



UNIVERSITY OF SASSARI
DEPARTMENT OF CHEMISTRY AND PHARMACY
PHD SCHOOL IN CHEMICAL SCIENCES AND TECHNOLOGIES
CURRICULUM CHEMICAL SCIENCES

**SYNTHESIS AND REACTIVITY OF CYCLOPLATINATED
ROLLOVER COMPLEXES, AN EXPERIMENTAL AND
THEORETICAL APPROACH**

**PHD THESIS OF
DR. LUCA MAIDICH**

**SUPERVISOR
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**COORDINATOR
PROF. STEFANO ENZO**

CYCLE XXVI, 2010-2013



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- *Mesoionic Complexes of Platinum(II) Derived from "Rollover" Cyclometalation: A Delicate Balance between Pt-C(sp³) and Pt-C(sp²) Bond Cleavage as a Result of Different Reaction Conditions*; Luca Maidich, Giuseppina Zuri, Sergio Stoccoro, Maria Agostina Cinellu, Marco Masia, and Antonio Zucca*; *Organometallics*, **2013**, 32(2), pp 438-448. DOI: 10.1021/om300824d. Publication Date (Web): January 11, 2013. Published In Issue January 28, 2013. Copyright © 2013 American Chemical Society.
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- *Rollover Cyclometalation with 2-(2'-Pyridyl)quinoline*; Antonio Zucca*, Diletta Cordeschi, Luca Maidich, Maria Itria Pilo, Elisabetta Masolo, Sergio Stoccoro, Maria Agostina Cinellu, and Simona Galli; *Inorg. Chem.*, **2013**, 52(13), pp 7717-7731. DOI: 10.1021/ic400908f. Publication Date (Web): June 14, 2013. Published In Issue July 01, 2013. Copyright © 2013 American Chemical Society.

Abstract

Cyclometalation reactions constitute one of the evergreen fields in synthetic chemistry because of the variety of applications, from substrate functionalization to catalyst production and model for C-H activation. A variation on this theme is rollover cyclometalation where a bidentate donor, such as 2,2'-bipyridine, upon C-H activation leads to a species with a free donor atom that is able to influence the properties, hence the reactivity, of the complex.

We explored the similarities/differences between classical and rollover cyclometalation to check the importance of the second nitrogen donor by comparing suitably substituted 2,2'-bipyridines and 2-phenylpyridines; moreover the properties of the ligands were tuned to investigate the impact of stereoelectronic modification on the C-H activation process. The reactivity of the newly synthesized cyclometalates having formula $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)\text{-(L)}]$ ($\kappa^2\text{-N,C}$ = cyclometalated ligand, L = neutral ligand) was tested in different conditions: ligand substitutions, protonolysis, oxidative additions and reductive eliminations. A wide variety of mono and dinuclear complexes was obtained and fully characterized by NMR spectroscopy.

Further insight has been sought from *in silico* experiments using DFT calculations that led to a nice agreement with the chemistry observed.

Part of this thesis was done in the Department of Chemistry of the University of Warwick (United Kingdom) under the supervision of Prof. Jonathan P. Rourke.

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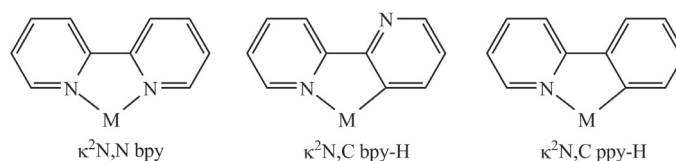
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C–H activation

1.1 Introduction

Classical spectator ligands such as 2,2'-bipyridine (bpy) were used in the past to simply complete the coordination sphere of a metal, providing electronic and steric properties to the complex, without being directly involved in chemical transformations. In contrast, in recent years attention has been devoted to the design of ligands with improved functions, able to enhance or change the reactivity of the metal centre in response to alterations in the solution environment, such as changes in pH.^{1,2} Nitrogen donors capable of forming N-H bonds, recently defined "ligands with multiple personalities",³ seem particularly suitable for this purpose, showing interesting perspectives in different fields, such as the design of molecular devices (for example, molecular machines^{4,5} and organometallic sensors⁶) or C-H bond activation.² Among classical ligands bpy plays an important role, being one of the most studied ligand in inorganic chemistry;⁷ in its common coordinative behaviour it acts as a chelated ligand even if monodentate⁸ and bridging coordinations^{9–13} are also known. In addition to the classical coordination as a neutral κ^2 -N,N ligand, bpy may behave in a different way (Scheme 1.1): starting from a chelated complex, displacement of one of the nitrogen atoms is followed by rotation of the pyridine ring, promoting the activation of the C-H bond in position 3 to give a five-membered cyclometalated complex.^{14–23} This unusual reaction, called "rollover" cyclometalation, is raising a growing interest as demonstrated by the publication of a very recent review.²⁴ It is worth noting that the reaction is not restricted to 2,2'-bipyridines: other chelated heteroar-

matic ligands, such as pyrazolylmethanes,²⁵ N-(2'-pyridyl)-7-azaindole,²⁶ aminopyrimidinyl phosphanes,²⁷ aminopyrimidinyl pyridines,²⁸ and 2-phenylpyridines,²⁹ may react in a similar way. Moreover, cyclometalated complexes of bpy closely resemble those of cyclometalated 2-phenylpyridine (ppy), whose platinum(II) complexes showed interesting properties in catalysis, reactivity, and medicinal chemistry,^{30–35} with the additional function of the second nitrogen atom.



Scheme 1.1

Much effort has been devoted to shed light into the mechanism of the rollover process. The fundamental mechanistic difference between "classical" and "rollover" cyclometalation lies in the nature of the species from which the reaction starts. Rollover cyclometalation originates by definition from a chelated adduct, and the crucial point is the internal rotation of the ligand, which occurs before the C-H bond activation. In the case of platinum(II) with bpy derivatives, the studies on the topic showed first the nucleophilic nature of the metal ion in the course of the C-H bond activation.^{20,23} Successive studies in the gas phase demonstrated a clear preference for an oxidative-addition/reductive-elimination mechanism for platinum, whereas σ -bond metathesis is favoured for nickel. In the case of palladium the situation is more delicate and the preferred mechanism depends on the nature of the anionic ligands coordinated to the metal.³⁶

The mechanism for the rollover cyclometalation with electronrich metal precursors is still unknown but some hypothesis have been made both from experimental data and from theoretical calculations^{20,36,37} and these were recently reviewed.²⁴ The mechanism proposed for the 2,2'-bipyridine derivatives has the following steps (Figure 1.1): (a) chelate coordination (κ^2 -N,N) of the bpy, (b) detachment of one of the nitrogen donors, (c) rotation around the C₂-C_{2'} bond, (d) interaction with the metal centre, (e) activation of the C-H bond, (f) elimination of R-H and (g) coordination of a ligand L to complete the coordination sphere of the metal.

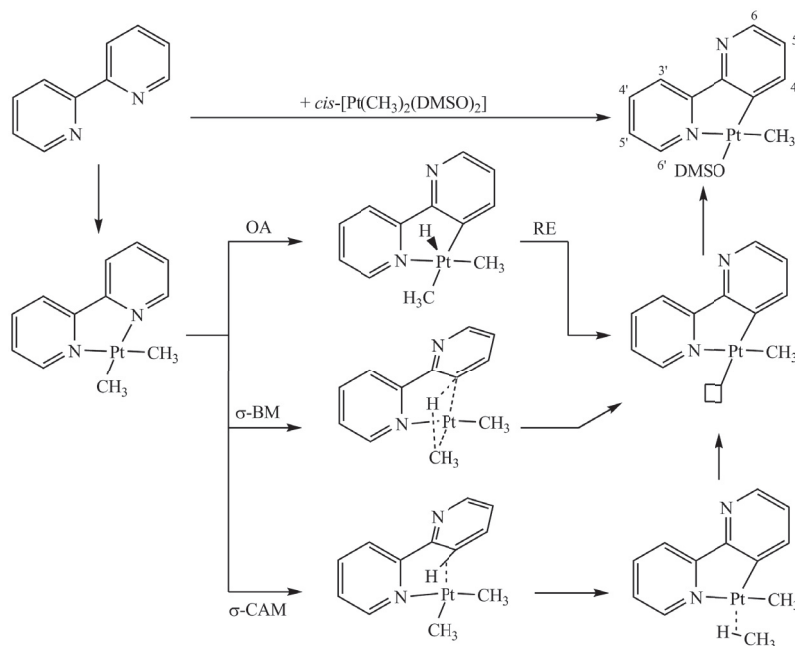


Figure 1.1: Rollover cyclometalation with 2,2'-bipyridine (bpy) and possible activation pathways.

The fundamental step of bond activation can follow different pathways which have been extensively reviewed.^{38–44} Among the possibilities we can find oxidative addition (OA), electrophilic substitution (ES), σ -bond metathesis (σ -BM),⁴⁵ σ -complex assisted metathesis (σ -CAM).⁴⁶

Oxidative additions require the addition of two new ligands to the coordination sphere of the metal and imply a formal oxidation of the metal centre, it is not surprising that this processes are typical when dealing with electron-rich complexes with metals in a low oxidation state.

Electrophilic substitutions, as the name suggests, follow a mechanism where the metal moiety is thought as a substituent in respect to the hydrogen of an aromatic ring, in this case the metal complexes involved are electron-poor.

Metathesis reactions, σ -complex assisted and σ -bond, are the respective counterparts that yield activation without formal change in the oxidation number of the metal. A further distinction between the last two mechanism is the aspect of the potential energy surface (PES) associated with the reaction coordinate, in fact the σ -BM process is commonly depicted as having a single transition state with no intermediates between reactants and

products while in the σ -CAM process several intermediates, in the form of σ -complexes, are involved.⁴⁶

The general mechanism here reported doesn't want to be comprehensive in describing all the possible rollover C-H activation processes because, as in many cases in chemistry, different mechanisms can operate in different experimental conditions, with different co-ligands and even with different substituents in the same ligand class (*vide infra*). Mechanistic studies have used a wide variety of ligands and conditions but a clear cut conclusion has not been reached yet.

In a series of papers Schwarz and co-workers investigated in some detail by mass spectrometry the cyclometalation process with bpy in the gas-phase reporting some interesting observations such as, for example, different reaction pathways depending on the sequence in which the co-ligands are lost³⁷ and evidences of catalytic behaviour by the cyclometalated compounds.⁴⁷⁻⁵⁰ Another interesting phenomenon observed on Pt(II) by Schwarz *et al.*³⁷ and on Rh(I) by Zuber *et al.*⁵¹ is the exchange of the protons in position 3 and 3' on the bpy.

In their work Zuber *et al.* studied Rh(I) cationic complexes with bpy in basic solutions and observed a scrambling between protons occupying analogous positions, *i.e.* 3-3', 4-4', 5-5' and even 6-6', with a deuterium atom from the CD₃OD solvent molecule. In this case the operating mechanism proposed is an initial oxidative addition of a C₃-H bond of the bpy to the Rh(I) centre, this affords a Rh(III) hydride complex that can be observed in the ¹H NMR spectrum (resonances between -14 and -28 ppm depending on the case). Once the hydride is on the metal an H-D exchange involving one, or possibly two methanol-*d*₄ molecules, occurs and it is followed by a reductive elimination of the C₃-D and formation of the κ^2 -N,N adduct. The authors state that very likely the mechanism for the exchange observed in the position 4-4' and 5-5' is different and could resemble the one proposed by Constable for a similar reaction on Ru(bpy) complexes.^{52,53} This reversibility observed at room temperature is very interesting in the perspective of a catalytic application of the rollover/retro-rollover process.

If an oxidative addition/reductive elimination sequence is operative in the case of rollover activation with 2,2'-bipyridines the step in which the electron density at the metal centre plays a key role is clearly the oxidative addition: in this case the metal formally gives two

electrons to the incoming hydrogen of the C-H bond and it is straightforward that all the factors that enhance the electron density on the metal will have a positive effect on the activation.^{23,43}

Reductive elimination of methane, in the case of dimethylhydrideplatinum intermediates, very likely is a regiospecific process on the basis of *trans*-influence because the methyl *trans* to the newly formed Pt-C bond is in an unfavourable configuration and therefore is more prone to react. Elimination of methane has also another strong point on its side because it is a volatile and inert compound it helps in driving the reaction to completion ruling out any possible reversibility in the conditions used. Methane elimination process has been studied using model complexes and it has been shown that there is a concrete chance of having a σ -complex with an agostic interaction between one of the C-H bonds of CH₄ and the metal centre.⁵⁴

Rollover cyclometalation may create a highly delocalized system thus, in this sense, we have decided to investigate a more delocalized ligand, such as 2-(2'-pyridyl)-quinoline, pyq. The latter, compared to bpy, possesses an additional fused ring, potentially imparting different electronic and steric properties, and has been investigated until now only by classical coordination means: examples available in the literature involve iron,⁵⁵ rhodium,⁵⁶ platinum,⁵⁷ and gold.⁵⁸

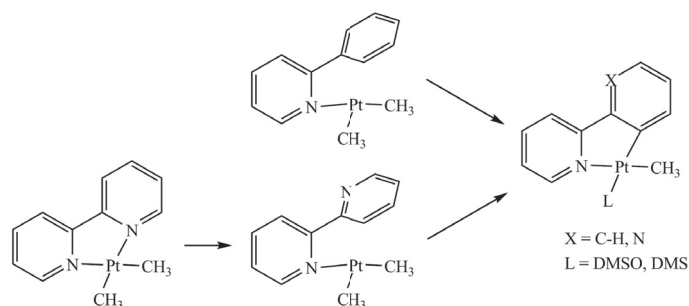
The extension of the delocalization can also be decreased and, in order to do this we decide to use the 2-vinylpyridine (vpy) ligand that already showed good results in cyclometalation reactions with Ru and Os,⁵⁹⁻⁶⁷ Co,⁶⁸ Pd,⁶⁹ Ir,⁷⁰ Pt,⁷¹ Au,⁷² and Re.⁷³

Cyclometalated complexes of 2-vinylpyridine were studied with rhodium in regioselective β -alkylations where the products had an anti-Markovnikov character.⁷⁴ Interesting results were also found with gold derivatives with the products showing a good cytotoxic activity.⁷²

1.2 Synthesis of the reagents

The ligands to be synthesized were carefully chosen in order to compare the effect of the presence/absence of a second nitrogen atom in the cyclometalation reactions, with particular interest in the different behaviour between *classical* and *rollover* cyclometala-

tion. The most natural and obvious choice was then to synthesize some substituted 2-phenylpyridines and the corresponding, wherever possible, substituted 2,2'-bipyridines. If we think about the two proposed mechanism for the cyclometalation it is easy to notice the close similarity between them once the κ^2 -N,N bpy detaches one nitrogen atom from the metal centre: from now on both the adducts with ppy and bpy are very similar, the only difference being the pyridinic vs phenyl ring (Scheme 1.2).



Scheme 1.2

1.2.1 2,2'-bipyridine derivatives

Given that 2,2'-bipyridine is one of the most studied ligand in chemistry⁷ it is not surprising that there are many possible and different ways to build the bipyridinic scaffold. Methyl-substituted bpy needed are mostly synthesized using coupling reactions such as Stille,⁷⁵ Negishi,^{76–78} Hiyama⁷⁹ and Suzuki-Miyaura⁸⁰ due to their high yield and easy workup, nonetheless some papers synthesized them using the Kröhnke approach.^{81,82} The synthesis of 6-methyl-2,2'-bipyridine (bpy^{6CH₃}) was accomplished following the procedure reported by Garber *et al.*⁸³ that used CH₃Li in Et₂O to selectively alkylate bpy in position 6. Functionalization of the position 5 is not trivial and the Negishi coupling of 2-bromopyridine and 5-methyl-2-bromopyridine was the reaction that gave the best results.^{84,85} Suzuki-Miyaura coupling in classical conditions afforded the product in very low yield after a longer purification process.

Trifluoromethyl-substituted bipyridines are less investigated in literature and the only entries found for the 5-CF₃ and 6-CF₃ substituted ones are the Suzuki-Miyaura⁸⁰ and the Hiyama⁷⁹ coupling, both of them relative to the 5-trifluoromethyl-2,2'-bipyridine

(bpy^{5CF₃}). The procedure chosen was the former due to the commercial availability of the coupling partners. 6-trifluoromethyl-2,2'-bipyridine (bpy^{6CF₃}) is unknown in literature and was synthesized using the same protocol that led to bpy^{5CF₃} just changing one of the partners in the coupling, the details of the synthesis can be found in the Experimental Section.

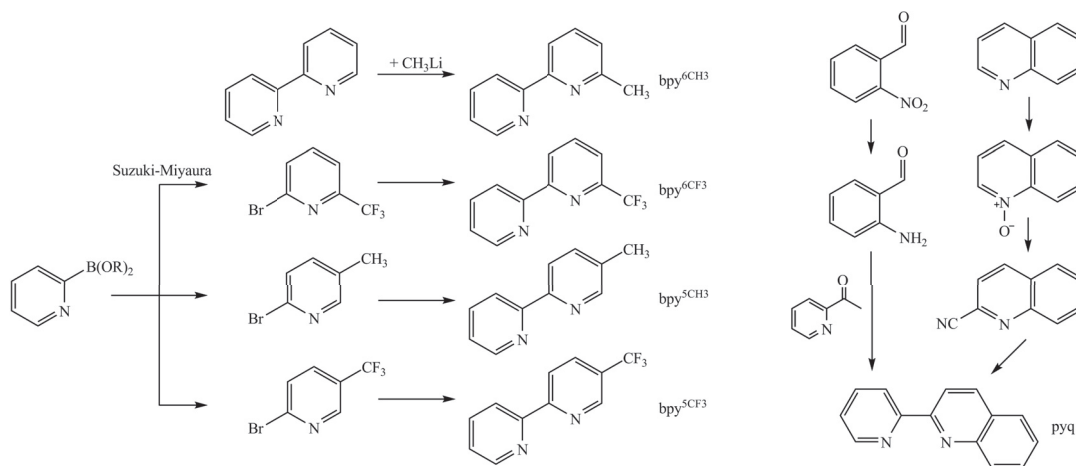


Figure 1.2: Synthesis of the bpy derived ligands used.

Finally, 2-(2'-pyridyl)quinoline (pyq) was synthesized following two different procedures. In the first one we used the well-known cyanation *via* N-oxide of the quinoline followed by co-cyclotrimerization with acetylene in the presence of Bönemann catalyst, [Co(Cp)(COD)] where Cp = η^5 -cyclopentadienyl and COD = 1,5-ciclooctadiene.^{86–88} A slightly improved yield is obtained using a different protocol that takes advantage of the cyclization of the 2-acetylpyridine with *o*-aminobenzaldehyde obtained *in situ* reducing *o*-nitrobenzaldehyde with iron powder.^{55, 89, 90}

In Table 1.1 the ¹H and ¹⁹F chemical shifts of the ligands are reported with the values for 2,2'-bipyridine included for comparison. The signals relative to the protons of the substituted ring are the most affected by the R group, the trend is in agreement with what is expected from the electronwithdrawing/releasing effects: trifluoromethylated bipyridines show more deshielded signals while the methylated ones have resonances more shielded than bpy.

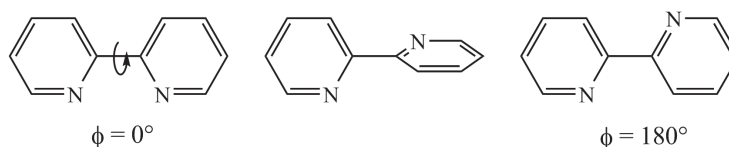
Table 1.1: ^1H and ^{19}F chemical shift of the substituted 2,2'-bipyridines synthesized registered in CDCl_3 .

	bpy	bpy ^{6CH₃}	bpy ^{6CF₃}	bpy ^{5CH₃}	bpy ^{5CF₃}
H ₃	8.42	8.14	8.64	8.29	8.57
H ₄	7.73	7.68	7.99	7.62	8.06
H ₅	7.21	7.15	7.70	-	-
H ₆	8.65	-	-	8.51	8.94
H _{3'}	8.42	8.33	8.53	8.36	8.47
H _{4'}	7.73	7.78	7.86	7.79	7.87
H _{5'}	7.21	7.27	7.37	7.28	7.38
H _{6'}	8.65	8.65	8.69	8.66	8.72
CH ₃	-	2.62	-	2.40	-
CF ₃	-	-	-68.0	-	-62.3

Particularly interesting is the fact that a small effect of the substituent is visible on the other pyridyl ring but its trend is harder to explain because while H_{3'} and H_{4'} follow the reasoning above, H_{5'} experiences always a deshielding effect regardless the substituent and H_{6'} is only very slightly affected. These observations could be true indicators that the substituent on one ring exerts an influence on both pyridyl rings thus implying the existence of some correlation between the rings.

The ligands were also studied with Density Functional Theory (DFT) methods to have a better insight in the electronic structure and possibly correlate it with the reactivity; in particular we concentrated our preliminar analysis to the investigation of the energetics of the rotation around the C₂-C_{2'} bond, *i.e.* the torsion angle between the two rings. In Figure 1.3 is reported the scan of the N₁-C₂-C_{2'}-N_{1'} dihedral angle ϕ evaluated using the ZORA formalism⁹¹⁻⁹³ along with the hybrid PBE0⁹⁴⁻⁹⁶ functional and the def2-SVP basis set⁹⁷ as implemented in ORCA package.⁹⁸⁻¹⁰⁰

All the bipyridines synthesized show two minima and two transition states (TS) when



Scheme 1.3

scanning the dihedral angle $N_1-C_2-C_2'-N_1'$ (ϕ) from 0 to 180° , for each one of them the global minimum is associated with a *transoid* conformation of the two nitrogen atoms ($\phi = 180$) while a local minimum is found around $\phi = 30$ and has a *cisoid* arrangement. The two transition states are located at $\phi = 0$ and around $\phi = 80$. The fully coplanar conformation at $\phi = 0$ is negatively affected by the repulsive interactions between the lone pairs on the sp^2 hybrid orbitals of the nitrogen atoms and between the H_3 and H_3' protons. The global maximum is located almost 10° before reaching the perpendicularity between the rings, a conformation which is expected to have very little (if any) contribution due to the inter-ring electron delocalization. These two observations are in agreement with previous studies by Göller and Grummt,^{101,102} but also with the more recent work of Lützen *et al.*¹⁰³

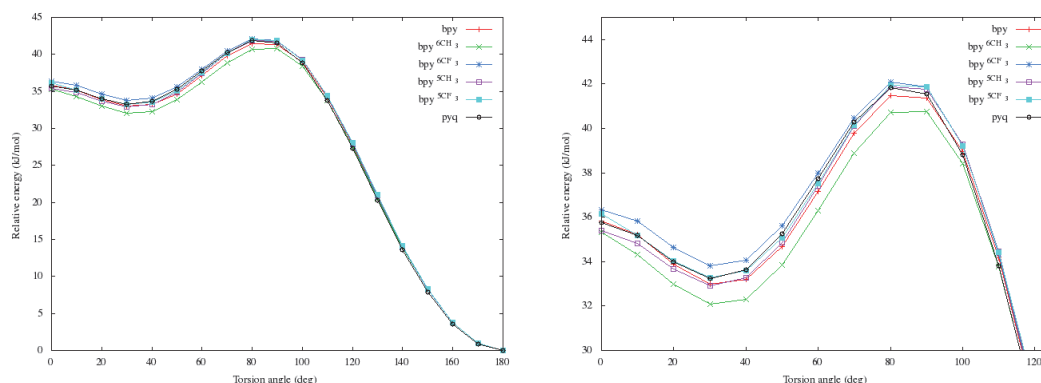


Figure 1.3: Potential energy surface scan in $\text{kJ}\cdot\text{mol}^{-1}$ associated to the torsion of the dihedral $N_1-C_2-C_2'-N_1'$, ϕ , in bpy derived ligands. The energies are relative to the global minimum found for $\phi = 180$ at ZORA-PBE0/def2-SVP level.

1.2.2 2-phenylpyridine derivatives

Substituted 2-phenylpyridines are not less studied than 2,2'-bipyridines because of their usefulness in the cyclometalation reactions with a plethora of different metals.⁴³ On the whole even in this case the C-C coupling reactions play a major role, therefore we found examples with Stille,¹⁰⁴ Hiyama,⁷⁹ Suzuki-Miyaura³⁴ and Kumada.^{105,106} Different methodologies are also present: for example cyclotrimerization¹⁰⁷ and a reaction involv-

ing lithium¹⁰⁸ for the synthesis of *m*-tolyl-2-pyridine or a sequence of amination, annulation and aromatization used to obtain 4-fluorophenylpyridine.¹⁰⁹ A summary of the methodologies used for the synthesis of the substituted 2-phenylpyridines, ppy^X where $X = 3\text{F},^{110,111} 3\text{CH}_3,^{112,113} 3\text{CF}_3,^{111,114} 4\text{F},^{34}$ is visible in Figure 1.4.

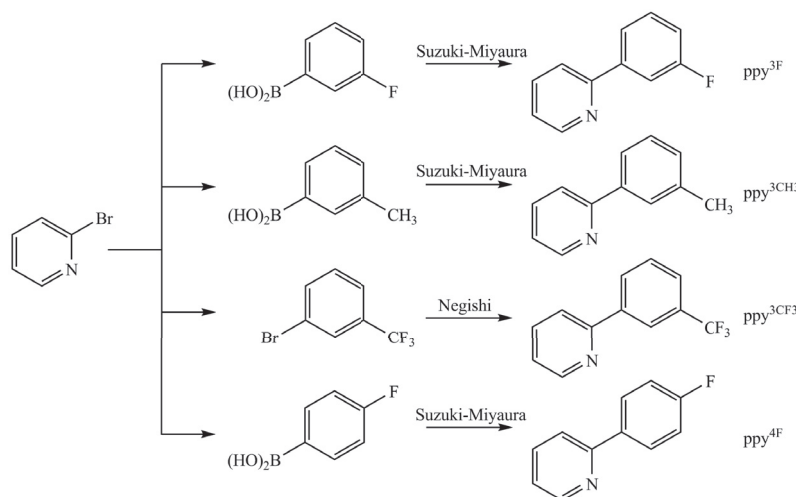


Figure 1.4: Synthesis of the substituted 2-phenylpyridines used.

In Figure 1.5 is depicted the potential energy surface associated with the torsion of the dihedral $\text{N}_1\text{-C}_2\text{-C}_{1'}\text{-C}_{2'}$, ϕ . The overall aspect of the graph is different than the one observed with 2,2'-bipyridines (see Figure 1.3) because now we see two minima for $\phi = 0$ and $\phi = 180$ while a TS is located around $\phi = 90$ giving to the surface a bell-shaped aspect.

1.3 Stereoelectronics

We need to distinguish between the two concepts of steric *hindrance* and steric *effect*: while the former simply indicates the physical volume required by a certain group or substituent, the second is defined by IUPAC as "the effect on a chemical or physical property (structure, rate or equilibrium constant) upon introduction of substituents having different steric requirements".¹¹⁵ In the past the two groups, *i.e.* CH_3 and CF_3 , were considered very similar in respect to the steric hindrance even if in some cases trifluoromethyl was thought to be more closely related to the isopropyl group.¹¹⁶ Recently a theory that takes

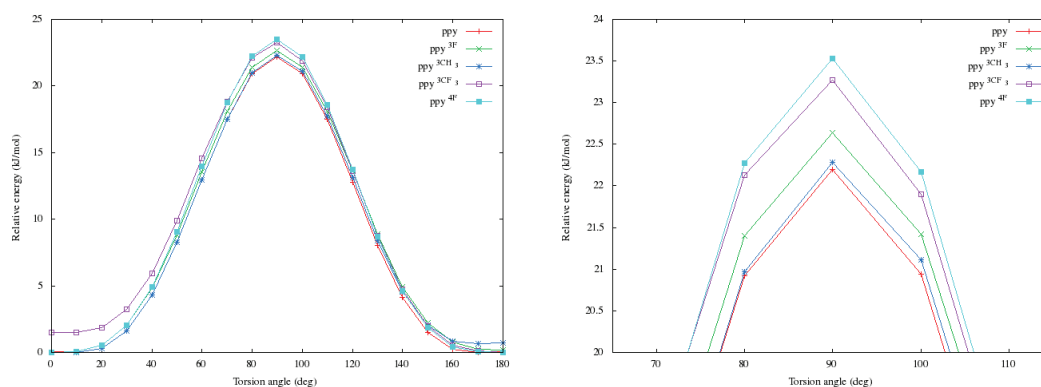


Figure 1.5: Potential energy surface scan in $\text{kJ}\cdot\text{mol}^{-1}$ associated to the torsion of the dihedral $\text{N}_1\text{-C}_2\text{-C}_{1'}\text{-C}_{2'}$, ϕ , for the ppy derived ligands. The energy are relative to the global minimum found for each ppy at ZORA-PBE0/def2-SVP level.

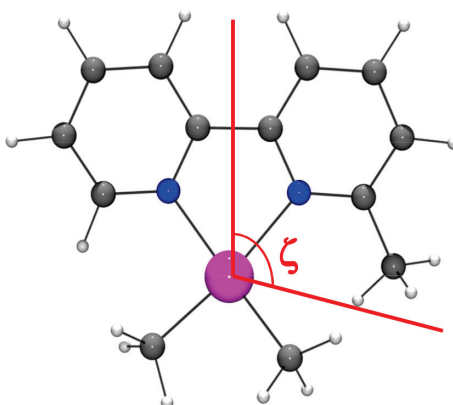


Figure 1.6: Definition of the ζ angle used to evaluate the steric hindrance by geometrical means.

in account Van der Waals volumes and the shapes of various alkyl groups suggested that the ethyl group best resemble CF_3 , with the isopropyl being bigger.^{117, 118}

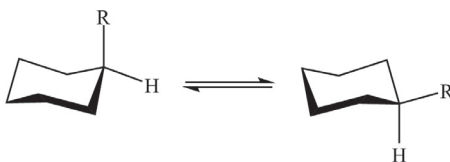
On a pure geometrical reasoning we can roughly estimate the steric hindrance of the methyl vs. trifluoromethyl group evaluating how much coordination plane is requested by the two bipyridines. Assuming that the bpy ligand is coplanar with the $\text{Pt}(\text{CH}_3)_2$ fragment and that also the substituent on bpy lies in the same plane, we can define an angle ζ between two planes perpendicular to the coordination one: one bisects the N-Pt-N angle while the second is the one tangent to the outermost Van der Waals surface of the substituent passing through the metal centre, as depicted in Figure 1.6.

The problem can be solved in two dimensions and it is possible to derive^a the data in Table 1.2 where some interesting values are visible and deserve comments. It is interesting that bpy occupies 8.8 degrees more than the theoretical 90° that would arise from a symmetrical division of the plane, the substitution of the hydrogen next to nitrogen with a fluorine has the effect of increasing the steric hindrance by ca. 10 degrees. A methyl group is more demanding as intuitively can be hypothesized (ca. 125 degrees) but the fact that the CF₃ occupies more than "one quarter and half" of the coordination plane is worthy of note.

Table 1.2: Steric requirements and A-values (relative to the substituent) of various substituted bpy. The angle ζ is defined in Figure 1.6.

Ligand	ζ (deg)	A-value (kcal·mol ⁻¹)
bpy	98.8	0
bpy ^{6F}	107.3	0.15
bpy ^{6CH₃}	125.1	1.70
bpy ^{6CF₃}	137.6	2.10

Another way to look at the sterics is to analyse the effect it has on the reactivity of a class of compounds, in this respect it has been defined a quantity called A-value that corresponds to the ΔG^0 , expressed in kcal·mol⁻¹, of the equilibrium reaction between the two chair conformations of a monosubstituted cyclohexane (Scheme 1.4).¹¹⁵ This value gives an idea of the conformational preference of a substituent for the more stable equatorial position, in fact when the substituent is in axial position it is affected by the 1,3-diaxial interactions that make this conformer less stable than the equatorial one.



Scheme 1.4

The difference between steric hindrance and steric effect is well represented in this case

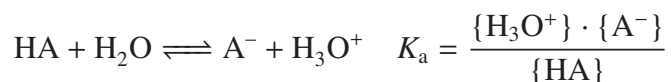
^aThe procedure used is described in Appendix A.

by the comparison of the *t*-butyl group with the trimethylsilyl one; while the former is smaller it has a bigger steric effect as highlighted by the A-value (> 4.0 vs 2.5). The reason behind this behaviour is the difference in the bond lengths between C-C and C-Si: due to the fact that bond distances involving silicon are intrinsically longer than those with carbon therefore in the axial conformer of trimethylsilylcyclohexane the 1,3-diaxial repulsions are weaker than in the corresponding *t*-butylcyclohexane leading to a lower A-value. It is worthy of note that this difference means that at the equilibrium less than the 0.1% of the *t*-butylcyclohexane will be in the axial form while with the trimethylsilyl analogue the percentage raises to 1.4%, *i.e.* one order of magnitude.

1.3.1 Basicity vs proton affinity

Evaluation of the donor capabilities of the nitrogen atoms in 2,2'-bipyridines is not an easy task both experimentally and theoretically. The very first issue that one encounters when facing this problem is the solubility connected to the bpy ligands, in fact not all of them are soluble in water and a suitable solvent needs to be found.

Acid dissociation constants, expressed in term of pK_a , are worldwide used as a reference to distinguish the easiness connected to the loss of the proton from a species HA



however, using non-aqueous solvents did not prevent chemists to find alternative ways to correlate the pK_a found in this way with the classical ones evaluated in aqueous solutions. Usually Brønstedt-Lowry bases are compared in terms of pK_a of the conjugated acid, for example amines, NR_3 , are ordered following the pK_a of the ammonium salts HNR_3^+ ; if the values are measured in water it is also possible to use the pK_b value, obtained as difference between pK_w and pK_a , *i.e.*

$$pK_b = pK_w - pK_a \quad (\text{for aqueous solutions})$$

Another complication when using 2,2'-bipyridines is due to the spatial proximity of the two nitrogen atoms that strongly influence each other thus modifying the observed pK_a values; in addition two different conformations, *i.e.* cisoid and transoid, are possible for

each protonation state.^b It is clear that with an unsymmetrically substituted bpy the situation becomes even more complicated to describe.

If the experimental approach turns out to be cumbersome, the theoretical one is not easier. High level theoretical calculations, due to their intrinsic approximations, can give only a static and therefore incomplete vision of the phenomenon of the equilibrium of weak acids/bases.

Proton affinities (ΔH) and gas-phase basicities (ΔG) can be accurately calculated in various and different ways.^{119–122}

Given the issues described above, in order to have a clue about the different donor abilities of the nitrogen atoms present in the ligands we decided to synthesize, a survey of the literature was performed to check if the pK_a and proton affinity values of the corresponding pyridine could help in analysing the reactivity. We are aware of the fact that a direct comparison between substituted pyridines and bipyridines cannot be quantitative but only qualitative.

All the data we were able to find in literature are summarized in Table 1.3.^c No surprise that a correlation between the acid dissociation constant and proton affinity can be drawn, more interesting is the fact that apparently there are no experimental values for py^{2CF_3} .

What emerges comparing the effect of the CH_3 and the CF_3 is that the trifluoromethyl group enhances the acidity of the pyridilium ion, $\text{py}^{\text{R}}\text{H}^+$, by two pK_a units and this corresponds to ca. $60 \text{ kJ}\cdot\text{mol}^{-1}$ difference in proton affinity values.

There is not a perfect parallelism between the reported values as highlighted by the fact that the more delocalized quinoline and isoquinoline have bigger ΔH but lower pK_a compared to the monocyclic pyridyl derivatives.

Judging from the difference in proton affinity values (ca. $5 \text{ kJ}\cdot\text{mol}^{-1}$) it is somewhat puzzling that we didn't find any data for the pK_a of py^{2CF_3} ; anyway a possible clue for this observation can be found in a paper published in 2005 written by Timperley *et al.*¹²⁷ where

^bCisoid and transoid are referred to the relative position of the two nitrogen atoms. For example with bpy there are 6 possible conformations for the 3 states relative to neutral, monocationic and dicationic species.

^cA pK_b was found for bpy at http://www.chemicalbook.com/ProductMSDSDetailCB5195697_EN.htm but only the value is present (9.67).

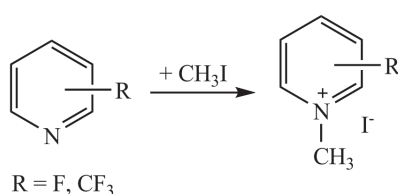
Table 1.3: Acid dissociation constant and proton affinity values for different pyridinic derivatives.

	pK_a at 25 °C	ΔH (kJ·mol ⁻¹) ¹²³
py	5.23	930.0
py ² CH ₃	6.00	949.1
py ³ CH ₃	5.70	943.4
py ⁴ CH ₃	5.99	947.2
py ² CF ₃		887.1
py ³ CF ₃	3.36	892.5
py ⁴ CF ₃	3.59	893.9
quinoline	4.90 ^a	953.2
isoquinoline	5.40 ^a	951.7
bpy	-	933.4 ¹²⁴

^a At 20 °C.^{125, 126}

the authors studied the quaternarization of monosubstituted pyridines with iodomethane (Scheme 1.5).

The starting pyridines used in the paper bear an electronwithdrawing group such as F or CF₃ and their influence on the reactivity was tested in dependence of the substitution pattern, *i.e.* whether it was in position ortho, meta or para to the nitrogen atom.

**Scheme 1.5**

The quaternarized pyridilium cations were obtained only when the substituents were in position meta or para and this was explained in terms of electronic factors for py²F and by "the combination of electronwithdrawal and steric congestion" for py²CF₃.¹²⁷

The higher electronic delocalization of quinoline compared to pyridine deserves a few comments: because of the additional condensed ring, the quinoline nitrogen is expected to be more basic, having the possibility to delocalize the positive charge, after protonation, on a larger area. Actually, other effects contribute to the basicity, such as solvation and

steric congestion. In particular, the *peri*-effect,¹²⁸ generating repulsion between the N-H hydrogen and the adjacent C₈-H one in the N-protonated quinoline, lowers the stability of this species, so that the basicity scale is quinoline < pyridine < isoquinoline (pK_b = 9.15, 8.83, 8.54, respectively).¹²⁹ On the whole, the electronic effects for pyq are not trivial and may furnish, together with the augmented steric hindrance and delocalization, additional interesting potentialities with respect to bpy.

1.3.2 Metal precursors

All the platinum(II) compounds of general formula $[Pt(X)_2(L)_2]$ were synthesized according to known procedures starting from the commercially available potassium tetrachloroplatinate, $K_2[PtCl_4]$, the general synthetic scheme is depicted in Figure 1.7.

A deep red aqueous solution of $K_2[PtCl_4]$ can be treated with excess DMSO at room temperature for 24 h to obtain *cis*- $[Pt(Cl)_2(DMSO)_2]$ easily isolated by filtration.¹³⁰ Subsequent treatment with excess $Sn(CH_3)_4$ at 80° in anhydrous conditions^{130,131} afforded in moderate to good yields (60-90%) the electron rich *cis*- $[Pt(CH_3)_2(DMSO)_2]$. The analogous phenyl containing product was obtained following the same scheme but treating with $Sn(CH_3)_3(Ph)$ the intermediate *cis*- $[Pt(Cl)_2(DMSO)_2]$.¹³¹

On the other hand we wanted to test the effect of a different neutral ligand but related with DMSO so the natural choice was dimethylsulphide (DMS). In this case an aqueous solution of $K_2[PtCl_4]$ and DMS was refluxed in inert atmosphere for 1 h to obtain a mixture of *cis* and *trans* isomers of $[Pt(Cl)_2(DMS)_2]$ which was treated with RLi , $R = CH_3, C_6H_5$, in Et_2O at 0 °C to obtain the bridging dimer $[Pt_2(CH_3)_4(\mu-DMS)_2]$ or *cis*- $[Pt(Ph)_2(DMS)_2]$ without any attempt to separate the two isomers as their ratio doesn't affect the following alkylation/arylation reaction.¹³²⁻¹³⁵

The DMS containing products could be converted in the corresponding, more stable, DMSO counterparts in clean and quantitative way by treatment with 10% excess DMSO in CH_2Cl_2 solutions. This very last route seems particularly interesting because avoids the handling of the very toxic triorganotin(IV) compounds (as the byproduct of the alkylation/arylation with $Sn(R)_4$ is $Sn(R)_3Cl$) although care must be taken in handling the alkyl/aryllithium solutions.

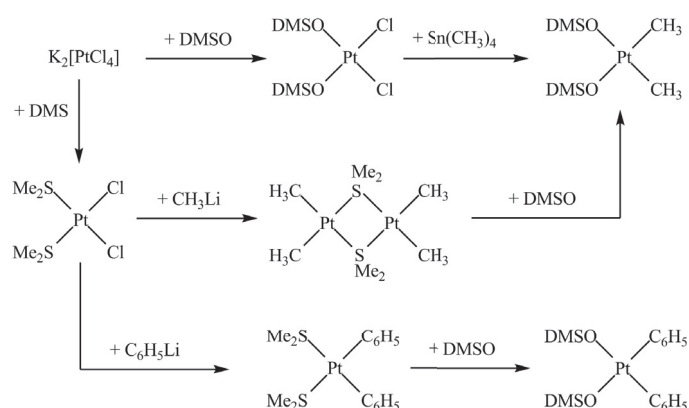


Figure 1.7: Synthesis of the metal precursors used.

1.4 Results and discussion

1.4.1 2,2'-bipyridine

The cyclometalation of the bpy^{X} and ppy^{X} pro-ligands synthesized in Section 1.2 has been investigated following two approaches: the first aimed to evaluate their feasibility in the cyclometalation process while the second tried to investigate the mechanism involved in this reactivity.

Using Pt(II) electronrich derivatives such as $\text{cis-}[\text{Pt}(\text{CH}_3)_2(\text{DMSO})_2]$ it is possible to achieve the activation of a remote C-H bond on the 2,2'-bipyridine (bpy) scaffold. At room temperature the isolated species is the coordination compound where bpy displaced two DMSO molecules, *i.e.* $[\text{Pt}(\text{bpy})(\text{CH}_3)_2]$ (**1a**).

The activation of the remote C-H bond in bpy requires harsher conditions in respect to the corresponding 6-substituted analogues, in fact while the 6-methyl-2,2'-bipyridine ($\text{bpy}^{6\text{CH}_3}$) undergoes rollover metalation in inert atmosphere at room temperature,^{20,136} bpy needs to be refluxed in toluene for at least 1 h to obtain the activation.¹⁶

The reaction gives as final product an orange-yellow air-stable Pt(II) complex which is formulated as $[\text{Pt}(\text{bpy-H})(\text{CH}_3)(\text{DMSO})]$ (**2a**) where the four coordination sites of the square planar d^8 metal ion are occupied by a methyl, a dimethylsulfoxide (DMSO) and the cyclometalated bpy ($\kappa^2\text{-C,N}$ mode, see Scheme 1.1). In absence of a crystal structure the characterization relies on ^1H and ^{13}C NMR data: (a) coordination of the methyl is evident from the singlet with satellites, due to the coupling with the NMR active ^{195}Pt

(33.8% natural abundance), at 0.70 ppm ($^2J_{\text{Pt-H}} = 82$ Hz); (b) S-coordinated DMSO gives a singlet with satellites at δ 3.25 ($^3J_{\text{Pt-H}} = 18.3$ Hz);^{21,22,137} (c) cyclometalation is highlighted by the presence of only seven signals in the aromatic region associated with the heteroaromatic ligand, in particular signals corresponding to H₆ (9.71 ppm, $^3J_{\text{Pt-H}} = 14$ Hz) and H₄ (8.01 ppm, $^3J_{\text{Pt-H}} = 56$ Hz) show the expected multiplicity and are flanked by satellites. Signals in agreement with the proposed formulation are also visible in the ^{13}C NMR spectrum where, among the resonances of the Pt-CH₃ (δ -13.4, $J_{\text{Pt-C}} = 763$ Hz) and the methyls of the DMSO (δ 43.7, $^2J_{\text{Pt-C}} = 42.1$ Hz), a small singlet with satellites ($J_{\text{Pt-C}} = 1090$ Hz) is ascribable to the metalated C₃ carbon. Finally, having two positions blocked by the cyclometalating ligand, the relative disposition of the remaining groups is in agreement with antisymbiosis,^{138–140} the *trans*-choice¹⁴¹ and *trans*-phobia^{142,143} concepts which place the S-coordinated DMSO *trans* to the high *trans*-influencing metalated C₃ and the methyl *trans* to the pyridinic nitrogen (see Figure 1.1).

1.4.2 6-substituted-2,2'-bipyridines

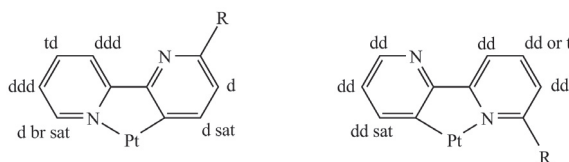
Reactions involving bpy^{6CH₃} and Pt(II) derivatives were already studied in the past,²⁰ but they have been repeated to have a more precise comparison keeping all the experimental settings as constant as possible between all the experiments.

A colourless acetone-*d*₆ solution of *cis*-[Pt(CH₃)₂(DMSO)₂] was prepared in an NMR tube, then an excess of bpy^{6CH₃} was added and the ^1H NMR were recorded at regular intervals. Very quickly the solution changed colour to orange-red and the spectrum showed the presence of a new platinum containing species and free DMSO (singlet at δ 2.52). The new species is characterized by seven aromatic signals and two methyl groups so it is easily assigned to the coordination compound [Pt(bpy^{6CH₃})(CH₃)₂] (**1b**) where the heteroaromatic ligand displaced two DMSO molecules, this kind of intermediate is not unexpected.²⁰ Formation of the coordination compound **1b** happens very slowly at low temperatures (below -10 °C) and starts to become detectable around 0 °C.

The asymmetry of the two pyridyl rings in bpy^{6CH₃} makes the two Pt-CH₃ groups slightly different and now they appear as two singlets with satellites at δ 1.03 ($^2J_{\text{Pt-H}} = 89.5$ Hz) and

1.04 ($^2J_{\text{Pt-H}} = 87.3$ Hz), all the signals of the $\text{bpy}^{6\text{CH}_3}$ experience a coordination shift and in particular the H_6 , next to nitrogen shows satellites ($^3J_{\text{Pt-H}} = 22.6$ Hz) and a $\Delta\delta = +0.48$ compared to the free ligand. A ^{195}Pt - ^1H HMQC confirmed the presence in solution of the starting material and the coordination compound that showed signals at -4150 ppm and -3334 ppm, respectively, along with the expected correlations.

When the reaction is carried on in a flask in refluxing acetone to speed up the process, eventually all the platinum ends up in the cyclometalated species $[\text{Pt}(\text{bpy}^{6\text{CH}_3}\text{-H})(\text{CH}_3)\text{-(DMSO)}]$ (**2b**) in which the coordination sphere is occupied by the $\kappa^2\text{-C,N}$ $\text{bpy}^{6\text{CH}_3}$ a methyl group (0.69 ppm, $^3J_{\text{Pt-H}} = 82.1$ Hz) and S-bound DMSO (δ 3.24, $^3J_{\text{Pt-H}} = 18.6$ Hz). Cyclometalation is confirmed by the presence in the aromatic region of only six signals where H_6 and H_4 are clearly visible with their satellites ($^3J_{\text{Pt-H}}$ are 14 and 53 Hz respectively), moreover it is equally visible from the multiplicity of the signals that the pyridyl ring that underwent cyclometalation is the substituted one: H_4 and H_5 are a triplet of doublets and a distorted ddd rather than two doublets of doublets with the former flanked by satellites (see Scheme 1.6).



Scheme 1.6

As we wanted to compare groups as similar as possible we synthesized 6-trifluoromethyl-2,2'-bipyridine ($\text{bpy}^{6\text{CF}_3}$) which, compared to $\text{bpy}^{6\text{CH}_3}$, should have a similar steric hindrance but a very different electronic influence due to the presence of the strongly electron-withdrawing CF_3 group.

Under the same conditions, *i.e.* acetone- d_6 solution of $\text{cis-}[\text{Pt}(\text{CH}_3)_2(\text{DMSO})_2]$ with subsequent addition of ligand in excess, no signs of reaction are visible at temperatures as low as -40 °C, not even coordination to platinum with displacement of one (or two) DMSO molecules. As the sample was warmed up to -20 °C the first evidence of reaction became visible with tiny singlets with satellites in the region of the coordinated DMSO (four of them between 3.41 and 2.95 ppm) but, unfortunately, we were not able to completely

identify all these species due to their low concentration. Around 0 °C the appearance of a new signal at δ 9.84, the growth of the singlet with satellites at δ 3.30 ($^3J_{\text{Pt-H}} \approx 18$ Hz), the singlet with satellites accounting for three protons at 0.71 ppm ($^2J_{\text{Pt-H}} \approx 84$ Hz) and the signal of methane confirmed that the cyclometalation was going on; in agreement with these evidences a singlet at -67.8 ppm grew in the ^{19}F NMR.

The sample was then warmed to room temperature and the reaction reached completion giving a pale yellow solution. As with $\text{bpy}^{6\text{CH}_3}$ the product is confidently deduced as $[\text{Pt}(\text{bpy}^{6\text{CF}_3}\text{-H})(\text{CH}_3)(\text{DMSO})]$ (**2c**) on the basis of the presence of H_6 (δ 9.85, $^3J_{\text{Pt-H}} = 18.8$ Hz) and H_4 (δ 8.22, $^3J_{\text{Pt-H}} = 55.1$ Hz) in the aromatic region and the already mentioned DMSO and Pt-CH_3 groups. Cyclometalation of the substituted pyridyl ring is again evident by the multiplicity of the signals of the ligand and was confirmed by a ^1H - ^1H COSY that showed two spin systems having four and two protons respectively rather than two systems with three protons each.

Complex **2c**, arising from a new ligand has some points of interest, therefore we decided to characterize it thoroughly by mono- and bi-dimensional NMR spectroscopy in order to correctly assign all the signals and evaluate the coupling constants.

The striking difference between $\text{bpy}^{6\text{CH}_3}$ and $\text{bpy}^{6\text{CF}_3}$ is that with the fluorinated one we do not have evidences of the formation of the adduct $[\text{Pt}(\text{bpy}^{6\text{CF}_3})(\text{CH}_3)_2]$ (**1c**) in appreciable quantities but with this we cannot exclude its existence in solution. Reasonably the strongly electronwithdrawing character in conjunction with the increased steric hindrance of the CF_3 group have a dramatic effect on the donor properties of the adjacent nitrogen atom modifying its coordinating abilities. The lone pair in the sp^2 hybridized orbital on nitrogen is less prone to react because it is attracted to a bigger extent by the nucleus; this, as a consequence, makes the nitrogen harder than usual and also less basic so that not only the coordination on the soft Pt(II) metal ion is less favourable but even the displacement of a DMSO molecule is more difficult. In conclusion we can note that evidently not even the formation of a chelate helps the stabilization of the $\kappa^2\text{-N,N}$ adduct demonstrating that entropy is not sufficient to overcome the enthalpic barrier.

In solution however it must be present an intermediate where the $\text{bpy}^{6\text{CF}_3}$ is bound to the metal centre at least as $\kappa^1\text{-N}$ adduct, where the coordinated nitrogen is presumably the one of the unsubstituted pyridyl ring, in order to facilitate the cyclometalation in a fash-

ion that resembles the mechanism followed with 2-phenylpyridines. The supposed κ^1 -N intermediate was not observed probably because of its proness to undergo C-H activation on the C₃ position of the CF₃-substituted ring; this very high reactivity could be explained by the fact that the bond is located in *para* position to the CF₃ and in *meta* to the nitrogen, a situation that enhances the electron-deficiency at the C₃-H bond and presumably makes the hydrogen atom more easily removable.

The bpy^{6CH₃} ligand cyclometalates following the steps already described for bpy, *i.e.* formation of the coordination compound κ^2 -N,N followed by C-H activation, and selectively metalates on the C₃ position of the substituted pyridyl ring showing that a substituent in position 6 have a paramount influence on the regioselectivity of the activation. The substituent has a destabilizing effect on the ground state of the reactant (κ^2 -N,N-adduct) facilitating the detachment of the pyridyl an thus making the activation on that ring much more favoured.

In first instance it is possible to say that both ligands show a similar steric effect that leads to the selective activation of the pyridyl ring bearing the substituent but, on the contrary, they have very different electronic effects on the C-H activation process as evident from the "activation temperature" that is 263 K for bpy^{6CF₃} and 273 K for bpy^{6CH₃}.^d The observed difference in the temperature at which cyclometalation becomes detectable is reflected also in the time requested to reach completion at room temperature: only a couple of hours for bpy^{6CF₃} while at least 12 h are required for bpy^{6CH₃}.

While the selectivity could be ascribed to a steric factor the lower activation temperature observed for the trifluoromethyl-substituted bpy cannot be related clearly with the electronic properties. In general drawing a clear line distinguishing between steric and electronic factors that influence a particular reaction is tough and this case shows no exception because a rigorous comparison is hampered by the fact that possibly the operating mechanism is different, *i.e.* we do not observe the coordination compound **1c** nor any other intermediate species.

The NMR data presented for bpy^{6CH₃} and bpy^{6CF₃} in Table 1.4 permit to eventually see the influence of the electronic properties of the substituent while keeping the steric ones

^dThe *activation temperature*, T_{act} , is the temperature at which detection of the ongoing cyclometalation is evident, in our case this was investigated by NMR spectroscopy.

almost comparable.¹⁴⁴

Table 1.4: Selected ^1H NMR chemical shifts (ppm) and ^{195}Pt coupling constants (Hz, in brackets) of the $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{DMSO})]$ complexes where $\kappa^2\text{-N,C}$ is a cyclometalated 6-substituted bpy.

Proton	bpy	bpy ^{6CH₃}	bpy ^{6CF₃}
H ₃ ,	8.29	8.31	8.40
H ₄ ,	7.95	7.91	7.98
H ₅ ,	7.36	7.31	7.40
H ₆ ,	9.71 [14]	9.68 [14]	9.73 [20]
H ₄	8.01 [56]	7.88 [53]	8.15 [56]
H ₅	7.17	7.04 [19]	7.48
H ₆	8.36	-	-
(DMSO)	3.25 [18]	3.24 [18]	3.26 [19]
Pt-CH ₃	0.70 [82]	0.69 [82]	0.73 [82]
R on bpy	-	2.52	-

The most notable differences in the ^1H NMR spectra are relative to the aromatic protons of the N-bounded pyridyl ring that are always slightly more deshielded.

An evaluation of the electronic effects of the substituent could be made by analysing the cyclometalated products. For instance an inspection of the $^3J_{\text{Pt-H}}$ coupling constants of the methyls of the DMSO ligand should give a crude esteem of the electronwithdrawing/donating abilities of the ligands used. The data, visible in Table 1.4, show that the values are 18.3, 18.3 and 19.2 Hz respectively for bpy, bpy^{6CH₃} and bpy^{6CF₃} (bpy has been included for the sake of comparison). It is evident that all the values are pretty close to each other with a bigger coupling for the complex with bpy^{6CF₃}, this is in agreement with what could be expected on the basis of the properties of the substituent: it is reasonable that the CF₃ pulls electron density from the pyridyl ring making it more demanding towards platinum, this in turn is reflected to the DMSO, located in *trans* to the metalated C₃ carbon, that is forced to donate more to the metal centre in order to satisfy its "hunger" of electrons.^c

^cSee also $J_{\text{Pt-P}}$ for $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{PR}_3)]$ complexes in Chapter 2

1.4.3 5-substituted-2,2'-bipyridines

The 5-substituted-2,2'-bipyridines were investigated aiming at a "sterically purified" C-H activations meaning that the substituent isn't close to the metal centre so that it cannot influence the regioselectivity of the process. In a precedent work it was observed that in the conditions where the $\text{bpy}^{6\text{CH}_3}$ gives cyclometalation the corresponding 5- CH_3 substituted one afforded only the adduct $[\text{Pt}(\text{bpy}^{5\text{CH}_3})(\text{CH}_3)_2]$.²⁰ We decided to explore a bit more the reactivity of this ligand and found that indeed undergoes cyclometalation even if in longer times (more than one week at room temperature) or using harsher conditions (refluxing toluene for at least 2 h).

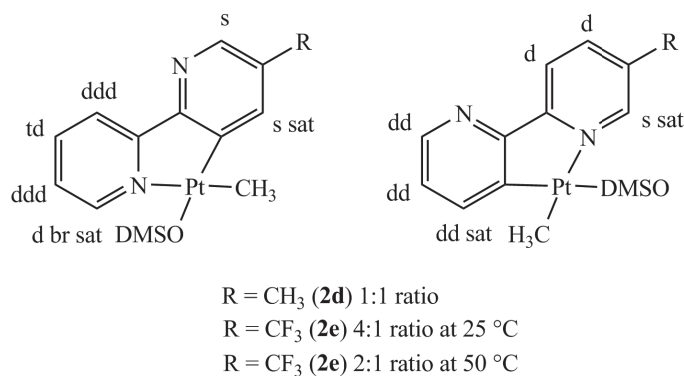
The investigation of the steric effect on the cyclometalation was carried out synthesizing $\text{bpy}^{5\text{CH}_3}$ and $\text{bpy}^{5\text{CF}_3}$, for the details of the synthesis see Section 1.2 and the Experimental Section. Now the substituent is not so close to the metal centre thus might have a different impact on the C-H activation process and this allows, at least in principle, to distinguish between electronic and steric effects.

Addition of $\text{bpy}^{5\text{CH}_3}$ to a colourless acetone- d_6 solution of *cis*- $[\text{Pt}(\text{CH}_3)_2(\text{DMSO})_2]$ in an NMR tube afforded rapidly an orangish solution where the only new species detected when recording the first spectrum were the starting materials and the coordination compound $[\text{Pt}(\text{bpy}^{5\text{CH}_3})(\text{CH}_3)_2]$ (**1d**), the formation of the adduct reaches completion in ca. 5 min. Displacement of the two DMSO molecules is confirmed by the signal at δ 2.52 (free DMSO) and by the coordination shift detected for the aromatic protons of the heteroaromatic ligand, diagnostic signals are H_6 and H_6' which are clearly assigned due to their multiplicity: 9.24 (d sat, $^3J_{\text{Pt-H}} = 21.6$ Hz) the former and 9.06 (s sat, $^3J_{\text{Pt-H}} = 22.0$ Hz) the latter. Coordination is supported also by the Pt- CH_3 resonances that are almost coincident around 1.11 ppm showing also a comparable coupling constant with ^{195}Pt (ca. 85 Hz).

Leaving the solution at room temperature for one week doesn't lead to the quantitative formation of the cyclometalated product, $[\text{Pt}(\text{bpy}^{5\text{CH}_3-\text{H}})(\text{CH}_3)(\text{DMSO})]$ (**2d**), however the following data allow to confirm that cyclometalation is taking place: (a) two singlets with satellites at 3.13 and 3.14 ppm ($^3J_{\text{Pt-H}}$ ca. 18 Hz) that might be assigned to a DMSO S-coordinated to a group with high *trans*-influence such as a C_{sp^2} metalated carbon; (b) two singlets with satellites at 0.64 and 0.65 ppm ($^2J_{\text{Pt-H}}$ ca. 84 Hz); (c) in the aromatic

region a singlet with satellites (δ 9.61, $^3J_{\text{Pt-H}} \approx 15$ Hz) and a broad doublet with satellites (δ 9.34, $^3J_{\text{Pt-H}} \approx 13$ Hz) are the only clearly visible resonances in this crowded region. The ratio between the two new signals is roughly 1:1 and on the whole they account roughly for $\frac{1}{50}$ of the coordination compound **1d**.

In order to obtain a quantitative conversion to the cyclometalated product we decided to use the same conditions needed for the cyclometalation of the simple bpy, *i.e.* refluxing a toluene solution of *cis*-[Pt(CH₃)₂(DMSO)₂] and bpy^{5CH₃} for at least 2 h; this choice led to a yellow solution and to the isolation of a mixture of the two cyclometalated products arising from the activation of the substituted and unsubstituted pyridine ring (Scheme 1.7) as suggested by the NMR follow-up experiment. The assignment is made on the basis of the NMR data of the diagnostic signals that are pretty close to each other both in chemical shift and in Pt-coupling.



Scheme 1.7

Switching to 5-trifluoromethyl-2,2'-bipyridine (bpy^{5CF₃}) any electronic effect, if present, should become evident. Following by ¹H and ¹⁹F NMR spectroscopy the reaction of *cis*-[Pt(CH₃)₂(DMSO)₂] in acetone-*d*₆ with bpy^{5CF₃} it is possible to identify the initial formation of the coordination compound, [Pt(bpy^{5CF₃})(CH₃)₂] (**1e**), visually suggested by the colour change to orange-red and clearly evident from the spectra, even in this case the asymmetry of the ligand made non-equivalent both the two methyls on platinum and the protons next to the nitrogen atoms of the pyridinic rings. Two singlets with satellites are visible in the aliphatic portion of the ¹H NMR at 1.08 and 1.02 ppm with a similar $^3J_{\text{Pt-H}}$ of ca. 86 Hz; seven signals are attributable to the bpy^{5CF₃} in the aromatic region and

chelation is demonstrated by the presence of satellites for the signals assigned to H_6 and H_6' . A ^1H - ^1H COSY helped in the assignment of all the signals and ^{19}F NMR showed a minimal coordination shift of -0.4 ppm for the CF_3 group from -62.9 to -63.3 ppm.

The sample was left at room temperature for almost three weeks before heavy decomposition prevented further analysis. During this time it was evident that cyclometalation was taking place on both pyridyl rings judging from the already mentioned typical features (DMSO, CH_3 , H_6 and CF_3 signals), the striking difference in respect to the case with bpy^{5CH_3} is that the ratio between the cyclometalated products was not 1:1 but 4:1 with the predominant isomer being the one arising from the activation of the substituted ring (Scheme 1.7).

Operating under kinetic control, *i.e.* acetone room temperature, it is possible to obtain a 4:1 mixture of the two possible cyclometalated compounds arising from the C_3 -H or C_3' -H activation. From the multiplicity of the signals the major species was assigned to the one in which the substituted ring has been activated (indicated without prime, C_3 -H): if the ring that undergoes C-H activation is the substituted one the aromatic region of the ^1H NMR spectrum should show two singlets relative to H_6 and H_4 (this one flanked by satellites due to ^{195}Pt coupling) and 4 signals relative to a 2-substituted pyridine coordinated to platinum, while in the other case the number of the singlets would be only one being relative to H_6 with a smaller $^3J_{Pt-H}$ value. Experimentally for the major species we observe a pattern in agreement with the first case (Scheme 1.7).

Product distribution was shown to depend on the temperature at which the reaction was carried on; in fact when another sample was heated to 50 °C for two weeks the ratio between the two isomers was 1:2 with the activation of the substituted ring still yielding the most abundant one, again further spectroscopy analysis was unsuccessful due to decomposition of the sample.

Comparison of the values of the coupling constants for the DMSO protons gives also in this case a clue on the electronic characteristics of the cyclometalated ligands. The values in Table 1.5 demonstrate again that when the metalated ring is substituted with the CF_3 group the $^3J_{Pt-H}$ coupling constant in *trans* position is higher (19.0 vs 18.0 Hz). It is worthy of note that in this case looks like that the electron-releasing effect of the methyl

Table 1.5: Selected ^1H NMR chemical shifts (ppm) and ^{195}Pt coupling constants (Hz, in brackets) of the $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{DMSO})]$ complexes where $\kappa^2\text{-N,C}$ indicates a 5-substituted cyclometalated bpy.

Proton	bpy	$^a\text{bpy}^{5\text{CH}_3}$	$^b\text{bpy}^{5\text{CH}_3}$	$\text{bpy}^{55'\text{CH}_3\text{145}}$	$^a\text{bpy}^{5\text{CF}_3}$	$^b\text{bpy}^{5\text{CF}_3}$
$\text{H}_{3'}$	8.29			8.17		
$\text{H}_{4'}$	7.95			7.54		
$\text{H}_{5'}$	7.36			-		
$\text{H}_{6'}$	9.71 [14]	9.54 [15]	9.42 [15]	9.46 [14]	9.76 [n.r.]	
H_4	8.01 [56]			7.71 [53]	8.21 [55]	
H_5	7.17			-		
H_6	8.36			8.42		
(DMSO)	3.25 [18]	3.08 [18]	3.08 [18]	3.18 [18]	3.27 [19]	3.23 [n.r.]
Pt- CH_3	0.70 [82]	0.55 [82]	0.54 [81]	0.69 [82]	0.73 [81]	0.75 [78]
R on bpy	-	2.25/2.21	2.21/2.25	2.34/2.31		

^a The metalated ring is the substituted one.

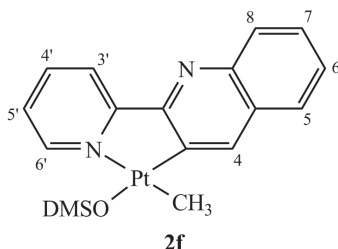
^b The metalated ring is the unsubstituted one.

group might be evident even if a 0.3 Hz is not a very big difference and could well be included in the uncertainties connected with the experiment.

1.4.4 2-(2'-pyridyl)quinoline

Cyclometalation of what could be defined as an exotic bpy derivative such as 2-(2'-pyridyl)quinoline, pyq, was also investigated in the same conditions:¹⁴⁶ the ligand was added in stoichiometric ratio to a colourless acetone- d_6 solution of *cis*- $[\text{Pt}(\text{CH}_3)_2(\text{DMSO})_2]$ yielding to a rapid colour change to dark red. The formation of the coordination compound $[\text{Pt}(\text{pyq})(\text{CH}_3)_2]$ (**1f**) was detected in solution by the presence of two coordinated methyl groups, with Pt satellites in line with N-Pt- CH_3 arrangements, at δ 1.23 ($^2J_{\text{Pt-H}} = 86.7$ Hz) and 1.16 ($^2J_{\text{Pt-H}} = 88.9$ Hz). The $\text{H}_{6'}$ proton, as expected, is slightly deshielded and coupled to ^{195}Pt (δ 8.90, $^3J_{\text{Pt-H}} = 24.4$ Hz), this evidence confirmed the coordination of the pyridine ring. Unfortunately, as in the case of $\text{bpy}^{6\text{CH}_3}$, the simultaneous presence in solution of the starting compounds, *cis*- $[\text{Pt}(\text{CH}_3)_2(\text{DMSO})_2]$ and pyq, does not allow the isolation of **1f** as a pure product. Moreover, the formation of the cyclometalated species

[Pt(pyq-H)(CH₃)(DMSO)] (**2f**) starts before all the reagents are converted to the coordination compound hampering the isolation of the intermediate.

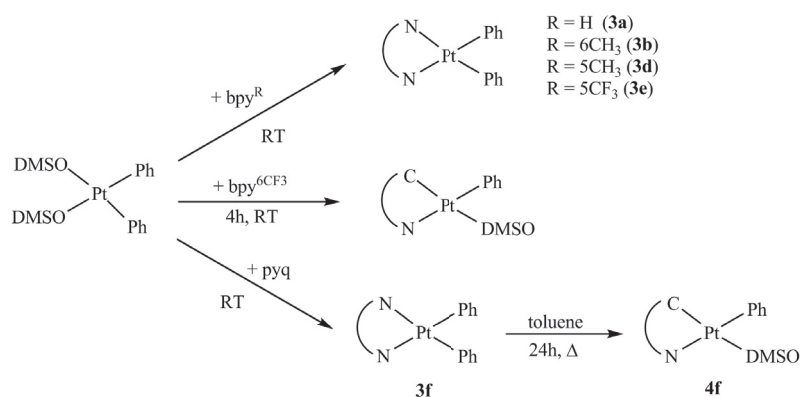


Scheme 1.8

Complex **2f** was thoroughly characterized by means of analytical and spectroscopic methods. In the absence of structural characterization, a detailed NMR study (¹H, ¹³C, 2D-COSY, NOE-1D experiments) confirmed the proposed molecular structure (Scheme 1.8). The ¹H NMR spectrum confirms metalation, showing only nine aromatic protons. In particular, the formation of the Pt-C₃ bond is demonstrated by the lack of the signal of the H₃ proton, by the signal of the H₄ proton (a singlet with satellites at 8.41 ppm, ³J_{Pt-H} = 60.4 Hz) and by the signal, in the ¹³C NMR spectrum, of the quaternary metalated C₃ (140.8 ppm, J_{Pt-C} = 1090 Hz). The coordination of the nitrogen on the pyridinic ring is confirmed by the coupling with platinum (³J_{Pt-H} = 14.2 Hz). The coordination sphere of the metal centre is completed by the methyl group and by a DMSO moiety, both showing spectroscopic data in agreement with a methyl coordinated *trans* to a pyridinic nitrogen (¹H: 0.82 ppm, ²J_{Pt-H} = 82 Hz; ¹³C: -13.1 ppm, J_{Pt-C} = 766 Hz) and a DMSO ligand in *trans* to an *sp*² carbon (¹H: 3.29 ppm, ³J_{Pt-H} = 18.3 Hz; ¹³C: 43.8 ppm, ²J_{Pt-C} = 42 Hz); an indication of the DMSO being *cis* to the N-bound edge of the cyclometalated ligand comes from the deshielding of the H₆ proton at 9.82 ppm (Δδ = +0.52 in respect to **1f** and +1.08 compared to free pyq). The geometry of the complexes was also ascertained by a series of NOE-1D NMR spectra, which show, *inter alia*, an NOE contact between the coordinated methyl group and the H₄ proton. Finally, a ¹H-¹H COSY experiment enabled to completely assign the signals.

All the reactions described up to now were investigated with a different Pt(II) precursor that in the past showed also a tendency to undergo rollover activation with bpy²³ and sub-

stituted bpys:^{21, 147} *cis*-[Pt(Ph)₂(DMSO)₂]. In general these reactions when carried on at room temperature afforded only the coordination compounds [Pt(κ^2 -N,N)(Ph)₂], where κ^2 -N,N = bpy (**3a**), bpy^{6CH₃} (**3b**), bpy^{5CH₃} (**3d**), bpy^{5CF₃} (**3e**), pyq (**3f**), without traces of formation of the metalated compound before decomposition occurs (Scheme 1.9). The only notable example is bpy^{6CF₃} that in 4 h at room temperature gave the corresponding metalated product [Pt(bpy^{6CF₃}-H)(Ph)(DMSO)] (**4c**) characterized in the ¹H NMR spectrum by a deshielded signal at 9.70 ppm (³J_{Pt-H} = 10.2 Hz) ascribable to the H_{6'} proton next to the coordinated nitrogen and spatially close to a DMSO coordinated to the metal centre by the sulphur atom (³J_{Pt-H} = 18.4 Hz).



Scheme 1.9

Upon heating, even prolonged, the situation didn't change that much for most of the ligands used and only pyq showed metalation after being refluxed for 24 h in toluene; even in this case the product [Pt(pyq-H)(Ph)(DMSO)] (**4f**) showed two characteristic signals, *i.e.* the H_{6'} (δ 9.75, ³J_{Pt-H} = 16.2 Hz) proton and the S-bound DMSO (δ 2.99, ³J_{Pt-H} = 17.5 Hz).

Another evidence of the successful cyclometalation is the fact that the DMSO can be displaced by a neutral two electron donor L, *e.g.* PCy₃, leading to a complex where the J_{Pt-P} coupling constant supports the P *trans* C arrangement (see Chapter 2).

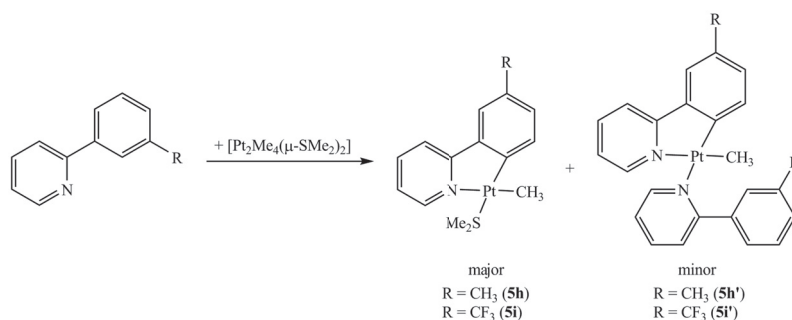
1.4.5 Substituted 2-phenylpyridines

We wanted to compare the effect of the presence/absence of a second nitrogen atom on the cyclometalation process so we used as ligands the analogous substituted 2-phenylpyridine. An acetone- d_6 solution of $[\text{Pt}_2(\text{CH}_3)_4(\mu\text{-SMe}_2)_2]$ was treated with an excess of $\text{ppy}^{3\text{CH}_3}$, 2-(3'-methylphenyl)pyridine, at $-20\text{ }^\circ\text{C}$ and no signs of reaction, not even coordination were detected up to room temperature when some new signals in the aromatic part of the spectrum started to appear, the most interesting being a doublet with satellites at δ 8.73 ($^3J_{\text{Pt-H}} \approx 15\text{ Hz}$) and another doublet with satellites at δ 7.58 ($^3J_{\text{Pt-H}} \approx 62\text{ Hz}$); along with these two a new DMS peak (δ 2.47, $^3J_{\text{Pt-H}} \approx 25\text{ Hz}$), a new singlet at δ 2.26 and a Pt- CH_3 resonance (δ 0.92, $^2J_{\text{Pt-H}} \approx 84\text{ Hz}$) substantially confirmed the formation of the complex $[\text{Pt}(\text{ppy}^{3\text{CH}_3}\text{-H})(\text{CH}_3)(\text{DMS})]$ (**5h**). After some time another couple of signals in the aliphatic region showed up at δ 2.20 and 2.21 (singlets) and 0.74 (s sat, $^3J_{\text{Pt-H}} \approx 85\text{ Hz}$) with an integral 4 times smaller, demonstrating along with the broad doublet with satellites at 9.07 ppm ($^3J_{\text{Pt-H}} \approx 19\text{ Hz}$) in the same ratio, the presence of a second Pt- CH_3 moiety and another coordinated ligand (Scheme 1.10).

The assignment of the second complex as $[\text{Pt}(\text{ppy}^{3\text{CH}_3}\text{-H})(\text{CH}_3)(\kappa^1\text{-ppy}^{3\text{CH}_3})]$ is supported by the fact that the reaction was carried out in excess of cyclometalating ligand, it is known that in this conditions formation of the *pendant* complex has to be expected.^{34, 148–153}

Keeping constant all the conditions an acetone- d_6 solution of $\text{ppy}^{3\text{CF}_3}$ was treated with $[\text{Pt}_2(\text{CH}_3)_4(\mu\text{-SMe}_2)_2]$ at $-20\text{ }^\circ\text{C}$ and both ^1H and ^{19}F NMR confirmed that no reaction took place. Nothing happened up to $0\text{ }^\circ\text{C}$ when a new singlet appeared in the ^{19}F spectrum at δ -62.2 ppm ($\Delta\delta = +0.6\text{ ppm}$ in respect to the free ligand), moreover in the ^1H spectrum the singlet due to CH_4 (0.16 ppm)⁴⁸ was present and the signals of the starting material decreased in intensity. Warming up the sample to room temperature speeds up the reaction and also in the aromatic region of the ^1H NMR some signals start to appear at 9.10 and 9.01 ppm (probably two H_C) suggesting the presence of two coordinated $\text{ppy}^{3\text{CF}_3}$ plus something else in the aromatic region. New singlets with satellites are visible at δ 2.50 ($^3J_{\text{Pt-H}} \approx 26\text{ Hz}$), at δ 0.76 ($^2J_{\text{Pt-H}} \approx 86\text{ Hz}$) and δ 0.99 ($^2J_{\text{Pt-H}} \approx 84\text{ Hz}$). Signal at 2.50 ppm is twice the one at 0.76 in a suitable ratio for a DMS-Pt- CH_3 fragment; the ratio between the signals at 0.76 and 0.99 ppm is close to 1:2 and agrees with that calculated

for the signals at -62.3 and -62.4 ppm in the ^{19}F NMR spectrum. In the aromatic region are clearly visible two sets of signals (sometimes overlapping) that a ^1H - ^1H COSY helped to separate: those belonging to the major species are 9.01 (d sat), 8.44 (s), 8.21 (d), 8.12 (td) while for the minor species are 9.10 (d sat), 8.54 (s), 8.26 (td), 7.63, 7.27, 7.19 (dd sat). Even in this case the species detected in solution are in agreement with a mixture of cyclometalated DMS and pendant complexes (Scheme 1.10).



Scheme 1.10

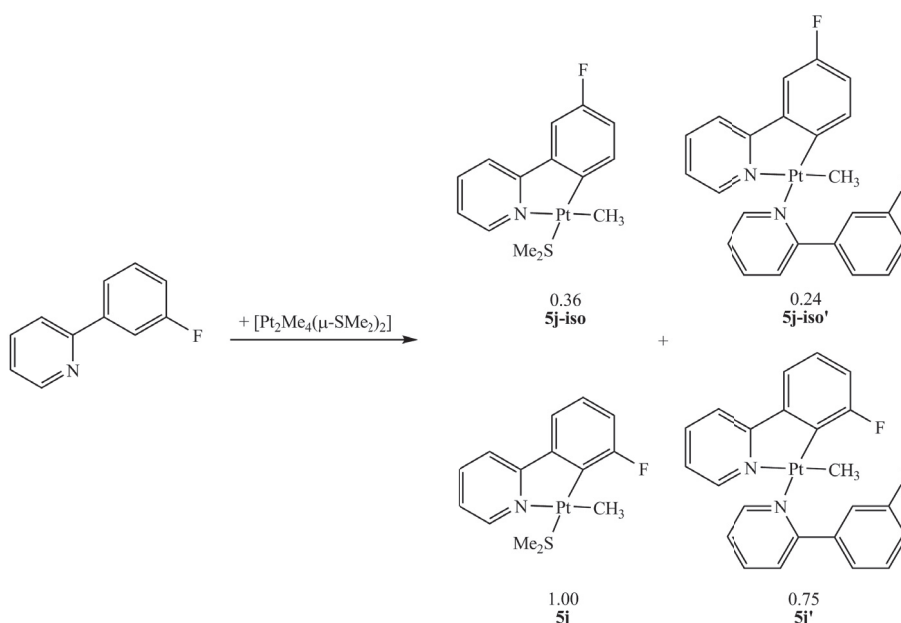
Treatment of an acetone- d_6 solution of $[\text{Pt}_2(\text{CH}_3)_4(\mu\text{-SMe}_2)_2]$ with excess of $\text{ppy}^{3\text{F}}$ at -40°C didn't lead to fast cyclometalation and the ^1H NMR is just the sum of the spectra of the two reagents, the ^{19}F NMR also confirms that there are no signs of any kind of reactivity. The situation did not change up to 0°C where evolution of methane became visible together with a singlet with satellites due to a DMS coordinated on Pt (δ 2.44, $^3J_{\text{Pt-H}} \approx 26$ Hz) and with a coordinated methyl (δ 1.23, $^2J_{\text{Pt-H}} \approx 82$ Hz). The fluorine NMR spectrum shows five resonances that can be divided into three groups depending on the region in which they appear: around -95, -114 and -123 ppm. The most intense signal is the one of the free ligand at -114.5 ppm then, in order of decreasing intensity, there are the two at -94.9 and -96.0 ppm (1:0.3 ratio) and finally those at -122.5 and -124.6 ppm (0.18:0.07 ratio). Among all these signals only the one at -94.9 shows satellites ($^3J_{\text{Pt-F}} \approx 128$ Hz) and it is easily assigned to the fluorine of a $\text{ppy}^{3\text{F}}$ that has cyclometalated in position 2' (complex **5j** Scheme 1.11) from the high value of the coupling constant.

Warming the sample to room temperature led to another change in the aspect of the NMR spectra. Now all the four fluorine singlet resonances show satellites and their ratio corresponds roughly to that of four singlets with satellites in the Pt-CH_3 region of the ^1H NMR,

the picture is completed by two singlets with satellites ascribable to two DMS at 2.44 and 2.48 ppm (see Table 1.6).

Table 1.6: ^{19}F and ^1H NMR resonances for the follow-up of the cyclometalation of $\text{ppy}^{3\text{F}}$. ^{195}Pt coupling constants are given in Hz in brackets.

ratio	5j	5j'	5j-iso	5j-iso'
Pt-CH ₃	1.25 [82.4]	1.04 [82.4]	0.93 [84]	0.72 [86]
^{19}F	-94.9 [129.6]	-96.0 [149.9]	-122.75 [13.6]	-124.8 [11.0]



Scheme 1.11

The reactivity of 2-(4-fluorophenyl)pyridine, $\text{ppy}^{4\text{F}}$, towards the cyclometalation with $[\text{Pt}_2(\text{CH}_3)_4(\mu\text{-SMe}_2)_2]$ was tested by mixing the reagents at $-40\text{ }^\circ\text{C}$ in an acetone- d_6 solution, even in this case no reaction was visible up to $0\text{ }^\circ\text{C}$ when in the ^{19}F NMR four new signals (-113.3 , -113.6 , -113.7 and -113.9 ppm) became visible with only one clearly showing satellites (-113.3 ppm, $^4J_{\text{Pt-F}} \approx 78$ Hz) probably also because it is the most intense peak. After some time at $0\text{ }^\circ\text{C}$ also the signal at -113.9 ppm showed satellites ($^4J_{\text{Pt-F}} \approx 82$ Hz) and the ratio between the new resonances in the ^{19}F changed with the one at -113.7

ppm becoming less intense. Correspondingly in the ^1H NMR two new singlets with satellites became visible: δ 2.47 ($^3J_{\text{Pt-H}} \approx 27$ Hz) and δ 0.89 ($^2J_{\text{Pt-H}} \approx 84$) that can be assigned to a DMS and to a methyl coordinated to the same metal centre taking in account the 2 to 1 ratio between them.

The sample was warmed up to room temperature and let to react for one day, after this time the aliphatic region of the ^1H NMR showed a new singlet with satellites at δ 0.69 ($^2J_{\text{Pt-H}} \approx 85$) along with the other two that were already present; a doublet of doublets with satellites was clearly detected at 7.40 ppm ascertaining the cyclometalation; moreover, two sets of aromatic signals in the same ratio of the two methyl signals at 0.69 and 0.9 ppm indicated the presence of two Pt-containing species in solution. A ^{195}Pt - ^1H HMQC experiment allowed the distinction between the two species with the assignment of the signals that correlate with platinum. In detail two platinum signals were detected at -3970 and -3507 ppm with the former correlating with signals at 8.95, 7.40, 2.49 and 0.90 while the latter correlates with signals at 9.07, 7.27 and 0.69. The difference in ^{195}Pt chemical shift is closely related to the electron density on the metal centre and it is in line with the donor characteristics of the two neutral ligands, *i.e.* DMS and $\text{ppy}^{4\text{F}}$.

Using the similar *cis*- $[\text{Pt}(\text{CH}_3)_2(\text{DMSO})_2]$ as a platinum source the situation does not change very much and the cyclometalated products are the same without notable exceptions.

The reaction of $\text{ppy}^{4\text{F}}$ with *cis*- $[\text{Pt}(\text{Ph})_2(\text{L})_2]$, with $\text{L} = \text{DMSO}$ or DMS , was also monitored by ^1H and ^{19}F NMR spectroscopy and showed in both cases the formation of the cyclometalated product $[\text{Pt}(\text{ppy}^{4\text{F}}\text{-H})(\text{Ph})(\text{L})]$. Diagnostic signals in the ^1H NMR spectrum are those relative to the H_6 , that resonates at δ 8.84 (CDCl_3 , $^3J_{\text{Pt-H}} \approx 14$ Hz) when $\text{L} = \text{DMS}$ and at δ 9.55 ($\text{acetone-}d_6$, $^3J_{\text{Pt-H}} = 12$ Hz) with $\text{L} = \text{DMSO}$; the H_3 , appears very shielded due to the presence of the phenyl ring and its $^3J_{\text{Pt-H}}$ is around 80 Hz in both cases being larger for the DMS derivative; finally methyls on sulphur show a larger coupling constant in the case of dimethylsulphide. The general observation that $[\text{Pt}(\text{ppy}^{4\text{F}}\text{-H})(\text{Ph})(\text{DMS})]$ (**6k**) shows larger coupling constants is visible even in the ^{19}F NMR where $^4J_{\text{Pt-F}}$ are 72.7 and 69.7 Hz for DMS and DMSO complexes, respectively.

The formation of the cyclometalated product in the case of $[\text{Pt}(\text{ppy}^{4\text{F}}\text{-H})(\text{Ph})(\text{DMSO})]$ (**4k**) was also confirmed by X-ray diffraction analysis with crystals grown from an acetone

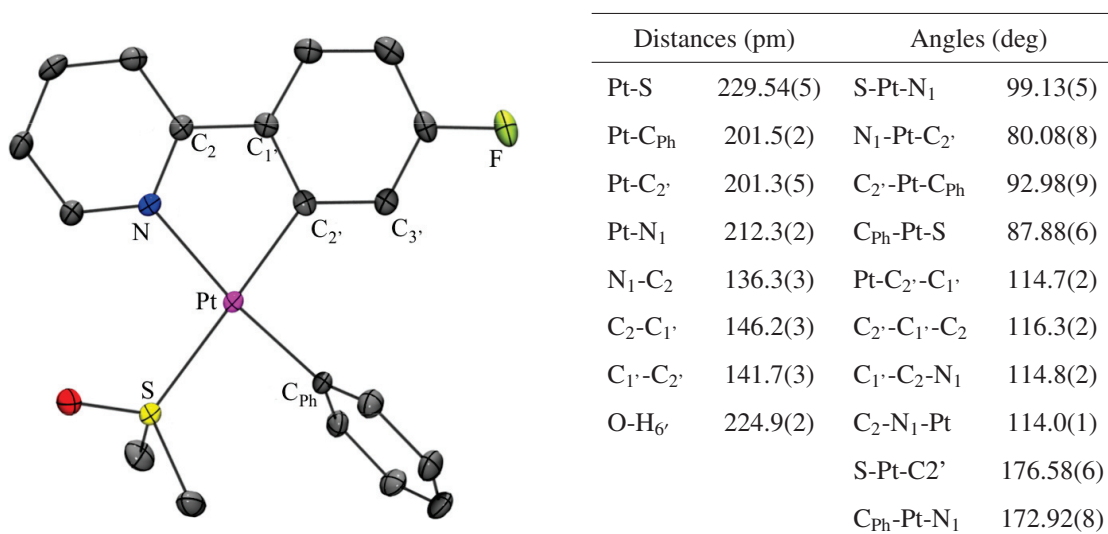


Figure 1.8: ORTEP for **4k**. Ellipsoids drawn at 50% probability level and hydrogens removed for clarity.

solution (Figure 1.8). The complex crystallizes in the $C2/c$ space group and the asymmetric unit contains a platinum complex with a metalated 2-(4-fluorophenyl)-pyridine, a phenyl and a DMSO. The geometry around the metal centre is square planar (maximum deviation 0.051 Å for C_{Ph}) with a minimal tetrahedral distortion as can be seen from the angle between the best planes through C_{2'}-Pt-N₁ and S-Pt-C_{Ph} that measures 3.7°. The same value is observed for the angle between the coordination plane and the ligand plane (all 13 non-hydrogen atoms) showing that they don't lie on the same plane, it is interesting to note a kind of butterfly bending visible for the two rings of the ligand: the angle between the two best planes is 7.3°.

A possible π stacking between the ppy^{4F} units is present even if they are not parallel (13.3° between the ligand mean planes) and the closest contact is between C₅ and C_{5'} of another ppy^{4F} measuring 3.2501(46) Å; the two units are rotated one in respect to the other. Finally the phenyl ring is almost perpendicular to the coordination plane with an angle of 76.9°.

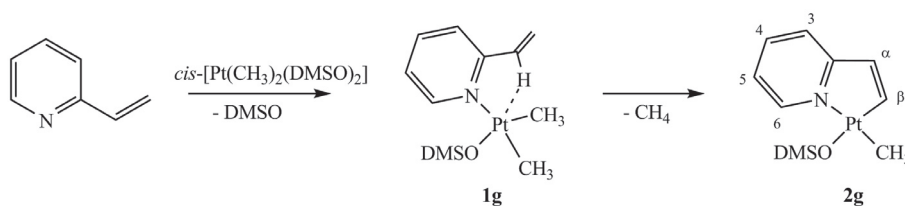
Selected bond distances and angles are collected in the inset of Figure 1.8. The slightly distorted square planar coordination around the metal centre is highlighted by the angle between the donor groups located in *trans* position, sulphur-C_{2'} and N₁-C_{Ph}, which are both close to 180°. The sum of the internal angles of the metallacycle is 539.9° in perfect

agreement with the theoretical value of 540° for a regular polygon showing that the angular strain doesn't play a significant role in destabilizing the structure probably because it is compensated to a certain extent by the distortion in the bond distances.

1.4.6 2-vinylpyridine

Modification of the extension of the delocalized cyclometalated system was the aim behind the use of the 2-vinylpyridine (vpy) ligand as substrate for C-H activation, in this context the straightforward comparison is with the 2-phenylpyridines just discussed.

Following the same scheme we first reacted vpy with the electronrich *cis*-[Pt(CH₃)₂(DMSO)₂] in excess of ligand in acetone-*d*₆ solution at room temperature monitoring eventual changes by ¹H NMR spectroscopy. The colourless solution of starting Pt complex readily reacts with vpy as demonstrated by the yellow colour presumably forming a coordination compound arising from the displacement of one (or possibly two) DMSO molecules from the metal centre. Indeed the ¹H NMR spectrum confirms that no C-H activation took place and that the main species is the complex *cis*-[Pt(vpy)(CH₃)₂(DMSO)] (**1g**). Coordination of the vpy moiety is confirmed by the signal of the H₆ at δ 8.84 that shows ¹⁹⁵Pt satellites of ca. 18 Hz in agreement with a N-Pt-C *trans* arrangement. The two methyls on platinum are different due to the asymmetry of the complex and resonate at 0.33 and 0.47 ppm with ²J_{Pt-H} of 79.1 and 88.4 Hz, judging from the coupling constants and from the chemical shift the first signal is relative to the CH₃ *trans* to the DMSO while the second is *trans* to the nitrogen; DMSO methyls give a singlet with satellites at 2.79 ppm (³J_{Pt-H} = 14.5 Hz). An interesting feature of this complex is the strongly deshielded signal ($\Delta\delta = +1.59$) ascribable to the vinylic CH which also shows satellites (J_{Pt-H} = 39 Hz), this observation can be interpreted as an evidence of an *anagostic* interaction between the vinyl and the metal centre.¹⁵⁴



The reaction was also repeated in acetone at 40 °C for 4 h and yielded to the same product suggesting that the activation of the vinylic C-H bond is harder to achieve than in the 2-phenylpyridines.

Looking at the bond dissociation energies and radical formation data it is possible to find that it is slightly easier to break a C-H bond in ethylene rather than in benzene, 464 vs 473 kJ·mol⁻¹.^{155,156} These data seems to be in contradiction with the experimental findings, *i.e.* we found easier to cleave the C-H in ppy rather than in vpy, but if we think that the most probable mechanism of the cyclometalation is electrophilic the data have perfectly sense: it is well known that aromatic hydrocarbons, in contrast to alkenes, prefer substitution over addition.

Formation of the cyclometalated compound was fruitful changing the conditions to toluene and heating to 80 °C using a 2:1 ligand:Pt ratio. The complex [Pt(vpy-H)(CH₃)(DMSO)] (**2g**) is very soluble in the common organic solvents and was almost completely found in the mother liquor after treatment of the concentrated reaction mixture with Et₂O and filtration of the precipitate.

The complex was characterized by ¹H and ¹³C NMR means showing signals in agreement with the proposed formulation. A broad doublet for the H₆ proton showing satellites (δ 9.24, ³J_{Pt-H} = 11.4 Hz) confirms that the pyridinic nitrogen is coordinated to the metal in *cis* position to a DMSO while the presence of six aromatic signals gives a compelling evidence of the achieved C-H activation. Further confirmation is given by the presence of only one Pt-CH₃ group characterized by a singlet with satellites at δ 0.69 (²J_{Pt-H} = 82.5 Hz) located in *trans* to the low *trans*-influencing nitrogen.

Activation occurred at the CH₂ end of the vinylic system as confirmed by the presence of two doublets forming an AX system for the remaining protons. This spin system has noteworthy characteristics: first of all the chemical shift associated with the H_β proton (*i.e.* the one closest to the metal) is almost 2 ppm deshielded in respect to the free ligand (7.42 vs 5.47, Δδ = +1.95) and, secondly, ¹⁹⁵Pt coupling constants for both protons are very high ²J_{Pt-H} = 171 Hz for H_β and ³J_{Pt-H} = 108 Hz for H_α.

Proton deshielding and high values of Pt couplings, in particular that for H_α, let us think to a partially delocalized cyclometalated system invoking possible metalloaromatic character for the platinacycle where the ring current has a deshielding effect on the protons

lying in the plane.^{157–160}

A survey of the literature looking for similar systems showed that no examples of vpy cyclometalated on a Pt-CH₃ fragment, nor Pt(II) nor Pt(IV), are currently present^f therefore the analysis was made with the benzylimines which have comparable donor atoms. Among the plethora of examples present we restricted our interest to those having a N-Pt-CH₃ and C-Pt-S-donor *trans* arrangement and found the following results regarding the coupling constant of the iminic proton, *i.e.* the one similar to our H_α: (a) unsubstituted benzylimines show a ³J_{Pt-H} of ca. 53 Hz;^{161,162} (b) halogenated benzylimines have a slightly larger coupling of ca. 55 Hz with no obvious difference between chloro,^{163,164} fluoro¹⁶⁵ and trifluoromethyl¹⁶⁶ substituent but depending on the number of halogen atoms present on the phenyl ring;¹⁶⁷ (c) changing the phenyl ring for a thienyl one doesn't seem to affect the coupling constant that stays around 55 Hz;^{168,169} (d) C,N,N terdentate systems (not having the sulphur donor) have a ³J_{Pt-H} approximately of 60 Hz, relatively insensitive to the substitution pattern.^{170–172}

On the whole however, it must be kept in mind that the group *trans* to the imine is not a relatively low *trans*-influencing DMSO but the strong CH₃ that certainly has the effect of diminishing the coupling.

The observed metalation could be explained both with statistical and thermodynamic reasons. If we neglect the possibility of having an N-bound vpy and an activated one on the same metal centre, as evident from the ¹H NMR, the only possibilities for C-H activation affording a cyclometalated species are those on the vinylic substituent; in this respect the two protons on the CH₂ are statistically favoured to undergo activation rather than the single CH. We do not observe any metalation on the carbon atom directly attached to the pyridinic ring because it would give a thermodynamically less stable four-membered ring in respect to the five-membered one resulting from the activation of the vinylic CH₂. The combination of these two factors nicely explains the observed results.

In conclusion an NOE-1d experiment confirmed the proposed geometry: irradiation of the singlet of the Pt-CH₃ at δ 0.69 produces an enhancement of the signals at δ 3.07 (coordinated DMSO) and at 7.42 ppm (H_β), this observation confirms that the last two are in *cis* position relative to the methyl group and that the pyridinic nitrogen must be in *trans*.

^fReaxys, version 2.15859.10; Elsevier Information Systems GmbH. End of October 2013.

In Table 1.7 some selected ^{13}C NMR resonances relative to complexes having general formula $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{DMSO})]$, where $\kappa^2\text{-N,C}$ is a cyclometalated moiety, are collected and some comments can be made.

The resonance relative to the DMSO methyls doesn't seem to be affected very much as its coupling constant with ^{195}Pt is always around 41 Hz, even if the compound having the cyclometalated ppy displays a lower value. Similarity of these values is somewhat remarkable taking into account the differences in the metalated carbon group located in *trans* that is either a vinyl, a phenyl, a pyridyl derivative or a quinolyl.

Looking at the $J_{\text{Pt-C}}$ of the carbons directly bound to the metal can give information that should be more easily correlated with the nature of the bond, there is in fact a trend in agreement with the electronic nature of the metalated group. Taken into account the difference between a vinylic carbon and a phenyl/pyridyl one it is not unexpected that vinylpyridine shows a value that seems an outlier. A comparison of the other groups shows that the coupling constant increases in the order $\text{ppy} < \text{bpy} \approx \text{pyq} < \text{bpy}^{6\text{CF}_3}$ that reproduces the electron-richness and the electron-withdrawing tendencies of the respective groups.

Perhaps the most interesting comparison can be made considering the resonance of the methyl group because, in each case, it is relative to a methyl that has a substituted pyridine in *trans* therefore we don't have issues due to the angle influence on the coupling constant as with DMSO or due to the nature of the metalated carbon. Worthy of note the chemical shift is practically constant (around -13 ppm) with vpy showing a more shielded resonance at ca. -20 ppm; on the other hand coupling constants show a slight variation that could be indicative of a sort of *cis*-effect due to the metalated group even if no clear trends were detected.

Having in hand the results obtained with the *cis*- $[\text{Pt}(\text{CH}_3)_2(\text{DMSO})_2]$ we switched our attention to the phenyl analogue to check whether it had a different behaviour or not. Heating to 80 °C a toluene solution of *cis*- $[\text{Pt}(\text{Ph})_2(\text{DMSO})_2]$ with excess of vpy led to the cyclometalated compound $[\text{Pt}(\text{vpy-H})(\text{Ph})(\text{DMSO})]$ (**4g**), that was obtained as a yellow solid rather than as an orangish oil like $[\text{Pt}(\text{vpy-H})(\text{CH}_3)(\text{DMSO})]$. According to the *trans*-phobia and *trans*-influence ideas and in analogy with the methylated compound we

Table 1.7: Selected CDCl_3 ^{13}C NMR chemical shifts (ppm) and ^{195}Pt coupling constants (Hz, in brackets) of the $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{DMSO})]$ complexes where $\kappa^2\text{-N,C}$ indicates a cyclometalated moiety.

Ligand	C_3	DMSO	Pt- CH_3
vpy	163.2 [1035]	43.5 [40]	-19.9 [756]
ppy ¹³⁷	150.4 [1063]	43.3 [35]	-12.4 [776]
bpy	145.1 [1090]	43.7 [42]	-13.4 [760]
bpy ^{6CF₃}	149.5 [1100]	43.8 [43]	-13.4 [761]
pyq	140.8 [1090]	43.8 [42]	-13.1 [766]

propose a geometry where the phenyl group is coordinated *trans* to the pyridinic nitrogen and the DMSO to the metalated vinylic carbon.

Our suggestion is corroborated by the ^1H NMR spectrum where we see a singlet with satellites at δ 2.89 ($^3J_{\text{Pt-H}} = 16$ Hz) suggesting an S-bound DMSO *trans* to a group with high *trans*-influence, this is also in agreement with the deshielded signal of the H_6 proton, *i.e.* the one next to the nitrogen, which is a broad doublet with satellites at δ 9.28 ($^3J_{\text{Pt-H}} = 13$ Hz). Due to the substitution of the methyl for a phenyl the aromatic region becomes more crowded but no dramatic shifts are noted for the vpy protons, *e.g.* H_β resonates at δ 7.38 ($^2J_{\text{Pt-H}}$ ca. 162 Hz) while H_α can be found at 6.90 ppm ($^3J_{\text{Pt-H}} = 118$ Hz, $^3J_{\text{H-H}}$ ca. 8 Hz).

1.5 DFT calculations

1.5.1 $[\text{Pt}(\kappa^2\text{-N,N})(\text{CH}_3)_2]$ species

Density Functional Theory (DFT) calculations were performed on the complexes having general formula $[\text{Pt}(\kappa^2\text{-N,N})(\text{CH}_3)_2]$, where $\kappa^2\text{-N,N}$ indicates a bpy derivative, in order to have some clues about the reactivity they displayed (see Section 1.4). All the coordination compounds investigated were characterized experimentally by NMR spectroscopy apart from $[\text{Pt}(\text{bpy}^{6\text{CF}_3})(\text{CH}_3)_2]$ but its structure was included in the comparison for completeness. Geometrical parameters resulting from the optimizations are collected in Table 1.8. A search in the Cambridge Crystallographic Data Centre (CCDC)¹⁷³ for $[\text{Pt}(\kappa^2\text{-N,N})-$

(CH₃)₂] structures gave only 7 results relative to only six different compounds because [Pt(bpy)(CH₃)₂] appears twice;^{174,175} among the five remaining hits only two are relative unsymmetrically substituted bpys, *i.e.* [Pt(bpy^{6NH₂})(CH₃)₂] and [Pt(bpy^{4BPh₃})(CH₃)₂].^{176,177} In general all the structures display a remarkable symmetry between the two halves, the mirror plane being the one through Pt and the midpoint of the C-C bond between the pyridyl rings perpendicular to the coordination plane.

Table 1.8: Bond distances (pm) and angles (deg) for the optimized complexes of general formula [Pt(κ^2 -N,N)(CH₃)₂]. Geometries obtained at PBE0/def2-SVP level using ZORA formalism with RI-J approximation.

		bpy	bpy ^{5CF₃}	bpy ^{5CH₃}	bpy ^{6CF₃}	bpy ^{6CH₃}	pyq
Distances	Pt-N ₁	209.8	209.5	210.1	217.3	217.1	214.8
	Pt-N ₁ ′	211.0	210.2	210.1	208.0	209.2	209.1
	Pt-CH ₃ ^a	203.3	203.0	203.1	202.4	202.7	202.9
	Pt-CH ₃	203.0	203.0	203.1	203.4	203.8	203.7
	N ₁ -C ₂	135.2	135.3	135.1	135.8	135.6	133.6
	C ₂ -C ₂ ′	147.3	147.3	147.3	147.6	147.6	147.3
	C ₂ ′-N	135.3	135.3	135.3	135.1	135.1	135.3
Angles	CH ₃ ^a -Pt-N ₁ ′	100.1	96.5	96.3	94.6	94.5	95.1
	N ₁ ′-Pt-N ₁	77.6	77.8	77.9	77.3	77.2	77.1
	N ₁ -Pt-CH ₃	96.1	96.2	96.3	102.1	102.4	101.9
	CH ₃ -Pt-CH ₃ ^a	86.3	89.6	89.5	85.5	85.9	85.7
	CH ₃ ^a -Pt-N ₁	177.6	174.2	174.1	171.8	171.7	172.2
	CH ₃ ′-Pt-N ₁ ′	173.7	174.0	174.2	169.8	171.0	169.9

^a Methyl group *trans* to N of the substituted ring.

Comparison of the structures relative to [Pt(bpy)(CH₃)₂] with the one obtained by DFT calculations highlights the goodness of the chosen model: mean absolute error (MAE) lies in the intervals 0.8 ÷ 1.6 and 1.4 ÷ 1.7 for bonds (in pm) and angles (in degrees) respectively.^g

Looking at the bond distances there are no trends or big differences worthy of note, with

^gThe evaluated bonds are those involving the metal centre and those of the chelate ring while only the angles involving Pt as central atom were used in the comparison.

the obvious exception of Pt-N bonds in 6-substituted bipyridines all the others do not show variations bigger than 2 pm. If there aren't sterical constraints, *i.e.* if the substituent is not in position 6, all the complexes display a coplanar geometry for the heteroaromatic ligand and the coordination plane and the bond distances involving platinum centre are not very much affected. In every case the metallacycles display bonds in agreement with an α,α' -diimine with short C-N bonds and a longer C-C bond connecting the two pyridyl rings. The same reasoning holds for the angles which do not display peculiarities; the bite angle of all the ligands is around 77.5°.

When the methyl or the trifluoromethyl are located in position 6 the effect on the geometry is more pronounced and affects mainly the Pt-N bonds. The nitrogen next to the substituent displays a longer bond with Pt while the other is only slightly shorter, this fact is explainable looking at the variations of the N₁-C₂, C₂-C_{2'} and C₂'-N_{1'} bonds that arrange themselves in order to minimize the destabilization brought by the steric hindrance. Worthy of note is the angle between the best plane calculated for the all 13 non-hydrogen atoms of the substituted bpy and the one calculated for the Pt(CH₃)₂ fragment (3 non-hydrogen atoms) which is 33.5° and 25.2° for bpy^{6CF₃} and bpy^{6CH₃}, respectively. Another distortion is observed in the ligand: the two pyridyl rings are not coplanar and are bent in a "butterfly-like" fashion, the angle between the best planes calculated for the two pyridyl rings (6 non-hydrogen atoms) is again larger for the trifluoromethylated ligand, 12.4° vs 9.7°.

The optimized complexes were also analysed using the Atoms in Molecules (AIM) theory developed by Bader¹⁷⁸ to investigate the nature of the involved bonds, selected results for [Pt(bpy)(CH₃)₂] (**1a**) are visible in Table 1.9 and an extensive table can be found in the Experimental Section.

First of all it is possible to distinguish the type of interaction between atom pairs by looking at the values of the electron density $\rho(\mathbf{r})$ and of the Laplacian $\nabla^2\rho(\mathbf{r})$ at the bond critical point $\rho(\mathbf{r}) = \rho(\mathbf{r}_c)$. All the bonds display electron density at the bond critical point (BCP) although to a different extent, this gives a clear idea about the strength of the interaction. The sign of $\nabla^2\rho(\mathbf{r})$ is discriminant to assess if the interaction is *closed* or *shared*. In Figure 1.9 the $\nabla^2\rho(\mathbf{r})$ projections on the coordination plane are depicted along with

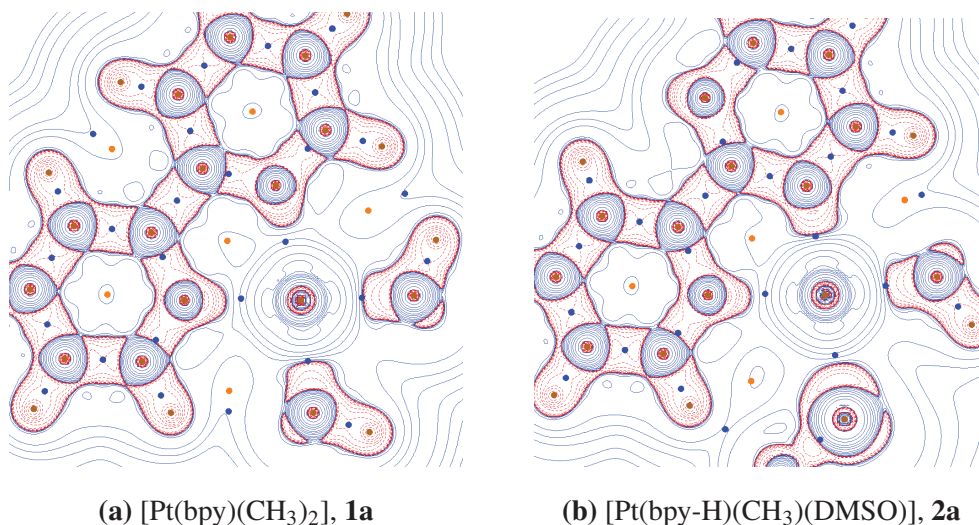


Figure 1.9: Projection on the coordination plane of $\nabla^2\rho(\mathbf{r})$ relative to the bpy adduct (left) and cyclometalated complex (right). Positive and negative values are indicated in blue and red respectively. Blue dots indicate bond critical points (BCP), orange dots ring critical points (RCP).

the critical points found with the Bader analysis for the adduct and for the corresponding cyclometalated complex with bpy. Blue contours are relative to positive values of $\nabla^2\rho(\mathbf{r})$ thus indicating charge depletion; conversely red ones indicate charge accumulation.

An inspection of the reported values suggests that the bonds in the bpy ligand are characterized as *shared* interactions because they display $\nabla^2\rho(\mathbf{r}) < 0$ and a quite large value of $\rho(\mathbf{r})$ at BCP; moreover, the degree of covalency Γ_{cov} supports the covalency of the bonds in the bpy scaffold.

Looking at the interactions with the metal it appears that they are of *closed* type, implying thus a situation where the donor atom doesn't share its valence electron upon bonding. However the Pt-N and Pt-C interactions are slightly different, in fact despite being both of *closed* type in nature they have different values of $\nabla^2\rho(\mathbf{r})$ which is closer to zero for the Pt-C interaction suggesting a more *intermediate* character. The situation, along with Γ_{cov} values, is also in agreement with the electronegativity of the donor groups: the more electronegative nitrogen shows a smaller degree of covalency and also a lesser ellipticity value, ϵ . The ellipticity measures the distortion of the electron density in the plane perpendicular to the bond path and therefore is an indicator of the π character of a bond.^{179–181}

As expected taking into account the close similarity between the N-bound pyridine and the

methyl *trans* to it in each $[\text{Pt}(\kappa^2\text{-N,N})(\text{CH}_3)_2]$ complex, the AIM analysis correctly gives similar values for the electronic density at the BCP for the Pt-N bond ($\approx 0.10 \text{ e}\cdot\text{bohr}^{-3}$) and for the Pt-C bond *trans* to it ($\approx 0.15 \text{ e}\cdot\text{bohr}^{-3}$).

On the whole no particular observations or trends clearly emerge from the analysis, the only differences worthy of note are those involved with the bpy having the substituent in position 6; these differences are not dramatic and probably not unexpected considering the geometrical distortion of the complex.

Table 1.9: Atom In Molecules (AIM) analysis for complex **1a**. Geometries obtained at PBE0/def2-SVP level using ZORA formalism with RI-J approximation.

	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	$G(\mathbf{r})$	ε	$\frac{\lambda_1}{\lambda_3}$	$\frac{G(\mathbf{r})}{\rho(\mathbf{r})}$	Γ_{cov}
Pt-N ₁	0.10396	0.45775	0.14472	0.03616	0.15366	1.39205	23.2
Pt-N _{1'}	0.10150	0.43658	0.13816	0.08830	0.16262	1.36124	23.8
Pt-CH ₃ ^a	0.14862	0.04727	0.09881	0.06384	0.45330	0.66485	46.8
Pt-CH ₃	0.14941	0.04865	0.09977	0.05561	0.45071	0.66774	46.7
N ₂ -C ₇	0.33040	-0.97522	0.28936	0.12404	1.87676	0.87580	78.0
C ₇ -C ₈	0.27333	-0.67744	0.06380	0.13052	1.56114	0.23342	74.6
C ₈ -N ₉	0.32973	-0.98001	0.28499	0.12319	1.91421	0.86433	78.3

^a Methyl *trans* to N₁.

Energy Decomposition Analysis (EDA) according to Su and Li partitioning scheme¹⁸² was performed on the equilibrium geometries and the results are summarized in Table 1.10, between the reported quantities and the total interaction energy ΔE^{KS} holds the relationship

$$\Delta E^{\text{KS}} = \Delta E^{\text{ele}} + \Delta E^{\text{ex}} + \Delta E^{\text{rep}} + \Delta E^{\text{pol}} + \Delta E^{\text{disp}} \quad (1.1)$$

where the single contributions have the following meaning: ΔE^{ele} is the electrostatic interaction between the occupied molecular orbitals (MOs) of the fragments that does not involve electron exchange; ΔE^{ex} quantifies the interaction between occupied and unoccupied MOs in the different fragments; ΔE^{rep} indicates the repulsive interactions which are connected to the exchange of electrons; ΔE^{pol} accounts for the interaction that causes the mixing of occupied and vacant MOs on the same fragment and, finally, ΔE^{disp} collects all

the dispersive interactions.^h

An inspection of the contributes to the overall interaction energy shows that they are all of the same order and they seem to be related to the nature and the position of the substituent. Electrostatic interaction, ΔE^{ele} , is attractive and around the value of $450 \text{ kJ}\cdot\text{mol}^{-1}$ being larger in absolute value (even if only less than $5 \text{ kJ}\cdot\text{mol}^{-1}$) for the 5-substituted bpy and smaller for the corresponding 6-substituted when compared to bpy.

In general the interaction of $\text{bpy}^{5\text{CF}_3}$ and $\text{bpy}^{5\text{CH}_3}$ with the $\text{Pt}(\text{CH}_3)_2$ fragment is comparable with that of bpy and is influenced only to a small extent by the electronic nature of the group attached in position 5. On the other hand, $\text{bpy}^{6\text{CF}_3}$ and $\text{bpy}^{6\text{CH}_3}$ have a smaller interaction energy that is in fair agreement with the experimental finding that they give cyclometalation more easily than bpy. It is also interesting to note that the $\text{bpy}^{6\text{CF}_3}$ shows the lowest interaction energy with the dialkylmetal fragment having a $\Delta E^{\text{KS}} = -214.2 \text{ kJ}\cdot\text{mol}^{-1}$.

Table 1.10: LMO Energy Decomposition Analysis (EDA) for the optimized complexes of general formula $[\text{Pt}(\kappa^2\text{-N,N})(\text{CH}_3)_2]$. Geometries obtained at PBE0/def2-SVP level using ZORA formalism with RI-J approximation. Fragments are the bpy ligand and the $\text{Pt}(\text{CH}_3)_2$ moiety. Values in $\text{kJ}\cdot\text{mol}^{-1}$.

	bpy	$\text{bpy}^{5\text{CF}_3}$	$\text{bpy}^{5\text{CH}_3}$	$\text{bpy}^{6\text{CF}_3}$	$\text{bpy}^{6\text{CH}_3}$	pyq
ΔE^{ele}	-458.54	-462.80	-465.32	-440.19	-446.93	-460.15
ΔE^{ex}	-400.71	-405.57	-405.20	-390.91	-392.09	-406.50
ΔE^{rep}	1178.05	1199.05	1193.25	1159.36	1147.57	1193.41
ΔE^{pol}	-455.81	-459.97	-460.67	-425.53	-428.48	-445.37
ΔE^{disp}	-115.37	-115.35	-115.59	-116.95	-118.03	-120.81
ΔE^{KS}	-252.38	-244.63	-253.53	-214.21	-237.96	-239.42

1.5.2 Cyclometalated species

Products of the cyclometalation of the bpy ligands with *cis*- $[\text{Pt}(\text{CH}_3)_2(\text{DMSO})_2]$, namely $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{DMSO})]$, were also analyzed by the same DFT methods used in subsection 1.5.1. Bond distances and angles are compared in Table 1.11 and, as expected

^hIn some papers ΔE^{ex} and ΔE^{rep} are summed together and identified as Pauli interaction, ΔE^{Pauli} ; on the other hand ΔE^{pol} and ΔE^{dis} are sometimes reported as orbital interaction ΔE^{orb} .

from the experimental results, the nature of the substituent doesn't seem to affect that much the geometry of the complex. The most notable differences are visible when comparing bpy derivatives with vpy, in particular the C₂-C₃ bond, *i.e.* the vinyl, is very short in [Pt(vpy-H)(CH₃)(DMSO)] (**2g**) suggesting that electron delocalization is not playing a substantial role in the metallacycle. However care must be taken in drawing conclusion by comparing different systems, in fact we have vinylic *vs* aromatic carbon atoms involved thus their nature is very different right from the beginning.

All the complexes display a planar structure with the coordination plane including the cyclometalated ligand, *i.e.* coplanarity is observed. In all cases a possible hydrogen bond is detected between the oxygen of the DMSO and the proton next to nitrogen in the N-bound pyridyl, this interaction is in good agreement with the experimental observation that the chemical shift of the H₆ is always very deshielded.

Information on the electron delocalization in the platinacycle can be extracted from the analysis of the C₂-C_{2'} bond distances that can be compared with the same in the adduct (Table 1.8). At first glance it is evident that there is a very slight shortening of the inter-ring bond but its small extent, less than 1 pm, is definitely not meaningful. Moreover, comparison of the C₂-C_{2'} and C₂-C₃ bonds in Table 1.11 indicates a situation of localized single and double bonds respectively.¹⁸³

Another approach that can give insights into the possible electron delocalization (connected with partial aromatic) in the metallacycle is the one proposed by Schleyer *et al.*^{185,186} called Nucleus Independent Chemical Shift (NICS). According to this procedure the chemical shift of a ghost atom is evaluated at the geometrical centre of the interested system and the obtained value is taken with the opposite sign. In order to avoid possible spurious contributions (σ -bond current, etc.) to the calculated value it has been suggested to calculate the NICS above the ring plane: if the NICS is evaluated at the geometrical centre is indicated as NICS(0) and if it is evaluated x Ångstrom above the plane is indicated as NICS(x).ⁱ

Comparison of the NICS data obtained for a series of rollover cyclometalated complexes

ⁱIn Appendix C more details on how the NICS have been evaluated and benchmarked can be found.

Table 1.11: Bond distances (pm) and angles (deg) for the optimized complexes of general formula $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{DMSO})]$. Geometries obtained at PBE0/def2-SVP level using ZORA formalism with RI-J approximation.

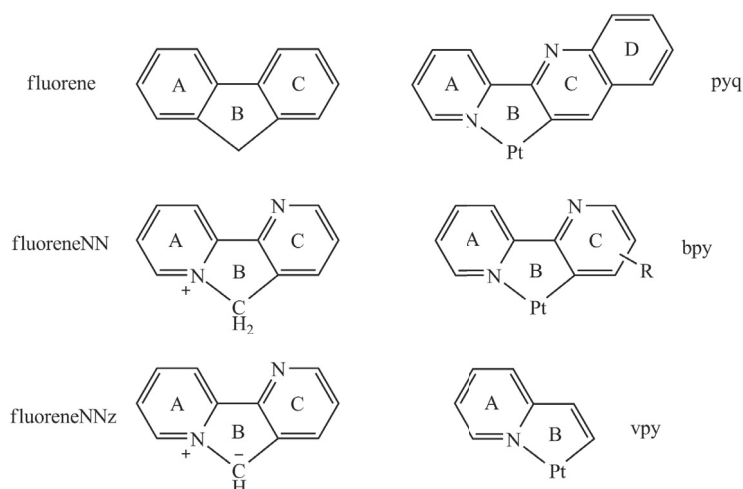
	bpy	bpy ^{6CF₃}	bpy ^{6CH₃}	pyq	vpy
Distances	Pt-C ₃	201.6	201.3	201.6	199.0
	Pt-N ₁	213.6	213.8	213.6	213.7
	Pt-S	228.6	228.7	228.5	229.0
	Pt-CH ₃	205.2	205.2	205.2	204.8
	C ₃ -C ₂	141.3	141.5	141.2	143.4
	C ₂ -C ₂	147.3	147.3	147.3	147.6
	C ₂ -N	135.0	135.0	135.1	135.0
	O...H ^a	202.4	202.1	202.6	201.4
Angles	S-Pt-N ₁	98.8	98.8	98.9	99.5
	N ₁ -Pt-C ₃	80.2	80.3	80.1	80.5
	C ₃ -Pt-CH ₃	90.6	90.5	90.5	90.5
	CH ₃ -Pt-S	90.4	90.5	90.5	90.3
	S-Pt-C ₃	178.9	178.8	178.9	179.2
	CH ₃ -Pt-N ₁	170.8	170.8	170.7	170.9

^a $r_{\text{vdW}}(\text{H}) + r_{\text{vdW}}(\text{O}) = 120 + 152 = 272 \text{ pm.}^{184}$

with general formula $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{DMSO})]$ is visible in Table 1.12 along with the corresponding values calculated for some all-organic corresponding fluorene derivatives. First of all it can be noted that there is a parallelism between the values obtained at the centroid and with those calculated starting from the ring critical point (RCP). We thought to calculate the NICS value in these two different points to check if there were some changes or trends; nevertheless, as evident by the calculations on the fluorene derivatives, the two approaches are almost superimposable if the atoms involved in the cycle belong to the same period.

A confirmation can be found in the comparison of the NICS(0) values for the platinacycle that differ more than 1 ppm for a displacement of only 0.2 pm: this gives a clear evidence of the importance of the choice of the point where the NICS is going to be evaluated.

A common feature of all the cyclometalated complexes analysed is the aromatic charac-



Scheme 1.12

ter of the pyridinic rings and the non-aromatic character of the metallacycles, this result constitutes no surprise if we recall the fact that the bond distances of this ring do not show substantial delocalization and are more in agreement with an α,β -unsaturated situation. Taking as reference the complex with bpy we can note the following trends. (1) All the N-bound pyridinic rings show a comparable aromatic character, this is perfectly reasonable due to the close similarity of this part between all the complexes. (2) The NICS value of the metalated pyridinic ring show a slight dependence on the group attached to it and a rough aromaticity scale can be built in ascending order: $\text{bpy}^{6\text{CH}_3} < \text{bpy} < \text{bpy}^{6\text{CF}_3} < \text{pyq}$. (3) The platinacycle has a general non-aromatic character but an order can be found also in this case, remarkably it is inversely related to the one of the metalated pyridinic ring and the complex with the small vpy shows the highest aromatic character; the NICS(1) value shows a levelling effect for the bpys while keeping the vpy and the pyq at the extremes.

On the whole some general precautions have to be kept in mind while investigating by theoretical means the aromaticity of complex systems such those presented; in fact different effects could be operative from the σ -current (mainly affecting NICS(0) value) to the effect of condensed adjacent aromatic rings that can have an impact on NICS(1) values, last but not least the effect of the metal centre has to be added to the list.¹⁸⁷

LMO-EDA was performed on some of the cyclometalated complexes obtained experi-

Table 1.12: NICS(0) and NICS(1) evaluated with the IGLO approach using ZORA-PBE/def2-TZVP with ECP on Pt for the optimized complexes of general formula $[\text{Pt}(\kappa^2\text{-N,C})\text{-(CH}_3\text{)(DMSO)}]$. Geometries obtained at PBE0/def2-SVP level using ZORA formalism with RI-J approximation. Labels according to Scheme 1.12.

		Evaluated at centroid				Evaluated at RCP			
		A	B	C	D	A	B	C	D
NICS(0)	bpy	-4.5	3.7	-4.3	-	-4.5	2.5	-4.3	-
	bpy ^{6CF₃}	-4.6	4.0	-4.8	-	-4.7	2.8	-4.8	-
	bpy ^{6CH₃}	-4.5	3.7	-4.2	-	-4.5	2.6	-4.2	-
	pyq	-4.3	4.4	-5.2	-7.2	-4.3	3.2	-5.2	-7.2
	vpy	-5.0	2.9	-	-	-5.0	2.0	-	-
	fluorene	-6.9	1.3	-6.9	-	-7.0	1.1	-7.0	-
	fluoreneNN	-5.7	-0.5	-6.1	-	-5.7	-0.6	-6.1	-
	fluoreneNNz	-6.5	-15.8	-7.4	-	-6.5	-15.8	-7.4	-
NICS(1)	bpy	-7.8	-0.4	-8.3	-	-7.8	-0.7	-8.3	-
	bpy ^{6CF₃}	-8.0	-0.4	-8.4	-	-8.0	-0.7	-8.5	-
	bpy ^{6CH₃}	-7.8	-0.4	-8.1	-	-7.8	-0.7	-8.1	-
	pyq	-7.7	0.0	-9.0	-9.5	-7.7	-0.3	-9.0	-9.5
	vpy	-7.8	-1.0	-	-	-7.8	-1.2	-	-
	fluorene	-9.2	-2.4	-9.2	-	-9.3	-2.5	-9.3	-
	fluoreneNN	-8.1	-2.4	-9.5	-	-8.1	-2.4	-9.5	-
	fluoreneNNz	-7.9	-13.9	-10.2	-	-7.9	-13.9	-10.2	-

mentally and the results are collected in Table 1.14. Aiming at a complete description of the interactions that interplay we analysed three different possible fragmentations: cyclometalated ligand, DMSO and methyl.

The global interaction energies, ΔE^{KS} , for methyl and for the $\kappa^2\text{-N,C}$ moiety are comparable while for the DMSO the value is ca. one order of magnitude smaller. Another similarity between the carbon donors is the relative importance of the single contributors showing that polarization and electrostatic, ΔE^{pol} and ΔE^{ele} , are the components that have the biggest stabilizing effect while the exchange is almost half of the former.

Regarding the DMSO again ΔE^{pol} is the largest stabilizing contribution to ΔE^{KS} but now electrostatic and exchange contributions are roughly the same. All the interaction energies are around $160 \text{ kJ}\cdot\text{mol}^{-1}$ and give an idea of the relative donor capabilities of the

Table 1.13: Atom In Molecules (AIM) analysis for the optimized complexes of general formula [Pt(bpy-H)(CH₃)(DMSO)] (**2a**). Geometries obtained at PBE0/def2-SVP level using ZORA formalism with RI-J approximation.

	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	$G(\mathbf{r})$	ε	$\frac{\lambda_1}{\lambda_3}$	$\frac{G(\mathbf{r})}{\rho(\mathbf{r})}$	Γ_{cov}
Pt-N _{1'}	0.0984	0.3837	0.1236	0.0634	0.1718	1.2561	25.0
Pt-C ₃	0.1520	0.1005	0.1132	0.0147	0.3925	0.7451	43.8
Pt-CH ₃	0.1425	0.0523	0.0945	0.0249	0.4352	0.6629	46.2
Pt-S	0.1080	0.3052	0.1190	0.1173	0.1883	1.1021	26.3
N _{1'} -C _{2'}	0.3295	-0.9100	0.3134	0.0838	1.5644	0.9512	75.0
C _{2'} -C ₂	0.2771	-0.7000	0.0656	0.1239	1.5856	0.2368	75.0
C ₂ -C ₃	0.2992	-0.7370	0.0952	0.1592	1.6485	0.3180	75.4

C₃ is the metalated carbon.

different *trans* metalated carbons, interaction energies follow the order $\text{bpy}^{6\text{CF}_3} > \text{pyq} \approx \text{bpy} \approx \text{bpy}^{6\text{CH}_3} > \text{vpy}$.

The given sequence is in agreement with the electronic characteristic of the metalated group in fact the more electron-withdrawing trifluoromethyl is expected to pull more electron density from the metal, as was suggested by the $^3\text{J}_{\text{Pt-H}}$ coupling constant, while the vinylic carbon should be more donating in nature so that the DMSO is not requested to donate heavily. The close similarity in the values for pyq and for the couple bpy, $\text{bpy}^{6\text{CH}_3}$ is interesting because seems that, once the cyclometalation is completed, they don't have a big effect on the ligand in *trans* as evident by the comparison of the $^3\text{J}_{\text{Pt-H}}$ for the methyls of the DMSO (see Section 1.4.2 and 1.4.4).

It has been found experimentally that using $\text{bpy}^{5\text{CH}_3}$ or $\text{bpy}^{5\text{CF}_3}$ as cyclometalating ligand a mixture of isomers relative to both activation products were detected in solution, *i.e.* activation of substituted and unsubstituted pyridyl ring.

In order to get an insight on the different stabilities of these isomers we performed DFT calculations for all the four species (two for each ligand $\text{bpy}^{5\text{CH}_3}$ and $\text{bpy}^{5\text{CF}_3}$) using the RI-J approximations along with ZORA at the PBE0/def2-SVP level. The geometries were confirmed as minima on the potential energy surface due to the absence of imaginary frequencies in the Hessian evaluated at the same level of theory and are visible in Figure

Table 1.14: LMO Energy Decomposition Analysis (EDA) for the optimized complexes of general formula $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{DMSO})]$. Geometries obtained at PBE0/def2-SVP level using ZORA formalism with RI-J approximation. One of the fragments used for the calculations is indicated in the first column. Values in $\text{kJ}\cdot\text{mol}^{-1}$.

		bpy	bpy ^{6CF₃}	bpy ^{6CH₃}	pyq	vpy
NC	ΔE^{ele}	-995.44	-972.89	-980.09	-976.80	-1048.40
	ΔE^{ex}	-530.36	-530.09	-519.36	-529.80	-557.50
	ΔE^{rep}	1576.31	1574.68	1536.52	1574.86	1666.98
	ΔE^{pol}	-1021.98	-1011.72	-1017.22	-1024.16	-1078.08
	ΔE^{disp}	-135.48	-132.94	-133.19	-134.73	-135.89
	ΔE^{KS}	-1106.95	-1072.96	-1113.35	-1090.63	-1152.89
DMSO	ΔE^{ele}	-258.03	-255.07	-259.12	-260.01	-253.94
	ΔE^{ex}	-273.38	-269.93	-274.49	-274.48	-267.49
	ΔE^{rep}	802.63	793.60	806.58	807.38	787.12
	ΔE^{pol}	-339.01	-339.31	-340.23	-340.29	-330.43
	ΔE^{disp}	-93.20	-93.05	-93.34	-93.50	-89.16
	ΔE^{KS}	-160.99	-163.75	-160.59	-160.91	-153.90
methyl	ΔE^{ele}	-946.43	-963.90	-938.67	-934.23	-939.04
	ΔE^{ex}	-448.87	-447.60	-448.99	-448.86	-435.99
	ΔE^{rep}	1282.12	1281.19	1281.84	1282.66	1255.29
	ΔE^{pol}	-822.59	-825.56	-824.11	-827.06	-821.77
	ΔE^{disp}	-97.76	-99.38	-97.30	-98.30	-91.43
	ΔE^{KS}	-1033.52	-1055.25	-1027.23	-1025.79	-1032.96

1.10.

The resulting energy differences obtained are in good agreement with experimental findings (see Section 1.4.3). The enthalpic difference (ΔH in $\text{kJ}\cdot\text{mol}^{-1}$ *in vacuo*) predicts that when bpy^{5CH₃} is used a roughly 1:1 ratio between the two activation product is to be expected; we recall here that the integrals, relative to the two cyclometalated complexes, observed in the ¹H NMR during and at the end of the cyclometalation were in 1:1 ratio. It is also worthy of note that the most stable isomer is the one with the substituted ring N-bound to platinum, which is also what could be thought on the basis of the electronic effects of the methyl group.

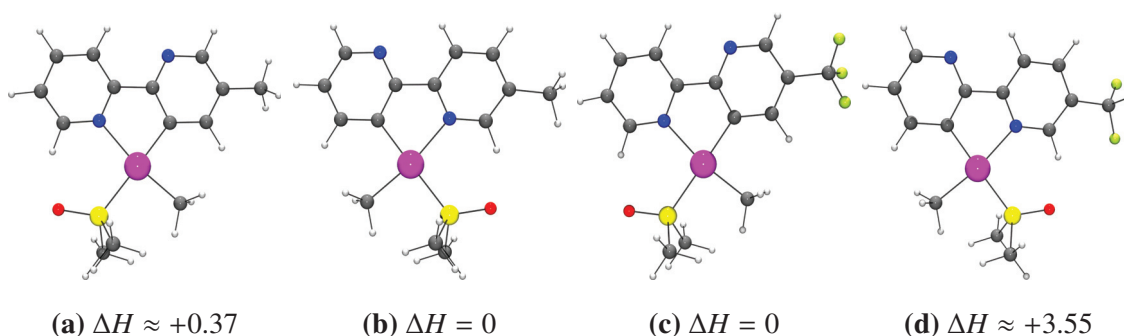


Figure 1.10: Equilibrium geometries for the isomers of $[\text{Pt}(\text{bpy}^{5\text{R}}\text{-H})(\text{CH}_3)(\text{DMSO})]$ for $\text{R} = \text{CH}_3$ (**2d**), CF_3 (**2e**). ΔH values are calculated *in vacuo* and expressed in $\text{kJ}\cdot\text{mol}^{-1}$ corrected with zero point energy (ZPE).

On the other hand, when the ligand used is $\text{bpy}^{5\text{CF}_3}$ a bigger ΔH is obtained and now the most stable isomer is the one where the metalated ring is the one bearing the substituent. Again the theory reproduces well the experiment being in agreement with the predominant species detected in solution by NMR means.

1.6 Conclusions

The cyclometalation reaction of heteroaromatic ligands was studied with electronrich platinum(II) derivatives with formula $[\text{Pt}(\text{X})_2(\text{L})_2]$ (X = anionic ligand, L = neutral ligand). Two well known families were investigated aiming at the disclosure of similarities and differences: substituted 2-phenylpyridines (ppy) and corresponding 2,2'-bipyridines (bpy).

A series of ligands was synthesized for this scope by coupling reactions and one previously unknown bipyridine has been successfully synthesized and fully characterized, *i.e.* 6-trifluoromethyl-2,2'-bipyridine. The substituent were carefully chosen in order to obtain ligands with a wide variety of different steric and electronic properties in order to systematically study the relationships between structure and reactivity.

In the case of bpps the substituents were placed in position 5 and 6 to check the impact of steric hindrance in the proximity of the metal centre during the rollover C-H activation process. The electronic properties of the substituent in the two different positions mentioned were investigated by comparing methyl and trifluoromethyl.

All the ligands afforded the corresponding cyclometalated product, either classical or deriving from rollover activation; this latter kind of activation is rather new and the parameters controlling the process are still yet to be completely elucidated.

Our results demonstrate that the position of the substituent dictates the regioselectivity of the rollover activation process by selectively activating the substituted pyridyl ring. In fact with $\text{bpy}^{6\text{CH}_3}$, $\text{bpy}^{6\text{CF}_3}$ and pyq only one isomer is obtained and the unsubstituted pyridyl ring was always N-bounded to the metal centre. Notably $\text{bpy}^{6\text{CF}_3}$ gives rollover activation very quickly and without detection of the $\kappa^2\text{-N,N}$ chelated coordination compound, in clear contrast with other bpys.

The ppy counterparts showed in addition that if the substituent is sufficiently large, *i.e.* as in $\text{ppy}^{3\text{CH}_3}$ or $\text{ppy}^{3\text{CF}_3}$, only the position in *para* to the substituent is selectively activated on the phenyl ring. On the contrary with $\text{ppy}^{3\text{F}}$ a mixture of isomers, where the positions activated are *ortho* and *para* to the substituent, is obtained clearly showing the presence of a steric threshold to achieve 100% selectivity with 2-phenylpyridines.

Moving the substituent to position 5 on the bpy scaffold changes the situation and now a mixture of isomers deriving from the activation of both pyridyl rings is obtained. The electronic nature of the substituent plays a clear role because with $\text{bpy}^{5\text{CH}_3}$ the ratio between the products is 1:1 while $\text{bpy}^{5\text{CF}_3}$ the substituted ring is the predominant species.

The effect of the anionic ligands present on platinum(II) starting compounds was also investigated, it is confirmed that in order to achieve rollover metalation with bpy derivatives having either a methyl or a phenyl is a mandatory requirement. When the phenyl is used the cyclometalation requires harsher conditions to proceed with 6-substituted ligands and, in the conditions tried, was not successful with the others. Presence of one or two chloride atoms in the $[\text{Pt}(\text{X})_2(\text{L})_2]$ inhibits completely the reaction with every bpy.

A different behaviour was found for the phenylpyridines that showed to be much more prone to cyclometalate with every anionic ligand used in the substrate, $\text{X} = \text{CH}_3, \text{Ph}, \text{Cl}$. Classical and rollover cyclometalated complexes were completely characterized by NMR spectroscopy and further insights were sought by DFT calculations that showed a very good correlation with the experimental phenomena observed.

Substitution reactions

2.1 Introduction

The chemistry of cyclometalated compounds is of great current interest because of the wide range of potential applications they may have in many areas, such as organic synthesis, homogeneous catalysis, photochemistry, and design of advanced materials and biologically active agents.¹⁸⁸

Compounds derived from "rollover" cyclometalation represent a new emerging class of cyclometalated complexes, due to the presence of the uncoordinated nitrogen atom, able to strongly influence the reactivity of the complex. In the case of platinum(II) these species have shown noteworthy potentialities, *e.g.* in platinum-¹⁸⁹ and palladium-mediated¹⁹⁰ C-C bond forming and in dehydrosulfurization and oxidative C-C bond coupling of thioethers in the gas phase.^{36,50,191} Moreover, insertion reactions in the metal-carbon bond have been successfully used for the synthesis of C₃ substituted bipyridines,¹⁹⁰ while double rollover metalation on the bipyridine ligand has afforded polymeric organometallic species²³ or bimetallic complexes where the metal centres are connected by a highly delocalized planar system.^{14,18} Very recently, two independent research groups have found catalytic applications involving rhodium-mediated "rollover" cyclometalation in the hydroarylation of alkenes and alkynes with 2,2'-bipyridines and 2,2'-biquinolines,¹⁹² and in the transformation of 3-alkynyl and 3-alkenyl-2-arylpyridines into 4-azafluorene compounds.¹⁹³

Among the most recent studied applications that mono and dinuclear complexes with

bisphosphanes have found we can cite for example those in photoluminescence,^{194–196} optical-limiting materials,¹⁹⁶ as molecular wires,¹⁹⁷ or in medicinal chemistry as antitumorals.¹⁹⁸

All these applications cited so far have the fundamental contribution of a metal moiety with other co-ligands, *e.g.* carbonyls, hydrides, cyclometalated heteroaromatic ligands, etc. Different transition metals have been successfully reacted with various bisphosphine and examples are present in literature for Cr,¹⁹⁹ Fe,^{200–203} Cu,^{204,205} Mo,²⁰⁶ Ru,^{207–209} Rh,²¹⁰ Pd,^{211,212} Ag,^{213,214} Ir,^{210,215} Re,^{216,217} and Au.^{194,218–222}

A lot of work has also been done with platinum and in the last decade probably the most prominent contributor to this field was the group of Rashidi and co-workers that studied many aspects connected to this class of ligands, from the synthesis to the reactivity.^{4, 18, 196, 223–232}

Among the wide variety of bisphosphines that can be synthesized the most commonly used are those having from 1 to 4 methylenic carbon atoms between the diphenylphosphino units, *i.e.* $\text{Ph}_2\text{P}-(\text{CH}_2)_n-\text{PPh}_2$ with $n = 1 \div 4$. From a general point of view as the alkyl chain becomes longer the tendency towards a bridging behaviour between two metals is enhanced, even though chelates are known.^{19, 233–235}

The steric strain of a series of chelating bisphosphines is visible in crystal structures of the complexes *cis*-[Pd(Cl)₂(κ^2 -P,P)], where κ^2 -P,P = dpmm, dppe and dppp, reported by Steffen and Palenik back in 1976.²³⁵ All the structures possess a chelate cycle but with a different number of atoms that depends on the length of the alkyl chain.

When κ^2 -P,P = dpmm the angle at the CH₂ carbon between the two phosphorus atoms is 93° which is 16 degrees less than what is predicted on the basis of the VSEPR theory, moreover the angle P-Pd-P is 73° being 17 degrees less than the theoretical 90°; these two large angular strains are not compensated by the 4° widening of the angle at phosphorus. The situation is different when the complex has a dppe where the five-membered chelate ring is less strained due to the larger bite angle of the ligand due to the presence of two methylenic spacers; now all the reported angles are much closer to the theoretical ones. A recent article substantially confirmed by DFT means that the trend just described is also effective in Ni complexes.²³⁶

In general it is therefore not surprising to expect that dpmm will be less prone than dppe

to give chelate complexes, as well it is conceivable that longer chains will reluctantly give chelates due to the fact that they spend more time far from the metal centre to which one phosphorus is bound.

It has been observed that dinuclear derivatives of cyclometalated platinum complexes could have a different reactivity compared to the mononuclear ones.^{237,238} Depending on the bridging group connecting the two metal centres we synthesized two classes of complexes: diphosphane or bpy bridged ones.

The first class of dinuclear derivatives is relative to bidentate ligands having phosphorus donor atoms, namely the series of the 1,X-bis(diphenylphosphino)alkanes, among these we can find dpdm, dppe, dppp, etc., they have general formula $\text{Ph}_2\text{P}-(\text{CH}_2)_n-\text{PPh}_2$. In this case the linkage between the metals is mediated by the diphosphine and the information transfer between them is less effective if not completely absent. On the other hand these systems have the possibility of interact in the space and, through π -stacking or metal-metal interactions, originate more or less ordered supramolecular structures,⁵ or influence the reactivity of the metal centre.

It is evident that by choosing carefully metal, co-ligands and bridging groups a wide variety of complexes can be easily synthesized.

Chelating bisphosphines have found many different applications in catalysis with square planar complexes, this is because they occupy two coordination sites in relative *cis* position and wise modification of the substituents on phosphorus atoms permits to tune the selectivity and the reactivity of the metal centre.

It has been observed that complexes having general formula $[\text{Pt}(\text{X})_2(\text{dRpe})]$, where X indicates a monoanionic ligand and R is the substituent on phosphorus, if dissolved in hydrocarbon solvents are prone to oxidatively add a solvent molecule and reductively eliminate HX, thus constituting another possible application in the C-H activation field.^{239,240} Dinuclear platinum(II) cyclometalated complexes with bridging dpdm have been studied for their photochemical properties.^{241,242} A good number of examples have been described where these complexes show tendency to adopt a close conformation driven by $\text{Pt} \cdots \text{Pt}$ interactions, this arrangement has a great effect on photoluminescence.²⁴³⁻²⁴⁵

Recently a work has reported a system able to modify its conformation just by changing the pH of the solution, this is possible due to the presence of an uncoordinated nitrogen

atom that can be easily protonated/deprotonated. This system has been described as a pivot hinge.²⁴⁶

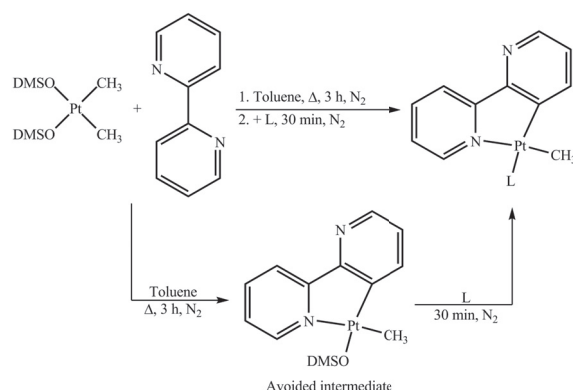
2.2 Substitution with phosphanes

Starting from the parent compound [Pt(bpy-H)(CH₃)(DMSO)] (**2a**), a series of complexes of general formula [Pt(bpy-H)(CH₃)(L)], with L = neutral ligand can be isolated in the solid state and characterized. The substitution of the DMSO occurs often in mild conditions such as room temperature in acetone or CH₂Cl₂ and slight excess (no more than 10%) of entering ligand, but in some cases it is necessary to use harsher conditions to push the reaction to the final product.

Particularly easy is the replacement of the dimethylsulfoxide with phosphanes and this is due to two main factors: (a) binding weakness of the DMSO and (b) strong affinity of the phosphanes for the Pt(II) metal centre. We already showed both experimentally and by DFT means (see Section 1.5.2) that in cyclometalated species of general formula [Pt(κ^2 -N,C)(CH₃)(DMSO)] the lowest interaction energy is found for the Pt-DMSO bond, likely due to the presence of a metalated carbon coordinated in *trans* position.

The clean synthesis of the methyl species [Pt(bpy-H)(CH₃)(L)] has been recently reported.¹⁶ The reaction occurs in two steps under strictly controlled conditions and is not immune from problems. A new and more effective route to such complexes has now been refined: the new protocol does not rely on the isolation in the solid state of the intermediate species **2a**, a critical step, but follows a "pseudo" one-pot reaction (see the Experimental Section), where the desired ligand is added directly to the hot solution at the end of the rollover process (Scheme 2.1).²⁴⁷ This procedure permits to prepare in good yields even complexes that cannot be obtained with the classical substitution reaction: *i.e.*, with L = PCy₃, P(OPh)₃.

A more detailed description of the data obtained for [Pt(bpy-H)(CH₃)(PMe₃)] (**7a**) will be given as it will be useful for its reactivity (see Chapter 4) and because the general characteristics of the NMR spectra are more easily described because the lack of overlapping between signals in the aromatic region. The complex was obtained as a yellow solid in



Scheme 2.1

high yield by the improved synthetic method²⁴⁷ that avoids the troublesome workup of the intermediate **2a** (Scheme 2.1). The success of the reaction was determined by the analysis of the ^1H and ^{31}P NMR spectra: in the aliphatic region of the ^1H spectrum the coordination of the methyl appears as a doublet with satellites due to the coupling with phosphorus and ^{195}Pt (3H, 0.85 ppm, $^3J_{\text{P-H}} = 8$ Hz, $^2J_{\text{Pt-H}} = 84$ Hz); another doublet with satellites is ascribable to the coordinated PMe_3 (9H, 1.57 ppm, $^2J_{\text{P-H}} = 8$ Hz, $^3J_{\text{Pt-H}} = 21$ Hz). The aromatic region is diagnostic because there are seven different signals, each integrating one proton, for the cyclometalated ligand rather than the starting four, with each one integrating two protons. Characteristic protons are those which couple with the metal centre, *i.e.* a broad doublet with satellites that corresponds to $\text{H}_{6'}$ (8.86 ppm, $^3J_{\text{Pt-H}} = 22$ Hz), a ddd with satellites accounts for H_4 that couples with H_5 , H_6 and the phosphorus atom in *trans* to the metalated ring (8.09 ppm, $^3J_{\text{Pt-H}} = 44.4$ Hz), H_5 which is also a ddd with satellites (7.16 ppm, $^4J_{\text{Pt-H}} = 15.2$ Hz). A ^{195}Pt - ^1H HMQC experiment confirms that all these signals are due to protons bonded to the same platinum, *i.e.* they belong to the same species, that which gives a doublet at -4106 ppm. ^{31}P NMR spectroscopy confirms the presence of only one phosphorus bound to Pt showing a singlet with satellites ($J_{\text{Pt-P}} = 2112$ Hz) at -18.6 ppm, the value of the coupling constant is typical of a phosphorus coordinated *trans* to a group having strong *trans*-influence that in this case turns out to be the aromatic carbon.²⁴⁸ Moreover the *trans*-phobia^{142, 143} concept supports this description as it keeps the methyl and aromatic carbon apart.

The new series of complexes $[\text{Pt}(\text{bpy-H})(\text{CH}_3)(\text{L})]$ ($\text{L} = \text{PPh}_3$ (**8a**), PCy_3 (**9a**), $\text{P}(\text{OPh})_3$

Table 2.1

	MW (u)	m.p. (°C) ^a	θ (deg) ²⁴⁹	ν _{CO} (cm ⁻¹) ²⁴⁹
PMe ₃	76.1	-86	118	2064.1
PPh ₃	262.29	79÷81	145	2068.9
PCy ₃	280.43	76÷78	170	2056.4
P(<i>p</i> -tol) ₃	304.37	144÷146	145	2066.7
P(OPh) ₃	310.29	22÷24	128	2085.3
dppm	384.40	118÷119	140/136 ^b	2066.7/2067.0 ^b

^a Retrieved from <http://www.chemspider.com>.

^b First value is for PPh₂Et, second for PPh₂Me.

(**10a**), P(*p*-tol)₃ (**11a**), dppm (**12a**)) was chosen in order to furnish different steric and electronic properties to the complexes, PPh₃ and P(*p*-tol)₃ lying in the middle for both electronic and steric parameters (Table 2.1). All synthesized complexes were characterized by ¹H and ³¹P NMR spectroscopy and elemental analysis.

Only one of the two possible geometric isomers for **7a-12a** is formed, *i.e.* that with a P-Pt-C(*sp*²) *trans* geometry, as confirmed by NMR spectra, which show coupling constants in line with phosphorus coordinated *trans* to the C₃ carbon (*e.g.*, ²J_{P-C₃} = 119.6 Hz, ²J_{Pt-Me} = 4.7 Hz, and ¹J_{Pt-P} = 2229 Hz for **8a**). Furthermore, in the ¹H NMR spectrum the methyl resonances appear as doublets, due to the phosphorus atom in a *cis* position, with satellites.

Selected NMR signals for different phosphanes with cyclometalated bpy, *i.e.* [Pt(bpy-H)-(CH₃)(L)] series, are collected in Table 2.2 for comparison.

Keeping in mind the differences in solvents and concentrations that can influence the chemical shift a rough analysis of the phosphanes' effects on the complexes can be made. It is evident that whenever an aromatic ring is directly attached to phosphorus the H_{6'} proton experiences a strong shielding effect and it is no more easily detectable in the simple ¹H because overlaps with the aromatic protons of the phenyl rings; this conclusion is also supported by the X-ray crystal structure (*vide infra*). When this proton is visible it is always the most deshielded one resonating between 8.5 and 9.5 ppm, the aspect is usually that of a multiplet due to the coupling with H_{5'}, H_{4'} and phosphorus flanked by

Table 2.2: Selected ^1H and ^{31}P NMR chemical shifts (ppm) with ^{195}Pt coupling constants (Hz, in brackets) for the $[\text{Pt}(\text{bpy-H})(\text{CH}_3)(\text{L})]$ series of complexes where L is a phosphane.

	H_4	$\text{H}_{6'}$	Pt-CH_3	^{31}P
$^a\text{PMe}_3$	8.09 [44]	8.86 [22]	0.85 [84]	-18.6 [2112]
$^b\text{PPh}_3$	8.28 [48]	ov aromatics	0.74 [83]	33.6 [2229]
$^b\text{PCy}_3$	8.20 [45]	8.75 [12]	1.00 [84]	19.3 [2083]
$^b\text{P(OPh)}_3$	7.93 [42]	9.41 [16]	0.83 [84]	118 [3848]
$^c\text{P}(p\text{-tol})_3$	8.18 [48]	ov aromatics	0.66 [84]	30.0 [2245]
$^b\text{dppm}$	8.16 [48]	ov aromatics	0.79 [83]	19.7 [2209]

^{a} Acetone- d_6 . ^{b} CDCl_3 . ^{c} CD_2Cl_2 .

broad satellites due to the coupling with ^{195}Pt .

The stereoelectronic properties of the phosphane have an effect on the $^3J_{\text{Pt-H}}$ of the $\text{H}_{6'}$, even though whatever correlation should be evaluated and analysed with great care due to the different parameters influencing the values. There seems to be a relationship between the sterics and the value of the coupling constant in the form that the bulkier PCy_3 leads to the smallest J-value while the compact PMe_3 has the largest. This observation could be regarded as an evidence of a *cis*-effect that is not visible in the Pt-CH_3 coupling constants: all the values are in a narrow range around 84 Hz.

Inspection of the coupling constant for the H_4 proton searching for a *trans*-effect shows, in first instance, that $^3J_{\text{Pt-H}_4}$ has little dependence on the nature of the phosphane, in fact all the values are ca. 45 Hz. There is probably a common interaction between the PPh_3 congeners that permits to the group in *trans* to bind more tightly to the metal, the reasons beyond this effect can be found in the subtle equilibrium between steric and electronic properties of the phosphane: moving away both sterically or electronically decreases the coupling constant of the *trans* group, possibly affecting its bond strength.

Analysis of the one bond coupling constant between phosphorus and ^{195}Pt should give a more reliable information on the nature of the Pt-P bond. Looking at the values in Table 2.2 a reasonable correlation is present between the $J_{\text{Pt-P}}$ and the Tolman electronic parameter displaying an R^2 of 0.852 including all the data and using the value of PMePh_2 for dppm .²⁴⁹ Removal of the triphenylphosphite drops the correlation coefficient to 0.754; this observation could indicate that for rollover $[\text{Pt}(\text{bpy-H})(\text{CH}_3)(\text{L})]$ compounds alkyl/aryl

and phenoxy substituent on phosphorus have more similarities than differences.

Many authors tried to find correlations between the one bond $J_{\text{Pt-P}}$ constants and other parameters (*e.g.* bond distances, nature of *trans* or *cis* group, *s* character in Pt-P bond, etc.) often with good results,^{250–256} sometimes with no appreciable trend.²⁵⁷

One of the most important parameters affecting the value of the ^{195}Pt - ^{31}P coupling constant is the electronic nature of the substituent on the P(III) atom, in fact an opposite dependence of the $J_{\text{Pt-P}}$ on the π -acidity of the substituent on phosphorus was found by Cobley and Pringle on one side and Waddell *et al.* on the other: while in the former the trend was direct,²⁵⁵ in the latter was inverse.²⁵⁰ The reason beyond this apparent discrepancy can be found in the different class of phosphanes examined: *para*-substituted triarylphosphines and $\text{P(OMe)}_x\text{Ph}_{(3-x)}$. Nevertheless the authors warn the reader about that reliable conclusion can be drawn only for a narrow series of complexes.²⁵⁰

It is worth noting that Cobley and Pringle,²⁵⁵ comparing similar Pt(II) and Pt(0) series of complexes, observed an inverse correlation between the $J_{\text{Pt-P}}$ coupling constant and the Hammett substituent constant σ_{P} .^{115,258,259} Their explanation for this trend is that in Pt(0) compound the more electronrich metal centre backdonates to the empty orbitals of suitable symmetry present on the phosphine which, in turn, increases its σ -donation resulting in a larger coupling constant. Following this reasoning in Pt(II) compounds backdonation from the metal centre to the phosphine is negligible if not completely absent and the electronwithdrawing effect of the substituent diminishes the $\text{P} \rightarrow \text{Pt}$ donation, as highlighted by the smaller ^{195}Pt - ^{31}P coupling.

A different aspect can be investigated by analysing the effect of the other co-ligands present in the Pt-species, in this context in a series of complexes $[\text{Pt}(\text{dppe})(\text{CH}_3)(\text{py}^{4\text{R}})]^+$ it was found that both the $J_{\text{Pt-P}}$ become larger as the Hammett σ parameter goes from negative to positive values,²⁵⁶ this is a clear evidence of the impact of *trans* and *cis* groups. A similar observation was put forward by Rigamonti *et al.*²⁵¹ with the precaution that whenever correlations between bond distances and coupling constants are made it is important to keep in mind that they are affected by different phenomena: in fact bond distances are more sensible to the interactions present in the solid state (mainly sterics) while, on the other hand, $J_{\text{Pt-P}}$ are predominantly subject to the electron density (*i.e.* $\text{P} \rightarrow \text{Pt}$ donation). However even in solution steric hindrance plays a role as elegantly demonstrated by

Romeo and Alibrandi studying the uncatalysed isomerisation of $[\text{Pt}(\text{Me})(\text{PR}_3)_2(\text{MeOH})]^+$,²⁵³ and by Haar *et al.*²⁵² that concentrated their attention on the evaluation of the substitution enthalpies in $[\text{Pt}(1,5\text{-COD})(\text{Me})_2]$, where 1,5-cyclooctadiene is substituted by two molecules of PR_3 (R = alkyl, aryl).

Another interesting comparison is possible if we consider the effect of the cyclometalated moiety on the $[\text{Pt}(\text{CH}_3)(\text{PPh}_3)]^+$ fragment. Looking at the $J_{\text{Pt-P}}$ values in Table 2.3 a nice trend is visible even if the difference in the numerical values is not dramatic.

The trifluoromethyl substituted bpy complexes show a larger coupling in fair agreement with what is expected on the basis of the electronic effects of the CF_3 group. Interestingly pyq and bpy have very similar $J_{\text{Pt-P}}$ despite the difference of a condensed phenyl ring in the former (2235 *vs* 2229 respectively). The electron-releasing nature of the methyl-substituted bpys fits well with the fact that their cyclometalated complexes have a lower $J_{\text{Pt-P}}$, in this case the phosphine is not required to donate more electron density to the metal centre.

Apparently no evident correlation is visible for the values relative to the Pt-CH_3 .

Table 2.3: Selected ^1H and ^{31}P NMR chemical shifts (ppm) with ^{195}Pt coupling constants (Hz, in brackets) for the $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{PPh}_3)]$ series of complexes where $\kappa^2\text{-N,C}$ is a cyclometalated bpy derivative.

		H_4	Pt-CH_3	^{31}P
8a	bpy	8.24 [48]	0.74 [83]	33.6 [2229]
8b	$\text{bpy}^{6\text{CH}_3}$	8.13 [46]	0.74 [83]	32.6 [2226]
8c	$\text{bpy}^{6\text{CF}_3}$	8.39 [48]	0.79 [83]	32.1 [2279]
8d	$^a\text{bpy}^{5\text{CH}_3}$	ov aromatics	0.76 [n.r.]	33.8 [2216]
8d'	$^a\text{bpy}^{5\text{CH}_3}$	ov aromatics	0.73 [n.r.]	33.6 [2224]
8e	$\text{bpy}^{5\text{CF}_3}$	8.46 [39]	0.77 [86]	33.2 [2312]
8f	pyq	8.66 [52]	0.89 [83]	32.4 [2235]
8g	vpy	-	0.80 [84]	28.5 [2020]

^a Both isomers.

The substitution of the DMSO in complex $[\text{Pt}(\text{bpy}^{5\text{CF}_3}\text{-H})(\text{CH}_3)(\text{DMSO})]$ (**2e**) should lead to a mixture of isomers as in the case of the $\text{bpy}^{5\text{CH}_3}$ but, surprisingly, only one isomer is

visible in the NMR spectra, *i.e.* the one having the PPh₃ coordinated *trans* to the activated substituted ring. We suggest as explanation that the difference in the ratio of the parent compounds with DMSO leads to a low concentration of the substituted product that probably is lost during the workup.

Starting from [Pt(pyq-H)(CH₃)(DMSO)] (**2f**) the corresponding PPh₃ and PCy₃ containing complexes, **8f** and **9f**, can be isolated and characterized. All the discussion made so far is still valid: (a) only the isomer with the phosphine *trans* to the metalated carbon is obtained as evident from the J_{Pt-P} coupling constant (ca. 2200 Hz); (b) the coupling constant in the P-Pt-C₃ *trans* arrangement, *i.e.* J_{Pt-P} and ³J_{Pt-H} for H₄, are both higher for PPh₃ suggesting a synergic effect acting on those bonds; (c) ¹⁹⁵Pt chemical shifts, taken from a ¹⁹⁵Pt-¹H HMBC experiment, are -4177 and -4036 ppm for the PPh₃ and PCy₃ complex respectively, this difference seems significative even if the solvent used was different (CDCl₃ and acetone-*d*₆). Moreover, the geometry of **8f** was ascertained by an X-ray Powder Diffraction (XRPD) analysis (*vide infra*).

Substitution reactions with cyclometalated vpy, [Pt(vpy-H)(CH₃)(DMSO)] (**2g**), proceed at room temperature and with a small excess (10% ca.) of entering ligand with both PPh₃ and PCy₃ leading to **8g** and **9g**, respectively. The products thus obtained are less soluble than the parent compound with DMSO therefore their isolation as solids has been possible. Characterization rests on NMR spectroscopy, both ¹H and ³¹P, but also on single crystal X-ray crystallography (*vide infra*).

³¹P NMR shows the presence of only one signal with satellites at δ 28.5 (J_{Pt-P} = 2020 Hz) that supports the formation of only one isomer, namely the one with the PPh₃ in *trans* to the metalated carbon, in agreement with the analogous complexes obtained with substituted bpys. In the ¹H NMR the methyl signal appears as a doublet with satellites due to the coupling with ³¹P and ¹⁹⁵Pt at 0.80 ppm (²J_{Pt-H} = 84 Hz, ³J_{P-H} = 8 Hz), notably most of the signals are beneath those of the PPh₃ and therefore an extensive analysis is hampered. An exception is the resonance of the H_β proton clearly visible at 7.90 ppm as a triplet with satellites (²J_{Pt-H} = 164 Hz); the triplet is a consequence of the fact that the coupling with the other vinylic proton (*i.e.* H_α) and the phosphorus in *trans* is very similar.

The simple substitution methodology did not afford complex **9g** as in the case of cyclometalated bpy ligands, which was therefore obtained by the one-pot two-step approach. All

the spectroscopic characteristics are in agreement with the already described **8g** the only notable differences are connected with the $J_{\text{Pt-P}}$ coupling constant and with $^3J_{\text{P-H}}$ of Pt-CH₃ that with the bulkier and more donating PCy₃ are smaller, *i.e.* 1875 Hz and 6.0 Hz respectively, this trend is also observed in the bpy series.²⁴⁷

Using [Pt(vpy-H)(Ph)(DMSO)] (**4g**) as starting material for the reaction with PPh₃ or PCy₃ in mild conditions afforded the complexes [Pt(vpy-H)(Ph)(PPh₃)] (**13g**) and [Pt(vpy-H)(Ph)(PCy₃)] (**14g**) that showed an NMR characterization similar to the corresponding methylated derivatives. Comparison of the $J_{\text{Pt-P}}$ leads to the conclusion that when the anionic ligand on Pt is phenyl coupling constants are ca. 30 Hz smaller than with the methyl. Crystals suitable for X-ray diffraction analysis were obtained for the complex [Pt(vpy-H)(Ph)(PCy₃)] (*vide infra*).

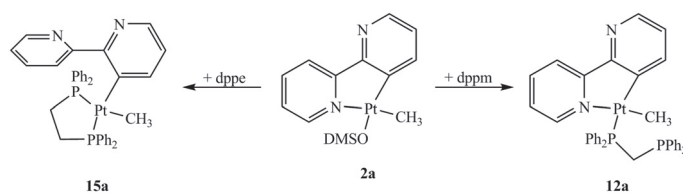
2.3 Bisphosphanes

Mononuclear derivatives

Reaction of complex [Pt(bpy-H)(CH₃)(DMSO)] (**2a**) with dppm in 1:1 ratio leads to the unusual species [Pt(bpy-H)(CH₃)(κ¹-dppm)] (**12a**) where the bisphosphine acts as a monodentate ligand.

The ¹H and ³¹P NMR data are in agreement with the formulation proposed. In the phosphorus NMR there are two doublets with satellites at very different chemical shifts δ 19.7 ($J_{\text{Pt-P}} = 2209$ Hz) and δ -24.8 ($^3J_{\text{Pt-P}} = 57.2$ Hz), the coupling between the two chemically different nuclei is $^2J_{\text{P-P}} = 78.6$ Hz. The similarity in the chemical shift of the free phosphorus atom with the one of the free dppm (δ -22) is not surprising and further supports the formulation.^{256, 260–263}

The signals in the ¹H NMR confirm that the chelated cyclometalated system still exists as evident by the H₄ ($^3J_{\text{Pt-H}} = 48$ Hz) and the H_{6'} ($^3J_{\text{Pt-H}} = \text{n.r.}$) both showing satellites due to ¹⁹⁵Pt, even if in the latter case they are too broad to permit a precise evaluation. Relative geometry is, as expected, methyl *trans* to nitrogen (0.79 ppm, $^2J_{\text{Pt-H}} = 83$ Hz, $^3J_{\text{P-H}} = 8$ Hz) and phosphorus *trans* to metalated bpy carbon.



Scheme 2.2

Stoichiometric reaction of dppe with **2a** in CH_2Cl_2 leads to the formation of a $\kappa^2\text{-P,P}$ adduct **15a** rather than to a $\kappa^1\text{-dppe}$ where the nitrogen of the cyclometalated bpy has been kicked out (Scheme 2.2). Evidences of this behaviour can be found in the ^{31}P NMR where two singlets with satellites can be seen at δ 44.7 and 43.3, their respective coupling constants with ^{195}Pt are 1953 Hz and 1814 Hz in agreement with a phosphorus coordinated to a Pt(II) metal centre having in *trans* a strong *trans*-influencing group like carbon. The chemical shift of the phosphorus atoms is diagnostic for a chelated dppe and the similarity between the coupling constants is indicative of the fact that they have similar group in *trans* position, the only reasonable option is then the one depicted in Scheme 2.2. In addition the presence of the methyl coordinated on platinum is confirmed in the ^1H NMR by the doublet of doublets at 0.47 ppm ($^2J_{\text{Pt-H}} = 76$ Hz, $^3J_{\text{P-H}} = 7.6$ and 7.0 Hz).

The reaction is particularly interesting because generates a 3-substituted-2,2'-bipyridine where the substituent is a metal complex, it is worth to note that the position 3 is more difficult to functionalize compared to the other positions of the bpy. Last but not least this new bpy can be used as ligand for other metals.²⁶⁴

Chelation of the dppe is favoured by enthalpic factors but not from the entropic point of view, in fact a $\kappa^1\text{-dppe}$ has more degrees of freedom compared to the $\kappa^1\text{-C}$ coordinated bpy; on the other hand both the cyclometalated ring and the one formed by the dppe have five members so that the preference for the latter has to be ascribed only to the involvement of stronger bonds.

As a corollary it is worth to note that in presence of extensive electron delocalization in the cyclometalated ring, *i.e.* in case of metalloaromaticity, the Pt-N bond would have been stronger probably leading to different reactivity.

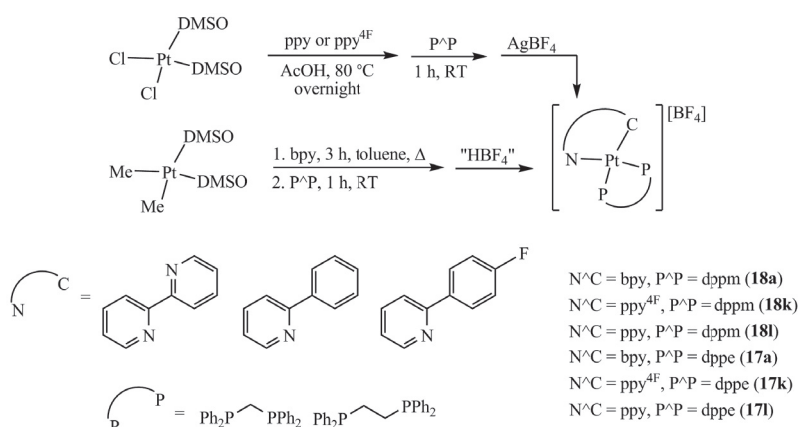
Reaction of $[\text{Pt}(\text{bpy-H})(\text{Cl})(\text{DMSO})]$ (**15a**, obtained as described in Section 3.4) with dppe leads to results very similar to the case of the corresponding methylated complex:

in the obtained $[\text{Pt}(\text{bpy-H})(\kappa^2\text{-dppe})]^+$ (**17a**) displacement of both the chloride and the DMSO ligand is a compelling evidence of the strong chelating proness of the dppe.

In the ^1H NMR almost all signals collapse in a wide region between 6.00 and 8.50 ppm and couplings are difficult to evaluate, thus preventing a complete assignment of the resonances. Due to the diastereotopic character of each of the 4 protons in the CH_2CH_2 bridge between the phosphorus atoms a broad resonance around δ 2.57 is visible and the only clearly identified signal.

^{31}P NMR is the most useful source of information to characterize the obtained complex, two singlets with satellites appear in the high frequency region of the spectrum at δ 51.8 ($J_{\text{Pt-P}} = 1949$ Hz) and δ 42.6 ($J_{\text{Pt-P}} = 3691$ Hz). The deshielding of the chelated dppe resonances in respect to the free ligand (δ -12 ppm)^{265–267} is diagnostic and the difference in the coupling constants with platinum is very well in agreement with the two different group in *trans* to each phosphorus, *i.e.* a pyridinic nitrogen and a metalated carbon.

As we wanted to compare the behaviour of the cyclometalated ligand we also performed the same reaction with ppy and ppy^{4F}. The synthetic approach used is depicted in Scheme 2.3 and proceeds through a one-pot two-step synthesis followed by treatment with AgBF_4 to remove the chloride (that can, at least in principle, coordinate) and make the chelation of the bisphosphane the most probable option (see the Experimental Section for more details).



Scheme 2.3

All the ^1H NMR spectra show extensive broadness of the signals suggesting a fluxional

behaviour in CDCl_3 solution. Some features worth to be noted: (a) for dppm complexes the CH_2 resonates around δ 4.75 for **18k** and **18l** and at 4.91 ppm for **18a** having always a $^2J_{\text{P-H}} \approx 11$ Hz; (b) a signal ascribable to the proton attached next to the nitrogen atom of the N-bound pyridine is always visible but its satellites are clear only for dppe complexes; (c) in **17k** and **18k** the signal of the proton next to the metalated carbon is always visible at ca. 6.65 ppm with satellites ($^3J_{\text{Pt-H}} \approx 50$ Hz).

Without doubt the ^{31}P NMR is the most appropriate tool to identify what's going on in solution and all the available data are collected in Table 2.4.

In general it is visible that the phosphorus atom *trans* to nitrogen, P_{N} , is always the most shielded one with a $\Delta\delta = \delta_{\text{P}_{\text{N}}} - \delta_{\text{P}_{\text{C}}}$ of ca. -7 and -10 ppm respectively for the dppm and dppe derivatives. The assignment of the phosphorus is made on the basis of the $J_{\text{Pt-P}}$ coupling constants with the metal centre, *i.e.* larger means *trans* to nitrogen and smaller *trans* to carbon.

Table 2.4: Selected ^1H , ^{19}F and ^{31}P NMR signal for complexes of general formula $[\text{Pt}(\kappa^2\text{-N,C})\text{-}(\kappa^2\text{-P,P})][\text{BF}_4]$. Chemical shifts are reported in ppm, coupling constants in Hz. Parentheses indicate coupling with ^{31}P , brackets with ^{195}Pt and braces with ^{19}F .

		bpy	ppy	ppy ^{4F}
dppm	CH_2	4.91 (10.8)	4.73 (10.7)	4.76 (10.7)
	P_{C}	-30.4 [1582] (51)	-26.7 [1403] (40)	-28.4 [1461] (41) {5.7}
	P_{N}	-36.9 [3186] (51)	-34.5 [3388] (40)	-35.9 [3318] (41)
	F	-	-	-108.5 [36] (5.7)
dppe	$^a\text{CH}_2\text{CH}_2$	2.57	2.57	2.56
	P_{C}	51.8 [1949]	50.5 [1832]	50.2 [1894] {5.2}
	P_{N}	42.6 [3691]	40.8 [3766]	40.7 [3706]
	F	-	-	-108.9 [40] (5.1)

^a Very broad signal, only the centre reported.

In the dppm series some trends are visible, as expectable the chemical shift of P_{N} doesn't seem to change very much and this is perfectly reasonable looking at the geometry of the complexes; however the coupling constant with ^{195}Pt in the bpy complex is ca. 200 Hz smaller compared to the other two. Interestingly the $J_{\text{Pt-P}_{\text{C}}}$ shows an inverse trend and is

ca. 100 Hz bigger.

The coupling constant between the two phosphorus, $^2J_{P-P}$, is bigger when the cyclometalated ligand is bpy and 10 Hz smaller with phenylpyridines (51 vs 40 Hz); it is interesting to compare its value with systems where the phosphorus atoms are connected only by the metal, namely those having general formula *cis*-[Pt(PR₃)₂XY], where X and Y are two different ligands. For example Romeo and Alibrandi reported a value of ca. 12 Hz for an extensive series of cationic complexes of the type *cis*-[Pt(PR₃)₂(Me)(MeOH)]⁺,²⁵³ another example can be found in this work in Section 3.3.2 where $J_{P-P} = 19$ Hz for the complex [Pt(bpy-H)(PR₃)₂]⁺, the comparison in this case is even more meaningful because the only difference is the absence of the CH₂ unit between the P atoms.²⁴⁷

The observed coupling in the ³¹P NMR of the chelating dppe species is the sum of two contributes both relative to a ^2J , thus having probably the same sign, one relative to the coupling through the metal centre and the other through the methylenic bridge. From the data reported it is possible to argue that the $^2J_{P-P}$ that goes through the metal centre gives a minor contribution to the observed value.

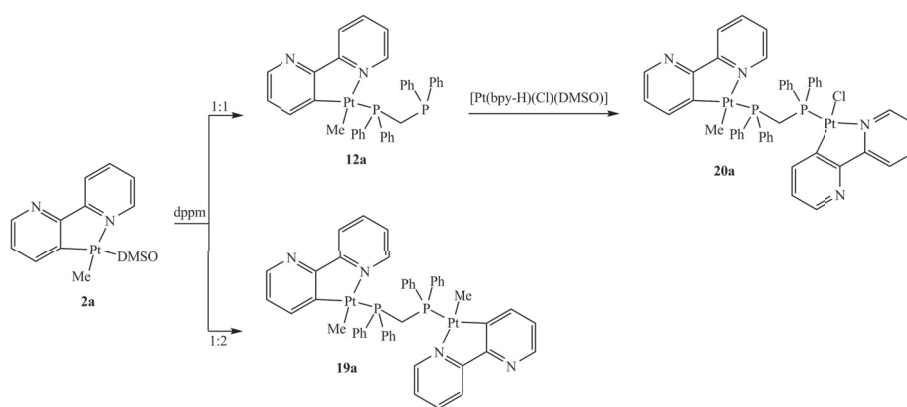
Turning the attention to the dppe series highlights a similar trend but with larger coupling constants between phosphorus and platinum and a smaller variation of the values on moving from bpy to ppys. No J_{P-P} coupling is observed in this case.

The fact that the reaction of dppe with **16a** leads to the bischelated cationic complex **17a** makes not so surprising the chelation of dppe at the expenses of the pyridinic nitrogen in **2a**. The explanation of this behaviour likely is due to the fact that dppe has the right length to form a five membered ring but also to the presence of two good donors for platinum such as phosphorus atoms. Other possible driving forces for the observed process are the formation of a second chelate ring that further stabilizes the metal centre and the intrinsic lability of the Pt-Cl bond.

Going back to the reaction with the complex [Pt(bpy-H)(CH₃)(DMSO)] (**2a**) it can be argued that in this case the ligand to be removed is not a chloride but a methyl that has a much stronger binding to platinum; in this situation the donor with lower affinity for Pt(II) is the pyridinic nitrogen and doesn't matter if it is involved in a 5-member chelate ring.

Dinuclear species with 1,1-bis(diphenylphosphino)methane

The synthesis of the dinuclear rollover μ -P,P derivatives with dppm can be achieved in different ways depending on the desired complex: multistep one-pot approach can be used if interested in a symmetric species while a classical multistep approach is mandatory if two different complexes have to be placed at the different ends of the bisphosphine (Scheme 2.4). The general principle, however, is to substitute the DMSO in $[\text{Pt}(\kappa^2\text{-N,C})\text{(X)}(\text{DMSO})]$, where $\kappa^2\text{-N,C}$ is a rollover cyclometalated ligand and X is an anionic ligand. The dinuclear complexes that have the same cyclometalated unit bound to both phosphorus atoms will be called *homodinuclear*, conversely *heterodinuclear* will be used if the two halves are different.



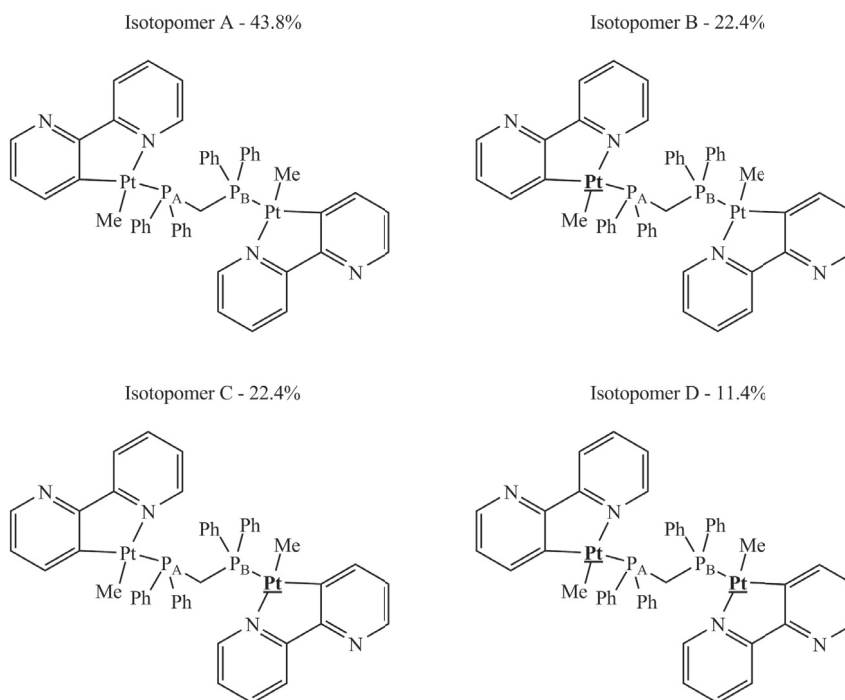
Scheme 2.4

Complex $[(\mu\text{-dppm})\{\text{Pt}(\text{bpy-H})(\text{CH}_3)\}_2]$ (**19a**) is synthesized using a one-pot approach adding 0.5 equivalent of dppm at the end of the rollover cyclometalation, usual workup leads to an orange solid that was characterized by ^1H and ^{31}P NMR spectroscopy. In the ^1H NMR all the expected signals are present but the most interesting one is the one due to the methyls at 0.74 ppm, the simulated pattern is reported in Figure 2.1a.

The peculiar pattern observed for the central signal is a consequence of the $A_3A'_3XX'$ spin system ($A = \text{CH}_3$, $X = \text{P}$) for which the coupling constants can be calculated: $^2J_{\text{Pt-H}} = 82.0$ Hz, $^3J_{\text{P-H}} = 7.1$ Hz and $^2J_{\text{P-P}} = 38.9$ Hz. The value of the coupling with ^{195}Pt ensures the coordination of the methyl *trans* to the pyridinic nitrogen.

Particularly interesting is also the deceptively simple ^{31}P NMR (Figure 2.1b) which is the

sum of different sub-spectra weighted using the relative percentage of the isotopomer that originates it. The structures of the isotopomers of **19a** are depicted in Scheme 2.5 along with the relative percentage according to ^{195}Pt natural abundance (*i.e.* 33.8%).



Scheme 2.5

Isotopomer A has two equivalent phosphorus and gives the singlet at 21.9 ppm. The satellites are mainly originated by the isotopomers B and C that give an ABX system where A = P_A is the phosphorus nucleus close to the NMR active metal centre, B = P_B is the other one and X = ^{195}Pt ; the corresponding coupling constants are $J_{\text{Pt-P}_\text{A}} = 2215$ Hz, $^2J_{\text{P-P}} = 38.9$ Hz and $^3J_{\text{Pt-P}_\text{B}} = 44.2$ Hz.

Isotopomer D, that accounts for 11.4%, is responsible for the AA'XX' system where both phosphorus atoms and both platinum atoms are chemically equivalent but magnetically different because they couple differently with a third nucleus chosen as reference.^{268, 269} Using a simulation software, gNMR,²⁷⁰ the higher order spectrum has been successfully reproduced (Figure 2.1b), this led also to the conclusion that the two platinum-phosphorus constants ($J_{\text{Pt-P}}$ and $^3J_{\text{Pt-P}}$) must have the same sign otherwise the smallest satellites would appear "outside".

We turned our attention also to the synthesis of the heterodinuclear species so we decided to react **12a** with **16a**. The synthesis in CH₂Cl₂ at room temperature resulted in a mixture of products where, among the desired species **20a**, also the signals of the corresponding homodinuclear complexes **19a** and **21a** were detected. ³¹P NMR data seem to suggest an exchange phenomenon in solution, ascribable to the continuous rupture and formation of the Pt-P bonds, that leads ultimately to the equilibrium mixture observed. In order to assess if we are in presence of a true equilibrium further tests are ongoing, in particular would be interesting to see whether a mixture of the two homodinuclear compounds gives the same spectroscopic result. A similar example, even if with a different metal and on a mononuclear complex, has been very recently reported in literature.²⁷¹

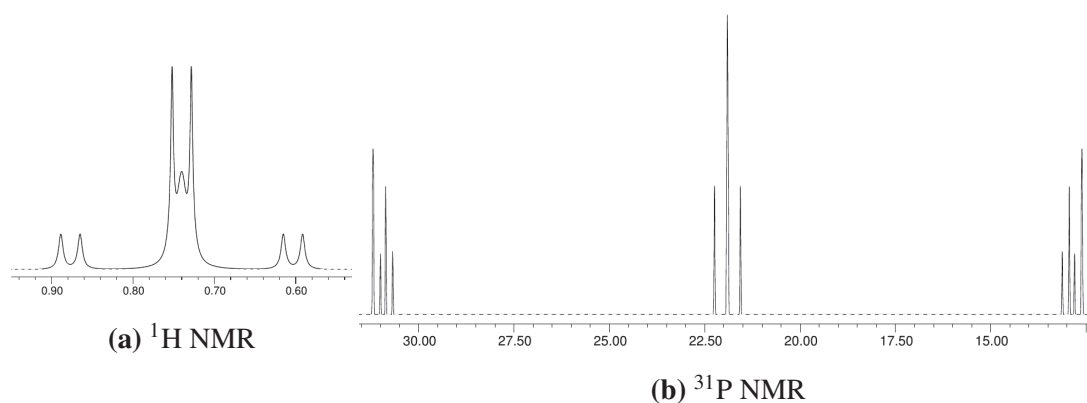


Figure 2.1: Simulated ¹H and ³¹P NMR spectra for complex [(μ-dppm){Pt(bpy-H)(CH₃)₂}]₂, **19a**.

2.3.1 Crystal structures

Single crystal X-ray of **8a**

Crystals suitable for X-ray analysis were obtained by slow evaporation of an acetone solution of [Pt(bpy-H)(CH₃)(PPh₃)] (**8a**).

The geometry around the metal centre deduced from NMR spectroscopy is confirmed by the structural analysis: a slightly distorted square planar Pt(II) complex with a κ²-N,C-cyclometalated unit, a PPh₃ and a methyl. *Trans*-influence principles are respected with methyl *trans* to nitrogen and PPh₃ *trans* to the metalated carbon.

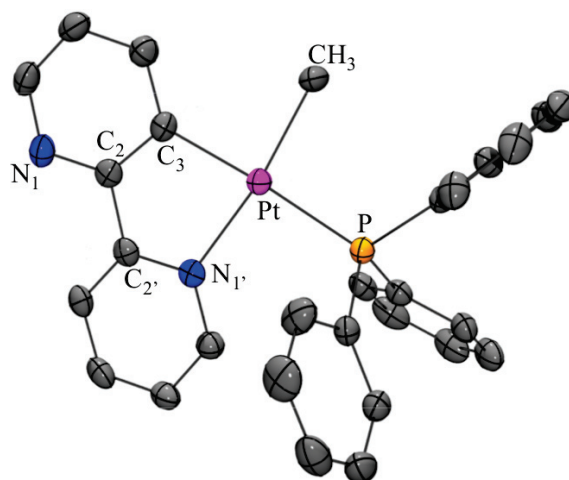


Figure 2.2: ORTEP for **8a**. Ellipsoids drawn at 50% probability level and hydrogens removed for clarity.

The structure is slightly distorted due to the presence of the bulky PPh_3 in the coordination plane and this is reflected by the angle $\text{N}_1\text{-Pt-CH}_3$, 169.3° . In order to minimize the distortion the phenyl rings adopt the disposition shown in Figure 2.2: two of them point towards the H_6 proton of the N-bound pyridine ring while the third is facing the methyl, this particular arrangement could also explain the observed shieldings of the chemical shifts of the corresponding protons (distance between proton and centroids is around 320 pm). In the crystal packing neighbouring complexes form discrete dimers interacting via a π - π overlap between the bpy ligand of one complex and a symmetry related bpy on a neighbouring complex. The interacting π systems are parallel (the interaction lies across an inversion centre) and the closest atomic contact is 329.65 (0.36) pm between C_5 of one bpy and C_7 of the symmetry related one.

Two other distortions are visible looking in more detail the groups directly attached to platinum. The first one gives an idea of the distortion of the square planar coordination towards the tetrahedral one and it is measured by the angle between the calculated mean planes through $\text{N}_1\text{'-Pt-C}_3$ and P-Pt-CH_3 which is 8.5° . The second one tells us how bent is the cyclometalated ligand compared to the mean plane containing the metal centre and the atoms directly attached, which in this case is 9.7° . Finally, the cyclometalated ligand

Table 2.5: Selected bond distances (in pm) and angles (in degrees) with corresponding ESDs in parentheses for complex **8a** compared with data obtained from DFT calculations at PBE0/def2-SVP level.

Distance	Exp	DFT	Angle	Exp	DFT
Pt-P	229.04(7)	234.9	P-Pt-CH ₃	91.41(9)	92.8
Pt-N _{1'}	213.0(2)	219.4	C ₃ -Pt-CH ₃	91.7(1)	90.1
Pt-C ₃	204.3(3)	203.7	C ₃ -Pt-N _{1'}	79.61(9)	79.5
Pt-CH ₃	207.7(4)	204.4	N _{1'} -Pt-P	97.92(6)	97.7
C ₃ -C ₂	140.5(4)	141.3			
C ₂ -C _{2'}	146.8(5)	147.0	P-Pt-C ₃	173.67(8)	176.8
C _{2'} -N _{1'}	136.0(3)	135.1	N _{1'} -Pt-CH ₃	169.3(1)	169.4

is not completely planar, the angle between the two best planes calculated through the six non-hydrogen atom of the two pyridinic rings have an angle of 6.6° bent like in an open book.

Selected bond distances and angles are visible in Table 2.5 along with the DFT calculated data.²⁴⁷ All the lengths are in the expected range and no particular deviations are worth noting, we should however point out the good agreement between optimized geometry and crystal structure with a mean absolute error of 2.6 pm on bond distances and 1 degree for angles.

Analysis of the geometrical parameters of the cyclometalated system allows us to point out that the N-bound pyridine ring does not differ very much from a normal pyridine while the metalated one has some interesting features. For instance, bonds adjacent to the 5 membered ring are slightly longer than the others and, furthermore, angles insisting on C₃, N₁ and C₅ measure less than 120 degrees while the other three compensate this being wider. Interestingly metalation has the effect of reducing the angle at C₃ to 115° and opening the one at C₂ to 125°.

Close inspection of the metallacycle does not give clues about the possible aromatic character of the ring.^{157,272}

Single crystal X-ray of **8l** and **11l**

Crystals suitable for X-ray analysis were obtained by slow evaporation of a CH_2Cl_2 solution of $[\text{Pt}(\text{ppy-H})(\text{CH}_3)(\text{PPh}_3)]$, **8l**.

^1H and ^{31}P NMR spectra are in agreement with those reported in literature²⁷³ so the product is confidently assigned; moreover, to the best of our knowledge^a, the geometry around the metal centre deduced from NMR spectroscopy is confirmed for the first time by the structural analysis: a slightly distorted square planar Pt(II) complex with a κ^2 -N,C-cyclometalated unit, a PPh_3 and a methyl. *Trans*-influence principles are respected with methyl *trans* to nitrogen and PPh_3 *trans* to the metalated carbon (Figure 2.3a).

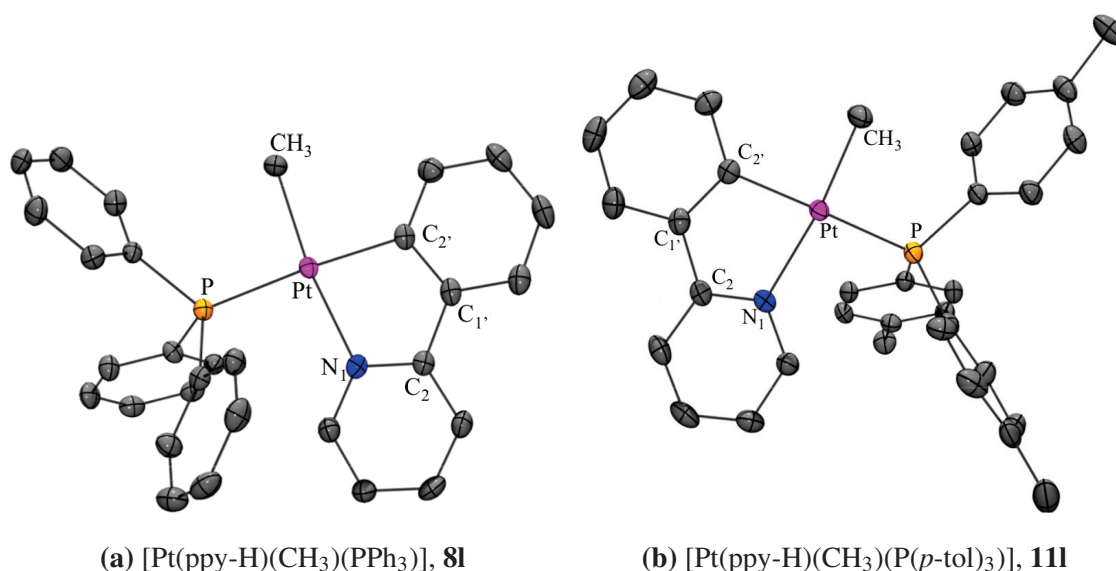


Figure 2.3: ORTEP for $[\text{Pt}(\text{ppy-H})(\text{CH}_3)(\text{L})]$. Ellipsoids drawn at 50% probability level and hydrogens removed for clarity.

In order to evaluate if the different electronic properties of the phosphanes have an influence on the structures we synthesized the corresponding complex with $\text{P}(p\text{-tol})_3$ (**11l**), this kind of substitution already demonstrated to influence the reactivity of some rollover cyclometalated complexes (see Chapter 3).²⁴⁷ Even in this case crystals suitable for X-ray analysis were obtained by slow evaporation of a CH_2Cl_2 solution. The NMR spectra are

^aReaxys, version 2.15859.10; Elsevier Information Systems GmbH. End of October 2013. CSD version 5.34 updates (November 2012).

very similar to those of **8l** and it is not surprising that the crystal structures are almost equal between the two complexes (Figure 2.3b and Table 2.6).

Both complexes crystallize in the monoclinic crystal system with a $P2_1/c$ space group, four molecules of complex are present in each of the asymmetric cells and there are no unusual interactions to report in the crystal packing.

Comparison of bond angles and distances do not show dramatic variations with the largest ones being an elongation of the Pt-P bond (≈ 1 pm) and a more distorted structure around metal centre that slightly diminishes the global planarity of the complex.

In both complexes are present a tetrahedral distortion, measured by the angle between the best planes through $C_{2'}-Pt-N_1$ and $P-Pt-CH_3$ that is larger for **11l** (11.7° vs 4.6°). The cyclometalated 2-phenylpyridine is not completely planar showing an angle between the two rings of ca. 7 degree.

Another common distortion in the two structures is the angle between the cyclometalated ligand (12 non-hydrogen atoms) and that calculated for the atoms in the coordination plane (platinum and those directly attached) that measure 8.1° and 10.4° for **8l** and **11l**, respectively.

Table 2.6: Selected bond distances (in pm) and angles (in degrees) with corresponding ESDs in parentheses for complex $[Pt(ppy-H)(CH_3)(L)]$.

Distance	8l	11l	Angle	8l	11l
Pt-P	229.55(9)	230.71(6)	P-Pt-CH ₃	91.8(1)	91.36(7)
Pt-N	213.6(3)	212.4(2)	C _{2'} -Pt-CH ₃	92.1(1)	91.39(9)
Pt-C _{2'}	204.4(3)	204.3(2)	C _{2'} -Pt-N	79.4(1)	79.78(7)
Pt-CH ₃	206.8(4)	204.9(2)	N-Pt-P	96.69(8)	98.50(5)
C _{2'} -C _{1'}	141.2(5)	141.4(3)			
C _{1'} -C ₂	146.9(5)	147.2(3)	P-Pt-C ₃	174.0(1)	170.48(6)
C ₂ -N ₁	135.9(5)	135.7(2)	N-Pt-CH ₃	171.5(1)	168.67(9)

Single crystal X-ray of **8g**

Crystals of $[Pt(vpy-H)(CH_3)(PPh_3)]$ suitable for X-ray analysis were obtained from a cooled ethereal solution of the complex. The solved structure (see Figure 2.4) confirms

the geometry deduced from the solution NMR studies: a four coordinated platinum(II) metal centre where the vpy is cyclometalated and the other two positions are occupied by the Me group and the PPh₃ in position *trans* to the nitrogen and to the metalated carbon (C_β) respectively. The principal geometrical parameters are collected in the inset in Figure 2.4. The complex shows a remarkable planarity both in the coordination plane and in the cyclometalated moiety, the largest deviation from the best plane comprising the metal and its bounded atoms is ascribable to the C_β which is 0.014 Å away from the plane.

The orientation of the aromatic rings attached to phosphorus give an explanation of the

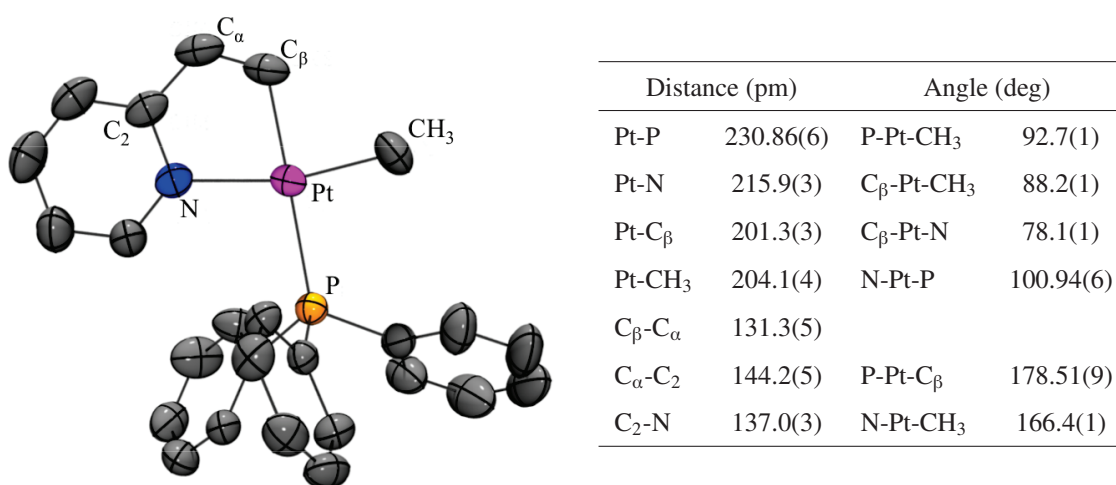


Figure 2.4: ORTEP for **8g**. Ellipsoids drawn at 50% probability level and hydrogens removed for clarity.

chemical shift observed for the H₆ and the CH₃ protons, these signals are more shielded because they are influenced by the shielding cones of the phenyls. The extent of this effect is particularly impressive on H₆ which has a difference of ca. 1 ppm if compared with its analogue in complex **9g** (see Experimental Section).

Angles around platinum are in line with the steric requirements of the ligands: cyclometalated vpy has a "bite" of 78.1° while the angles involving phosphorus are bigger than 90° which seems reasonable looking at the hindrance of the PPh₃.

The structure has a very slight pyramidal distortion highlighted by the angle between the best planes calculated through N-Pt-C_β and P-Pt-CH₃ which is only 1.2 degrees. Moreover the best plane through the cyclometalated ligand has an angle of 3.8 degrees with the fragment comprising the metal centre and the two other ligands. There are no unusual

interactions due to packing and no particular contacts worth noting.

Single crystal X-ray of **14g**

Crystals of $[\text{Pt}(\text{vpy-H})(\text{Ph})(\text{PCy}_3)]$ suitable for X-ray analysis were obtained from a cooled ethereal solution. The solved structure (see Figure 2.5) confirms the geometry deduced from the solution NMR studies: a four coordinated platinum(II) metal centre where the vpy is cyclometalated and the other two positions are occupied by the Ph group and the PCy_3 in position *trans* to the nitrogen and to the metalated carbon (C_β) respectively. The principal geometrical parameters are collected in the inset in Figure 2.5. The complex is planar with the largest deviation from the best plane comprising the metal and its bounded atoms ascribable again to the C_β which is 0.061 Å away from the plane.

Angles around platinum are similar to those in **8g** obeying to the steric requirements

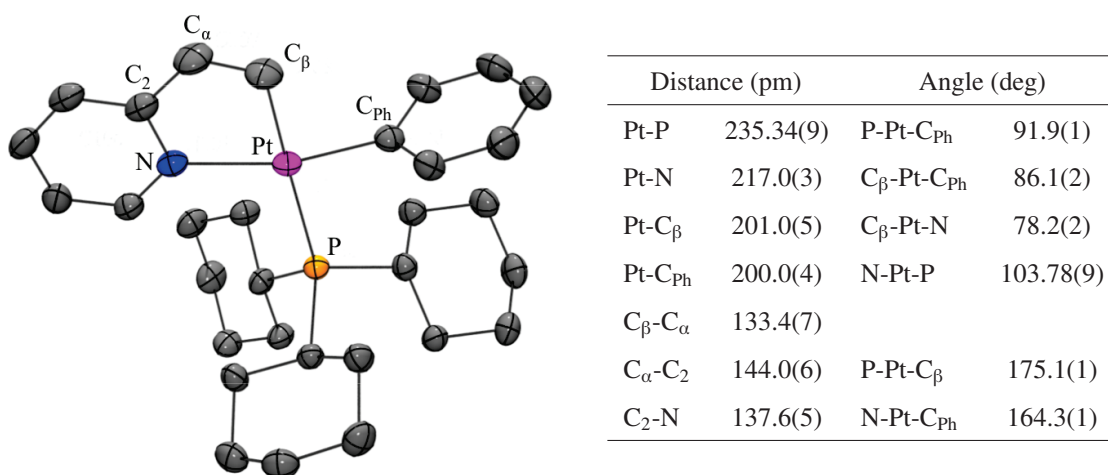


Figure 2.5: ORTEP for **14g**. Ellipsoids drawn at 50% probability level and hydrogens removed for clarity.

of the ligands: cyclometalated vpy has a "bite" of 78.2° while the angles involving the PCy_3 are wider, compared with **8g**, accounting for the increased cone angle of the phosphine.²⁴⁹ Steric strain is somewhat relieved by the presence of the phenyl which bends away from the phosphane taking advantage of its perpendicular coordination in respect to the cyclometalated plane (89.8°).

The structure has a slight pyramidal distortion highlighted by the angle between the planes

passing through N-Pt-C $_{\beta}$ and P-Pt-CH $_3$ which is only 4.5 degrees. Moreover the best plane through the cyclometalated ligand (all 8 non-hydrogen atoms) has an angle of 6.3 degrees with the fragment comprising the metal centre and the two other ligands. There are no unusual interactions due to packing and no particular contacts worth noting.

XRPD structure of **8f**

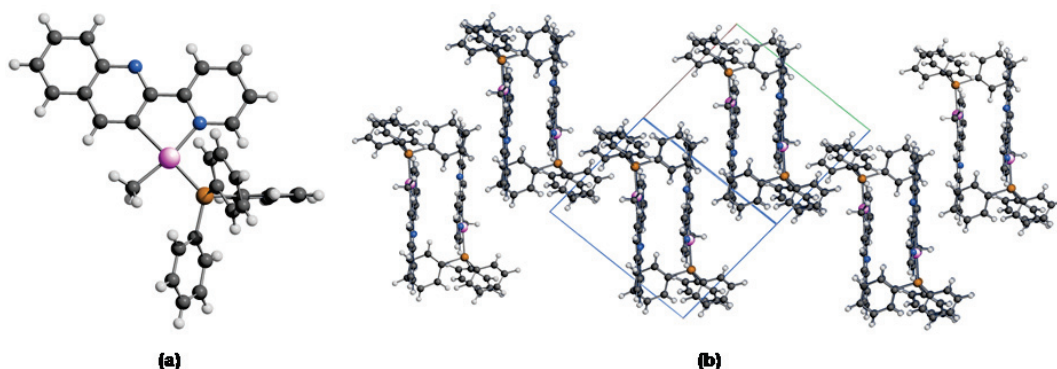
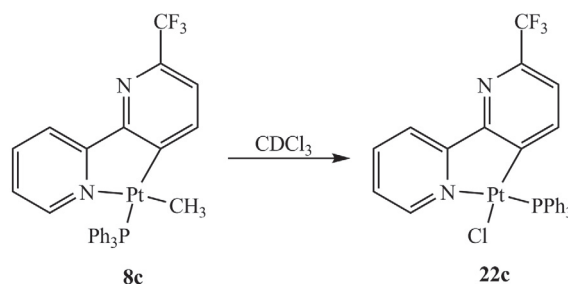


Figure 2.6: Portion of the crystal structure of species **8f**: (a) the Pt(II) complex; (b) the packing, from which the intermolecular π - π interactions involving couples of symmetry-related pyq ligands can be appraised.

Species [Pt(pyq-H)(CH $_3$)(PPh $_3$)] crystallizes in the triclinic space group $P\bar{1}$. Its asymmetric unit comprises one **8f** complex (Figure 2.6a), lying on a general position. The steric hindrance is responsible for the actual orientation of the PPh $_3$ moiety, no phenyl ring being obviously coplanar with the pyq ligand. The reciprocal disposition of the complexes is dictated by the formation of intermolecular π - π interactions between couples of parallel pyq ligands, lying approximately on the (11-2) plane, and facing each other at about 3.4 Å (Figure 2.6b). The two π - π interacting complexes are mutually related by a crystallographic inversion centre; thus, no Pt $\cdots$ Pt contacts can be appraised together with the π - π ones.

2.3.2 Reactions with CDCl_3

While analysing the $[\text{Pt}(\text{bpy}^{6\text{CF}_3}\text{-H})(\text{CH}_3)(\text{PPh}_3)]$ (**8c**) complex, after a couple of hours, we noticed some changes in the NMR spectra of the CDCl_3 solutions of the samples. In particular both the chemical shift of the phosphorus and the $J_{\text{Pt-P}}$ coupling constant changed respectively to 22.8 ppm and 4238 Hz from 32.1 ppm and 2279 Hz, demonstrating that in solution we have a Pt(II) complex with a phosphorus coordinated *trans* to a group with a lower *trans*-influence compared to carbon. More information are collected from the ^1H NMR which does not show anymore the doublet with satellites integrating three protons relative to the methyl group but, in the aromatic region, still six resonances are present with one of these very deshielded at δ 9.87 with satellites that is characteristic of an $\text{H}_{6'}$ spatially close to an halogen.^{16,34}



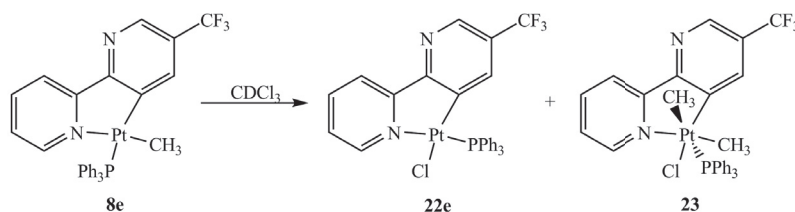
Scheme 2.6

All the data described point in the direction of a cyclometalated compound with an halogen and a phosphine coordinated on the metal centre so we safely describe the complex as $[\text{Pt}(\text{bpy}^{6\text{CF}_3}\text{-H})(\text{Cl})(\text{PPh}_3)]$ (**22c**) probably formed by reaction of the methylated compound with HCl (or DCl) formed with a photochemical reaction of the CDCl_3 solvent (Scheme 2.6); the geometry, dictated by the *trans*-influence, places the phosphine *trans* to the nitrogen and the chloride *trans* to the metalated carbon.

The same happens with $[\text{Pt}(\text{bpy}^{5\text{CF}_3}\text{-H})(\text{CH}_3)(\text{PPh}_3)]$ (**8e**) that upon reaction with HCl (or DCl) gives the corresponding chloride **22e** releasing methane (or CH_3D) by selective protonolysis of the Pt-CH_3 bond. The spectroscopic data in this case are a ^{31}P chemical shift of 21.9 ppm with $J_{\text{Pt-P}} = 4208$ Hz and a $\text{H}_{6'}$ that resonates at δ 9.90 due to the proximity with the chloride.

In the spectra another species is visible that is characterized by the presence of two methyls at δ 0.87 ($^2J_{\text{Pt-H}} = 57.6$ Hz, $^3J_{\text{P-H}} = 7.8$ Hz) and δ 1.50 ($^2J_{\text{Pt-H}} = 68.4$ Hz, $^3J_{\text{P-H}} = 7.8$ Hz) but also, in the ^{31}P , by a singlet with satellites at -4.0 ppm ($J_{\text{Pt-P}} = 958$ Hz). These two data indicate that a Pt(IV) dialkyl species is present in solution, namely $[\text{Pt}(\text{bpy}^{5\text{CF}_3}\text{-H})(\text{CH}_3)_2(\text{Cl})(\text{PPh}_3)]$ (**23e**, Scheme 2.7). The data are in nice agreement with other Pt(IV) compounds synthesized and characterized (see Chapter 4).

The behaviour of the trifluoromethyl-bpys is different compared to simple bpy and to the



Scheme 2.7

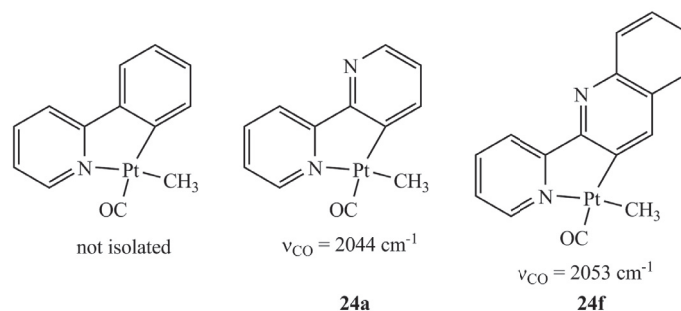
alkyl-substituted ones because they are more reactive, for example in the same conditions complex $[\text{Pt}(\text{bpy-H})(\text{CH}_3)(\text{PPh}_3)]$ (**8a**) does not react as it requires longer times.¹⁶ If the formation of the Pt(II) chloride complexes from the corresponding methyl ones can be explained (see Chapter 3), the presence of the Pt(IV) compound is somewhat puzzling and we are currently investigating this aspect.

2.4 Substitution with CO

Another interesting probe to evaluate the electronic effects of the cyclometalated ligand on the properties of the complex lies in the use of carbon monoxide, CO, as ligand. Characteristic infra-red (IR) stretching frequency of the CO has been used for long time as a parameter to evaluate the properties of the ligand coordinated in *trans* (or even *cis*) position.^{249,274–277}

As with the phosphanes (see Section 2.2) the substitution is performed in mild conditions starting from the relevant $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{DMSO})]$ compound or by bubbling CO in the reaction mixture at the end of the cyclometalation process.

The IR spectra of the carbonyl species $[\text{Pt}(\text{bpy-H})(\text{CH}_3)(\text{CO})]$ (**24a**) and $[\text{Pt}(\text{pyq-H})-$



Scheme 2.8

(CH₃)(CO)] (**24f**) show different CO stretching frequencies: a lower frequency for **24a** ($\nu_{\text{CO}} = 2044 \text{ cm}^{-1}$) and a higher frequency for **24f** (2053 cm^{-1} , Scheme 2.8). The difference can be ascribed to the different electronic effect of the pyridyl *vs* the quinolyl metalated group with the less delocalized one having a stronger donating effect. Both complexes may have some points of interest having three Pt-carbon bonds, each in a different hybridization state (*sp*, *sp*², *sp*³). Notably, as also confirmed by the XRPD structural analysis (*vide infra*), the complex contain an uncommon *trans* C-Pt-C arrangement, usually considered highly unstable because of the high *trans* influence of carbon donors (*trans*-phobia).^{142,143,261} It is interesting to note that from these complexes a relative *trans*-influence order or the *sp* hybridised carbon atoms can be deduced: C(*sp*³) > C(*sp*²) > C(*sp*). On the whole, however, this trend involves different groups attached to the carbon atoms, *i.e.* protons, *sp*² carbon atoms and oxygen, therefore a proper comparison is not possible strictly speaking.

Taking in account this arrangement a stability comparison can be made, in fact the complex with pyq is highly stable, differently from the analogous rollover complex **24a** which tends to decompose, and from the cyclometalated complex [Pt(ppy-H)(CH₃)(CO)], not isolated in the solid state.¹³⁷ The geometry of the complexes in solution was further confirmed by ¹H-NOE 1D spectra, which show NOE contacts between the Pt-CH₃ and the H₄ protons.

XRPD structure of **24f**

Species [Pt(pyq-H)(CH₃)(CO)] (**24f**) crystallizes in the monoclinic space group P2₁. The asymmetric unit contains two crystallographically independent complexes (Figure 2.7a).

The two independent complexes lie approximately on the (210) plane (and on the symmetry related one (2-10)), forming piles of staggered moieties along [210]. Along the piles, Pt...Pt contacts of about 3.4 Å can be envisaged between couples of consecutive complexes (Figure 2.7b). Visualized along the crystallographic axis *c*, the adjacent stacks describe a herringbone motif.

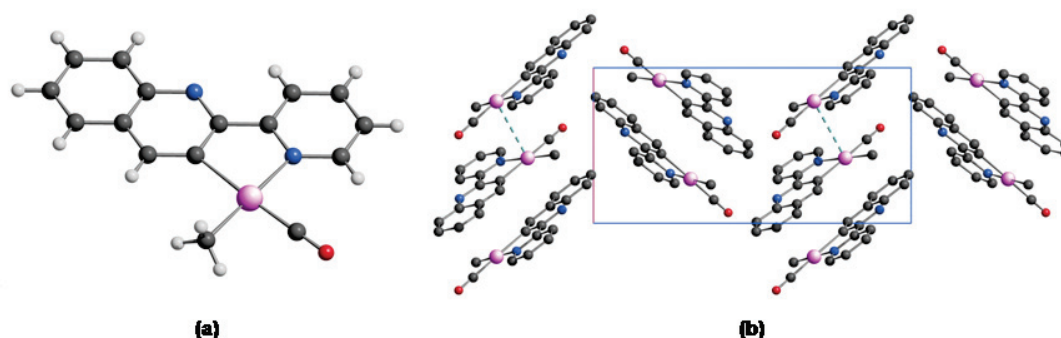
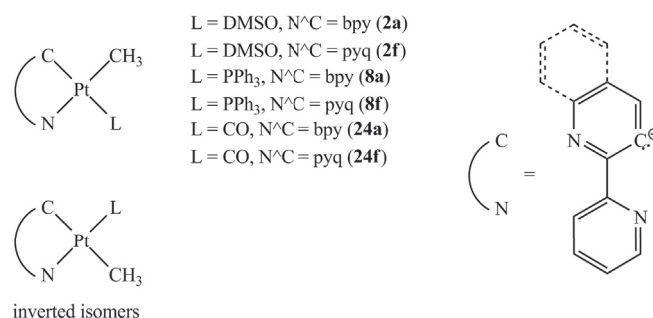


Figure 2.7: Portion of the crystal structure of species **24f**: (a) one of the two crystallographically independent complexes; (b) the packing, viewed along [001]. Horizontal axis, **a**; vertical axis, **b**. The Pt...Pt non bonding interactions are highlighted with cyan fragmented lines. Hydrogens atoms have been omitted in panel (b) for the sake of clarity.

2.5 DFT Calculations

In square planar complexes having a chelating ligand that blocks two positions, as in $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{L})]$, two isomers are possible, namely, one with the methyl residue *trans* to the nitrogen atom, and the other where the methyl group is *trans* to the metalated carbon atom (Scheme 2.9).

Complexes $[\text{Pt}(\text{bpy-H})(\text{CH}_3)(\text{DMSO})]$ (**2a**), $[\text{Pt}(\text{pyq-H})(\text{CH}_3)(\text{DMSO})]$ (**2f**), $[\text{Pt}(\text{bpy-H})(\text{CH}_3)(\text{PPh}_3)]$ (**8a**), $[\text{Pt}(\text{pyq-H})(\text{CH}_3)(\text{PPh}_3)]$ (**8f**), $[\text{Pt}(\text{bpy-H})(\text{CH}_3)(\text{CO})]$ (**24a**), $[\text{Pt}(\text{pyq-H})(\text{CH}_3)(\text{CO})]$ (**24f**), and their corresponding isomers with inverse geometry, *i.e.* C-*trans*-C and L-*trans*-N (Scheme 2.9), were optimized at the PBE0/def2-SVP level of theory. In each case the isomer deduced from the NMR data is the one that has the lowest energy and the biggest $E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}$ in agreement with the Maximum Hardness



Scheme 2.9

Principle (MHP),^{278–280} the calculated relative enthalpy differences (298.15 K and 1 atm) along with the E_{gap} for the two isomer of each complex are collected in Table 2.7 where the isomer having the lowest energy has been taken as reference. The calculated data fit well in the framework of *trans*-phobia^{142, 143, 261} and antisymbiosis¹³⁹ effect.

Table 2.7: Enthalpies, in $\text{kJ}\cdot\text{mol}^{-1}$, and E_{gap} , in eV, for some $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{L})]$ complexes obtained at PBE0/def2-SVP level.

		$\Delta H \text{ (kJ}\cdot\text{mol}^{-1})$	$E_{\text{gap}} \text{ (eV)}$
2a	exp	0.0	4.71
	inv	46.2	4.34
2f	exp	0.0	4.37
	inv	46.8	3.98
8a	exp	0.0	4.49
	inv	21.5	4.24
8f	exp	0.0	4.23
	inv	20.1	3.96
24a	exp	0.0	4.73
	inv	12.4	4.31
24f	exp	0.0	4.36
	inv	12.8	4.08

The series of phosphane complexes $[\text{Pt}(\text{bpy-H})(\text{CH}_3)(\text{PR}_3)]$, **8a-11a**, has been optimized

Table 2.8: Selected bond distances (in pm) and angles (in degrees) for complexes [Pt(bpy-H)(CH₃)(L)] optimized at PBE0/def2-SVP level.

L	PPh ₃	PCy ₃	P(OPh) ₃	P(<i>p</i> -tol) ₃
Pt-P	234.920	240.027	225.061	235.137
Pt-CH ₃	204.446	204.067	206.163	204.418
Pt-C ₃	203.727	203.832	204.933	203.725
Pt-N _{1'}	219.397	221.738	217.416	219.300
N _{1'} -C _{2'}	135.079	135.093	135.008	135.083
C _{2'} -C ₂	147.052	146.757	147.131	147.055
C ₂ -C ₃	141.345	141.271	141.211	141.361
P-Pt-CH ₃	92.77	91.77	88.29	92.74
CH ₃ -Pt-C ₃	90.12	88.19	89.89	90.20
C ₃ -Pt-N _{1'}	79.47	78.84	79.41	79.47
N _{1'} -Pt-P	97.68	101.26	102.42	97.64
N _{1'} -Pt-CH ₃	169.39	166.63	169.29	169.47
P-Pt-C ₃	176.84	178.74	177.39	176.80

at PBE0/def2-SVP level of theory and some selected bond distances and angles are visible in Table 2.8.

The particular functional/basis-set couple was chosen because, after a benchmark screening, it showed the best compromise between accuracy in reproducing geometrical parameters and computational time.

The data in Table 2.8 can be compared with experimental data resulting from ¹H and ³¹P NMR spectroscopy in Table 2.2; keeping in mind the differences between the two conditions only qualitative trends will be discussed.

In general we can observe that all the geometries are similar to each other displaying a square planar coordination for the platinum metal centre, bond distances and angles are in the expected ranges and no particular deviations are evident. The biggest variation, as expected, are visible in the proximity of the phosphane.

Platinum-phosphorus bond distances are in agreement with J_{Pt-P} coupling with the longest bond found for the complex with the lowest coupling, *i.e.* **9a**, and vice versa for **10a** that displays the the shortest bond and the largest J_{Pt-P}.

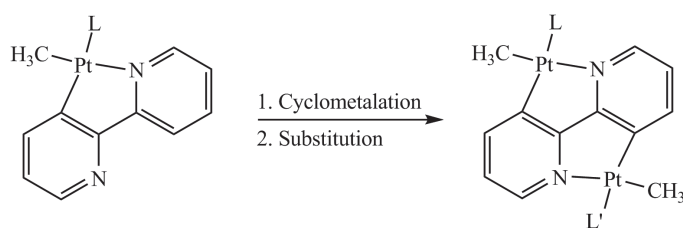
Reasonable correlations can be found also between the Pt-C₃ distances with the ³J_{Pt-H} for

the H_4 proton but, in this case, drawing conclusions is more tricky because coupling constants are influenced also by the angles. Taking into account this precautions a reasonable agreement is evident although with smaller variations in both distances and coupling constants.

The steric hindrance of the coordinated phosphanes can be evaluated by summing the values of the angles involving phosphorus, *i.e.* $P-Pt-CH_3$ and $N_{1'}-Pt-P$. The obtained values of 190.45 (**8a**), 193.03 (**9a**), 190.71 (**10a**) and 190.38 (**11a**) show the interesting value obtained for $P(OPh)_3$ that is comparable with arylphosphines PPh_3 and $P(p-tol)_3$; as expected PCy_3 , being the largest on the basis of Tolman cone angle, has the largest value.

2.6 Doubly cyclometalated bpy

The rollover cyclometalated compounds closely resemble the analogous derivatives of 2-phenylpyridine.^{31–35} A striking difference between the two families of complexes is the presence (or absence) of the uncoordinated nitrogen atom. For this reason compounds $[Pt(bpy-H)(CH_3)(L)]$ and $[Pt(bpy-H)(Cl)(L)]$ are able to further react to give dinuclear species of general formula $[(L)(X)Pt(\mu-bpy-2H)Pt(X')(L')]$ ($X, X' = Me, Cl$; $L, L' = PPh_3, DMSO, CO$, etc.), where the doubly deprotonated 2,2'-bipyridine acts as a planar, delocalized dianionic bridging ligand (Scheme 2.10).²⁸¹



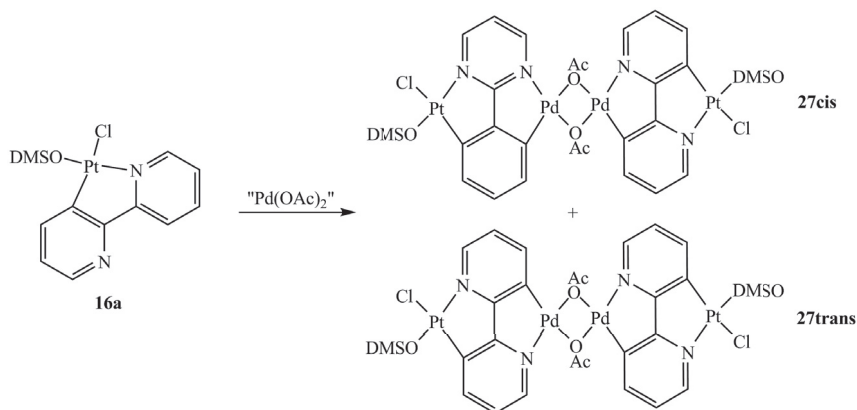
Scheme 2.10

This synthetic route has made possible the synthesis of both symmetric ($L = L', X = X'$; *e.g.* $[(PPh_3)(Me)Pt(\mu-bpy-2H)Pt(Me)(PPh_3)]$, **25**) and unsymmetrical ($L \neq L', X \neq X'$; *e.g.* $[(PPh_3)(Me)Pt(\mu-bpy-2H)Pt(Cl)(CO)]$, **26**) species. A logical consequence of this approach is that the second cyclometalation may involve a different metal from the first one and hence may produce heterodinuclear species where the metal centres are strictly

connected by the delocalized bridging ligand.

The synthesis of these dinuclear complexes, however, is not trivial. As shown by the X-ray crystal structure of $[\text{Pt}(\text{bpy-H})(\text{Cl})(\text{PPh}_3)]$ (**22a**),¹⁶ the distance between the hydrogen atom bonded to $\text{C}_{3'}$ and the uncoordinated nitrogen is 257.9 pm (average distance in two independent molecules), slightly less than the sum of van der Waals radii (109 + 155 pm). According to these data the uncoordinated nitrogen may not be easily available for coordination, at least on the basis of steric considerations.

As a starting point we reacted $[\text{Pt}(\text{bpy-H})(\text{Cl})(\text{DMSO})]$ (**16a**) with palladium acetate in refluxing benzene to obtain the tetranuclear species $[(\text{DMSO})(\text{Cl})\text{Pt}-(\mu\text{-bpy-2H})\text{Pd}-(\mu\text{-OAc})_2]$ (**27**, Scheme 2.11).

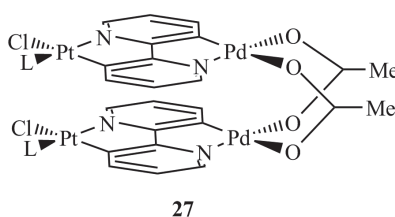


Scheme 2.11

The ^1H NMR spectrum of the isolated product shows two sets of resonances, indicating the presence of two species in a 4:1 molar ratio. The subspectra of these species are very similar: in both cases the aromatic region contains six protons, suggesting a second C-H bond activation. In the aliphatic region the main species has two signals ascribable to coordinated DMSO ligands (δ 3.83 ppm, 6H, $^3J_{\text{Pt-H}} = 17$ Hz; δ 3.49 ppm, 6H, $J_{\text{Pt-H}} = 19$ Hz) and only one for the acetato groups (δ 2.22 ppm, 6H). In contrast, the minor species possesses two signals for the DMSO methyls (3.79 and 3.49 ppm, 6H + 6H partially overlapping) and two singlets for the acetato ligands (2.64 and 2.17 ppm, 3H + 3H). This is in line with the proposed tetranuclear species **27**, present as the **27trans** and **27cis** isomers. The main species, **27trans**, should have two equivalent acetato bridging ligands;

the DMSO ligands should be chemically equivalent as well (Scheme 2.11).

Acetato dimeric species usually have a folded structure,^{282,283} which in our case should render diastereotopic the methyls of the same DMSO (planar chirality, Scheme 2.12). The minor species **27cis** possesses chemically inequivalent acetato ligands but equivalent coordinated DMSO. Due to the folded conformation of the complex, in this case, again the methyl groups in the same DMSO should be diastereotopic.



Scheme 2.12

In the absence of a structural characterization we investigated the nature of acetato complexes through mono- and multidimensional ^1H NMR spectroscopy (COSY and GOESY²⁸⁴ experiments). For complex **27trans** the ^1H GOESY experiments show, *inter alia*, enhancement of the signals at 7.04 (H_4) and 7.55 ppm ($\text{H}_{6'}$) after irradiation of the acetato signal, confirming that they are adjacent to the Pd atom. Irradiation of aromatic signals confirms that peaks that in a planar conformation would not be expected to be in close proximity to each other actually are: *e.g.*, irradiation at 7.04 ppm (H_4) enhances the signal at 7.55 ppm ($\text{H}_{6'}$) and vice versa. In addition an extremely small, but significant, enhancement is present between the H_5 and $\text{H}_{5'}$ protons.

The DMSO signal at 3.85 ppm enhances the peaks at 8.26 ($\text{H}_{4'}$) and 8.55 (H_6), whereas the other signal, at 3.49 ppm, enhances only the $\text{H}_{4'}$ peak. All these data fit with a bent molecule having, on the NMR time scale, a nonrotating DMSO, with the S=O bond in the plane, one methyl (at 3.85 ppm) inside the folded molecule, and the other one (at 3.49 ppm) pointing out.

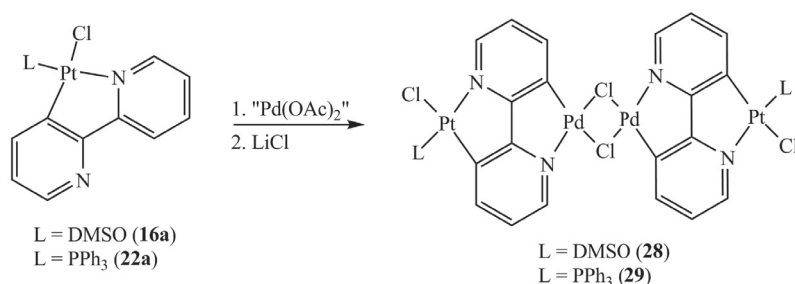
In addition, the spectra seem to indicate that there may be some exchange between the two Me groups on the same DMSO, as both are diminished in intensity upon irradiation of the other one, rather than each enhancing the other. This is consistent with a dynamic behaviour of the molecule which inverts the structure, so that the methyl pointing out be-

comes in and vice versa.

Furthermore, irradiation of some of the peaks of the major compound causes a small amount of negative enhancement of the peaks of the minor component. This would imply that they are in slow chemical exchange.

In agreement with the proposed formulation the IR spectrum shows bands in the region 1390-1570 cm^{-1} (see the Experimental Section) consistent with bridging acetato ligands.²⁸⁵

The reaction of **16a** with palladium acetate may be followed by treatment with LiCl, to give the corresponding chloride $[(\text{DMSO})(\text{Cl})\text{Pt}(\mu\text{-bpy-2H})\text{Pd}(\mu\text{-Cl})_2]$ (**28**). Analogously, starting from **22a**, $[(\text{PPh}_3)(\text{Cl})\text{Pt}(\mu\text{-bpy-2H})\text{Pd}(\mu\text{-Cl})_2]$ (**29**) may be isolated in the solid state in good yields and characterized. In contrast to the acetato species, the chloride-bridged complexes are flat, with evidence coming from the ^1H NMR spectra which show only one resonance for the DMSO protons (Scheme 2.13).



Scheme 2.13

The ^1H NMR spectra of the tetranuclear complexes with bridging chlorides show only one set of signals and support the given formulation. In particular, the coupling constants of the DMSO signal in the ^1H spectrum of **28** ($^3J_{\text{Pt-H}} = 25.2$ Hz) and of the coordinated phosphorus in **29** ($J_{\text{Pt-P}} = 4154$ Hz) agree with neutral ligands coordinated *trans* to a nitrogen atom.

Starting from the tetranuclear species **28** and **29** subsequent reactions lead to cleavage of the anionic bridge between the two palladium centres and the generation of relatively simple bimetallic species. Starting from **28**, apart from opening the chloride bridge, the neutral ligand may also displace the coordinated DMSO: the reactions with PPh_3 or 3,5-lutidine, driven with at least a 4:1 ligand:complex molar ratio, gave the heterodinuclear

"symmetric" species **30** ($L = L' = \text{PPh}_3$) and **31** ($L = L' = 3,5\text{'-lutidine}$).

The ^1H and ^{31}P NMR spectra of complex $[(\text{PPh}_3)(\text{Cl})\text{Pt}(\mu\text{-bpy-2H})\text{Pd}(\text{Cl})(\text{PPh}_3)]$ (**30**) clearly show the different influences of palladium and platinum on the chemical shifts. In the ^{31}P NMR spectrum the phosphorus coordinated to platinum is unambiguously assigned by the presence of satellites. The coupling constant value ($J_{\text{Pt-P}} = 4155 \text{ Hz}$) is in agreement with a *trans* P-Pt-N arrangement. The chemical shifts of the two phosphorus atoms are very different (41.9 ppm, P-Pd; 19.8 ppm, P-Pt), as previously observed in corresponding cyclometalated palladium and platinum complexes.^{286,287}

The protons adjacent to the nitrogen, H_6 and $\text{H}_{6'}$, are slightly deshielded by coordination; as is often observed, the deshielding effect of the platinum is greater than that of palladium (δ next to Pt 9.05 ppm, δ next to Pd 8.85 ppm). A comparison between analogous mono- and dinuclear rollover species (Scheme 2.14 and Table 2.9) evidences the shielding of the $\text{H}_{6'}$ proton upon the second metalation (9.85, 9.06, and 9.05 ppm in **30**, $[\text{Pt}_2(\mu\text{-bpy-2H})(\text{PPh}_3)_2(\text{Cl})_2]$ (**30'**), and **22a**, respectively), apparently independent from the nature of the second metal. The second metalation has consequences also in the ^{31}P NMR spectra, in both chemical shift and coupling constant values.

Operating under mild conditions, starting from **29**, the "unsymmetrical" complex $[(\text{PPh}_3)(\text{Cl})\text{Pt}(\mu\text{-bpy-2H})\text{Pd}(\text{Cl})(3,5\text{-lut})]$ (**32**) can be isolated in the solid state by reaction with 3,5-lutidine. As expected, 3,5-lutidine opens the chloride bridge but does not displace PPh_3 .

The NMR spectra confirm in solution the coordination of the neutral ligands *trans* to the bpy nitrogen, as indicated by $J_{\text{Pt-P}}$ and $^3J_{\text{Pt-H}}$ (ortho lutidine protons) coupling constants (4155 and 55.8 Hz, respectively). Furthermore, the position of H_4 and $\text{H}_{4'}$ in the spectrum (multiplet at ca. 6.6-6.8 ppm) is due to the shielding effect of the adjacent PPh_3 and lutidine, respectively. The structure of **32** was definitely confirmed by the resolution of the crystal structure in the solid state by X-ray diffraction (Figure 2.8).

Distances and angles are in line with those previously reported for the analogous homodinuclear rollover complex **30'** (e.g., Pt-Cl = 235.2 pm, Pt-C = 211.3 pm, Pd-C = 200.4 pm, Pd-Cl = 239.4 pm).¹⁶ The bpy-2H bridging ligand is almost completely planar.

Electronic delocalization through the two planar deprotonated bpy rings and the cyclomet-

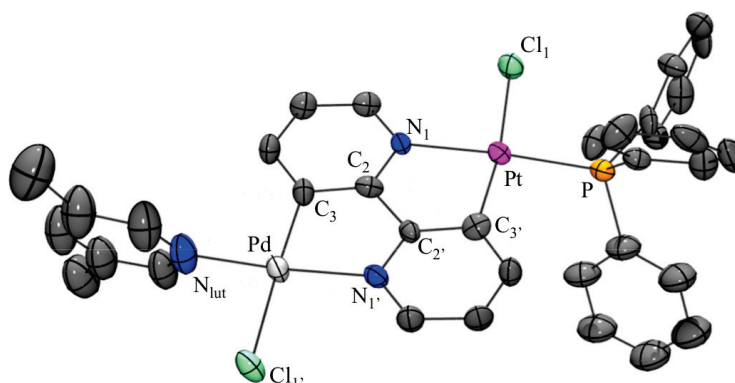
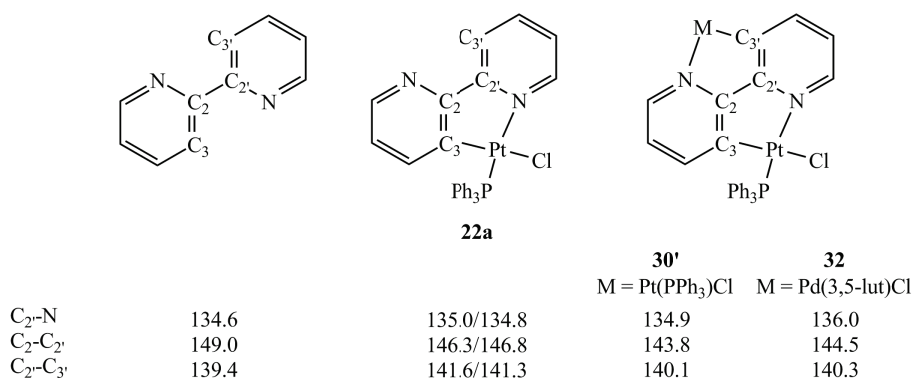


Figure 2.8: ORTEP of the solid-state structure of one of the crystallographically independent but chemically identical molecules in the asymmetric unit of **32**. Hydrogens and disordered solvent have been removed for clarity. Ellipsoids are drawn at the 50% probability level.

alated rings (metalloaromaticity) may be deduced by the short $C_2-C_{2'}$ bond, whose length decreases from 149.0 pm in free 2,2'-bipyridine²⁸⁸ to 146.3/146.8 pm in **22a**, 143.8 pm in **30'**, and 144.5 pm in **32** (see Scheme 2.14). Similar trends were used to identify metalloaromaticity in palladium(II) five-membered cyclometalated species.¹⁵⁷ It should be noted, however, that in species **22a**, **30'** and **32** no clear corresponding elongation is observed in C_2-N and $C_{2'}-C_3$ bond lengths and the shortening of the $C_2-C_{2'}$ bond may be due to double chelation effects of the bpy-2H ligand.



Scheme 2.14

NMR Spectra

The ^{195}Pt NMR spectra of **22a**, **27**, **30-32** and **33** were obtained by means of ^{195}Pt - ^1H correlation spectra using a variant of the HMBC pulse sequence. A first comparison of the spectra shows, as expected, that the major influence on the chemical shift is provided by the nature of the ligands on the platinum centre, so that the species having the same $\text{Pt}(\kappa^2\text{-N,C})(\text{PPh}_3)\text{Cl}$ environment (**22a**, **30**, **32** and **33**) have similar chemical shifts (see Table 2.9), whereas complex **33**, having a 3,5-lutidine instead of a PPh_3 , shows a deshielding of more than 1000 ppm. This is in line with literature data, which indicate the same trend when a nitrogen donor is replaced by a phosphine.²⁸⁹ The same behaviour is observed for complexes **27** (*trans* and *cis*), which have a Pt-S instead of a Pt-P bond.

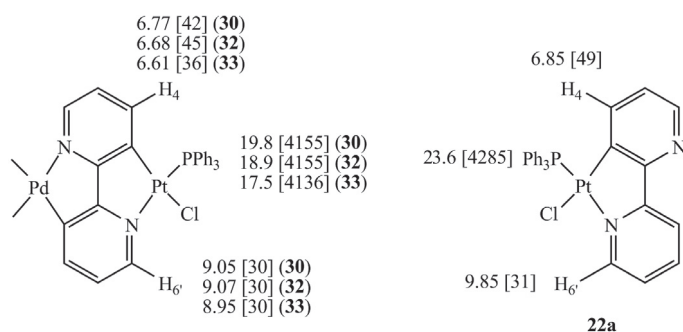
Table 2.9: Selected ^{195}Pt , ^1H and ^{31}P NMR chemical shifts (ppm) with ^{195}Pt coupling constants (Hz, in brackets) for some of the complexes synthesized.

	$\delta(^{195}\text{Pt})$	$\delta(^{31}\text{P})$	$\delta(\text{H}_6')$
22a	-4195	23.6 [4285]	9.85 [31]
27trans	-3562	-	-
27cis	-3568	-	-
30	-4050	19.8 [4155]	9.05 [30]
31	-2953	-	8.81 [29]
32	-4034	18.9 [4155]	9.07 [30]
33	-4136	17.5 [4136]	8.95 [30]

The differences in chemical shift values between the dinuclear complexes **30-33** is only attributable to the different environments around the palladium (ca. 100 ppm between **30** and **33**), reflecting the influence of the palladium centre on the platinum atom, connected via the delocalized planar doubly cyclometalated 2,2'-bipyridine. The substitution of a PPh_3 on the palladium with a 3,5-lutidine results in a 16 ppm shift to lower field of the ^{195}Pt , following the trend expected for a P/N substitution, but with a smaller effect due to the Pt-Pd distance.

A comparison between the ^1H and ^{31}P spectra of **22a**, **30**, **32**, and **33**, all having a $\text{Pt}(\kappa^2\text{-N,C})(\text{PPh}_3)\text{Cl}$ coordination, shows a clear difference between the H_6 chemical shifts in

mono- and dinuclear species (9.85, 9.05, 9.07, and 8.95 ppm in **22a**, **30**, **32** and **33**, respectively), a sharp effect due to the second cyclometalation. Conversely, the second metalation has minor consequences on the chemical shift of the $H_{6'}$ proton but greater effects on its ^{195}Pt -H coupling constants, showing also a clear dependence on the nature of the palladium centre. Furthermore, the ^{31}P NMR spectra also show consequences, both in chemical shift and coupling constant values (Scheme 2.15), due to the second cyclometalation.



Scheme 2.15

2.7 Conclusions

Starting from the $[\text{Pt}(\kappa^2\text{-N,C})(\text{X})(\text{DMSO})]$ ($\text{X} = \text{CH}_3, \text{Ph}$) rollover cyclometalated products obtained in Chapter 1 we were able, by simple substitution, to obtain a series of mono and dinuclear Pt(II) complexes with different characteristics both steric and electronic.

The complexes were completely characterized by NMR and IR spectroscopy and, in some cases, by X-ray crystallography either from single crystal or from powder diffraction. Each member of the series of complexes obtained can be used as parent compound for further reactivity as we will see in Chapter 2 and Chapter 3.

We have been able to compare the crystal structures of two cyclometalated derivatives differing only for the presence of an uncoordinated nitrogen atom, *i.e.* arising from classical and rollover metalation. The geometrical parameters deduced (bond distances and angles) highlights a very close similarity between them, at least from this point of view.

Two methodologies for synthesizing dinuclear derivatives have been exploited with diphenylphosphinoalkanes and rollover cyclometalated bpy by itself. In both cases a second

metal can be connected to the Pt(II) metal centre opening up the possibility of different combinations that can enrich the chemistry of rollover derivatives. Similar cyclometalated complexes have found applications in very important fields such as photoluminescence and catalysis.

Reactions with acids

3.1 Introduction

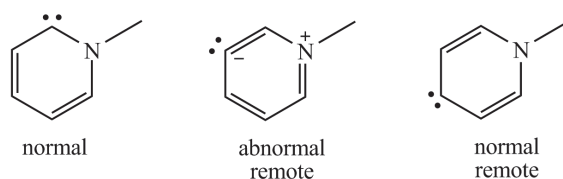
Protonolysis of Pt-C bonds has been the subject of extensive research. Significant mechanistic insights were gained from this reaction, regarded as the microscopic reverse of the C-H activation step of hydrocarbons, a process of great practical implications.^{290,291} A particular attention has been devoted to Pt-alkyl systems, whose protonolysis follows two alternative mechanisms: (1) a concerted electrophilic attack at the metal-carbon bond and (2) protonation at the metal to generate a platinum(IV) hydride, from which, after reductive elimination, alkane is lost. In general, the distinction between the two pathways is problematic, but it has been shown that for Pt(II) complexes with good electron donor ligands protonation of the metal centre is favoured.²⁹² Pt(IV) hydrido alkyl species have been observed at low temperature, and in many cases it has been asserted that the metal is the preferred site of protonation.^{293–300}

The peculiarity of rollover complexes derives from the presence of an uncoordinated donor atom, usually a nitrogen or a sulphur, which may influence the reactivity and properties of the whole complex and the growing interest in this emerging field is evidenced by the publication of a very recent review dedicated to this topic.²⁴

Rollover derivatives of bpy may be compared to the analogous complexes of 2-phenylpyridine, with the striking difference that the formally anionic, deprotonated rollover bpy is no more a spectator ligand, but may be an active participant in the course of the chemical transformations of the complex, through, for example, coordination or protonation.

In particular, protonation of the uncoordinated nitrogen atom allows the synthesis of uncommon cationic complexes which may be regarded either as mesoionic species,^{301,302} or abnormal pyridylenes.³⁰³

It is interesting to remember that the first complex of the rollover family appeared in the literature in late 1970s was an iridium species with three coordinated 2,2'-bipyridines; it was completely characterized, through a single-crystal X-ray determination, only at the end of a long and controversial debate as $[\text{Ir}(\text{bpy})_2(\text{bpy}^*)]^{3+}$.³⁰⁴ The zwitterionic bpy^* ligand is an $\kappa^2\text{-N,C}$ -bonded isomer of 2,2'-bipyridine (bpy), and this iridium complex has been described also as the first abnormal pyridylene complex.³⁰³ In the last decade due to growth of the interest in these species different coordination motifs arose and a new nomenclature was coined that called "abnormal" those heterocyclic carbenes for which a canonical valence bond representation requires additional formal charges on some nuclei, whereas the term "remote" indicates that no heteroatom is located in a position α to the carbene carbon (Scheme 3.1).^{301,303}



Scheme 3.1

The class of pyridylenes is receiving growing interest due to their intriguing properties;³⁰⁵ among them, the real nature of C_3 abnormal-remote pyridylenes has not yet been completely defined and the distinction between the two forms, zwitterionic and carbenic, may be subtle and, overall, only semantic. Moreover, according to IUPAC nomenclature abnormal carbenes are included in the class of mesoionic compounds;³⁰² however, the term "carbene" is often used to highlight the relationship of these species with normal heterocyclic and Fischer carbenes.

In protonolysis reaction rollover complexes can, in principle, show a competition between two Brønsted-Lowry bases, *i.e.* the uncoordinated nitrogen and the platinum lone pairs, in addition to electrophilic attack at the $\text{Pt-C}(sp^2)$ and $\text{Pt-C}(sp^3)$ bonds. The nitrogen is

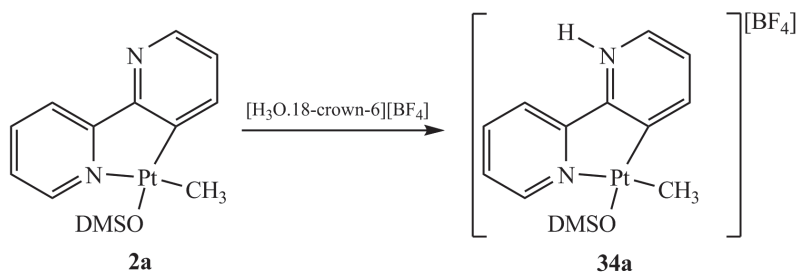
likely to be the kinetic protonation site to give the uncommon cationic species $[\text{Pt}(\text{bpy}^*)(\text{CH}_3)(\text{L})]^+$, which contains the unusual bpy^* ligand described as an abnormal-remote pyridylene or as a mesoionic cyclometalated ligand.^{16, 146, 247}

The N-protonated rollover complexes may convert into the corresponding $\text{Pt}(\kappa^2\text{-N,N})$ adducts through a "retro-rollover" reaction.²⁴⁷ The reversibility of the rollover process, found in ruthenium,^{306–308} rhodium,⁵¹ and platinum complexes,^{29, 191} is extremely attractive, offering, in principle, the possibility to design catalytic cycles based on "rollover"/"retro-rollover" paths, employing the $\text{bpy}/\text{bpy-H}$ ligands as a hydrogen atom reservoir/acceptor system. As for the more common cyclometalated species, also in the case of rollover compounds the properties of the complexes may be modulated on the basis of the nature of the cyclometalated ligand.

3.2 Acids having weakly coordinating anion

Reactivity of the parent cyclometalated complexes of general formula $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{DMSO})]$ was tested using an acid bearing a weakly coordinating anion such as $[\text{H}_3\text{O} \cdot 18\text{-crown-6}][\text{BF}_4]$, following a known synthetic protocol.¹⁶ In the case of $[\text{Pt}(\text{bpy-H})(\text{CH}_3)(\text{DMSO})]$ (**2a**) the success of the reaction was confirmed mainly by ^1H NMR but also from infra-red (IR) spectroscopy (Scheme 3.2). To sum up the characterized product shows the following data: (a) presence of a broad singlet at 13.8 ppm integrating one proton assigned to N-H; (b) a shift to higher frequencies, *i.e.* deshielding, of all the signals; (c) presence of N-H stretchings around 3200 cm^{-1} .

The more delocalized analogous complex $[\text{Pt}(\text{pyq-H})(\text{CH}_3)(\text{DMSO})]$ (**2f**) is extremely



Scheme 3.2

stable in solution and in the solid state, both in air and in the presence of moisture. As a

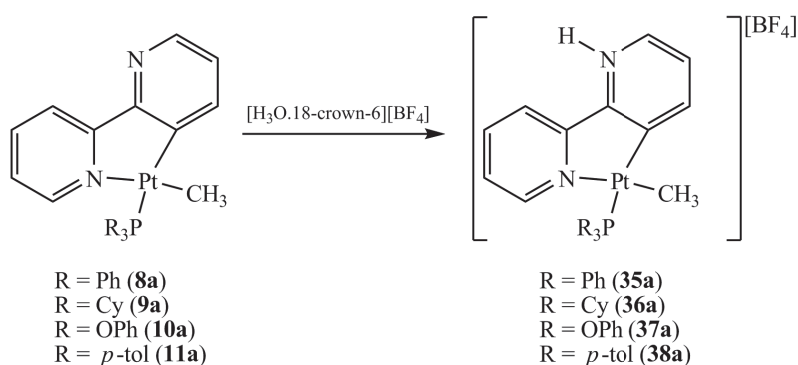
matter of fact, its stability is higher than that of **2a** which tends to decompose in solution. In the absence of any data regarding decomposition pathways, we can tentatively ascribe the extra stability of pyq rollover complexes to the peculiar electronic properties of the quinoline ring, able to stabilize additional charges through delocalization in a better way than pyridine.

As with the bpy complexes the Pt-C bonds in **2f** remain intact and only protonation of the uncoordinated nitrogen atom occurs, giving the cationic derivative [Pt(pyq*)(CH₃)-(DMSO)][BF₄], **34f**, where pyq* is the κ^2 -C,N neutral ligand formed by deprotonation of the C₃-H atom and protonation of the quinoline nitrogen.

The ¹H NMR spectrum of **34f** shows a broad signal at 13.9 ppm, accounting for one hydrogen atom, ascribable to the N-H proton, which disappears after addition of D₂O. As a further confirmation, the IR spectrum shows bands above 3000 cm⁻¹, due to the N-H stretching. The scarce solubility of **34f** did not allow the acquisition of a ¹³C NMR spectrum. The analysis of its ¹H NMR spectrum, compared to that of **34a**, showed that the Pt-H coupling constants involving the *trans* Pt-C(*sp*²) and Pt-S bonds are greater in the former than in the latter (*e.g.*, ³J_{Pt-H₄} and ³J_{Pt-DMSO}, see the Experimental Section), whereas the contrary is observed for the *trans* Pt-N and Pt-C(*sp*³) bonds (*e.g.*, ³J_{Pt-H_{6'}} and ²J_{Pt-Me}).²⁴⁷ Protonation of [Pt(bpy-H)(CH₃)(PPh₃)] (**8a**) with [H₃O · 18-crown-6][BF₄] smoothly proceeds to the corresponding cationic complex [Pt(bpy*)(CH₃)(PPh₃)][BF₄] (**35a**), which was isolated and characterized. The same complex may also be obtained by a substitution reaction, from **34a** and PPh₃.

In order to better describe the nature of **35a** and its relationship with **8a** (Scheme 3.3), we performed a deep NMR characterization of both complexes. All ¹H, ¹³C, and ³¹P NMR signals were attributed by means of one- and two-dimensional experiments (¹H, ¹³C, ³¹P, 1D-NOE, 2D ¹H-¹H COSY, and ¹H-¹³C HETCOR).

First, the ¹³C NMR spectra allowed us to identify the cyclometalated C₃ resonance with its satellites. Due to the protonation the C₃ signal shifts downfield from δ 158.4 (**8a**) to δ 163.4 (**35a**) while ¹J_{Pt-C} increases from 970 (**8a**) to 997 Hz (**35a**). These data may be compared to those recently reported for the analogous complex [Pt(L₁*)(Me)(PPh₃)]⁺ (δ 160.3 ppm, ¹J_{Pt-C} = 990 Hz, L₁ = (5S,7S)-5,7-methane-6,6-dimethyl-2-(pyridin-2-yl)-5,6,7,8-



Scheme 3.3

tetrahydroquinoline).³⁰⁹ The C_3 signal is not particularly shifted to high frequencies for a carbon which may be defined as "carbenic", but it can be compared to the signals for platinum(II) C_2 -pyridylene complexes reported by Bercaw and co-workers¹³⁷ (δ ca. 160-170 ppm). Furthermore, in contrast to C_2 and C_4 "normal" pyridylenes, which often show chemical shift values above 190 ppm, "abnormal" C_3 -pyridylenes usually have values of chemical shifts lower than those of the "normal" homologues. It has been recently concluded that chemical shift values for C_3 -pyridylenes must be considered with great care, being affected by a number of factors,³⁰³ and in addition the bond with the metal cannot be simply described in terms of valence bond theory.³⁰⁵

The enhancement of the Pt- C_3 coupling constant from **8a** to **35a** suggests an enhancement in the Pt- C_3 bond strength after protonation. A complete analysis of the ^{13}C NMR spectra enabled us to note that the coupling constant values of the metalated pyridine ring carbons are greater than those of the N-bonded pyridine ring. These values are in agreement with the coordination geometry, *i.e.* nitrogen *trans* to methyl and C_3 *trans* to a less *trans*-influencing donor atom, such as phosphorus. Neutral and cationic complexes have a good thermal stability; for example, **8a** and **35a** are stable up to 215 and 183 °C, respectively, after which decomposition occurs.

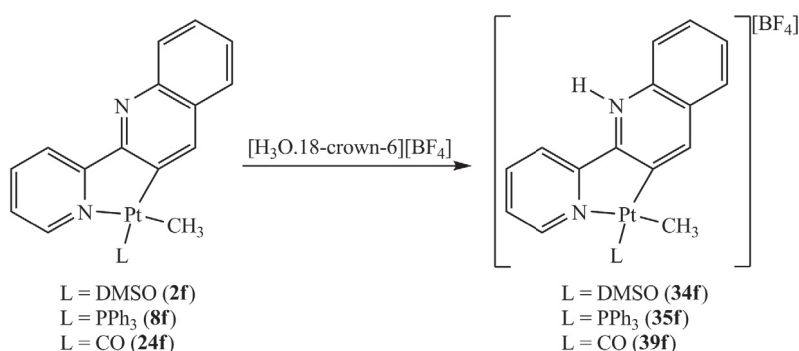
It is worth to note that the ligands bpy* and bpy are isomers and constitute an uncommon Brønsted-Lowry acid-base conjugated couple. The nature of the former deserves a few comments: it may be described as a mesoionic ligand, but also as an abnormal remote pyridylene.³⁰³ The nature of the metal-carbon bond in compounds containing $\kappa^2\text{-N,C}^*$ ligands has not been fully ascertained and two possible representations can be proposed,

zwitterionic or carbenic. However the distinction between the two is very subtle and probably good for semantic discussions.^{303,310–312}

Having notable potentialities in catalysis,^{313,314} such uncommon species have received wide attention in recent years, thus, the catalytic activity of $\kappa^2\text{-N,C}^*$ complexes is reasonably worth of thorough investigation.

Protonation of the complex $[\text{Pt}(\text{bpy}^{6\text{CH}_3}\text{-H})(\text{CH}_3)(\text{PPh}_3)]$ (**8b**) is confirmed by the NMR spectra: in the ^{31}P the singlet with satellites resonates now at 33.3 ppm and the $J_{\text{Pt-P}}$ is increased to 2497 Hz; in the ^1H the presence of only one species is confirmed because there is only one set of signals that are more deshielded compared to the neutral complex and, among these, the broad singlet at 13.25 ppm is assigned to N-H, thus confirming protonation.

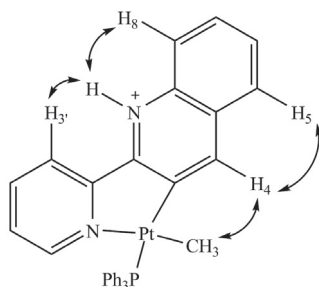
Complex $[\text{Pt}(\text{bpy}^{6\text{CF}_3}\text{-H})(\text{CH}_3)(\text{PPh}_3)]$ (**8c**) behaves differently (*vide infra*) and no evidences of an N-protonated species could be detected by NMR spectroscopy, whether ^1H , ^{19}F or ^{31}P ; our explanation for this behaviour is closely related to the discussion in Chapter 1 regarding the nature of the $\text{bpy}^{6\text{CF}_3}$. Probably, even in this case, the relative *ortho* position of the CF_3 substituent in respect to the nitrogen atom kinetically deactivates the lone pair on the sp^2 hybrid orbital preventing its reactivity.



Scheme 3.4

As already observed with **2f**, the reaction of the methyl complexes $[\text{Pt}(\text{pyq-H})(\text{CH}_3)(\text{PPh}_3)]$ (**8f**) and $[\text{Pt}(\text{pyq-H})(\text{CH}_3)(\text{CO})]$ (**24f**) with $[\text{H}_3\text{O} \cdot 18\text{-crown-6}][\text{BF}_4]$ gave the analogous mesoionic species **35f** and **39f** (Scheme 3.4) which were isolated in the solid state as tetrafluoroborate salts. As expected, the protonation of the uncoordinated nitro-

gen atom produces, in the ^1H NMR spectra, a generalized deshielding of the signals of the aromatic protons. This effect is particularly evident for the H_4 protons (δ 8.64, **8f**; 9.35, **35f**; 8.46, **24f**; 9.17, **39f**). The NH proton gives a broad signal at about 13.8 ppm. A NOE difference spectrum of complex **35f** shows that irradiation at 13.8 ppm promotes enhancement of the doublets at 8.91 and 8.53 ppm, due to the $\text{H}_{3'}$ and H_8 protons (Scheme 3.5). In addition, irradiation of the singlet at 9.35 ppm (H_4) shows NOE contacts at 8.05 ppm (d, H_5) and 0.90 ppm (d, Me), confirming the purported geometry of the complex in solution.



Scheme 3.5

The $J_{\text{Pt-P}}$ value increases from 2236 Hz in **8f** to 2507 Hz in **35f**, as previously observed for the analogous bpy complexes.^{16,247} The CO stretching frequency in **39f**, 2079 cm^{-1} , is higher than in **24f**, 2053 cm^{-1} , as expected because of the minor retrodonating properties of platinum(II) in the cationic complex. These data may be compared to those of the analogous bpy-containing couple **24a** and **39a** (2044 and 2087 cm^{-1} , see Section 2.4): the increase of the stretching frequencies, 26 cm^{-1} for pyq vs 43 cm^{-1} for bpy, is very different for the two ligands and may be explained with the greater capacity of L in delocalizing a positive charge, due to the quinoline fragment, so that the Pt-C-O bonds are less affected by the additional charge than in the bpy-based complexes, for which the protonation directly results in a stronger change in the C-O bond order.

3.2.1 NMR data of neutral and protonated phosphane species

The analysis of ^1H , ^{31}P , and ^{13}C NMR spectra of phosphane species shows, after protonation, an enhancement of the coupling constants related to the mutually *trans* Pt-L and

Pt-C(sp^2) bonds (*e.g.*, $^1J_{\text{Pt-C}_3}$ = 970 Hz in **8a** and 997 Hz for **35a**, $^3J_{\text{Pt-H}_4}$ = 46.4 Hz in **10a** and 49 Hz in **37a**; $^1J_{\text{Pt-P}}$ = 2229 Hz in **8a** and 2500 Hz in **35a**). In contrast, coupling constants related to Pt-L bonds *cis* to C_3 show a small decrease after protonation (*e.g.*, the Pt-CH₃ bond: $^1J_{\text{Pt-C}}$ = 725 Hz in **8a** and 716 Hz, **35a**). Pt-N bonds may be evaluated by comparison of the $^3J_{\text{Pt-H}_6'}$ values (*e.g.*, 16.0 Hz in **10a** and 15 Hz in **37a**). On the whole, the rationale of the observed NMR trends for species [Pt(bpy-H)(CH₃)(L)] and [Pt(bpy*)(CH₃)(L)] is not as straightforward and great care should be taken in the analysis of NMR data in solution, because several factors may have effects on spin-spin coupling constants.

One-bond coupling constants are dominated by the Fermi contact interaction of nuclei with *s* electrons and are usually taken as an estimate of bond strength,^{255,274,315–317} provided such bonds involve hybrid orbitals with some *s* character;²⁵¹ as an example, a correlation of Pt-P bond lengths with Pt-P coupling constants has been recently reported by Wollins and co-workers.²⁵⁰

In those cases in which greater values of $J_{\text{Pt-P}}$ are associated with shorter Pt-P bonds, the trend is likely to derive from the sensitivity of both parameters to the *s* orbital bond order.³¹⁸ In addition, charge effects may operate and the presence of a protonated nitrogen in species [Pt(bpy*)(CH₃)(L)]⁺ should influence the coupling constant values; however, back-donation in Pt(II) complexes may be considered of little relevance²⁵⁵ and it has also been reported that Pt^{II}-P bonds are weaker when the metal atom is less positively charged²⁵⁰ with a negligible Pt-P π donation in cationic complexes.

As for chemical shift value, protonation of species [Pt(bpy-H)(CH₃)(L)] produces a shift to high frequencies of most of the metalated bpy hydrogens, as may be expected from the presence of a positive charge. This effect is more evident in the metalated-protonated pyridine ring, and it is clearly associated with the electron deficiency of the complex.

3.2.2 Bisphosphanes

Protonation of [Pt(bpy-H)(CH₃)(κ^1 -dppm)] (**12a**) with [H₃O · 18-crown-6][BF₄] leads to the formation of a new species identified by NMR spectroscopy as the cationic bischelated product [Pt(bpy-H)(κ^2 -dppm)]⁺ (**18a**) which was isolated in the solid state as tetrafluorob-

Table 3.1: Selected ^1H and ^{31}P NMR chemical shifts (ppm) with ^{195}Pt coupling constants (Hz, in brackets) for the $[\text{Pt}(\text{bpy-H})(\text{CH}_3)(\text{L})]$ and corresponding $[\text{Pt}(\text{bpy}^*)(\text{CH}_3)(\text{L})]^+$ series of complexes where L is a phosphane. Cationic complexes isolated as tetrafluoroborate salts.

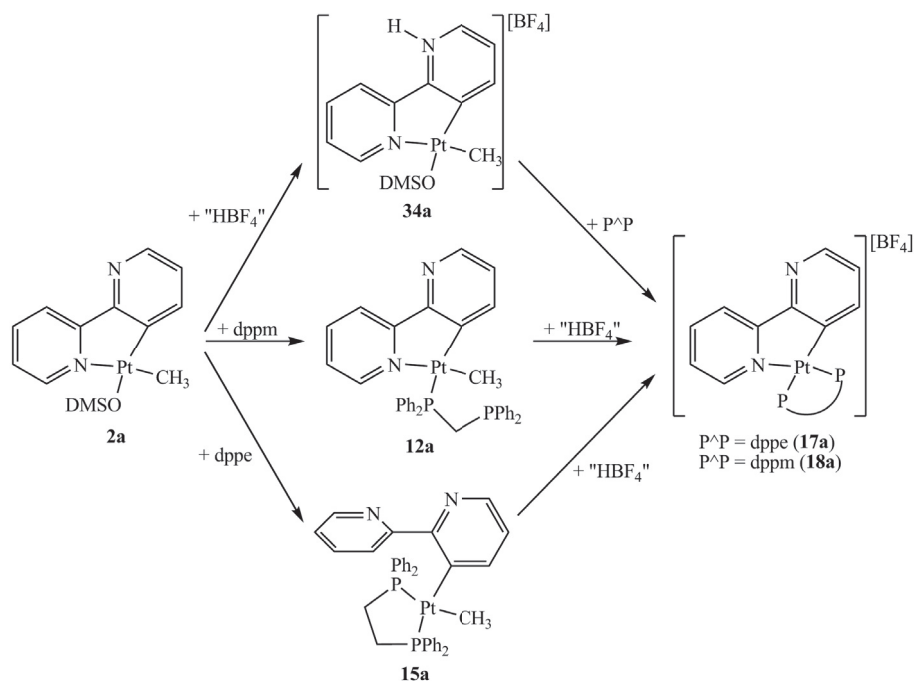
	H_4	$\text{H}_{6'}$	Pt-CH_3	DMSO	^{31}P
2a	8.01 [56]	9.71 [14]	0.70 [82]	3.25 [18]	-
34a	n.d.	9.95 [15]	0.78 [81]	3.30 [20]	-
2f	8.41 [60]	9.82 [14]	0.82 [82]	3.29 [18]	-
34f	9.02 [63]	10.00 [13]	0.85 [81]	3.33 [20]	-
8a	8.24 [48]	ov aromatics	0.74 [83]	-	33.6 [2229]
35a	8.97 [50]	7.88 [10]	0.83 [82]	-	32.1 [2500]
8b	8.13 [46]	ov aromatics	0.74 [83]	-	32.6 [2226]
35b	8.81 [51]	ov aromatics	0.80 [82]	-	33.3 [2497]
8f	8.66 [52]	ov aromatics	0.89 [83]	-	32.4 [2235]
35f	9.35 [55]	ov aromatics	0.91 [82]	-	32.0 [2507]
10a	7.93 [42]	9.41 [16]	0.83 [84]	-	118.0 [3848]
37a	8.01 [n.r.]	9.75 [15]	0.92 [82]	-	111.6 [4255]
11a	8.18 [48]	ov aromatics	0.66 [84]	-	30.0 [2245]
38a	8.99 [50]	8.00 [14]	0.82 [83]	-	28.7 [2502]

orate salt.

In the ^1H NMR all the signals are broad indicating a certain degree of fluxionality but at 4.91 ppm is present the triplet due to the methylenic unit of the dppm, in addition it is flanked by satellites of ca. 11 Hz. Clear evidence of chelation of the bisphosphine is found in the ^{31}P NMR where two doublets ($^2J_{\text{P-P}} \approx 51$ Hz) with satellites appear very shielded at δ -30.4 ($J_{\text{Pt-P}} = 1582$ Hz, *trans* to carbon) and δ -36.9 ($J_{\text{Pt-P}} = 3186$ Hz, *trans* to nitrogen) as typical for compounds having a chelate dppm.^{256,260–263} Complex $[\text{Pt}(\text{bpy-H})(\kappa^2\text{-dppm})]^+$ can also be obtained following another route by reacting $[\text{Pt}(\text{bpy-H})(\text{Cl})(\text{DMSO})]$, **16a**, with dppm (see Section 2.3).

Worthy of note is the formation of a sterically strained, thus unfavoured, 4-membered chelate cycle in the product complex rather than keeping the dppm in a monodentate coordination. Probably the reason behind this is the protonolysis of the Pt-CH_3 bond with irreversible elimination of methane; once methane has left the complex the highly reactive

14-electron cationic complex tend to complete its coordination sphere by binding to the second phosphorus atom (which is not too far away from the metal centre) in a mechanism probably very similar to that proposed for the retro-rollover reaction (*vide infra*).²⁴⁷ The data just presented demonstrate that dppm and dppe show a different behaviour if they react with neutral **2a**, *i.e.* substitution for dppm and chelation with displacement of pyridinic nitrogen for dppe, but on protonation with $[\text{H}_3\text{O} \cdot 18\text{-crown-6}][\text{BF}_4]$ they both lead to the bischelated cationic complexes having general formula $[\text{Pt}(\kappa^2\text{-N,C})(\kappa^2\text{-P,P})]^+$. On the other hand if the order of the reactions is reversed, *i.e.* substitution with bisphosphine is tried on the cationic **34a**, both dppm and dppe give the bischelated $[\text{Pt}(\kappa^2\text{-N,C})(\kappa^2\text{-P,P})]^+$ after elimination of methane (Scheme 3.6).

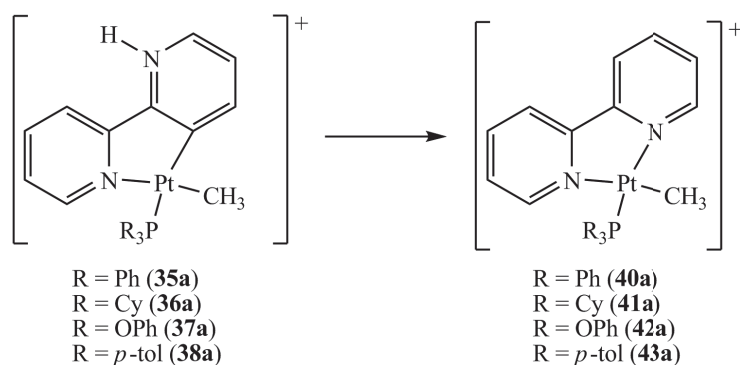


Scheme 3.6

3.3 "Retro-rollover" reaction

A new reaction was observed when complex **35a** was left in solution for several days: it slowly converts into a new species with a completion time of ca. one month. The compound formed was isolated in the solid state and characterized as the adduct $[\text{Pt}(\text{bpy})(\text{CH}_3)(\text{PPh}_3)][\text{BF}_4]$ (**40a**). In the ^{31}P NMR spectrum a strong $J_{\text{Pt-P}}$ coupling constant (4351

Hz) is in agreement with a phosphorus *trans* to a pyridinic nitrogen (Scheme 3.7).



Scheme 3.7

The $^3J_{\text{P-H}}$ and $^2J_{\text{Pt-H}}$ values in the $\kappa^2\text{-N,N}$ adduct **40a** are particularly small: ca. 3 and 69 Hz, respectively (*vs* 7.1 and 82 Hz in $\kappa^2\text{-N,C}$). Complexes **35a** and **40a** are isomers; therefore, this reaction corresponds to an isomerisation process. The rate of the reaction may be influenced by addition of DMSO to the solution: the reaction evolves completely in 2 days either in CD_2Cl_2 with 10 drops of DMSO or in $\text{DMSO-}d_6$ solution. It is also worth noting that excess $[\text{H}_3\text{O} \cdot 18\text{-crown-6}][\text{BF}_4]$ does not influence the rate of the process.

The reaction is unprecedented for bpy, being the very first example of a "retro-rollover" reaction in solution of a bpy complex with isolation of the product. Reversibility of the rollover process has been recently invoked in the gas phase to explain the exchange of hydrogen between the bpy fragment and dimethyl sulphide.³⁷ A related reversible reaction, driven by a change of solvent, has also been recently reported by Rourke and co-workers for a cyclometalated phenylpyridine.²⁹

At variance with **35a**, the protonated complex **36a** shows an enhanced reactivity and rapidly converts into the corresponding adduct **41a**. Even with short reaction times at room temperature a mixture of **36a** and **41a** is formed (*e.g.*, 9:1 molar ratio after 10 min) so that complex **36a** cannot be isolated in pure form but only detected in solution: *e.g.*, by means of NMR spectroscopy. Full conversion is achieved in a couple of hours.

In contrast, the cationic complex **37a** is kinetically much more stable and can be easily characterized. The subsequent isomerisation to the adduct **42a** is extremely slow with a completion time of about 3 months at room temperature.

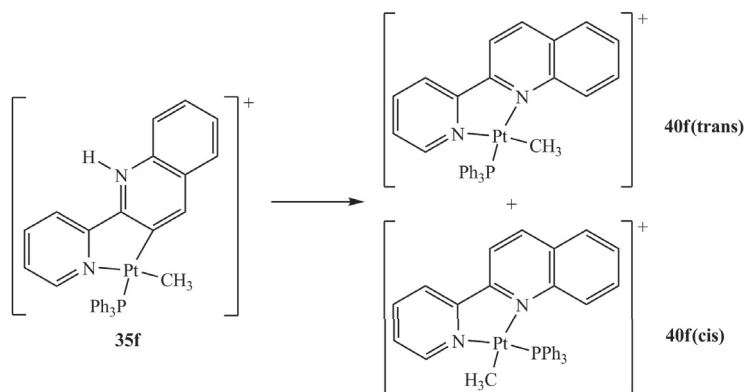
The series of complexes **11a-38a-43a** was studied in order to evaluate only the electronic factors by direct comparison with the PPh_3 series (**8a-35a-40a**). The $\text{P}(p\text{-tol})_3$ ligand, according to the Tolman cone angle θ , is equivalent to PPh_3 but it is more basic due to the presence of the methyl groups.²⁴⁹ Despite the close similarity between these two phosphines the observed difference is striking when 10^{-2} M solutions in CD_2Cl_2 of **35a** and **38a** are followed by means of ^1H and ^{31}P NMR spectroscopy at room temperature: after 6 days a 90% conversion was observed for **38a**, in contrast to the 33% conversion observed for **35a**.

These data show a clear dependence of the reaction rate from the donor properties of the phosphane and are in line with Tolman electronic parameters. On the whole, our experimental data show that the time requested to complete the retro-rollover reaction may range over almost 3 orders of magnitude by simply changing the nature of the fourth ligand. The reaction seems to be closely related to the electronic properties of the phosphane: the more basic donor, PCy_3 , is kinetically more active than the less basic $\text{P}(\text{OPh})_3$, with PPh_3 and $\text{P}(p\text{-tol})_3$ in the middle, a trend compatible with a hypothetical mechanism where the proton migrates to the $\text{Pt}(\text{II})$ centre to give a $\text{Pt}(\text{IV})$ hydride, from which, after reductive elimination of $\text{C}_3\text{-H}$, the final product is formed. On the basis of our experimental data, however, we cannot rule out the possibility of a concerted electrophilic attack at the metal-carbon bond. A second possible reaction pathway, that is, a concerted mechanism involving electrophilic attack of the platinum-carbon bond, cannot be completely ruled out, but in the case of electron-rich platinum(II) organometallic complexes it is unlikely;²⁹² moreover, a different mechanism may be operating for different phosphane donors.

According to the first mechanism, electron-richer complexes react faster than electron-poorer species. The most electron-rich $\text{Pt}(\text{II})$ centre in complex **36a** is likely to undergo the oxidative addition pathway more easily than **35a** and **37a**; however, it is important to note that steric factors may also play a role in the process and should not be completely ruled out.

The mesoionic species **34f** and **39f** are rather stable in solution and do not decompose in the presence of moisture or oxygen. In contrast, the NMR spectrum of complex **35f**, acquired in CDCl_3 , undergoes a slow change; as a matter of fact, both ^1H and ^{31}P NMR

show the conversion of **35f** into two new species **40f**, formed in a 1.3:1 molar ratio. The new complexes appear to be very similar, each having, *inter alia*, one methyl group and one phosphorus atom bound to platinum, with similar ^{195}Pt - ^1H and ^{195}Pt - ^{31}P coupling constant values (see the Experimental Section), suggesting P-Pt-N and Me-Pt-N *trans* coordination for both complexes.



Scheme 3.8

These similarities suggest that the two species are closely related, being the two geometric isomers of $[\text{Pt}(\text{pyq})(\text{CH}_3)(\text{PPh}_3)]^+$ (**40f**, Scheme 3.8), originated through a "retro-rollover" process, as reported for the analogous bpy complexes.²⁴⁷ In the starting complex **35f**, the C₃ atom is metalated, so the appearance of the signals due to the H₃ protons in the spectra of both species strongly corroborates our assumption. Furthermore, in the aromatic region, a signal with satellites is clearly visible which is typical of an H₆ proton *trans* to phosphorus,²⁴⁷ due to a N-Pt-P *trans* arrangement, whereas in the other isomer the signal due to H₆ is strongly upfield shifted (δ 7.65) by the shielding cones of the phosphine aromatic rings. In the light of this, the two species may be indicated as **40f(trans)** (phosphorus *trans* to quinoline) and **40f(cis)** (phosphorus *cis* to quinoline). As expected, complex **40f(trans)**, having the bulky PPh₃ far from the quinoline moiety, is the main species. In line with this assignment, NOESY-1D spectra showed contacts between the methyl group at 0.72 ppm (Pt-Me in **40f(trans)**) and a doublet at 8.40 ppm belonging to the adjacent H₈ proton. For the other Pt-Me hydrogens, that is, those of the **40f(cis)** isomer, a clear contact with the H_{6'} proton, at 8.94 ppm, is observed. A ^1H - ^1H COSY spectrum further helped in the assignments; in particular, two AB systems, due to the H₃

and H₄ protons, are clearly visible in the spectra.

The retro-rollover reaction rate is solvent-dependent: the process is slower in CDCl₃ (approximately 30% conversion in a 10⁻² M solution after 2 days) and faster in CD₂Cl₂ (100% conversion after 2 days). Addition of excess crown ether acid does not affect the reaction rate, probably because protonation of Pt does not occur on the cationic species [Pt(pyq*)(CH₃)(L)]⁺ but on the neutral complexes [Pt(pyq-H)(CH₃)(L)], originated from the former by deprotonation. Dilution of the solution results in a slower reaction rate, so it is likely that the process is not intramolecular, but may involve water. Saturation with H₂O almost inhibits the reaction, but this may be due to the presence of a water phase, so that H₃O⁺ is almost completely removed from the chloroform solution.

The analogous conversion of the bpy rollover²⁴⁷ complex **35a** is significantly slower, reaching completion in CD₂Cl₂ only after 30 days. In this case, the reaction rate was strongly dependent on the electron density on the metal centre. In particular, studying the effect of the phosphane properties in the rollover complexes [Pt(bpy*)(CH₃)(PR₃)]⁺, it emerged that better donors (*e.g.*, P(*p*-tol)₃ vs PPh₃) highly accelerate the process. Moreover, we have found that also the nature of the cyclometalated ligand affects the rate of reaction. The condensed aromatic ring on the cyclometalated pyridine is likely to strongly favour the retro-rollover process. However, although electronic effects seem to be dominant, also steric ones may play a non negligible role. In particular, repulsion between the N-H and the H₈ protons (in mutual *peri* position), added to the N-H vs H_{3'} repulsion, may also influence the process.

Complexes **40f** are not static in solution: a 1D-EXSY experiment in CD₂Cl₂ showed that irradiation of the methyl signal at 0.72 ppm (**40f(trans)**, main species), results in magnetization transfer to the other methyl group at 0.67 ppm, demonstrating a dynamic process in solution which rapidly interconverts the two isomers on the NMR time scale.

An analogous behaviour was observed by Romeo and co-workers in the case of the symmetric chelating ligand 2,9-dimethyl-1,10-phenanthroline (N,N) in a series of cationic [Pt(N,N)(CH₃)(PR₃)]⁺ complexes.^{319–323} By contrast, analogous complexes of the less-hindered ligands 1,10-phenanthroline and 2,2'-bipyridine, appear static in solution on the NMR time scale. The severe distortion of the square planar geometry around the platinum centre, due to the methyl groups on the bidentate ligand 2,9-dimethyl-1,10-

phenanthroline, was reported to be responsible for the fluxionality of the complexes. Detailed kinetic studies showed that the mechanism of the process may switch from associative to dissociative pathways according to several factors, such as solvent or counterion properties, the presence of external nucleophiles, the electronic and steric properties of the phosphane ligand, and so forth. In addition to the flipping of the bidentate N,N ligand, also rotation of the phosphane occurs. Indeed, it was shown that tuning the bulkiness of the PR_3 ligand, the two motions display identical rates. Because of this synchronized fluxional motion, these complexes act as a molecular gear.^{319,320}

To the best of our knowledge, complexes **40f(cis)** and **40f(trans)** are the first platinum(II) species with nonsymmetric κ^2 -N,N ligands which show a dynamic flipping of the chelated ligand. The possibility to design molecular gears whose dynamics can be controlled by the stereoelectronic properties of the ligands is of outstanding interest. Studies are in progress to evaluate, also in the present case, the possible behaviour as a molecular gear with different phosphane ligands.

Finally, it is worth noting that $[\text{Pt}(\kappa^2\text{-N,N})(\text{Me})(\text{neutral ligand})]^+$ cationic complexes are also of interest in the C-H bond activation of alkanes,^{41,324–330} even if their synthesis is not trivial, involving the use of silver salts and several steps. On the contrary, our methodology opens a new and simpler way to obtain this class of complexes, at least when the rollover reaction is accessible.

To the best of our knowledge, only the adduct $[\text{Pt}(\text{bpy})(\text{CH}_3)(\text{PPh}_3)]\text{Cl}$ has been reported in the literature,³³¹ being detected only in solution but not isolated as a pure species in the solid state. Complex **40a** has been previously obtained and fully characterized in our laboratory following a different synthetic procedure.³³²

The case of $\text{bpy}^{6\text{CF}_3}$

Addition of $[\text{H}_3\text{O} \cdot 18\text{-crown-6}][\text{BF}_4]$ to a solution of **8c** does not yield to the formation of the species in which the non-coordinating nitrogen is protonated. The ^{31}P NMR recorded right after the addition shows only the signals of the starting material (δ 33.2, $J_{\text{Pt-P}} = 2281$ Hz) while with the others the protonation was already completed.

Upon following the reaction by NMR spectroscopy we observe after 15 minutes the ap-

pearance of two new signals at 26.9 ppm ($J_{\text{Pt-P}} = 3142$ Hz) and 18.0 ppm ($J_{\text{Pt-P}} = 2378$ Hz) in 1:3 ratio.

The progress of the reaction is highlighted by the decrease in the signal of the starting compound and by the growth of the two new species that, after ca. 1 h are in 2:3 ratio. After some more time a new singlet with satellites appears in the ^{31}P spectrum at δ 21.3 having a $J_{\text{Pt-P}}$ of 4122 Hz in agreement with a phosphorus *trans* to a low *trans*-influencing group, *i.e.* a nitrogen. Confidently we assign this last species detected as the cationic adduct $[\text{Pt}(\text{bpy}^{6\text{CF}_3})(\text{CH}_3)(\text{PPh}_3)]^+$ (**40c**) resulting from the retro-rollover reaction.

After almost one week the majority of the platinum in solution appears as the final adduct, no signs of starting material are visible and the intermediate species are being consumed. On the whole the reaction has a complicated evolution that is not easily understandable, moreover signals in the ^1H NMR are of difficult interpretation due to the simultaneous presence of four species in solution.

3.3.1 Bisphosphanes

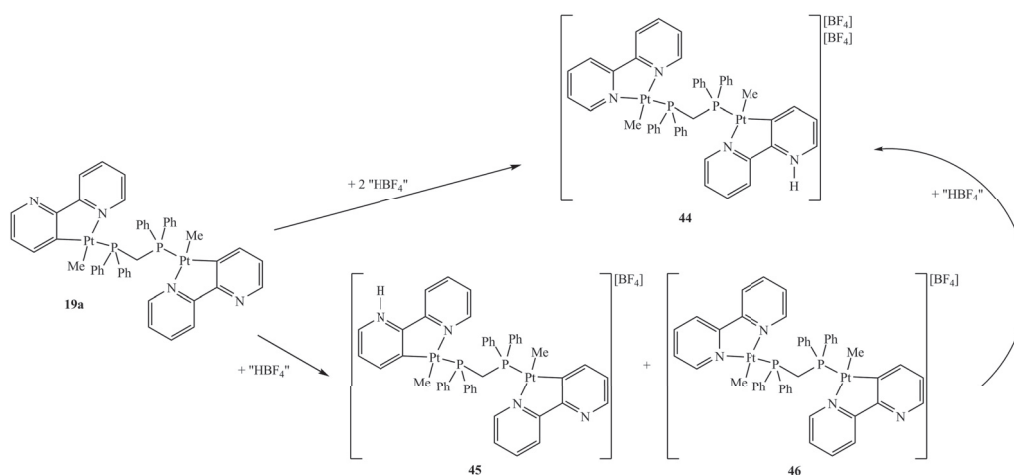
Similarly to what has been done with the mononuclear complexes the reaction with acids bearing a weakly coordinating anion, *i.e.* $[\text{H}_3\text{O} \cdot 18\text{-crown-6}][\text{BF}_4]$, was tested on dinuclear species.

Reaction of complex $[(\mu\text{-dppm})\{\text{Pt}(\text{bpy-H})(\text{CH}_3)\}_2]$ (**19a**) with Pt:H 1:1 ratio in CH_2Cl_2 makes the orange-yellow solution darker and leads to the isolation of a single species. ^1H and ^{31}P NMR confirm that only one species is present in solution, in particular in the ^{31}P spectrum two different singlets with satellites are visible. Analysis of the pattern is made following the discussion made before taking in account all the isotopomers (Section 2.3). The signal at δ 19.6 appears complicated due to the presence of different couplings however, on the whole, it can be described as a doublet with satellites ($J_{\text{Pt-P}} = 2304$ Hz, $^3J_{\text{Pt-P}} = 82.3$ Hz, $^2J_{\text{P-P}} = 45.0$ Hz); the same aspect can be deduced for the signal at 11.6 ppm ($J_{\text{Pt-P}} = 4444$ Hz, $^3J_{\text{Pt-P}} = 65.6$ Hz, $^2J_{\text{P-P}} = 45.0$ Hz).

Values of the coupling constants, compared with the results obtained with the mononuclear species, permits to confidently assign the first signal to a phosphorus coordinated on Pt(II) having a carbon atom in *trans* position; on the other hand the second is coordinated

trans to a nitrogen, strongly suggesting that a retro-rollover process took place in one half of the complex.

If the linkage between the atoms is now clear we still have to assess whether the non-coordinating nitrogen is protonated or not, even if on the basis of $J_{\text{Pt-P}}$ we can hypothesize a protonated bpy. A $5 \cdot 10^{-4}$ M solution of the complex was prepared and its conductivity was measured obtaining a value of $\Lambda_{\text{M}} = 190 \frac{\text{cm}^2}{\Omega \cdot \text{mol}}$ that is in agreement with an electrolyte having a 2:1 ratio between the ions. The complex present in solution could then be formulated as having one $\kappa^2\text{-N,N}$ bpy on one metal centre and a protonated $\kappa^2\text{-N,C}$ bpy on the other (Scheme 3.9).



Scheme 3.9

In order to have more information on the process observed we decided to add the acid stepwise one equivalent per time and follow the reaction by ^{31}P NMR spectroscopy.

Addition of only one equivalent of $[\text{H}_3\text{O} \cdot 18\text{-crown-6}][\text{BF}_4]$ to an NMR solution of **19a** leads to a colour change from yellow to intense red with formation of a dark red precipitate.

^1H NMR is not very useful in understanding what is going on because the aromatic region is overcrowded and therefore difficult to analyse; the aliphatic one is only slightly better because we note the presence of a second broad and unresolved resonance around 0.60 ppm. Much more useful is the ^{31}P NMR that shows the simultaneous presence of two species.

One species (**45**) has a pattern very similar to that of the starting dinuclear compound and resonates at δ 22.2 ($J_{\text{Pt-P}} = 2324$ Hz, $^3J_{\text{Pt-P}} = 52.7$ Hz, $^2J_{\text{P-P}} = 54.9$ Hz), due to the similarity with the reagent we can hypothesize that this species corresponds to the symmetric one where the proton is exchanged between the two non-coordinating nitrogen atoms of the two rollover bpps. This situation is also corroborated by the red colour of the solution, in fact this is diagnostic of Pt-Pt interactions.

The other species (**46**) has two different phosphorus atoms with resonances at δ 19.7 ($J_{\text{Pt-P}} = 2267$ Hz, $^3J_{\text{Pt-P}} = 79.4$ Hz, $^2J_{\text{P-P}} = 45.0$ Hz) and δ 11.4 ($J_{\text{Pt-P}} = 4458$ Hz, $^3J_{\text{Pt-P}} = 70.2$ Hz, $^2J_{\text{P-P}} = 45.0$ Hz), in this case it is evident that one phosphorus is coordinated *trans* to a nitrogen thus a retro-rollover process took place on one of the cyclometalated bpy.

It is remarkable that in this case the rate of the process is very different from that observed in the mononuclear compound **8a**, in fact it is similar to what has been observed with complex **9a**. We are prone to think that the observed enhancement in the reaction rate is due to the nuclearity of the complex because the same reaction on the mononuclear complex, *i.e.* $[\text{Pt}(\text{bpy-H})(\text{CH}_3)(\kappa^1\text{-dppm})]$ (**12a**), follows a different path eliminating methane and thus leading to the bischelatate complex $[\text{Pt}(\text{bpy-H})(\kappa^2\text{-dppm})]^+$ (**18a**).

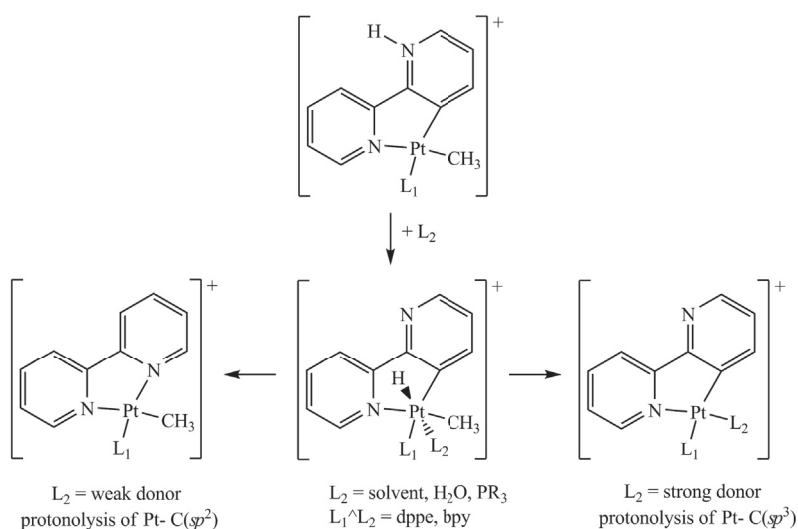
Addition of a second equivalent of $[\text{H}_3\text{O} \cdot 18\text{-crown-6}][\text{BF}_4]$ leads to a colour change from deep red to orange and the ^{31}P NMR signals change accordingly: 17.4 ppm ($J_{\text{Pt-P}} = 2516$ Hz, $^3J_{\text{Pt-P}} = 79.4$ Hz, $^2J_{\text{P-P}} = 42.0$ Hz) and 10.1 ppm ($J_{\text{Pt-P}} = 4421$ Hz, $^3J_{\text{Pt-P}} = 70.9$ Hz, $^2J_{\text{P-P}} = 42.0$ Hz). The NMR data of the last species obtained by stepwise addition of acid are not exactly the superimposable with those obtained using directly two equivalents, however they follow the same trend.

3.3.2 Pt-C(sp^2) vs Pt-C(sp^3) bond breaking

The isomerisation process from species $[\text{Pt}(\kappa^2\text{-N,C}^*)(\text{CH}_3)(\text{PR}_3)]^+$ to $[\text{Pt}(\kappa^2\text{-N,N})(\text{CH}_3)(\text{PR}_3)]^+$ shows that, under the experimental conditions described, only the Pt-C(sp^2) bond is attacked, leaving the Pt-C(sp^3) bond unaltered. However, the balance between the two Pt-C bond ruptures is subtle. Addition of a weak donor such as DMSO simply accelerates the reaction; in contrast, the presence of a strong donor in a solution of **8a** may drive the reaction toward a different route: addition of a second equivalent of PPh_3 results in

formation of methane and coordination of PPh_3 on the fourth coordination site, to give the complex $[\text{Pt}(\text{bpy-H})(\text{PPh}_3)_2]^+$ (**47**).

The same result was obtained by starting from **34a** and 2 equivalents of PPh_3 . Complex **47** was characterized in solution and in the solid state. In particular, the presence of two signals in the ^{31}P NMR spectrum with different Pt-P coupling constants accounts for P-Pt-C ($J_{\text{Pt-P}} = 2105$ Hz) and P-Pt-N ($J_{\text{Pt-P}} = 3938$ Hz) *trans* arrangements; the relative *cis* coordination of the two phosphorus atoms is forced by the presence of the cyclometalated chelating ligand and it is also confirmed by the value of the P-P coupling constant ($^2J_{\text{P-P}} = 19$ Hz).



Scheme 3.10

Furthermore, when the reaction is followed by means of ^1H NMR spectroscopy a signal at 0.22 ppm, due to free methane,³³³ is observed. The same behaviour is observed with bidentate donors, such as 1,2-bis(diphenylphosphino)ethane (dppe) and bpy. Addition of dppe or bpy to a solution of **34a** results in Pt-C(sp^3) bond cleavage, and $[\text{Pt}(\text{bpy-H})(\text{dppe})][\text{BF}_4]$ (**17a**) and $[\text{Pt}(\text{bpy-H})(\text{bpy})][\text{BF}_4]$ (**48**) may be isolated in the solid state and characterized.

Complex **48** has some points of interest, having two coordinated 2,2'-bipyridines, one in the classical $\kappa^2\text{-N,N}$ and the other in the $\kappa^2\text{-N,C}$ mode.

Complex **17a** was easily characterized by means of NMR spectroscopy (see Section 2.3).

In particular, the ^{31}P NMR spectrum shows two signals at high frequency, as is usual for chelated dppe, attributable to a P *trans* to C (δ 51.8 ppm, $J_{\text{Pt-P}} = 1949$ Hz) and a P *trans* to N (δ 42.6 ppm, $J_{\text{Pt-P}} = 3691$ Hz). The signals in the ^1H NMR spectrum appear as broad lines, probably due to a dynamic process in solution.

The presence of a good donor in solution seems to be of paramount importance in driving the reaction toward Pt-C(sp^3) instead of Pt-C(sp^2) protonolysis (Scheme 3.10). The vacant coordination site created in the first case is occupied by the external ligand, whereas in the second case the pyridine itself contains a nitrogen donor centre.

Both the observed Pt-C bond breaking reactions are irreversible, and in the retro-rollover process the second nitrogen coordinates only after the reductive elimination of C(sp^2)-H; thus, the differentiating factor between M-C sp^2 and sp^3 bond breaking operates before the reductive elimination step. For this reason we may assume coordination of the external ligand before the reductive elimination step.

3.4 Acids having coordinating anion

As previously reported, the reaction of $[\text{Pt}(\text{bpy-H})(\text{CH}_3)(\text{DMSO})]$ (**2a**) with an acid having a coordinating anion, such as HCl, gives the corresponding chloride $[\text{Pt}(\text{bpy-H})(\text{Cl})(\text{DMSO})]$ (**16a**) and free methane.¹⁶ The same product can be obtained with good yields by reaction of **1a** with $[\text{H}_3\text{O} \cdot 18\text{-crown-6}][\text{BF}_4]$ in acetone in the presence of LiCl. The reaction in this case likely proceeds through protonation of the uncoordinated nitrogen atom, followed by a mechanism similar to that operating in the presence of 2 equivalents of PPh_3 , with the anionic ligand Cl^- in place of neutral PPh_3 .

In agreement with the different *trans*-influence of chloride *vs* methyl, in **16a** a swap between the positions of the neutral and anionic ligand is observed; ^1H NMR data support this picture, in fact (a) no more resonances attributable to methyl are detected around 1 ppm, (b) an increase in the $^3J_{\text{Pt-H}}$ of the DMSO protons is observed (from 18.3 to 24.3 Hz) and (c) the signal of the H_4 is ca. 0.60 ppm deshielded being close in space with the chloride.

Extension of the delocalization did not affect the outcome of the reaction so that using **2f** as starting material and treating it with aqueous HCl resulted in Pt- CH_3 bond attack

with subsequent release of methane, giving the corresponding chloride, **16f**. Only one of the two possible geometric isomers is formed, that is, the one with DMSO *trans* to the nitrogen atom, instead of *trans* to the carbon atom, as in **2f**.

This is confirmed by the ^1H NMR spectrum of **16f** which shows a $^3J_{\text{Pt-H}}$ value for the coordinated DMSO strongly enhanced with respect to that found for **2f** (24.0 Hz vs 18.3 Hz), in line with the weaker *trans* influence of N with respect to C. A clear downfield shift is also present for the H_4 proton (δ 9.02 ppm), attributable to the effect in the space of the DMSO ligand. A combination of 2D COSY and NOESY experiments allowed complete assignment of the ^1H NMR signals and in the NOESY spectrum it is present, *inter alia*, a weak interaction between the DMSO protons, at 3.71 ppm, and the H_4 one, at 9.02 ppm, confirming the proposed geometry.

A more in depth comparison between the complexes **16a** and **16f** permits to observe an interesting trend in chemical shifts and coupling constants. These data are summarized in Table 3.2 and show that signals of the pyq complex are more deshielded than the bpy one and this effect, assuming that all other factors are similar, is probably due to the difference in the extension of the delocalized system that pulls electron density away from the N-bound pyridyl ring making its protons less shielded. The notable difference in the chemical shift relative to H_4 is probably due to sum of the effects of the neighbouring chloride and the quinolyl aromatic system.

Coupling constants with ^{195}Pt are influenced in different ways, if the DMSO protons do not seem to be affected by the ligand in *trans* on changing bpy for pyq, the H_4 and $\text{H}_{6'}$ show an inverse behaviour, *i.e.* increase and decrease, respectively, for the corresponding $^3J_{\text{Pt-H}}$. The observed values clearly speak in favour of a relative electronic influence between the quinolyl system and the pyridyl one, distinguishing between the two possibilities, *i.e.* correlation through the platinum metal centre or through the carbon skeleton, it is not possible with only these data and moreover could be tricky.

Alternative ways to chlorides

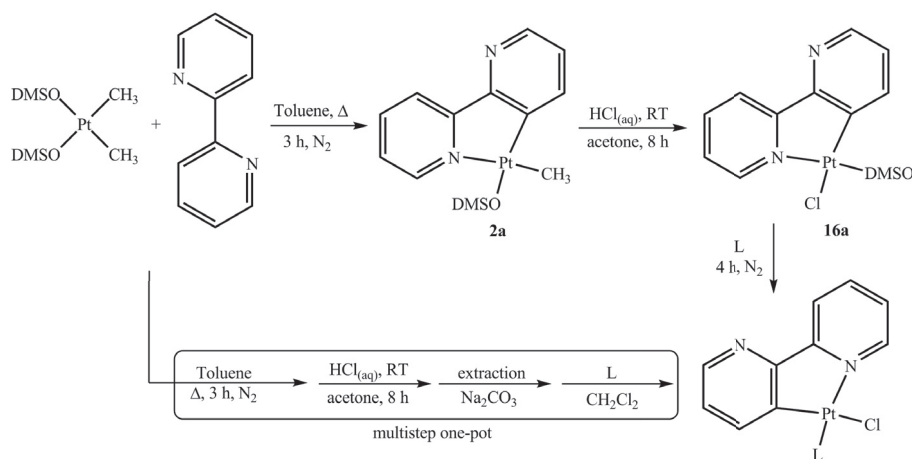
Finding new routes to known complexes is an important task in synthetic chemistry because sometimes it leads to better processes that can afford purer products in higher yields.

Table 3.2: Selected ^1H chemical shifts (ppm) with ^{195}Pt coupling constants (Hz, in brackets) registered in CDCl_3 for the complexes **16a** and **16f**.

	16a	16f
$\text{H}_{3'}$	8.22	8.55
$\text{H}_{4'}$	7.98	8.05
$\text{H}_{5'}$	7.40	7.48 (ov)
$\text{H}_{6'}$	9.59 [36]	9.71 [33]
H_4	8.60 [42]	9.02 [46]
DMSO	3.65 [24]	3.71 [24]

In this context optimization of the synthetic route to cyclometalated chloride complexes was explored because of the following facts: (1) the classic synthesis¹⁶ involves three steps, *i.e.* cyclometalation, treatment with aqueous HCl , substitution, isolating each intermediate; (2) reaction of $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{L})]$ with HCl is strongly dependent on the conditions and the ligands, even weak or very weak, present in solution.

Inspired by the multistep one-pot approach used for the synthesis of a series of complexes having general formula $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{L})]$, L = various neutral 2-electron donors, we decided to develop a similar protocol to obtain the corresponding chlorides. We indeed succeeded in our plan obtaining in high yield and pure form the desired complexes starting from the precursors $\text{cis-}[\text{Pt}(\text{CH}_3)_2(\text{DMSO})_2]$ and bpy (Scheme 3.11).



Scheme 3.11

The standard approach that isolates all the intermediates is certainly useful because permits to break the synthetic process in some key-points from which different compounds can be easily obtained but, on the contrary, gives a fairly low yield of the final $[\text{Pt}(\kappa^2\text{-N,C})(\text{Cl})(\text{L})]$ compound that, in the best case, is 55% ca.

The one-pot synthesis has the same possibilities of customization and gives better yields (around 75-80%) because avoids isolation of the intermediates that sometimes are troublesome as in the case of **2a** and can have a dramatic impact in lowering the overall yield. In detail, see Scheme 3.11, the process involves the rollover cyclometalation of the desired heteroaromatic ligand with *cis*- $[\text{Pt}(\text{CH}_3)_2(\text{DMSO})_2]$; afterwards, rather than isolating the intermediate, an acetone solution of aqueous HCl (Pt:HCl ratio ca. 1:1.1) is added to the warm toluene solution. The use of acetone is very important because avoids the formation of a biphasic system giving an homogeneous mixture that diminishes other possible pathways for the reaction.

At this point the $[\text{Pt}(\kappa^2\text{-N,C})(\text{Cl})(\text{DMSO})]$ complex is extracted with CH_2Cl_2 , treated with Na_2SO_4 to remove traces of water and reacted with a stoichiometric amount of desired ligand L. Traditional workup leads to isolation of the complex in the solid state.

Up to now the multistep protocol has been applied only with $\kappa^2\text{-N,C} = \text{bpy-H}$ and $\text{L} = \text{PPh}_3$ in order to have a known system to optimize the reaction conditions, however these encouraging results are certainly promising and the flexibility of the method is currently under investigation.

A preliminary result connected to the protocol just described has been obtained using vpy as cyclometalating ligand, in fact the complex $[\text{Pt}(\text{vpy-H})(\text{Cl})(\text{DMSO})]$ (**16g**) has been obtained in high yield and purity as evident from the ^1H NMR spectrum. The diagnostic signals are, as usual, the lack of the resonance of the methyl in the aliphatic region, the increase in the value of the $^3J_{\text{Pt-H}}$ of the DMSO protons (3.54 ppm, ca. 26 Hz) as a consequence of the DMSO *trans* to pyridinic nitrogen arrangement and the deshielding of the signal of the H_6 due to the chloride (δ 9.10, $^3J_{\text{Pt-H}} = 35$ Hz).

Even in the case of the chlorides it is visible an AB system due to the vinylic protons that both couple with ^{195}Pt nucleus (H_β : δ 6.65, $^2J_{\text{Pt-H}} = 97$ Hz; H_α : δ 7.26 $^3J_{\text{Pt-H}} = 84$ Hz). It is interesting to note that H_β is not very deshielded as often happens when DMSO is spatially close and, by comparison with the corresponding $[\text{Pt}(\text{vpy-H})(\text{CH}_3)(\text{DMSO})]$

(**2g**) complex, it is evident that it is even more shielded. A reasonable explanation for this behaviour can be found in the distance between the DMSO and the proton that in this case is bigger due to the geometry of the ligand.

As already said for **2g**, even for the chloride one we were not able to find examples in literature^a but comparison can be made with similar arrangements. For instance H_α can be compared roughly with the iminic proton of cyclometalated benzyliminic derivatives.^{334–338}

Among the examples found only two complexes have a κ^2 -N,C cyclometalated ligand and in one case no coupling with ^{195}Pt is observed.³³⁶ In the other example the analogous $[\text{Pt}(\kappa^2\text{-N,C})(\text{Cl})(\text{SEt}_2)]$, with $\kappa^2\text{-N,C} = \text{N-isopropyl-benzylimine}$, show a ca. 30 Hz larger $^3J_{\text{Pt-H}}$ coupling constant.³³⁴ Even though the solvent is different, *i.e.* C_6D_6 vs. CDCl_3 , the observed difference seems reliable and could not be explained by the *trans*-influence because a chloride is thought to have a smaller effect than a sulphur donor.^{339,340}

A *trans* arrangement somewhat closer to the one observed in our complex, *i.e.* double bond *trans* chloride, can be obtained if the cyclometalating benzylimine can block three positions as in the complexes synthesized by López and co-workers using terdentate C,N,S ligands.^{335,337,338} In this case however the coupling of the iminic proton with platinum is even larger being around 130 Hz, in agreement with *trans*-influence order.

On the other hand the pyridinic part of **16g** can be compared with the ppy cyclometalated derivatives $[\text{Pt}(\kappa^2\text{-N,C})(\text{Cl})(\text{DMSO})]$ where $\kappa^2\text{-N,C}$ indicates a cyclometalated substituted ppy,^{34,341} benzo[*h*]quinoline,¹⁵⁰ or pyridyl-N-methylated indoles.³⁴² In this class of complexes the comparison is straightforward and there are no issues about different *trans* arrangements because pyridyl and DMSO are placed as in our vpy complex; in this case the values we found for $H_{6'}$ (δ 9.10, $^3J_{\text{Pt-H}} = 35$ Hz) and for methyls on DMSO (δ 3.54, $^3J_{\text{Pt-H}} = 26$ Hz) are in the same interval of the complexes reported in literature regardless the cyclometalating unit.

Single crystal X-ray of **22l**

The same synthetic protocol used to obtain $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{L})]$ complexes has been used starting from *cis*- $[\text{Pt}(\text{Cl})_2(\text{DMSO})_2]$ and 2-phenylpyridine (ppy) with addition of

^aReaxys, version 2.15859.10; Elsevier Information Systems GmbH. End of October 2013.

PPh₃ at the end of the cyclometalation process.

In this context it has been possible to obtain crystals suitable for X-ray analysis of the complex [Pt(ppy-H)(Cl)(PPh₃)] (**221**) that, to the best of our knowledge, is not present in the Cambridge Crystallographic Data Centre nor in published papers.^b

The complex crystallizes in the triclinic P-1 space group, the asymmetric unit contains the complexes and two of them are found in the unit cell (Figure 3.1). A π stacking between the cyclometalated ppy bearing to neighbouring complexes is present, this is characterized as atoms used to define the mean plane (12 non-hydrogen atoms of each ppy), the angle between mean planes through interacting π systems is 0 degrees, *i.e.* they are parallel, and closest atomic contact between the C₂ on one ppy and the C_{5'} in the symmetry related one of 330.9(2) pm.

The square planar geometry is confirmed and the groups coordinated to the platinum metal centre are a cyclometalated ppy, a chloride and a triphenylphosphine. A very slight pyramidal distortion is visible from the angle between the mean planes through N-Pt-C_{2'} and P-Pt-Cl (2.4°) with the Pt being 2.6 pm away from that plane. On the whole the complex is planar and the angle between the mean planes calculated for the ppy and for the coordination plane (platinum and atoms directly attached to it) is 2.6 degrees. Finally, the phenyl and pyridyl rings are not coplanar as demonstrated by the 6.2° angle between the two mean planes.

Geometrical parameters, *i.e.* bond distances and angles, are visible in Table 3.3 and are compared with two closely related structures, *i.e.* they all share the general formula [Pt(κ^2 -N,C)(Cl)(PPh₃)], already published.^{16,343}

Complex [Pt(ppy-H)(Cl)(PPh₃)] can be envisaged as the common link between the other two structures because in one case it is possible to evaluate the influence of substituting an hydrogen with a fluorine atom and, in the other case the influence of the isoelectronic fragments C-H and N-(lone pair) can be investigated.

In the solid state all the structures crystallize with the same space group (P-1) and with very similar cell parameters (see Experimental Section for details) so that it is not unexpected that bond distances and angles are very similar in each case. No substantial

^bReaxys, version 2.15859.10; Elsevier Information Systems GmbH. End of October 2013. CSD version 5.34 updates (November 2012).

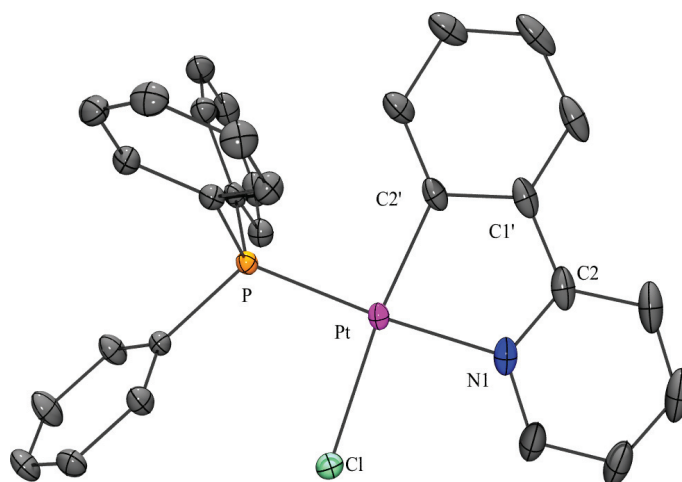


Figure 3.1: ORTEP for **22I**. Ellipsoids drawn at 50% probability level and hydrogens removed for clarity.

differences are worth noting between **22I** and the one with $\text{ppy}^{4\text{F}}$, in fact the largest variations are ca. 1 pm and 1 degree and almost always overlapping with each other taking into account the standard deviations.

Comparison between the rollover and the classical cyclometalated species does not lead to different results, the only notable differences are connected with the fact that bonds involving the metalated pyridine are ca. 0.5 pm shorter while Pt-P, Pt-Cl and Pt-N are almost 1 pm longer.

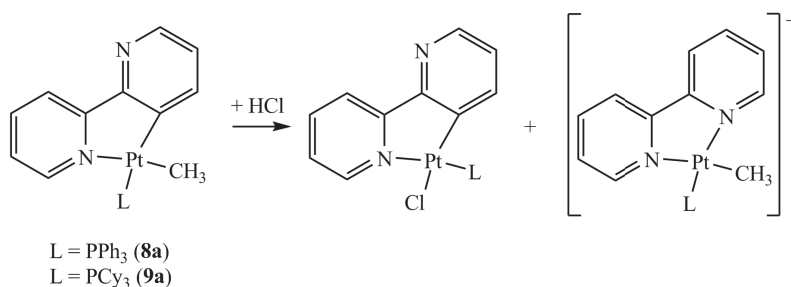
As with the corresponding methylated complexes (see Chapter 2) a family of derivatives can be easily synthesized by substituting the DMSO with another neutral ligand L, *e.g.* phosphanes, pyridines, carbon monoxide. Due to the stronger interaction between the DMSO and the metal centre substitutions are generally harder and require longer times or excess of entering ligand or both as in the case of 3,5-lutidine.¹⁴⁵ Thus, it would be very interesting and synthetically useful if the complexes $[\text{Pt}(\text{bpy-H})(\text{CH}_3)(\text{L})]$ could be converted into the corresponding chlorides directly by treatment with HCl, both using it directly as aqueous solution or generating it *in situ* using LiCl and a proton source.

The reaction of the species $[\text{Pt}(\text{bpy-H})(\text{CH}_3)(\text{L})]$ with HCl, however, is not as straightforward: the corresponding reaction of **8a**, having PPh_3 in place of DMSO, shows a competition between the two protonolysis processes, and a mixture of $[\text{Pt}(\text{bpy-H})(\text{Cl})(\text{PPh}_3)]$ (**40a**) and $[\text{Pt}(\text{bpy})(\text{CH}_3)(\text{PPh}_3)]\text{Cl}$ (**40a**) in a 1:4 molar ratio is formed (Scheme 3.12).

Table 3.3: Selected bond distances (in pm) and angles (in degrees) with corresponding ESDs in parentheses for complex **22I** along with those relative to the published bpy and ppy^{4F} cyclometalated analogues.^{16,343}

	bpy-H	ppy-H	ppy ^{4F} -H
Pt-P	223.33(7)	222.58(4)	222.69(7)
Pt-Cl	238.03(8)	237.57(6)	237.20(9)
Pt-N ₁	209.6(2)	208.6(1)	209.2(2)
Pt-C _{2'}	200.8(3)	201.2(2)	201.9(4)
C _{2'} -C _{1'}	141.6(3)	142.2(2)	142.8(4)
C _{1'} -C ₂	146.3(3)	146.3(3)	146.3(5)
C ₂ -N ₁	135.0(3)	135.5(2)	136.6(4)
P-Pt-Cl	92.75(2)	91.55(2)	91.61(3)
Cl-Pt-N ₁	90.77(5)	92.60(4)	92.06(6)
N ₁ -Pt-C _{2'}	80.75(8)	80.46(6)	80.9(1)
C _{2'} -Pt-P	95.81(7)	95.34(5)	95.33(9)
P-Pt-N ₁	176.23(5)	175.40(4)	175.61(6)
Cl-Pt-C _{2'}	170.96(7)	172.93(5)	172.81(9)

Their identification in solution was ascertained through NMR spectroscopy by comparison with literature data.^{16,137} In contrast, the reaction of **9a** with HCl gives the cationic adduct **41a** as the main species, in addition to a minor species (in a 1:3 molar ratio) not corresponding to the expected rollover complex [Pt(bpy-H)(Cl)(PCy₃)]. Despite several efforts, we were not able to separate and characterize the second species.



Scheme 3.12

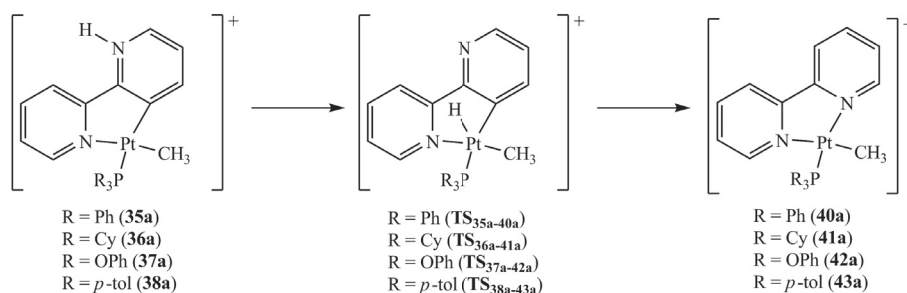
The role of the nature of the neutral fourth ligand appears therefore to be of paramount importance in driving the Pt-C bond breaking, with a marked propensity of phosphane

complexes to give Pt-C(sp^2) protonolysis followed by a retro-rollover reaction: overall, several factors may play a role in the reaction and will be the subject of future investigations.

3.5 DFT Calculations

In order to get more insights into the observed reaction kinetics of the retro-rollover process, we performed density functional theory (DFT) calculations on the species involved: *i.e.*, **8a-11a**, **35a-38a** and **40a-43a**. On the basis of the results of previous studies on similar reactions,^{293,344} we hypothesize that the formation of a hydride intermediate is the key step for the reaction mechanism of all species studied. Therefore, we optimized the geometry of reagents, (proposed) intermediates, and products for the four reactions discussed in Section 3.3 (Scheme 3.13).

Protonation of the neutral species **8a-11a** has very little influence on the bond distances



Scheme 3.13

and angles (Table 3.4); it is worth noting that there are no differences above 0.02 Å, the largest ones involving the elongation of Pt-P and Pt-N₁ bonds. As expected, all the bonds connected to the protonation site, *i.e.* the N₁ atom, are shorter after protonation.

Bonds in the metallacycle not directly connected to platinum undergo very slight and probably not meaningful changes. All species are distorted square planar (see Table 3.4), with the heteroaromatic ligand lying on the plane; the lowest values for the C₃-Pt-CH₃ and C₃-Pt-N₁ angles are found for the PCy₃ ligand.

A comparison of the proposed hydride intermediates **TS_{x-y}** permits us to note that all the

Table 3.4: Selected bond distances, in pm, and angles, in deg, for the PPh₃ series of complexes involved in the retro-rollover reaction.

	8a	35a	TS_{35a-40a}	40a^a
Pt-P	234.92	236.44	246.72	227.26
Pt-CH ₃	204.45	203.80	204.69	203.85
Pt-C ₃	203.73	202.87	204.12	212.16
Pt-N _{1'}	219.40	220.44	221.44	218.23
N _{1'} -C _{2'}	135.08	135.30	135.00	135.09
C _{2'} -C ₂	147.05	146.85	147.22	147.74
C ₂ -C ₃	141.34	140.74	141.05	135.18
N ₁ -H	-	-	101.689	-
Pt-H	-	-	-	150.983
P-Pt-CH ₃	92.77	91.90	90.59	90.44
CH ₃ -Pt-C ₃	90.12	90.64	92.38	92.85
C ₃ -Pt-N _{1'}	79.47	79.03	79.67	76.91
N _{1'} -Pt-P	97.68	98.47	97.27	99.99
N _{1'} -Pt-CH ₃	169.39	169.49	171.93	168.91
P-Pt-C ₃	176.84	177.30	175.78	175.83

^a Bonds and angles involve the N₁ rather than C₃.

bonds involving platinum are elongated with respect to both the protonated (**35a-38a**) and neutral (**8a-11a**) corresponding species, with the Pt-P bond experiencing the greatest change in absolute value. Pt-H distances follow a reverse trend in comparison to those of Pt-P; these observations are consistent not only with the change in geometry and coordination number around the Pt centre but also with the steric requirements of each phosphane. Finally, for species **40a-43a**, we notice that, by comparison with the corresponding species **8a-11a**, **35a-38a**, and **TS_{x-y}**, (a) the Pt-P distance decreases possibly because the *trans* influence of the nitrogen is weaker in comparison to that of the C(*sp*²) carbon of the cyclometalated bipyridine, (b) the distances Pt-CH₃ and Pt-N_{1'} increase and decrease respectively, (c) the C₂-C_{2'} distances remain substantially unchanged from **TS_{x-y}** but increase in comparison to those in **40a-43a**, and (d) P-Pt-CH₃ and C₃-Pt-N_{1'} angles tighten while C₃-Pt-CH₃ and N_{1'}-Pt-P widen. Figure 3.2 reports the geometry-optimized minimum structures of complexes **8a**, **35a**, **TS_{35a-40a}** and **40a**.

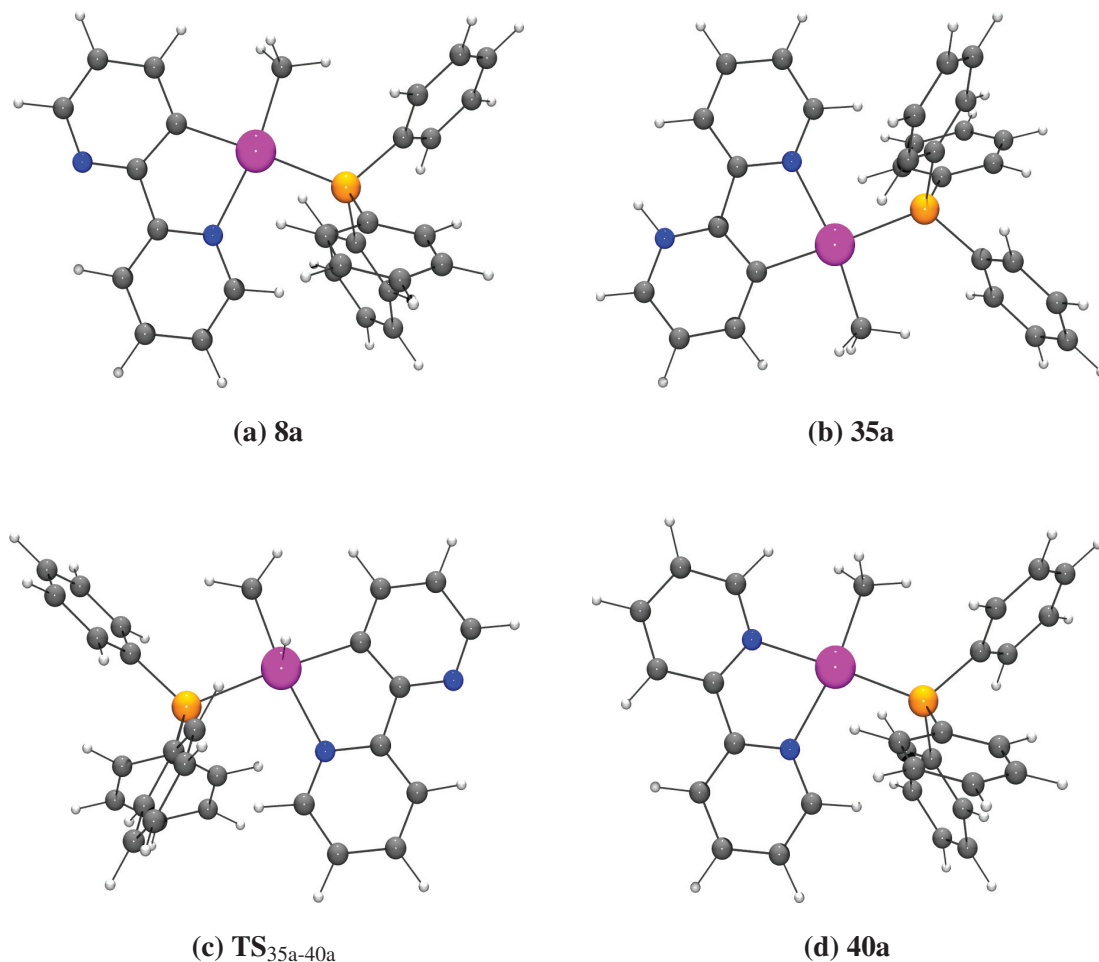


Figure 3.2: Equilibrium geometries structures of complexes **8a**, **35a**, **TS_{35a-40a}** and **40a** optimized at PBE0/def2-SVP level.

In Table 3.5 we report the zero point energy corrected enthalpies for all the species involved in the experimental study. In order to qualitatively correlate numerical results to experimental findings, since we do not have any data for the transition states (TS), we refer to the Hammond-Leffler postulate:^{345,346} assuming that the intermediates are structurally similar, and thus close in energy to the respective TSs, we hypothesize that the activation energies and enthalpies follow the same trend as the calculated values for the intermediate species. We notice that the smallest barrier is found for the complex containing the most basic ligand (PCy₃), while the highest barrier is found for the complex containing the most acidic ligand, in fair agreement with experimental observations. This is also coherent with experimental findings that P(*p*-tol)₃ is faster than PPh₃, the former

having a smaller energy barrier, thus suggesting that electronic factors effectively have a role in speeding up the reaction.

Looking at the final product of the process, we can see another factor which drives the reaction that is purely thermodynamic: the energy content of the adducts **40a-43a** is considerably higher, in absolute value, than that of the protonated complexes **35a-38a**, and this can give a good explanation why we do not observe an equilibrium. From a closer point of view we can note that the sum of the energies of Pt-C and N-H bonds is less than that of Pt-N and C-H bonds, all other bonds being kept constant.

Another result evident from Table 3.5 is connected with the proton affinity of the complexes.¹¹⁵ In a broader way the rollover cyclometalated complexes can be viewed as species having two lone pairs (*i.e.* one on the sp^2 hybrid orbital of the non coordinating nitrogen and one in the d_{z^2} orbital on platinum) that can compete for an electrophile, in this case a proton. From the data reported it is clear that the nitrogen is the thermodynamic protonation site because affords the most stable protonated species, in fact the corresponding hydridic species arising from protonation of the metal centre lies always more than 70 kJ·mol⁻¹ above in energy.

Table 3.5: Calculated enthalpies, in kJ·mol⁻¹ at 298.15 K and 101325 Pa, for the complexes optimized at the PBE0/def2-SVP level.

	κ^2 -N,C*	TS _{x-y}	κ^2 -N,N
PPh ₃	0.00	78.75	-92.78
PCy ₃	0.00	72.71	-96.57
P(Ph) ₃	0.00	93.01	-91.66
P(<i>p</i> -tol) ₃	0.00	73.75	-95.01

In Table 3.6 are reported the proton affinities for the complexes [Pt(bpy-H)(CH₃)(L)] with L = phosphane obtained from the optimization at PBE0/def2-SVP level. It is interesting to note that there is a rough correlation between the proton affinity of the non-coordinating nitrogen and the donor characteristics of the phosphane bound to the metal centre. The more donor the phosphane the higher the proton affinity, however the value relative to PCy₃ is suspiciously low compared to the Tolman electronic parameter²⁴⁹ and let us think

that there are other operating factors (probably steric).

Notably, if we restrict the comparison to the phosphanes having approximately the same steric hindrance (*i.e.* PPh_3 , P(Ph)_3 , $\text{P}(p\text{-tol})_3$) the correlation is really good indeed even though not appreciable experimentally because all the species, when treated with $[\text{H}_3\text{O} \cdot 18\text{-crown-6}][\text{BF}_4]$, yield almost instantaneously to the N-protonated derivative. This is most likely due to the levelling effect of the solvent that reduces the differences observed in the ΔH .

As described above, upon reaction with $[\text{H}_3\text{O} \cdot 18\text{-crown-6}][\text{BF}_4]$, complexes $[\text{Pt}(\text{pyq-H})(\text{CH}_3)(\text{L})]$ yield the cationic N-protonated analogues. As evident from the calculations, both protonation and change in the charge of the complex cause only slight modifications in bond distances and angles in a way very similar to what has been reported for bpy complexes (see Table 5.12 and Table 5.13 in the Experimental Section). Changes in bond distances involving platinum can be explained in terms of push-pull interactions between ligands *trans* to each other, that is, when a bond elongates, that in *trans* shortens. In detail, the highest variations, in absolute value, are evident for Pt-N_1 , Pt-CH_3 , and Pt-L bonds (ca. 1 pm). Quite surprisingly, the Pt-C_3 bond length is almost unchanged, showing a 0.1 pm difference which is too small to be considered significant.

The angles insisting on the metal centre do not show dramatic changes in their absolute value, but it can be noted that corresponding angles have the same trend, that is, $\text{N}_1\text{-Pt-C}_3$ and L-Pt-CH_3 close, while the other two become wider (Table 5.12). Finally, the planarity of the molecule is not affected by the protonation of the non-coordinating quinolinic nitrogen.

The effect of protonation on the cyclometalated ligand was also investigated (Table 5.13). As expected, the changes in the molecular structure are more pronounced in the surroundings of the protonation site and, particularly, in the $\text{N}_1\text{-C}_2$, $\text{C}_2\text{-C}_3$, $\text{N}_1\text{-C}_{10}$ and $\text{C}_9\text{-C}_{10}$ bond lengths, with elongations of about 3.0, 2.0, 1.4, and 1.2 pm, respectively. Interestingly, a kind of "contraction" of the metallacycle bonds is evident on the quinolinic moiety, that is, $\text{C}_2\text{'-C}_2$, $\text{C}_2\text{-C}_3$, and, to a lesser extent, Pt-C_3 . This is in line with the fact that the electron density is somewhat pulled toward the protonated nitrogen, which is more electron-deficient than in the neutral complex. The bonds in the pyridinic ring rearrange without significant or unexpected changes: all the differences are below 1 pm; in detail,

those bonds closer to the quinolinic system (*i.e.*, N_{1'}-C_{2'} and C_{2'}-C_{3'}) shorten, while the others are alternately shorter or longer.

Table 3.6: DFT-calculated, ZPE corrected, proton affinity (ΔH) and gas phase basicity (ΔG) for [Pt(κ^2 -N,C)(CH₃)(L)] complexes.^a

	ΔG	ΔH
2a [Pt(bpy-H)(CH ₃)(DMSO)]	995.1	993.1
8a [Pt(bpy-H)(CH ₃)(PPh ₃)]	1018.6	1016.1
9a [Pt(bpy-H)(CH ₃)(PCy ₃)]	1016.6	1017.2
10a [Pt(bpy-H)(CH ₃)(P(OPh) ₃)]	1000.2	999.2
11a [Pt(bpy-H)(CH ₃)(P(<i>p</i> -tol) ₃)]	1024.7	1023.4
24a [Pt(bpy-H)(CH ₃)(CO)]	964.8	963.2
2f [Pt(pyq-H)(CH ₃)(DMSO)]	1007.5	1005.3
8f [Pt(pyq-H)(CH ₃)(PPh ₃)]	1027.4	1026.8
24f [Pt(pyq-H)(CH ₃)(CO)]	980.3	978.6

^a All values in kJ·mol⁻¹.

The trend of the unscaled stretching frequencies of the CO bond in complexes **24a/24f** and **39a/39f**, recorded in Nujol, is correctly reproduced by the harmonic analysis. Finally, evaluation of the DFT-calculated proton affinity and gas phase basicity of the species [Pt(pyq-H)(CH₃)(L)] (Table 3.6) and comparison with the corresponding bpy analogues permits to note the following: (a) both with pyq and bpy the easiness of protonation depends on the neutral ligand coordinated *trans* to the metalated carbon atom and increases in the order PPh₃ > DMSO > CO; (b) complexes with cyclometalated bpy always show lower values than the corresponding with pyq. These observations are in good agreement and show a good correlation with the well-known donor properties of the neutral ligands involved in this work; moreover it seems that the basicity order expected for pyridine and quinoline is respected.

DFT calculations could also provide an interesting insight to the experimental observation that the mesoionic complex **35f** reacts faster than the corresponding **35a** in a 10⁻² CH₂Cl₂ solution. The key point here is the fact the on going from **35f** to the κ^2 -N,N pyq adduct **40f** there is an increase in the dipole moment of the platinum containing species: from

13.7 Debye to 15.5 and 17.3 for the two isomers of the final product.

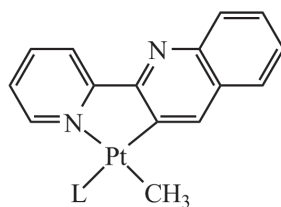
The enhanced polarity of the final cationic complex is probably better stabilized by the more polar dichloromethane that has a (relative) dielectric constant ϵ of 9.10, nearly twice the value for CHCl_3 (4.81). Moreover, CH_2Cl_2 has also a larger dipole moment: 1.60 vs 1.04 Debye.

On the other hand for **35a** the dipole moment is 12.8 D and for the final adduct, **40a**, "only" 7.95 D.

This observation is qualitative and by no means constitutes a definitive explanation for the different rates observed experimentally but, on the whole, it suggests that when the system is more polarizable the retro-rollover reactivity experiences a speed-up.²⁹

3.6 Electrochemical behaviour

Platinum derivatives **2f**, **8f**, **24f** and corresponding N-protonated **34f**, **35f**, **39f** (Scheme 3.14) were characterized by UV-Vis spectroscopy in CH_2Cl_2 . By comparison with the free ligand, the higher energy bands are attributable to ligand centred $\pi\text{-}\pi^*$ transitions and the lower ones are tentatively assigned to metal-to-ligand charge transfer transitions (380-430 nm).³⁴⁷ N-protonated cationic derivatives show MLCT absorptions at higher wavelengths than the corresponding neutral species, suggesting a more effective extension of the charge delocalization on the complex. It seems reasonable to ascribe this red-shift of the MLCT band to the effects that the protonation has on the electron density, as highlighted also by the DFT calculations (see Table 3.7). The same effect can be ob-



L = DMSO (**2f**)

L = PPh_3 (**8f**)

L = CO (**24f**)

Scheme 3.14

served comparing complexes **2f** and **2a**, which differ only for the cyclometalated ligand

(pyq and bpy, respectively) thus we are prone to think that the higher extent in the electronic delocalization originating from the quinoline system instead of a pure pyridine ring is the reason of the observed red-shift. The analysis of the UV-Vis bands position permits also to roughly estimate the σ -donor effect of the cyclometalated ligand.³⁴⁷ Complexes **2f** and **2a** show $\lambda_{\max}$ respectively at 403 and 380 nm suggesting that bpy-H has a stronger σ donating effect than pyq-H; the same trend is visible in the corresponding N-protonated species **34f**, $[\text{Pt}(\text{pyq}^*)(\text{CH}_3)(\text{DMSO})]^+$, and $[\text{Pt}(\text{bpy}^*)(\text{CH}_3)(\text{DMSO})]^+$ (460 vs 364 nm). The analysis of the energy-gap (E_{gap}) values derived from the UV-Vis spectra evidences, as predictable, a lower E_{gap} value for the cationic complexes (**34f**, **35f**, **39f**) than for the corresponding neutral ones (**2f**, **8f**, **24f**). E_{gap} values obtained from UV-Vis spectra were compared with estimated data by DFT method (see Table 3.7), confirming a decrease in E_{gap} values going from neutral to cationic species. Differences in experimental with respect to calculated E_{gap} data is between 18 and 36%: although such values seem quite high, they are in line with those reported for some Pt(II) derivatives with phenylpyridine and benzoquinoline ligands.³⁴⁸ We reasonably impute the difference to the functional/basis set used in the computations and the absence of the solvent which can play a not negligible role. Finally, the analysis of the molecular orbitals suggests that the higher E_{gap} displayed by the bpy-H complexes is due to a concurrent stabilization of the highest occupied molecular orbital (HOMO) and destabilization of the lowest unoccupied molecular orbital (LUMO).

The electrochemical behaviour of the neutral (**2f**, **8f**, **24f**) and of the corresponding cationic (**34f**, **35f**, **39f**) species was investigated in the CH_2Cl_2 -TEAPF₆ 0.1 M solvent system by cyclic voltammetry.

Neutral complexes show an anodic irreversible process between 0.6 and 1.4 V, while the oxidation of the free ligand occurs at about 1.6 V (Table 3.7). DFT calculations indicate that in the free ligand the HOMO is located on the whole of the molecule, while in the complexes it encompasses the quinoline fragment, the metal centre, and, especially in the case of **24f**, even the L ligand. Theoretical data support the hypothesis that the anodic processes involve primarily the pyq ligand, and to a minor extent the Pt(II) centre and, eventually, the L ligand. Moreover, DFT data show a dipole moment oriented toward the L ligand in **2f** and **8f**, and toward the pyridine ring in **24f**. The comparison between

the direction of the dipole moment, together with the fact that the oxidation process is mainly located on L, might explain the higher oxidation potential of the PPh₃ derivative (**8f**) compared to the CO one (**24f**): as a matter of fact, in **8f** the electron density on the quinoline ring is lower than in **24f**, thus the oxidation process in the latter is easier than in **8f**. In the case of the dimethylsulphoxide (DMSO) derivative (**2f**), the known lability of the Pt-DMSO bond makes it difficult to compare its electrochemical response with that of the analogues with PPh₃ and CO, **8f** and **24f**.

The cathodic portion of the voltammograms does not evidence the appearance of reductive processes in the potential range exploited. With regards to the LUMO values, the DFT calculations seem to confirm that the associated cathodic process would be at very negative onset potential values, reasonably not detectable in the CH₂Cl₂-TEAPF₆ solvent system.

As for the cationic species (**34f**, **35f**, **39f**), no oxidative process is evidenced in the potential range exploited. Evaluation of the HOMO energy values by DFT calculations suggests that the anodic response due to the cationic species, mainly located on the metal centre, would be at potential values higher than the anodic limit of the CH₂Cl₂-TEAPF₆ 0.1 M solvent system. Conversely, the cathodic behaviour shows a reduction process (Table 3.7) attributable to the reduction of the protonated portion. The DFT data indicate that the LUMO is always located on the pyq ligand, and the dipole moment is always oriented toward the cyclometalated ligand, accounting for the relatively small difference between the reduction potential values of **35f** and **39f**. Accordance between experimental and theoretical data is in the range of analogous comparisons reported in literature.³⁴⁸

3.7 Conclusions

Great efforts have been devoted to the comprehension of the mechanisms operating in alkane C-H activation by platinum²⁹² complexes. Significant mechanistic insights have been gained through investigations of the microscopic reverse of the C-H activation step: *i.e.*, protonolysis of alkylplatinum(II) model systems. The protonation reaction may occur with different mechanisms, but it has been demonstrated that in electron-rich platinum(II) diiminoalkyl complexes the metal is both the thermodynamic and kinetic site of protona-

Table 3.7: Electrochemical, optical and computational data for selected neutral and cationic complexes [Pt(κ^2 -N,C)(CH₃)(L)].

	λ (nm) ^a	$E_{\text{gap,opt}}$ (eV) ^b	$E_{\text{gap,DFT}}$ (eV) ^c	E_{ox} (V) ^d	E_{red} (V) ^d	HOMO _{exp} (eV)	HOMO _{DFT} (eV) ^e	LUMO _{DFT} (eV) ^e
2a [Pt(bpy-H)(Me)(DMSO)]	276, 307, 380	2.99	4.71	0.72		-5.13 ^e	-6.28	-1.57
34a [Pt(bpy*)(Me)(DMSO)] ⁺	255, 314, 364	2.95	3.75		-0.58	-7.42 ^f	-9.73	-5.98
2f [Pt(pyq-H)(Me)(DMSO)]	306, 366, 403	2.94	4.37	0.64		-5.04 ^e	-6.15	-1.78
34f [Pt(pyq*)(Me)(DMSO)] ⁺	325, 460	2.18	3.43		-0.85	-6.74 ^f	-9.54	-6.11
8f [Pt(pyq-H)(Me)(PPh ₃)]	262, 302, 381	2.88	4.23	1.35		-5.70 ^e	-5.89	-1.66
35f [Pt(pyq*)(Me)(PPh ₃)] ⁺	264, 329, 429	2.46	3.06		-0.50	-7.00 ^f	-8.87	-5.81
24f [Pt(pyq-H)(Me)(CO)]	256, 289	3.59	4.36	1.21		-5.61 ^e	-6.48	-2.12
39f [Pt(pyq*)(Me)(CO)] ⁺	275, 284, 350	2.96	3.71		-0.44	-7.69 ^f	-10.17	-6.46
pyq	253, 320, 335	3.62	4.95 (cis)	1.58		-5.59 ^e	-6.66 (cis)	-1.71 (cis)
			4.83 (trans)				-6.64 (trans)	-1.81 (trans)

^a Measured in CH₂Cl₂ solution. Concentration for UV-Vis measurements was about $2 \cdot 10^{-5}$ M.^b The energy-gap ($E_{\text{gap,opt}}$) value was determined from the λ_{onset} in the UV-Vis spectrum.^c Theoretical values obtained from DFT calculations at PBE0/def2-SVP level.^d Potential values reported vs Ag/AgCl in CH₂Cl₂-TEAPF₆ 0.1 M solvent system. Concentration $2 \cdot 10^{-3}$ M.^e Calculated from the anodic (HOMO) or cathodic (LUMO) onset potential value.^f The LUMO energy value was calculated from the equation $\text{LUMO(eV)} = \text{HOMO} + E_{\text{gap,opt}}$, and the HOMO value from $\text{HOMO(eV)} = \text{LUMO} - E_{\text{gap,opt}}$.³⁴⁹

tion.²⁹³

Protonolysis with acids having a weakly coordinating anion on rollover complexes $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{L})]$, $\kappa^2\text{-N,C}$ bpy derivative, L = neutral ligand, does not attack the two Pt-C bond present in the complex but affords instead the protonation of the non-coordinating nitrogen atom. The species thus generated has some interesting points because the cyclometalated ligand can now be seen as a mesoionic species able to influence differently the reactivity of the complex.

However, the protonated species evolve in solution with protonolysis of one of the two Pt-C bonds present in the complex. According to the reaction conditions Pt-C(sp^2) or Pt-C(sp^3) bond rupture may take place. In the first case, in the absence of a good external donor, a retro-rollover reaction occurs to give the cationic adducts $[\text{Pt}(\kappa^2\text{-N,N})(\text{CH}_3)(\text{L})]^+$, $\kappa^2\text{-N,N}$ = bpy derivative.

The rate of this isomerisation process is dramatically dependent on the nature of the neutral ligand L, when $\kappa^2\text{-N,N}$ = bpy the more basic PCy₃ ligand shows the fastest reaction among the phosphanes used. Moreover the observation that P(*p*-tol)₃ reacts faster than PPh₃ is a strong information supporting our thesis.

In contrast, in the presence of an external good donor elimination of methane is observed through Pt-C(sp^3) bond protonolysis. Theoretical studies are in qualitative agreement with the experimental observations, suggesting that the key factor influencing the kinetics is the (de-)stabilization of the electron density on the metal centre.

Several factors are active in the course of the protonolysis reaction, and a subtle balance between them may drive the reaction toward different routes. The comprehension of the factors leading the rollover and retro-rollover processes would give the possibility of designing catalytic cycles where the bpy and bpy* ligands will no longer operate as spectator ligands but will be active actors in the process: for example, acting as a hydrogen reservoir/acceptor system.

Reactivity involving Pt(IV)

4.1 Introduction

An intriguing possibility with platinum(II) rollover complexes is the oxidation to platinum(IV) which opens up a parallel world of reactivity. The importance of Pt(IV) complexes is well documented in many different fields of chemistry: they are intermediates in the Shilov-type functionalizations of alkanes,^{350,351} as catalysts/reagents in direct functionalization of saturated/unsaturated hydrocarbons by oxidation,^{352–355} in the C-X bond formation,^{239,356} in material science³⁵⁷ and in medicinal chemistry.^{358–365}

Reductive elimination is one of the most fundamental steps in stoichiometric and catalytic processes leading to C-C bond formation, representing the reaction where the final product is formed.³⁶⁶ A great attention has been focused on reductive elimination reactions from Pt(IV) complexes, which often take place after initial loss of a ligand to generate a more reactive five-coordinate intermediate.³⁶⁷ A great number of studies are concerned with reductive C(*sp*³)-C(*sp*³) elimination from methylplatinum(IV) compounds, and analogous studies have been carried out on arylplatinum(IV) compounds, including studying the competition between C(*sp*²)-C(*sp*²) and C(*sp*²)-halide bond formation,^{239,368–371} or C(*sp*³)- and C(*sp*²)-halide elimination.^{343,372}

In contrast, examples of C(*sp*²)-C(*sp*³) reductive elimination are very scarce,^{373–375} though they do include a catalytic process involving platinum(IV) compounds.^{376–379}

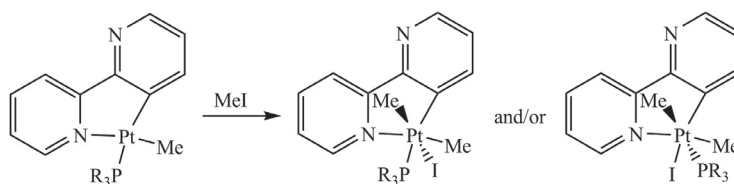
Pt(IV) complexes with chelated nitrogen ligands (both κ^2 -N,N and κ^2 -N,C) are often obtained through oxidative addition of C-X bonds. In the case of cyclometalated species,

the resulting Pt(IV) complexes $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)_2(\text{X})(\text{L})]$ (L = neutral ligand, X = halide) usually display a *fac*-PtC₃ arrangement, due to the natural tendency of carbon-bonded ligands to avoid mutual *trans* coordination (*trans*-phobia),^{142,143,261} and are stable at room temperature both in solution and in the solid state.

Here we use CH₃I as oxidizing agent, a well known and studied methodology in organometallic Pt(II) chemistry,^{231,380–382} with some 2,2'-bipyridine derived rollover complexes.

4.2 Results

In Chapter 2 it has been reported the synthesis of the rollover complexes $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{PR}_3)]$ with different cyclometalating ligands $\kappa^2\text{-N,C}$ and different phosphanes, PR₃. All these complexes are considered to be electronrich and, therefore, good substrate to undergo oxidative addition reactions with alkyl halides (Scheme 4.1).



Scheme 4.1

Our intention is to investigate how the outcome of the reaction is influenced by the properties of the Pt(II) compound; in order to do this, taking $[\text{Pt}(\text{bpy-H})(\text{CH}_3)(\text{PPh}_3)]$ (**8a**) as reference, we selected complexes having different characteristics: *e.g.* a small phosphine in the case of PMe₃, a more or less delocalized cyclometalated unit (pyq and vpy, respectively), different electron density at the metal centre in the case of bpy^{6CF₃}.

4.2.1 PMe₃

The first reaction we describe is with $[\text{Pt}(\text{bpy-H})(\text{CH}_3)(\text{PMe}_3)]$ (**7a**) because changes in the ¹H NMR spectra can be better appreciated, in fact the singlet with satellites of the PMe₃ does not affect the region of the spectrum we are interested in.

A solution of **7a** in acetone- d_6 was treated with an excess of CH_3I at room temperature and the reaction was monitored by ^1H and ^{31}P NMR techniques. As soon as the reagent was added the solution became paler and quickly almost colourless, correspondingly the spectra changed. Major changes are visible in the aliphatic region of the ^1H spectrum where the signals of the PMe_3 protons are deshielded (1.84 ppm vs 1.57 ppm in **7a**) and there is a clear change in the coupling constants: while the $^2J_{\text{P-H}}$ increases slightly to 9.5 Hz (from 8 Hz in **7a**) the coupling with platinum is nearly halved ($^3J_{\text{Pt-H}}$ from 21 to 12 Hz in **49a**); moreover there are now two doublets with satellites both integrating three protons at δ 1.40 ($^3J_{\text{P-H}} = 7$ Hz, $^2J_{\text{Pt-H}} = 69$ Hz) and at δ 0.82 ($^3J_{\text{P-H}} = 7$ Hz, $^2J_{\text{Pt-H}} = 69$ Hz). Protons that couple with phosphorus were detected by a $^1\text{H}\{^{31}\text{P}\}$ NMR experiment, and a single resonance in the ^{31}P spectrum at -44.6 ppm with Pt coupling was seen. Finally, a ^{195}Pt - ^1H correlation spectrum shows the presence of only one platinum resonance at -3429 ppm that couples with protons at δ 0.82 (CH_3), 1.40 (CH_3), 1.84 (PMe_3), 7.99 (H_4) and 8.92 (H_6): this further confirms that we have only one species in solution which can be formulated as $[\text{Pt}(\text{bpy-H})(\text{CH}_3)_2(\text{I})(\text{PMe}_3)]$, **49a**.

There are, in principle, seven possible isomers of the single product that forms, Figure 4.1. We can quickly discount two of the possible isomers, *i.e.* those having two methyls in reciprocal *trans* positions (**49aF** and **49aG**), because we would have seen only one resonance for the two Pt bound methyls integrating six protons in the ^1H NMR, whereas we see two signals, each integrating three. As a corollary we can also add that two groups with high *trans*-influence, such as two methyls, try to avoid being in competition for the same orbital leading to an arrangement expected to be higher in energy (*vide infra*). We can therefore narrow down the possibilities to five Pt(IV) isomers, *i.e.* **49aA-E**, depicted in Figure 4.1.

In order to understand which one of the isomers is present in solution we carried out extensive NMR characterization. From the proton NMR spectrum it is evident that the reaction didn't affect the cyclometalated ligand because there are still seven resonances due to the seven protons of the bpy-H moiety. A ^1H - ^1H COSY correctly showed the presence of two spin system having four and three protons respectively and allowed the assignment of all the signals of the aromatic protons (see Experimental Section).

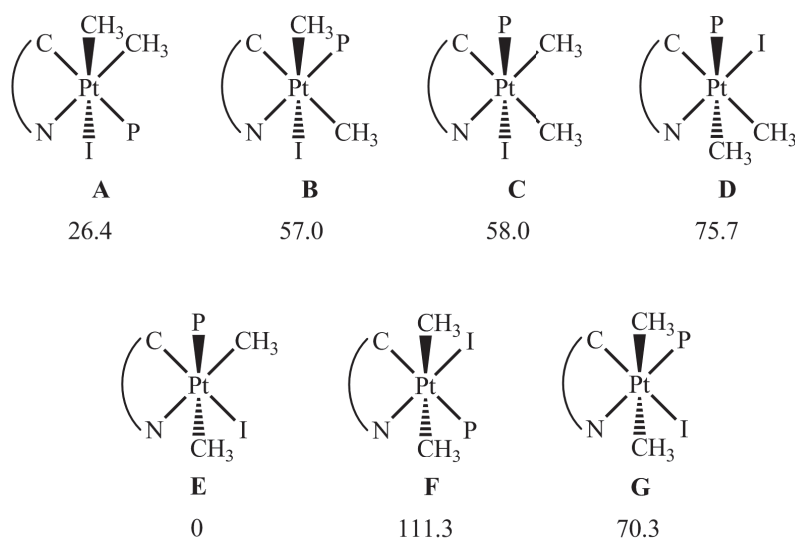
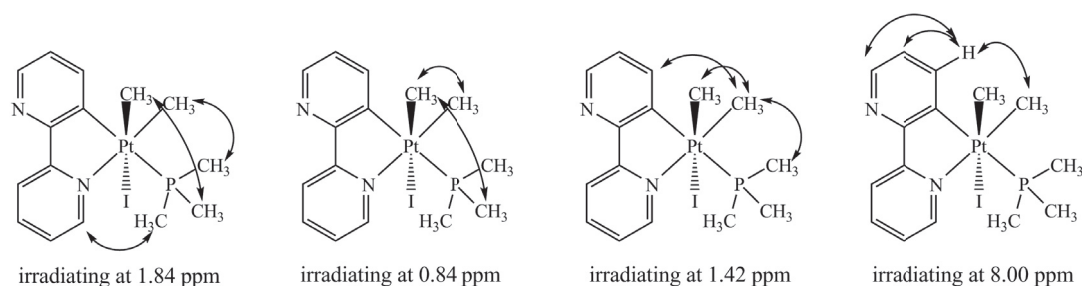


Figure 4.1: Possible isomers of complex **49a** and their relative stability (ΔH ZPE corrected in $\text{kJ}\cdot\text{mol}^{-1}$). For clarity cyclometalated bpy and substituent on phosphorus are omitted.



Scheme 4.2

A series of NOE-1d experiments identified clearly which isomer is present in solution (Scheme 4.2). Irradiation of the PMe_3 protons at 1.84 ppm leads to enhancements detected at δ 0.82, 1.40 (the two methyl groups attached to Pt) and 8.92 (H_6). The fact that the phosphine has influence only on a specific proton of the cyclometalated ring is a probe that the two must be close in space: comparing this observation with the possible structures left we realize that the only one that fits this data is **49aA**. We should note that we might not expect isomers **49aB**, **49aC** and **49aD** on the basis of *trans*-phobia, leading to **49aE** being the only other realistic isomeric form. However, we can easily distinguish our product as **49aA** as the NOE from the PMe_3 group would affect only one CH_3 (*i.e.* the one *trans* to the nitrogen) and non-specific aromatic protons in **49aE**.

In detail, when the NOE contacts of the two platinum bonded methyls were explored a distinction was observed since the one that resonates at 0.82 ppm shows contacts at 1.40 (the other CH₃) and 1.84 ppm (the PMe₃) while the other, *i.e.* at δ 1.40, has contacts with signals at δ 0.82, 1.84 and 7.99 (H₄).

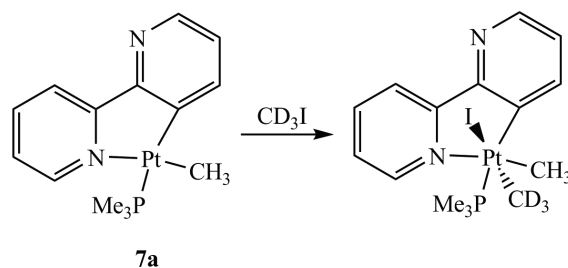
Last but not least, irradiating H₄ completes the NOE cycle and clearly confirms the geometry: the product obtained derives from the *trans* addition of CH₃I to complex **7a**, the PMe₃ is in the plane of the cyclometalated ligand (defined as "equatorial") and the iodide is perpendicular to the afore mentioned plane ("axial" position) *trans* to a methyl group. The ³¹P resonance shows a coupling to Pt of 1400 Hz, diagnostic of a carbon group *trans* to it as in the precursor **7a**.

Decrease in J_{Pt-P} coupling constant is attributable mainly to the increase in the oxidation number of the metal centre, this lowers the *s* character in the Pt-P bond from 0.25 to 0.16 considering "pure" *dsp*² and *d²sp³* hybrid orbitals respectively. It is also worth noting that the ratio between the J_{Pt-P} in **49aA** and in **7a** is 0.66, in line with the expected value of 0.67 which represents the ratio of *s* character present in the Pt^{IV}-P and Pt^{II}-P bonds.³¹⁸

In order to get some clues on the mechanism of the reaction we treated **7a** with CD₃I in the same conditions (acetone-*d*₆, room temperature). As before, the solution became paler and eventually almost colourless, as expected all the signals are the same apart from the fact that one methyl resonance, the one at 0.82 ppm, is not present. The absence of this signal is due to the stereoselective incorporation in the axial position of the CD₃ which is "mute" in the ¹H NMR (Scheme 4.3). This observation confirms that in this case the well established S_N2 mechanism for the reaction of Pt(II) complexes is operating.³⁸⁰ The alkyl halide undergoes nucleophilic attack by the electron pair formally occupying the *d_z²* orbital on platinum, iodide is the leaving group that can trap one of the two possible square pyramidal intermediates, *i.e.* PMe₃ *trans* to C(*sp*²) or C(*sp*³), and lead to the final six-coordinate saturated Pt(IV) complex.

Single crystal X-ray of **49aA**

Additional confirmation of the geometry of **49aA** comes from the X-ray structure. We were able to obtain crystals suitable for X-ray analysis: the solved structure is illustrated in Figure 4.2 and clearly shows the six coordination of the platinum(IV) metal centre and



Scheme 4.3

the PMe_3 in the equatorial position; in Table 4.1 a selection of parameters, *i.e.* bond distances and angles involving platinum, are listed and compared with the those obtained by theoretical means (*vide infra*).

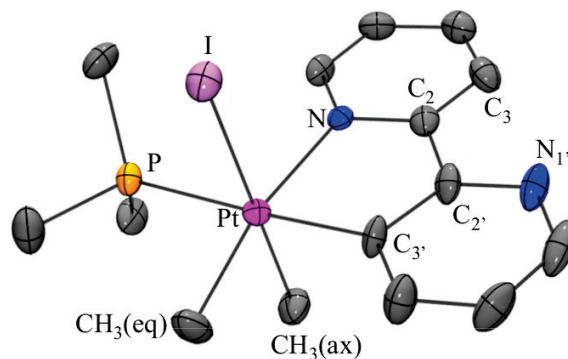


Figure 4.2: ORTEP view of the crystal structure of complex **49aA**. Thermal ellipsoids are drawn at 50% probability, and hydrogens are removed for clarity.

The inequivalence of the ligands leads to a slightly distorted octahedral geometry with the plane of the cyclometalated bpy not very far from the ideal as highlighted by the angles between $\text{P-Pt-C}(sp^2)$ and $\text{N-Pt-CH}_3(\text{eq})$ that are both close to 180 degrees. This plane is almost equally occupied by the four ligands except the cyclometalated one that has some constraints due to the linkage between the two rings.

The small difference, less than 2 pm, in the bond distance between the two methyls is in good agreement with the similarity of the $^3J_{\text{P-H}}$ and $^2J_{\text{Pt-H}}$ coupling constants (see Experimental Section) and gives a clue why this values are so close together. To the best of our knowledge, this is the first crystal structure of a Pt(IV) rollover complex with bpy.

Table 4.1: Experimental, ESD in parentheses, and theoretical values for selected bond distances (in pm) and angles (in degrees) for complex **49aA**.

Distance	Exp	DFT	Angle	Exp	DFT
Pt-P	236.7(2)	243.4	N _{1'} -Pt-C _{3'}	79.5(2)	79.0
Pt-N _{1'}	216.8(5)	221.6	C _{3'} -Pt-CH ₃ (eq)	92.2(3)	92.1
Pt-C _{3'}	202.6(7)	203.8	CH ₃ (eq)-Pt-P	90.1(2)	86.8
Pt-CH ₃ (eq)	208.1(7)	205.9	P-Pt-N _{1'}	98.36(14)	102.4
Pt-CH ₃ (ax)	206.8(8)	207.3	N _{1'} -Pt-CH ₃ (eq)	169.1(3)	169.7
Pt-I	277.18(5)	280.4	P-Pt-C _{3'}	177.6(2)	175.1

Crystal structures of dimethylplatinum(IV) cyclometalated complex are rather rare in literature and all the examples we were able to find have the neutral ligand in axial position. The only cases having an arrangement similar to that presented here, *i.e.* methyl and halide in mutual *trans* position, are those arising from C-H activation of dimethyl-aminoethyl-benzylimines of the type Me₂NCH₂CH₂N=CHAr with Ar = 3,5-C₆H₃Cl₂ or 4-(C₆H₅)-C₆H₄ synthesized by Crespo and co-workers^{170,383} similarity in this complexes is due to the C,N,N binding mode of the ligand which is forced to assume a planar conformation. All the other crystals found have halogenated benzylimines derivatives as cyclometalating unit and PPh₃^{161,376,384} or a sulphide^{385,386} as neutral ligand. Complex **49aA** is actually the kinetic product of the reaction while the thermodynamically favoured isomer is one with the PMe₃ in the axial position.

4.2.2 Bulky phosphanes

Complex **8a**, [Pt(bpy-H)(CH₃)(PPh₃)], was obtained both from **2a** by substitution of the labile DMSO ligand, or directly from *cis*-[Pt(CH₃)₂(DMSO)₂], bpy and PPh₃, in a "one pot" reaction.²⁴⁷ Complex **8a** is stable in air, both in solution and in the solid state, and was characterized in solution by means of NMR spectroscopy.

The reaction at room temperature of the electron rich complex **8a** with MeI gives the corresponding Pt(IV) complex [Pt(bpy-H)(Me)₂(I)(PPh₃)], **50a**, which was isolated in high yield and characterized. In the absence of an X-ray structural characterization compounds **50a** was analytically and spectroscopically characterized, in particular, through mono and

bi-dimensional NMR techniques.

Though the reaction may generate several isomers, due to *trans*-phobia, only *fac*-PtC₃ isomers are expected and considering the cyclometalated κ^2 -N,C restriction, only two isomers may be reasonably formed with the phosphane in "axial" or "equatorial" position (with respect to the bpy plane).

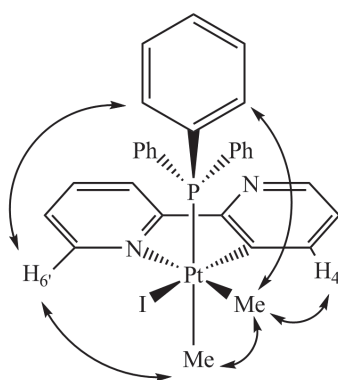
Table 4.2: Selected NMR data for some couples of Pt(II)/Pt(IV) complexes. Chemical shifts are given in ppm, coupling constants, in parentheses (coupling with ³¹P) and square brackets (coupling with ¹⁹⁵Pt), are given in Hz.

		¹ H (CH ₃)	³¹ P	¹³ C
7a	[Pt(bpy-H)(Me)(PMe ₃)]	0.85 (8) [84]	-18.6 [2112]	-17.0 (7.0) [n.r.]
8a	[Pt(bpy-H)(Me)(PPh ₃)]	0.74 (7.5) [83]	33.6 [2229]	-12.37 (4.5) [725]
8b	[Pt(bpy ^{6CH₃} -H)(Me)(PPh ₃)]	0.74 (8) [83]	32.6 [2226]	
9a	[Pt(bpy-H)(Me)(PCy ₃)]	1.00 (5.5) [84]	19.3 [2083]	
49aA	[Pt(bpy-H)(Me) ₂ (I)(PMe ₃)]	1.40 (7.5) [69]	-44.6 [1467]	2.88 (3) [593]
		0.82 (7.5) [69]		6.45 (4) [n.r.]
49aE	[Pt(bpy-H)(Me) ₂ (I)(PMe ₃)]	1.40 (8.5) [71]	-42.9 [1239]	
		0.76 (8) [56]		
50a	[Pt(bpy-H)(Me) ₂ (I)(PPh ₃)]	1.12 (8) [61]	-11.2 [992]	-6.87 (4) [632]
		1.64 (7.5) [71]		7.06 (113) [494]
51a	[Pt(bpy-H)(Me) ₂ (I)(PCy ₃)]	1.73 (6.5) [72]	-17.9 [957]	
		0.96 (7) [57]		
51b	[Pt(bpy ^{6CH₃} -H)(Me) ₂ (I)(PCy ₃)]	1.65 (7.5) [71]	-9.71 [967]	
		1.19 (7.5) [60]		

Complex **50a** was characterized as the axial isomer, *i.e.* **50a**, on the basis of analytical data and NMR spectroscopy, as detailed below. The ³¹P NMR spectrum of **50a** shows Pt-P coupling constant values in agreement with a Pt(IV) species ($J_{\text{Pt-P}} = 992$ Hz), and the ¹H NMR spectrum shows two different platinum-bonded methyls (δ 1.12 ppm, $^3J_{\text{P-H}} = 8$ Hz, $^2J_{\text{Pt-H}} = 61$ Hz; 1.64 ppm, $^3J_{\text{P-H}} = 7.5$ Hz, $^2J_{\text{Pt-H}} = 71$ Hz) as doublets with satellites due to coupling to ¹⁹⁵Pt and ³¹P nuclei. A comparison of ³¹P, ¹H and ¹³C NMR data of **50a** and **49aA** (see Table 4.2) suggests coordination of PPh₃ in "axial" position in **50a(ax)** with respect to the cyclometalated plane. Accordingly, the ¹³C NMR spectrum shows two

Pt-CH₃ carbon atoms, having very different P-C coupling constants, attributable to an "axial" methyl, coordinated *trans* to phosphorus (CH₃(ax): δ +7.06 ppm, $^2J_{P-C}$ = 113 Hz), and an "equatorial" methyl (CH₃(eq): δ -6.87 ppm, $^2J_{P-C}$ = 4 Hz) coordinated *cis* to phosphorus. Furthermore, in the same plane of the bpy, a ^{13}C - ^1H HSQC spectrum showed the following correlations: CH₃ *trans* to P, *i.e.* CH₃(ax) δ_{C} = 7.06 ppm, δ_{H} = 1.12 ppm, CH₃ *cis* to P *i.e.* CH₃(eq): δ_{C} = -6.87 ppm, δ_{H} = 1.64 ppm.

Different geometries between **50a** and **49a(eq)** were supported by ^{195}Pt - ^{31}P coupling constant values: whereas **8a** and **7a**, show similar $J_{\text{Pt-P}}$ values (**8a**: δ 33.6 ppm, $J_{\text{Pt-P}}$ = 2229 Hz; **7a** δ -18.6 ppm, $J_{\text{Pt-P}}$ = 2112 Hz), **50a** and **49a(eq)** have very different J values (**50a**: δ -11.2 ppm, $J_{\text{Pt-P}}$ = 992 Hz; **49a(eq)**: δ -44.6 ppm, $J_{\text{Pt-P}}$ = 1467 Hz). Also ^{31}P chemical shifts do not follow the same trend. Furthermore, 1D-NOE experiments on **50a** (Figure 4.4) clearly pointed out the geometry showing, after irradiation at 1.64 ppm (CH₃(eq)), enhancement at 7.05 (H_{4'}), 7.29 (H_{5'}) and 1.12 ppm (CH₃(ax)), and enhancements at 9.58 (H₆) and 1.64 ppm (CH₃) by irradiation at 7.21 ppm (H_{ortho}, PPh₃). Finally, irradiation at 1.12 ppm (CH₃(ax)) produces enhancement only at 1.64 ppm (CH₃(eq)). It follows that the signal at 1.12 ppm is the axial CH₃ while the signal at 1.64 is due to the equatorial one.



Scheme 4.4

On the basis of all these data we conclude that **50a** does indeed have a PPh₃ coordinated in "axial" position with respect to cyclometalated plane. The iodide, coordinated close to the N-bonded pyridine ring, is responsible for the downfield shift of the H_{6'} proton (δ 9.98) as usual. The different behaviour of PPh₃ and PMe₃ derivatives can be ascribed to

different electronic and steric properties of the two phosphanes, and in particular to the larger cone angle of PPh_3 , which destabilizes coordination in the same plane of the cyclometalated bpy.

The reaction of **8a** with CH_3I was followed by NMR spectroscopy, in order to identify the presence of the "kinetic" species with the phosphane in "planar" position and its isomerisation. No intermediate species were observed, and the reaction was then performed with CD_3I in NMR tube, in order to distinguish the previously coordinated methyl from that coming from MeI . Reaction of **8a** with CD_3I , however, gives from the beginning an equal distribution of the CD_3 group in axial and equatorial positions. This may be explained assuming that the first step of the reaction, *i.e.* the addition of Me^+ , is followed by rapid rearrangement of the five-coordinate intermediate before addition of I^- .

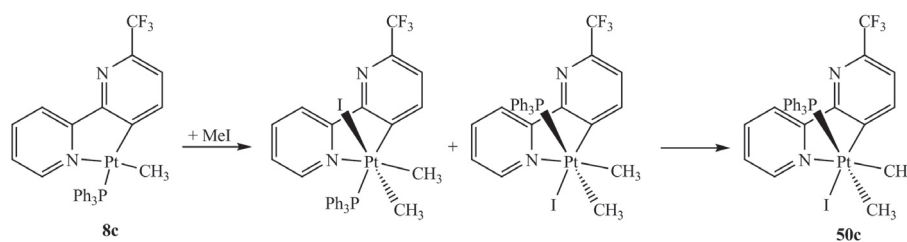
It is also worth noting that complex **50a** should be present as a racemic mixture, with PPh_3 coordinated "above" and "below" the cyclometalated plane.

4.2.3 6-substituted bpy

Starting from the cyclometalated products $[\text{Pt}(\text{bpy}^{6\text{R}})(\text{CH}_3)(\text{PPh}_3)]$, where $\text{R} = \text{CH}_3$ (**8b**) or CF_3 (**8c**), a comparison with bpy could be made by analysing the reactivity with MeI . The reaction of **8b** with iodomethane is very similar to the bpy case as it could be expected on the basis of the similarities found in other data (see Chapter 1 and Chapter 2). The general aspect of the NMR spectra is similar to the already described **50a** and therefore will not be discussed.

More intriguing is the same reaction with the trifluoromethylated bpy complex **8c**. NMR follow-up of the reaction in acetone- d_6 showed an interesting evolution. In the first recorded spectra (ca. 5 minutes after the addition) the aliphatic region of the ^1H NMR clearly showed, along with the starting material (0.72 ppm, $^2J_{\text{Pt-H}} = 84.2$ Hz, $^3J_{\text{P-H}} = 7.5$ Hz), the presence of four doublets with satellites (ascribable to the two methyl groups of each Pt(IV) complex) in agreement with the two possible isomers that can form from the oxidative addition, namely the one with the PPh_3 perpendicular to the bpy plane and the one where the phosphine is *trans* to the cyclometalated carbon (Scheme 4.5). Due to the low concentration and broadness of the signals it was not possible to evaluate the coupling

constants.



Scheme 4.5

After 20 minutes the formation of the two isomers is definitely ascertained by the analysis of the chemical shifts and the coupling constants: the species with equatorial PPh_3 gives resonances at δ 0.34 ($^2J_{\text{Pt-H}} = 67.3$ Hz, $^3J_{\text{P-H}} = 6.7$ Hz) and δ 1.49 ($^2J_{\text{Pt-H}} = 69.7$ Hz, $^3J_{\text{P-H}} = 6.8$ Hz); on the other hand the complex with axial PPh_3 shows doublets with satellites at 1.12 ppm ($^2J_{\text{Pt-H}} = 60.3$ Hz, $^3J_{\text{P-H}} = 7.4$ Hz) and 1.68 ppm ($^2J_{\text{Pt-H}} = 70.8$ Hz, $^3J_{\text{P-H}} = 7.6$ Hz).

Analysis of the coupling constants against the data reported in previous Sections permits to confidently describe the species, particularly diagnostic is the difference in the value of the $^3J_{\text{Pt-H}}$ for the two methyls (*i.e.* the one in the plane of the bpy and the one above/below it): they show an almost equal value when the PPh_3 is in the plane of the cyclometalated ligand while they differ of ca. 10 Hz when the phosphine is in axial position.

As the reaction proceeds to completion the starting material is consumed and eventually all the platinum ends up in a single complex: the one with the PPh_3 coordinated in axial position. The definitive assignment is supported also by the presence in the ^1H NMR of a very deshielded resonance at 9.65 ppm flanked by satellites ($^3J_{\text{Pt-H}} = 13.4$ Hz) that is in line with the data of an $\text{H}_{6'}$ next to a nitrogen and close in space to an halide (iodide in this case). This signal would not have been visible if the triphenylphosphine remained in *trans* to the metalated carbon due to the effect of the shielding cones of the aromatic rings.

^{31}P NMR spectroscopy shows data in agreement with the proton spectra: the starting material (δ 33.9, $J_{\text{Pt-P}} = 2309$ Hz) is converted firstly in a mixture of two species (PPh_3 equatorial, -3.0 ppm, $J_{\text{Pt-P}} = 1378$ Hz; PPh_3 axial, -10.6 ppm, $J_{\text{Pt-P}} = 988$ Hz) and finally

only one Pt(IV) product is present in solution.

The data just reported represent, to the best of our knowledge, the first observation of simultaneous presence in solution of both isomers deriving from the nucleophilic attack of the mononuclear cyclometalated rollover species to MeI. Rashidi *et al.* reported an NMR study where they identified the two isomers on a dinuclear complex.²³¹ Unfortunately the data we found for the reactivity of **8c** do not help in distinguishing which is the isomerisation pathway between isomerisation of the hexacoordinate or dissociation of one ligand (probably iodide) and the isomerisation on the pentacoordinate cationic compound (Figure 4.3).

The same reaction using as starting material **9c** does not show any particular evolution and in the first ^1H and ^{31}P NMR spectra the only detectable species is the product having the phosphine in axial position. Two methyls are visible in the aliphatic region in the ^1H NMR but only for the most shielded one at 0.89 ppm it is possible to evaluate the coupling constants ($^2J_{\text{Pt-H}} = 57.6$ Hz, $^3J_{\text{P-H}}$ ca. 7 Hz), in fact the other one is beneath the signals of the PCy_3 protons. Even in this case it is visible a signal at 9.95 ppm ($^3J_{\text{Pt-H}} = 16$ Hz) that points in the direction of a iodide in the plane of the cyclometalated bpy.

The fast kinetic observed for the complex having the PCy_3 can be related to a faster nucleophilic attack due to the enhanced donor properties of the phosphine, but also to the increased steric hindrance that strongly influences the equilibrium between the two possible intermediates after the $\text{S}_{\text{N}}2$ attack: in our opinion the bulkier PCy_3 has a stronger preference for the axial site in the pentacoordinate $[\text{Pt}(\text{bpy}^{6\text{CF}_3}\text{-H})(\text{CH}_3)_2(\text{PCy}_3)]^+$ making the concentration of this species in solution so high that the iodide can trap only this isomer, leading to the axial hexacoordinate complex where the halide is in *trans* to the metalated carbon.

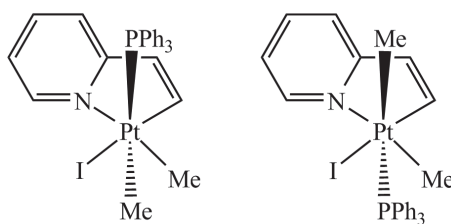
4.2.4 2-vinylpyridine, vpy

Oxidative addition reactions with MeI were also carried out with cyclometalated vpy complexes because we wanted to check if modification in the delocalized system, *i.e.* a contraction compared to bpy, can influence the reactivity. Moreover no examples of similar

compounds were found in literature,^a making this investigation more intriguing. Starting from [Pt(vpy-H)(CH₃)(PPh₃)] (**8g**) using the standard conditions (5-fold MeI excess in acetone at room temperature) it is possible to isolate and characterize the corresponding Pt(IV) compound [Pt(vpy-H)(CH₃)₂(I)(PPh₃)], **50g**. As in the other cases two methyl resonances are visible in the ¹H NMR at 1.11 ppm (²J_{Pt-H} = 60 Hz, ³J_{P-H} = 8 Hz) and at 1.80 ppm (²J_{Pt-H} = 69 Hz, ³J_{P-H} = 8 Hz), the proton next to the coordinated nitrogen (*i.e.* H₆) is visible at 9.06 ppm with satellites due to ¹⁹⁵Pt coupling (³J_{Pt-H} ca 11 Hz); in the ³¹P spectrum only one singlet with satellites is visible at -5.9 ppm (J_{Pt-P} = 1018 Hz) in agreement with a phosphorus coordinated to Pt(IV) centre.

The data presented so far are in good agreement with those observed in the rollover cyclometalated Pt(IV) complexes. In particular we can safely assign the geometry of the complex placing the PPh₃ in the axial position, perpendicular to the vpy plane, as suggested by several factors: (a) the value of the J_{Pt-P}, (b) the somewhat deshielded signal of the H₆, (c) the difference between the ²J_{Pt-H} of the methyls.

The Pt(IV) complex gives a racemic mixture of the two enantiomeric forms, *i.e.* the one having the phosphine above the plane of the cyclometalated ligand and the other having the phosphine below it (Scheme 4.6).



Scheme 4.6

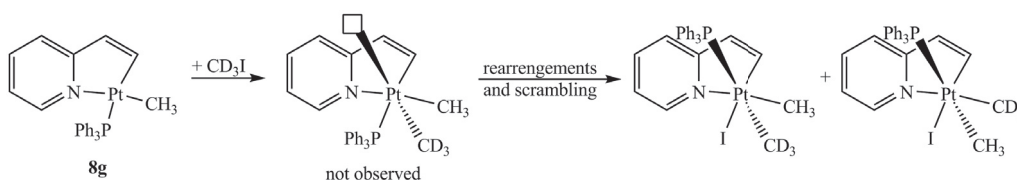
The reaction was also followed by ¹H and ³¹P NMR spectroscopy using both CH₃I and CD₃I aiming to detect eventual intermediates. When the reagent was the protiated MeI already 5 min after the addition in the ¹H NMR only one Pt(IV) species is detected along with the unreacted Pt(II) starting material. Reaction goes to completion smoothly and after 5 h only the already described Pt(IV) product is present in solution.

^aReaxys, version 2.15859.10; Elsevier Information Systems GmbH. End of October 2013.

This observation suggests that the formation of the final species is quite fast at room temperature, moreover the fact that no intermediates are detected in solution let us think that the steric bulk of the PPh_3 drives the reaction directly to the thermodynamic isomer having the phosphine in axial position.

Using the same conditions (acetone- d_6 , 5-fold excess MeI, room temperature) we performed the reaction with CD_3I to check whether there is or not selective incorporation of CD_3 in the complex. In the first ^1H NMR spectrum recorded after the addition there are two doublets with satellites in the same position where the methyl groups of the final product resonate. In the ^{31}P NMR spectrum two almost overlapping singlet with satellites are visible at δ -5.94 and -5.95 having the same coupling constant with ^{195}Pt ($J_{\text{Pt-P}} = 1011$ Hz).

The data obtained are in agreement with the picture of a fast isomerisation between the pentacoordinate intermediate arising from the nucleophilic attack of the Pt(II) complex to the alkyl halide, *i.e.* the one having the PPh_3 in the plane of the vpy, and the one with the PPh_3 perpendicular (Scheme 4.7). Probably during this rearrangement on the pentacoordinate species the CH_3 and the CD_3 find a way to scramble their positions yielding a statistical 50:50 mixture.



Scheme 4.7

4.3 DFT calculations

A series of DFT calculations was performed on all the seven possible isomers of complex **49a**, depicted in Figure 4.1 with their respective relative ΔH (in $\text{kJ}\cdot\text{mol}^{-1}$, ZPE corrected, *in vacuo*). Each complex was optimized and verified as a minimum on the potential energy surface (PES) at the PBE0/def2-SVP level of theory. Before this final step a survey

of the PES was carried out in order to find the minimum rotational angle for the phosphine with a lower level of theory, *i.e.* using the Vosko-Wilk-Nusair functional V (VWN5)³⁸⁷ and the SBKJC VDZ ECP basis set,^{388–391} the minimum energy geometries thus obtained were then used as starting guess for the following calculations.

A validation of the theoretical results can be obtained by comparing theoretical and experimental bond distances and angles in **49aA** which shows a very good agreement despite the rather small basis set used. As expected all the calculated distances are longer than the real ones, except the Pt-CH₃ (eq), possibly due to the approximations used in DFT calculations: only one molecule *in vacuo* at 0 K. Comparing the experimental data and the different values obtained for the ΔH we can rule out the isomers that have both methyls in a *trans* arrangement because: (a) they would have displayed the same chemical shift in the ¹H NMR and (b) they lie at very high energy 70 and 111 kJ·mol⁻¹ for **49aG** and **49aF** respectively. It is worth noting that even in the case of these high energy isomers the one more in agreement with the rules of *trans*-effect in the plane of the cyclometalated ligand (*i.e.* **49aG**) has the lowest energy.

The enthalpy values obtained from the theory respect the *trans*-phobia concept, in fact the lowest lying isomers are those with the highest *trans*-influence groups not in reciprocal *trans* position, *i.e.* **49aA** and **49aE**; afterwards we find those with a C(*sp*²)-to-C(*sp*³) *trans* arrangement, **49aB** < **49aC** < **49aD** in order of increasing energy, and the highest isomers are those with two methyls in axial position **49aG** < **49aF**. Taking into account all the approximations used in the calculations from these values we can conclude that methyl group has a stronger *trans*-influence than the metalated *sp*² carbon atom.

More interesting is the fact that the complex **49aA** is found to be ca. 26.4 kJ·mol⁻¹ less stable than **49aE** which is, in this case, the thermodynamic isomer in agreement with other calculations on similar systems performed by Rashidi *et al.*³⁸⁰ It appears thus that the crystal structure obtained is the kinetic isomer which is, to the best of our knowledge, the first and only case present in literature regarding this kind of reaction.

In analogy to the analysis carried out in the case of **49a** we performed DFT calculations on the two most probable isomers (*i.e.* axial and equatorial) of **50a**, **50b** and **50f**. We decided to concentrate only on axial and equatorial isomers assuming that, due to *trans*-phobia, *fac*-PtC₃ isomers would be more stable than the other isomers. Full optimization

at PBE0/def2-SVP level led to the conclusion that the axial isomer is always more stable than the equatorial one by 25.4, 25.7 and 27.2 kJ·mol⁻¹ (ΔH ZPE corrected *in vacuo*) for the complexes having cyclometalated bpy, bpy^{6CH₃} and pyq respectively.

The results obtained show a very similar energy difference to that for the two isomers of **49a**.³⁹² This result is interesting because shows that although the systems are quite different they seem to have the same effect on the stabilization of the axial isomer; whether this effect is due to steric or electronic factors is hard to say.

4.4 Discussion on oxidative addition

Oxidative addition of CH₃I to Pt(II) square planar complexes is a well studied reaction and almost everything has been elucidated.^{393,394} The reaction starts with the nucleophilic attack of the Pt(II) complex to the alkyl halide in a S_N2 fashion leading to inversion of the configuration if optically active halides are used.³⁹⁵ In some cases it is possible to trap the intermediate before the addition completes, *i.e.* before the coordination of the iodide.³⁹⁶ If the intermediate lives enough before being caught by the iodide, it can possibly rearrange to a more stable isomer according to the characteristics, both steric and electronic, of the ligands.

Once the octahedral complex is formed isomerisation can happen according to two main mechanisms: (a) on the six-coordinate species via a Bailar or R  y-Dutt twist, or (b) on a penta-coordinate species arising from dissociation of the most labile ligand through a Berry or turnstile twist. All these passages are shown in Figure 4.3.

Reaction of [Pt(bpy-H)(CH₃)₂(I)(PMe₃)] (**7a**) with CH₃I in acetone-*d*₆ at room temperature leads only to **49aA** with no other detectable species in solution and with CD₃I the selectivity of the process was ascertained, *i.e.* CD₃ is incorporated in "axial" position, and thus confirmed that the reaction mechanism proposed by Rashidi *et al.* for phenylpyridine cyclometalated complexes is followed even in our case.³⁸⁰

We observe only the kinetic isomer deriving from the *trans* addition of CH₃I to **7a** with no further evolution to the thermodynamic isomer with the bulkier PMe₃ perpendicular and the iodide planar with the cyclometalated ligand. We believe that the rationale for

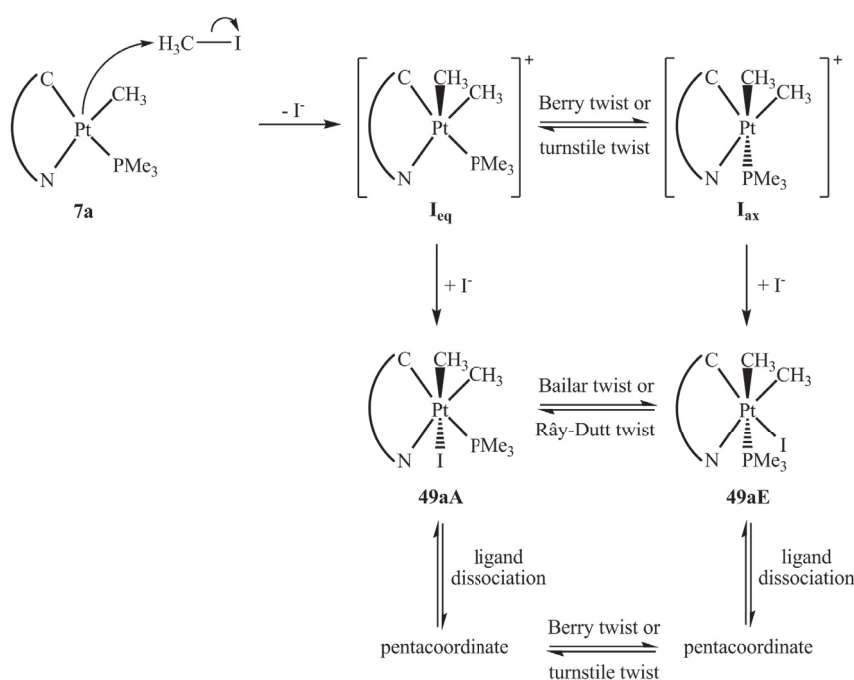


Figure 4.3: Possible isomerisation pathways following the nucleophilic attack of complex **1** to CH_3I .

this observation lies in the following explanations. First of all isomerisation in octahedral complexes (for example **49aA** $\rightarrow$ **49aE**) are predicted to be highly energy demanding due to the conversion through a trigonal-prismatic transition state.³⁹³ Secondly, on the basis of preliminary DFT calculations, dissociation of one of the ligands from **49aA** requires a not negligible amount of energy (around $90 \text{ kJ}\cdot\text{mol}^{-1}$ in gas phase). Thirdly, the Tolman electronic parameter and steric hindrance of PMe_3 are not extreme ($\nu = 2064.1 \text{ cm}^{-1}$ and $\theta = 118$ degrees²⁴⁹) so that there is not a strong preference for the axial site that is wider but also *trans* to a methyl. These two factors result perhaps in a slower equilibrium between the two isomers of the intermediate ($\text{I}_{\text{ax}} \rightarrow \text{I}_{\text{eq}}$ in Figure 4.3) thus the iodide attacks preferentially the *P-trans-C* isomer.

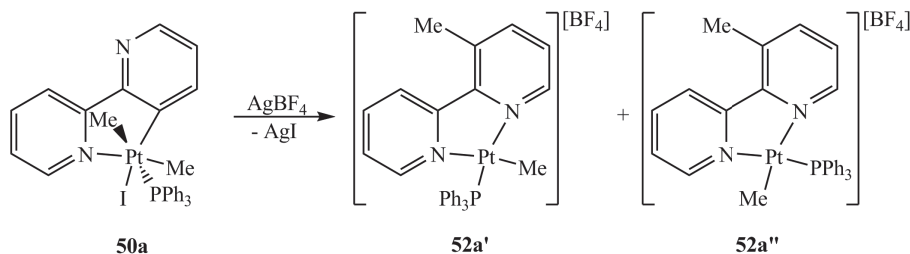
The accepted $\text{S}_{\text{N}}2$ mechanism proposed for this reaction requires the trapping of the five-coordinate intermediate formed by the nucleophilic attack of the $\text{Pt}(\text{II})$ on the alkyl halide to form the kinetic equatorial product which subsequently converts into the thermodynamic axial product. In the chemistry of cyclometalated $\text{Pt}(\text{IV})$ the isolated product of the reaction is usually the axial species, and isolation of the equatorial isomer is extremely rare.

4.5 Treatment of Pt(IV) complexes with Ag⁺

Compound **50a** is stable in the solid state and in solution, in the presence of air and moisture. It is well known, however, that five-coordinated Pt(IV) species are highly reactive towards reductive elimination reactions.³⁶⁷ For this reason we reacted **50** with silver salts in acetone solution in order to abstract the iodide ligand and create coordinatively unsaturated species. Unexpectedly, the reaction of **50a** with AgBF₄ gave the cationic Pt(II) adduct [Pt(bpy^{3CH₃})(Me)(PPh₃)]⁺, **52a**, as indicated by analytical and NMR data, where the ligand bpy^{3CH₃} = 3-methyl-2,2'-bipyridine is formed through an uncommon C(sp³)-C(sp²) coupling. The reaction is unique because, following a retro-rollover process, the newly-formed ligand stabilizes the complex by chelation, taking advantage of the formerly uncoordinated nitrogen.

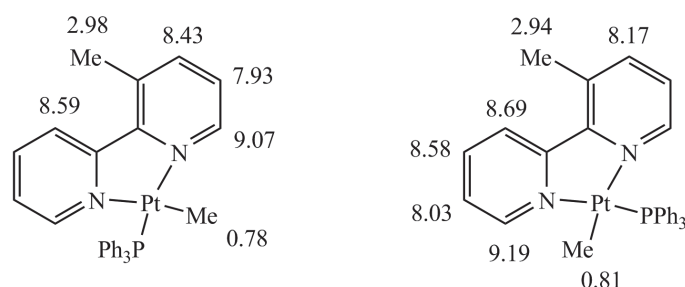
The ¹H and ³¹P NMR spectra of **52a** show two species in a 1:1 molar ratio; the analysis of the spectra allows their characterization as the geometric isomers **52a'** and **52a''**, as indicated in Scheme 4.8.

In particular, the ³¹P spectrum of **52a** shows two singlets with satellites at 19.2 and



Scheme 4.8

18.9 ppm with coupling constants ($J_{\text{Pt-P}} = 4294$ and 4318 Hz respectively) indicative of P *trans* to N in a platinum(II) complex. Also the ¹H NMR spectra show two Pt-CH₃ groups (**52a'**: 0.78 ppm, $^3J_{\text{P-H}} = 3.5$ Hz, $^2J_{\text{Pt-H}} = 71$ Hz; **52a''**: 0.80 ppm, $^3J_{\text{P-H}} = 3.5$ Hz, $^2J_{\text{Pt-H}} = 72$ Hz) in agreement with methyls coordinated in *cis* to a PPh₃ and *trans* to a nitrogen. Two singlets at 2.94 and 2.98 ppm were assigned to methyls on the bpy in 3 position. A ¹H-¹H NOESY helped in the characterization and assignment of the resonances (see Scheme 4.9).



Scheme 4.9

This reaction has points of interest: **52a** is generated by a reductive elimination reaction involving a very rare $C(sp^3)$ - $C(sp^2)$ coupling; no ethane evolution, formed through a more common $C(sp^3)$ - $C(sp^3)$ coupling, is observed. In addition, the reductive elimination is followed by a retro-rollover reaction, to give a chelated bpy adduct, and it may be that this assists the overall process.

At first sight, the elimination of ethane, rather than the observed $C(sp^3)$ - $C(sp^2)$ coupling, might be the expected outcome of the treatment of **50a** with Ag^+ . After all, in the case of ethane formation there is a favourable entropic contribution to the Gibbs free energy of the reaction that arises from the release of a molecule of gas. However, this thermodynamic factor is irrelevant in this case as neglects to take into consideration the spatial requirements of the coupling groups at the five coordinate intermediate. If we consider the geometry of **50a** we can see that removal of the iodide results in a vacancy in the equatorial plane defined by the cyclometalated bpy. Orbital considerations are clear: reductive coupling of groups within this vacancy-containing plane results in the population of a non-bonding orbital, whereas coupling of groups in a four coordinate plane requires occupation of a high-energy strongly antibonding orbital.^{397,398}

Thus the two Me groups occupy a four coordinate plane (elimination unfavoured) whereas one of the Me groups and the sp^2 carbon occupy a three coordinate plane (elimination favoured).

Even though the five coordinate intermediate is likely to be very fluxional, it is impossible for it to rearrange, and for the two methyl groups to occupy a three coordinate plane, without bringing the large PPh_3 group back into the equatorial plane defined by the cyclometalated group.

The free ligand $\text{bpy}^{3\text{CH}_3}$, **55**, was isolated by reaction of **52a** with dppe. The chelating bisphosphine easily displaces the bpy ligand so that species **55** can be isolated in good yield and analysed. The ^1H and ^{13}C NMR spectra clearly show the methyl in position 3 (^1H , 2.51 ppm, ^{13}C , 18.89 ppm) and a NOE-1d NMR spectrum showed a contact between the singlet at 2.51 ppm ($\text{CH}_3\text{-bpy}$) and the adjacent H_4 proton at 7.62 ppm. The aromatic region show 7 protons, with 4 and 3 spin systems for the unsubstituted and substituted pyridine rings, respectively, and a $^1\text{H}\text{-}^1\text{H}$ COSY spectrum allowed assignment of all ^1H NMR signals. Further evidence for the characterization of **55** was provided by a high-resolution mass spectrum, which shows the $(\text{M}+\text{H})^+$ peak with an excellent match between the calculated and experimental values (m/z found 171.0915, calculated for $\text{C}_{11}\text{H}_{11}\text{N}_2 (\text{M}+\text{H})^+$, 171.0917).

The synthesis of $\text{bpy}^{3\text{CH}_3}$ was previously reported in the literature, through co-cyclotrimerization,³⁹⁹ Negishi coupling⁷⁶ or Suzuki-Miyaura reactions.⁸⁰ Our new synthetic method, however, could be of general use and might be extended to other bidentate heterocyclic donors taking advantage of rollover C-H bond activation.

4.5.1 Assessing the generality of the coupling

In order to better understand the nature of the process we extended the study to the phosphanes PMe_3 and PCy_3 , both better donors than PPh_3 , but with minor and major steric hindrance, respectively. The general applicability of the method was also checked, extending the study to two bidentate heterocyclic ligands: $\text{bpy}^{6\text{CH}_3}$ and pyq, both able to give rollover cyclometalation.^{20,146}

When a substituent is present in the ligand in proximity of a nitrogen, rollover cyclometalation is facilitated (see Chapter 1). For this reason complexes **8b**, **8f**, **9f** can be obtained even at room temperature in acetone, following a one pot synthetic method. The ^1H and ^{31}P NMR spectra of **8b**, **8f**, **9a**, **9f** are very similar to those of **8a**, showing, *inter alia*, a methyl coupled to ^{195}Pt and ^{31}P in the ^1H NMR spectrum (*e.g.* **9f**: δ 1.11 ppm, $^2J_{\text{Pt-H}} = 84$ Hz, $^3J_{\text{P-H}} = 6.5$ Hz) and a phosphorus *trans* to a carbon in the ^{31}P spectrum (*e.g.* **9f**: δ 24.8 ppm, 2090 Hz).

The reaction of **7a** with MeI (Section 4.2.1) at room temperature was followed through

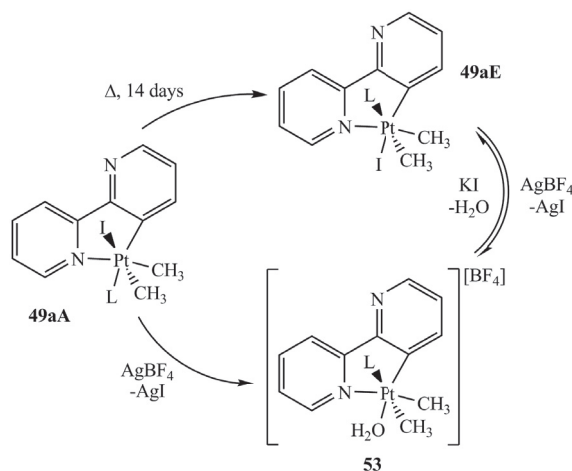
NMR spectroscopy: the reaction rapidly produces the Pt(IV) complex **49aA**, which converts very slowly (ca. 10 days at 60 °C in acetone- d_6) into the isomer having the phosphane in axial position, **49aE**, *i.e.* the thermodynamically stable species. NMR data of **49aE** are comparable to those of **50a**, in particular $^2J_{\text{Pt-H}}$ of Pt-bonded methyls and ^{195}Pt - ^{31}P coupling constant values (see Table 4.3).

Table 4.3: NMR data for PMe_3 complexes. Chemical shifts are given in ppm, coupling constants, in parentheses (coupling with ^{31}P) and square brackets (coupling with ^{195}Pt), are given in Hz.

	7a	49aA	49aE	53
CH_3 ax		0.82 (7.5) [70]	0.76 (8) [56]	0.57 (8) [50]
CH_3 eq	0.85 (8) [84]	1.40 (7.5) [69]	1.40 (8.5) [71]	1.35 (8) [66]
PMe_3	1.57 (8) [21]	1.84 (9.5) [12]	1.14 (10) [12]	1.16 (10.5) [12]
H_4	8.09 [44]	7.99 [30]	7.69 [44]	7.78 [54]
H_5	7.16 [15]	7.24 [10]	7.28 [14]	7.31 [15]
H_6	8.28	8.32	8.41	8.47
$\text{H}_{3'}$	8.33	8.51	8.50	8.61
$\text{H}_{4'}$	8.10	8.11	8.18	8.33
$\text{H}_{5'}$	7.44	7.52	7.60	7.84
$\text{H}_{6'}$	8.86 [22]	8.91 [10]	9.82 [12]	8.99 [9]
H_2O	-	-	-	7.10
^{31}P	-18.6 [2112]	-46.4 [1467]	-42.9 [1239]	-25.6 [1243]
^{195}Pt	-4107	-3429	-3411	-2676

In contrast to **50a**, treatment of **49aA** with AgBF_4 does not induce reductive coupling, but produces a solvato complex, identified as the cationic species $[\text{Pt}(\text{bpy-H})(\text{Me})_2(\text{PMe}_3)(\text{H}_2\text{O})]^+$, **53**, with a coordinated water in the equatorial position and the phosphane in an axial site, as indicated by NOE measurements (Scheme 4.10). Treatment of **53** with excess iodide does not return back to the starting complex **49aA** but gives the thermodynamic Pt(IV) complex **49aE**. In contrast to complex **50a**, addition of AgBF_4 to **49aE** does not result in reductive elimination but leads back to the water complex **53**. These results indicate a strong component of steric strain in the octahedral complexes with PPh_3 , relieved by reductive coupling; it also confirms that the isomer having the phosphine in

axial position is more stable as deduced from DFT calculations in Section 4.3.



Scheme 4.10

The leading effect in both oxidative addition and reductive elimination processes seems to be steric rather than electronic, because the analogous PCy_3 complexes **9a** and **51a**, behave as **8a** and **50a**, with a slight acceleration, likely due to higher steric congestion.

As for the reductive elimination process we may conclude that there is not such strain in the PMe_3 complexes **49aA** and **49aE**, and consequently the coupling does not take place. It is worth noting that the analogous cyclometalated Pt(IV) complexes originating from 2-phenylpyridine or 2-vinylpyridine, $[\text{Pt}(\kappa^2\text{-N,C})(\text{Me})_2(\text{I})(\text{PPh}_3)]$, do not show a corresponding behaviour, so this reactivity seems to be peculiar to rollover cyclometalated compounds.

Reaction of **8b**, **8f**, **9f** with MeI rapidly gave the corresponding thermodynamic Pt(IV) derivatives $[\text{Pt}(\text{bpy}^{6\text{CH}_3}\text{-H})(\text{Me})_2(\text{I})(\text{PPh}_3)]$, **50b**, $[\text{Pt}(\text{pyq-H})(\text{Me})_2(\text{I})(\text{PPh}_3)]$, **50f**, and $[\text{Pt}(\text{pyq-H})(\text{Me})_2(\text{I})(\text{PCy}_3)]$, **51f**, with high yields. ^1H and ^{31}P NMR data of **50b**, **50f**, **51f** are similar to those of **50a**, confirming that the PPh_3 ligand is coordinated in axial position (see the Experimental Section).

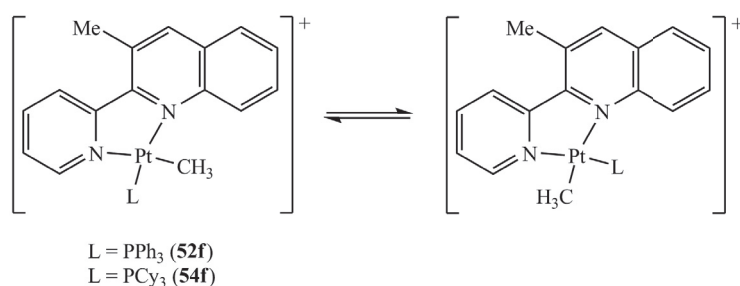
Compounds **8f** and **51f** were chosen for a thorough comparative NMR characterization (*e.g.* ^1H , ^{31}P , ^{195}Pt - ^1H HMQC, H-H COSY, NOE-1d). ^{195}Pt - ^1H HMQC experiments showed the expected correlations of the Pt signal with $\text{H}_{6'}$, H_4 , and the methyl protons in both **8f** and **51f**. As expected, the ^{195}Pt signal is strongly deshielded in the Pt(IV) com-

plex **51f** (-3345 ppm) when compared to the Pt(II) complex **8f** (-4177 ppm). The same trend was observed for **7a**, **49aA** and **49aE** (δ = -4107, -3429, and -3411 ppm, respectively).

A series of NOE-1d experiments on **51f** is in agreement with an axial structure: irradiating at 1.22 ppm (CH_3, ax) gives enhancements at 1.75 ppm (CH_3, eq), whereas irradiating at 1.75 ppm (CH_3, eq) gives enhancements at 1.22 (CH_3, ax), 7.27 (H_o , PPh_3), and 7.43 ppm ($\text{H}_{4'}$). Furthermore, irradiation at 7.44 ppm ($\text{H}_{4'}$) enhances signals at 1.75 (CH_3, eq), 7.27 (H_o , PPh_3), and 7.61 ppm (H_5), and irradiation at 9.73 ppm ($\text{H}_{6'}$) gives enhancements at 7.27 (H_o , PPh_3), and 7.50 ppm ($\text{H}_{5'}$).

Confirming the generality of the reductive coupling method, reaction of **50b**, **50f**, **51a**, **51f** with AgBF_4 gave reductive elimination with $\text{C}(\text{sp}^2)\text{-C}(\text{sp}^3)$ coupling, to give the adducts of the corresponding new methylated ligands, $\text{bpy}^{3\text{CH}_3}$ (**55**), $\text{bpy}^{3,6\text{CH}_3}$ (**56**) and 2-pyridyl-3-methyl-quinoline ($\text{pyq}^{3\text{CH}_3}$, **57**): $[\text{Pt}(\text{55})(\text{Me})(\text{PCy}_3)]^+$, **54a**, $[\text{Pt}(\text{56})(\text{Me})(\text{PPh}_3)]^+$, **52b**, $[\text{Pt}(\text{57})(\text{Me})(\text{PPh}_3)]^+$, **52f**, and $[\text{Pt}(\text{57})(\text{Me})(\text{PCy}_3)]^+$, **54f**.

In contrast to bpy, $\text{bpy}^{6\text{CH}_3}$ and pyq have a substituent in proximity to one nitrogen, so that in the $\kappa^2\text{-N,N}$ bidentate adducts **52b**, **52f**, **54f** steric repulsions may affect the molar ratio between the geometric isomers possible for these complexes (Scheme 4.11).



Scheme 4.11

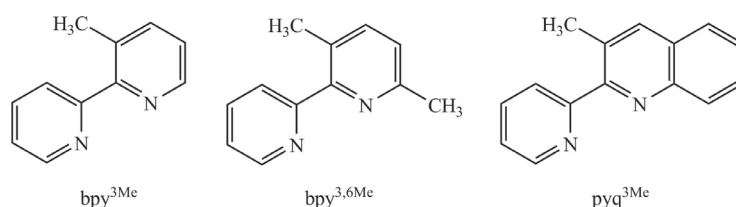
However, **52b'** and **52b''** are formed in almost 1:1 molar ratio, as demonstrated by ^1H NMR integrals; in one of the isomers (**52b''**) a Me in position 6 on the bpy is strongly shielded in the ^1H NMR spectrum (δ 0.47 ppm) with respect to other one (δ 0.95 ppm) likely due to its proximity to the PPh_3 ligand.

In the case of the pyq ligand the molar ratio of the isomers **52f'** and **52f''** in solution is slightly different, ca 4:3, and a third, unidentified species is also present in solution.

The main species, **52f'**, corresponds to the isomer having the PPh_3 ligand in *trans* to the quinoline nitrogen as may be expected by steric reasons and as it was observed in other occasions (see Chapter 3).¹⁴⁶ This is corroborated by a NOE-1d spectrum, which shows a NOE contact between the methyl at 0.47 ppm (Pt-Me, **52f'**) and the H_8 proton, a doublet at 8.28 ppm. In this case the phosphorus of the two isomers are slightly different, **52f'**: δ 18.5 ppm, $J_{\text{Pt-P}} = 4470$ Hz; **52f''**: δ 16.7 ppm, $J_{\text{Pt-P}} = 4325$ Hz, reflecting the Pt- PPh_3 environments. The ^1H and ^{31}P NMR spectra of complex **54f** show only one set of broad signals, indicating a fluxional behaviour in solution in the NMR time scale, likely due to the bulkiness of the PCy_3 ligand.

From **52b**, **52f**, **54f** the corresponding free ligands **56** and **57**, were isolated in the solid state and identified through high resolution mass spectrometry and NMR spectroscopy (Scheme 4.12).

High-resolution mass spectra show the $(\text{M}+\text{H})^+$ peaks with an excellent match with the calculated values (**56**: m/z found 185.1075, calculated for $\text{C}_{12}\text{H}_{13}\text{N}_2$ $(\text{M}+\text{H})^+$, 185.1073; **57**: m/z found 221.1073, calculated for $\text{C}_{15}\text{H}_{13}\text{N}_2$ $(\text{M}+\text{H})^+$, 221.1073).



Scheme 4.12

In detail, ^1H NMR of the 3,6-dimethyl-2,2'-bipyridine, **56**, clearly shows six aromatic signals (six protons) and two singlets (3 + 3 protons) at 2.58 ppm and 2.41 ppm which can be ascribed to the methyls. Quinoline derivative **57** shows the expected signals, among these the presence of the singlet attributable to the H_4 in the condensed pyridine ring and the presence of the singlet integrating for three protons due to the methyl on the C_3 are diagnostic.

To the best of our knowledge there is only one synthesis of **56** in the literature, by means of co-cyclotrimerization of 2-cyanopyridine with propyne.⁸⁸ Similarly, there is only one synthesis of **7** present in the literature proposed by Hoste in 1950.⁴⁰⁰

4.6 Conclusions

In the previous Chapters we concentrated our attention to Pt(II) rollover complexes studying particular aspects such as synthesis, substitution reactions and protonolysis. Intrigued by the possibility of using our complexes in catalysis we decided to investigate how they behave in one of the classical steps of a cycle, *i.e.* the oxidative addition.

We reported the synthesis and characterization of a new series of rollover cyclometalated complexes obtained by reaction of $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{PR}_3)]$ with CH_3I . Particular attention was paid to the influence of the phosphane, PR_3 , and of the cyclometalated ligand, $\kappa^2\text{-N,C}$.

Keeping constant the cyclometalated unit, *i.e.* bpy, and using bulky phosphanes such as PPh_3 or PCy_3 the only product obtained is the expected one with the PR_3 occupying an axial position, perpendicular to the plane of the bpy. Using the smaller PMe_3 we obtained and completely characterized what is thought of as the kinetic product of the reaction, arising from the *trans* addition of CH_3I to the metal complex. The operating mechanism was confirmed to be a $\text{S}_{\text{N}}2$ even in the case of rollover complexes.

Variation of the $\kappa^2\text{-N,C}$ unit led to interesting results showing that with cyclometalated $\text{bpy}^{6\text{CF}_3}$ both isomers, PR_3 in axial and equatorial position, are present in solution in the first stages of the reaction. In all the other cases only the final species was observed.

Theoretical calculations confirmed that the PR_3 in equatorial position, *trans* to the cyclometalated carbon, is not the thermodynamically favoured isomer being ca. $27 \text{ kJ}\cdot\text{mol}^{-1}$ less stable than the expected one with the phosphane in axial position; remarkably the energy difference seems to be rather insensitive to the nature of the phosphane and of the cyclometalated group.

The Pt(IV) complexes obtained, *i.e.* $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)_2(\text{I})(\text{PR}_3)]$, bear an iodide atom that was abstracted with silver salts in order to check whether its removal promotes or not a reductive elimination. Indeed we obtained the desired reaction with a rare $(sp^3)\text{-C}(sp^2)$ coupling, in place of the more common $\text{C}(sp^3)\text{-C}(sp^3)$ one, and whether this reductive elimination takes place or not seems to be governed principally by steric factors, as indicated by the behaviour of PPh_3 , PMe_3 and PCy_3 complexes. The reaction is unique to rollover complexes; as a comparison, the analogous phenylpyridine cyclometalated com-

plexes do not exhibit C-C coupling when treated with Ag^+ . The bpy derivatives thus obtained, *i.e.* $\text{bpy}^{3\text{CH}_3}$, $\text{bpy}^{3,6\text{CH}_3}$ and $\text{pyq}^{3\text{CH}_3}$ were isolated and characterized to confirm the coupling.

This route constitutes a new stoichiometric method for the activation and functionalization of C-H bond potentially usable in all the cases where rollover cyclometalation is achievable.

Experimental Section

5.1 General considerations

All reactions were carried out under an inert atmosphere. The solvents were purified and dried before use according to standard procedures.⁴⁰¹ Elemental analyses were performed with a Perkin-Elmer 240B elemental analyzer (Department of Chemistry and Pharmacy, University of Sassari, Sassari, Italy) or by the Warwick Analytical Service (University of Warwick, Coventry, United Kingdom). Infrared spectra were recorded with a FT-IR Jasco 480P using Nujol mulls. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded with Bruker AV 400, 500, or 600 MHz and Varian VXR 300 MHz spectrometers. Chemical shifts are given in ppm relative to internal TMS for ^1H and $^{13}\text{C}\{^1\text{H}\}$ and external 85% H_3PO_4 for $^{31}\text{P}\{^1\text{H}\}$ or referenced to the residual peak of the solvent.

Coupling constant values are given in Hz. ^{13}C apt, NOE difference (GOESY) and 2D-COSY experiments were performed by means of standard pulse sequences. ^{195}Pt NMR spectra were recorded on a Bruker Avance 500 using ^{195}Pt - ^1H correlation spectra; these were recorded using a variant of the HMBC pulse sequence with the ^{195}Pt chemical shifts quoted taken from the 2D HETCOR spectra and referenced to external Na_2PtCl_6 . All accurate mass spectra were run on a Bruker MaXis mass spectrometer.

UV-Vis spectra were recorded on a Hitachi U-2010 spectrophotometer. Cyclic voltammetric tests were performed using an Autolab PGSTAT12 (Ecochemie) potentiostat/galvanostat interfaced with a PC under GPES software, employing a single-compartment three-electrode cell, at room temperature, under Ar atmosphere, at a potential scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$.

A 2 mm diameter Pt disk electrode (CH Instruments) was used as working electrode, an aqueous Ag/AgCl (Amel) with suitable salt bridge was adopted as the reference electrode, and a graphite rod was the auxiliary electrode. All the experiments were carried out in CH₂Cl₂ (Sigma-Aldrich, anhydrous, ≥99.8%) using 0.1 M tetraethylammonium hexafluorophosphate (TEAPF₆, Sigma-Aldrich, for electrochemical analysis, ≥99.0%) as supporting electrolyte, with sample concentration about 2·10⁻³ M.

Single crystal X-ray data were obtained by Dr. Guy J. Clarkson (Department of Chemistry - University of Warwick- United Kingdom) as specified for each compound.

X-ray powder diffraction data collection and analysis was performed by Dr. Simona Galli (Dipartimento di Scienza e Alta Tecnologia - Università dell'Insubria - Italy).

DFT calculations benefitted of the resources given by the Cybersar Project managed by the "Consorzio COSMOLAB".

5.2 X-ray Powder Diffraction Structural Analysis

Polycrystalline samples of compounds [Pt(pyq-H)(CH₃)(PPh₃)] (**8f**), [Pt(pyq-H)(CH₃)-(CO)] (**24f**) and [Pt(pyq*)(CH₃)(CO)][BF₄] (**39f**), not containing single crystals of suitable quality, were deposited in the hollow of an aluminum sample-holder equipped with a quartz zero-background plate.^a For all the species, diffraction data were collected by means of overnight scans in the 2θ range of 5-105°, with steps of 0.02°, on Bruker AXS D8 Advance diffractometer, equipped with Ni-filtered Cu-K_α radiation (λ = 1.5418 Å), with a Lynxeye linear position-sensitive detector, and with the following optics: primary beam Soller slits (2.3°), fixed divergence slit (0.5°), receiving slit (8 mm). The generator was set at 40 kV and 40 mA. Standard peak search, followed by indexing through the Singular Value Decomposition approach⁴⁰² implemented in TOPAS-R,⁴⁰³ allowed the detection of the approximate unit cell parameters of all the species. The space groups were assigned on the basis of the systematic absences. Prior to structure solution, unit cells and space groups were checked by means of Le Bail refinements. Structure solutions were performed by the simulated annealing technique, implemented in TOPAS,

^aRemarkably, at least in the case of **8f** and **24f**, grinding the sample in an agate mortar provoked partial degradation of the material.

employing rigid, idealized models: in the case of **8f** and **39f**, a rigid group was defined comprising the whole Pt(II) complex (completed, for **39f**, by a rigid group describing the counterion). As for **8f**, two rigid groups were defined, comprising the PPh₃ moiety and the residual portion of the complex, respectively. Average values, retrieved by analyzing similar moieties present in the Cambridge Structural Database, were assigned to the bond parameters defining the stereochemistry at the metal ions, the ligands, and the counterion. The rollover nature of the complexes was established in all the cases by NMR. Thus, a rigid body comprising a C,N-chelating ligand was adopted. Nonetheless, the possibility of having a CH₃ moiety *trans* to the carbon atom, not to the nitrogen one, was investigated at the stage of structure solution. In all the cases, the geometry suggested by NMR resulted in structural models with lower figures of merit, which were thus adopted for the final structure refinements.

A heavy preferred orientation along [1 0 1] affected the diffractogram of **24f**: at the structure solution stage, the mere introduction of a correction in the March-Dollase formulation did not allow to reach convergence to a sensible structural model. A reasonable model was obtained only minimizing the preferred orientation by acquiring XRPD data on a batch of **24f** admixed with a dispersing, amorphous material (flour). For the refinement stage, to avoid the contribution of flour to the diffractogram, preferred orientation was hampered by side-loading **24f** onto the sample-holder. The final refinements were carried out by the Rietveld method, maintaining the rigid bodies introduced at the solution stage, but allowing the ligand to depart from planarity. The background was modeled by a Chebyshev polynomial function. One, isotropic thermal parameter was assigned to the metal atoms (B_M) and refined; lighter atoms were given a $B_{iso} = B_M + 2.0 \text{ \AA}^2$ thermal parameter. Final Rietveld refinement plots are shown in Supporting Information, Figure S1. Fractional atomic coordinates are supplied in the Supporting Information as CIF files. X-ray crystallographic data in CIF format have been deposited at the Cambridge Crystallographic Data Center as supplementary publications no. CCDC 933079 (**8f**), CCDC 933080 (**24f**) and CCDC 933081 (**39f**). Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (Fax: +44-1223-335033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

5.3 Abbreviations

Compounds

bpy	2,2'-bipyridine	ppy ^{3CH₃}	2-(3-methylphenyl)-pyridine
bpy ^{6CH₃}	6-methyl-2,2'-bipyridine	ppy ^{3CF₃}	2-(3-trifluoromethylphenyl)-pyridine
bpy ^{6CF₃}	6-trifluoromethyl-2,2'-bipyridine	ppy ^{4F}	2-(4-fluorophenyl)-pyridine
bpy ^{5CH₃}	5-methyl-2,2'-bipyridine	dppm	1,1-bis(diphenylphosphino)methane
bpy ^{5CF₃}	5-trifluoromethyl-2,2'-bipyridine	dppe	1,2-bis(diphenylphosphino)ethane
vpy	2-vinylpyridine	PPh ₃	triphenylphosphine
epy	2-ethylpyridine	PCy ₃	tricyclohexylphosphine
pyq	2-(2'-pyridyl)-quinoline	P(OPh) ₃	triphenylphosphite
ppy	2-phenylpyridine	PMe ₃	trimethylphosphine
ppy ^{3F}	2-(3-fluorophenyl)-pyridine	P(<i>p</i> -tol) ₃	tri- <i>p</i> -tolylphosphine
DMSO	dimethylsulphoxide	AcOH/AcO ⁻	acetic acid/acetate

NMR descriptors

s	singlet	m	multiplet
d	doublet	sat	satellites
t	triplet	br	broad
q	quartet		

5.4 Synthesis and characterisation

6-methyl-2,2'-bipyridine, bpy^{6CH₃}

The experimental procedure followed is the one by Rillema et al.⁸³ In a Schlenk tube bpy (2380 mg, 15.2 mmol, 1 eq) was dissolved in Et₂O (10 mL) and placed in an ice bath for 30 min. With a syringe CH₃Li 1.6M in Et₂O was added (9.2 mL, 14.7 mmol, 0.97 eq) and the colourless solution became suddenly intense red. Reaction mixture was left to warm to room temperature and then refluxed for 3 h, during this time no changes in appearance were noticed.

Reaction mixture was cooled down to room temperature and 50 mL of distilled H₂O were added yielding to a biphasic system where the aqueous layer is yellow and the organic one dark red. The aqueous phase was separated and extracted with Et₂O (3 × 30 mL), all the ethereal portions were mixed together, treated with Na₂SO₄, filtered and evaporated to

dryness obtaining a dark red oil. Quantitative yield. NMR signals are in agreement with those in literature. ^1H NMR (300 MHz, CDCl_3 , 298 K, ppm): 8.65 (d, 1H, $J_{\text{H-H}} = 4.8$ Hz, $\text{H}_{6'}$); 8.38 (d, 1H, $J_{\text{H-H}} = 8.0$ Hz, $\text{H}_{3'}$); 8.14 (d, 1H, $J_{\text{H-H}} = 7.9$ Hz, H_3); 7.78 (td, 1H, $J_{\text{H-H}} = 7.8, 1.8$ Hz, $\text{H}_{4'}$); 7.68 (t, 1H, $J_{\text{H-H}} = 7.7$ Hz, H_4); 7.27 (ddd, 1H, $J_{\text{H-H}} = 7.4, 4.9, 1.1$ Hz, H_5); 7.15 (d, 1H, $J_{\text{H-H}} = 7.6$ Hz, H_5); 2.62 (s, 3H, CH_3). ^1H - ^1H COSY (300 MHz, acetone- d_6 , 298 K, ppm): Signal at 8.65 correlates with those at 7.27, 7.78, 8.38; signal at 8.14 correlates with 7.68 and 7.15. ^1H NMR (700 MHz, acetone- d_6 , 298 K, ppm): 8.66 (d, 1H, $J_{\text{H-H}} = 4.5$ Hz, $\text{H}_{6'}$); 8.49 (d, 1H, $J_{\text{H-H}} = 7.9$ Hz, $\text{H}_{3'}$); 8.28 (d, 1H, $J_{\text{H-H}} = 7.8$ Hz, H_3); 7.90 (td, 1H, $J_{\text{H-H}} = 7.7, 1.8$ Hz, $\text{H}_{4'}$); 7.79 (t, 1H, $J_{\text{H-H}} = 7.7$ Hz, H_4); 7.39 (ddd, 1H, $J_{\text{H-H}} = 7.4, 4.7, 1.0$ Hz, H_5); 7.28 (d, 1H, $J_{\text{H-H}} = 7.6$ Hz, H_5); 2.58 (s, 3H, CH_3).

6-trifluoromethyl-2,2'-bipyridine, $\text{bipy}^{6\text{CF}_3}$

2-bromo-6-trifluoromethylpyridine (819.7 mg, 3.63 mmol, 1 eq) and 2-pyridineboronic acid N-phenyldiethanolamine ester (1.35 g, 5.04 mmol, 1.4 eq) were dissolved in a 5:1 toluene:MeOH mixture (10+2 mL) in inert atmosphere. K_2CO_3 (1.07 g, 7.75 mmol, 2.1 eq) and CuI (295.0 mg, 1.55 mmol, 0.4 eq) were dissolved in the same amount of the same mixture and then added to the former solution that changes colour from whitish to pale green. $[\text{Pd}(\text{PPh}_3)_4]$ (448.5 mg, 0.39 mmol, 0.1 eq) and 5+1 mL of solvent were finally added. The mixture is then heated to reflux and vigorously stirred for 24 h. Reaction is then quenched with 50 mL of saturated aqueous solution of EDTA (as sodic salt) and extracted with CH_2Cl_2 . Organic phase is treated with Na_2SO_4 filtered and evaporated to dryness. The product is purified by column chromatography on silica gel (3-5 cm diameter, 20 cm height) eluting with petroleum ether:ethyl acetate 10:1 + 5% NEt_3 mixture. The fraction containing the product is then evaporated to dryness yielding the product as a white solid. Yield: 60%. Melting point: 60 °C. Brute formula: $\text{C}_{11}\text{H}_7\text{N}_2\text{F}_3$. FW: 224.1853. ^1H NMR (400 MHz, CDCl_3 , 298 K, ppm): 8.69 (dd, 1H, $J_{\text{H-H}} = 4.8, 0.9$ Hz, $\text{H}_{6'}$); 8.64 (d, 1H, $J_{\text{H-H}} = 8.0$ Hz, H_3); 8.53 (dt, 1H, $J_{\text{H-H}} = 7.9, 1.1$ Hz, $\text{H}_{3'}$); 7.99 (t, 1H, $J_{\text{H-H}} = 7.7$, H_4); 7.86 (td, 1H, $J_{\text{H-H}} = 7.5, 1.7$ Hz, $\text{H}_{4'}$); 7.70 (dd, 1H, $J_{\text{H-H}} = 7.6, 0.9$ Hz, H_5); 7.37 (ddd, 1H, $J_{\text{H-H}} = 7.5, 4.8, 1.1$ Hz, H_5). ^{13}C NMR (100.6 MHz, CDCl_3 , 298 K, ppm): 156.6 (s, C_2 or $\text{C}_{2'}$); 154.7 (s, $\text{C}_{2'}$ or C_2); 149.2 (s, $\text{C}_{6'}$); 147.7 (q, $^2J_{\text{F-C}} = 36$ Hz, C_6); 138.2 (s, C_4); 137.2 (s, $\text{C}_{4'}$); 124.5 (s, $\text{C}_{5'}$); 123.5 (s, C_3); 121.6 (s, $\text{C}_{3'}$); 121.6 (q,

$J_{F-C} = 274$ Hz, CF_3); 120.2 (q, $^3J_{F-C} = 11$ Hz, C_5). ^{19}F NMR (376.4 MHz, $CDCl_3$, 298 K, ppm): -68.0 (s, CF_3).

5-methyl-2,2'-bipyridine, bpy^{5CH_3}

This procedure is adapted following Fraser et al.^{85,404} For a successful synthesis it is extremely important to operate in inert atmosphere and all the glassware used need to be dried in oven for at least an hour before usage. 10 mL of dry THF were placed in a two neck round bottomed flask under N_2 flow and degassed twice with a vacuum/ N_2 cycle, then was cooled down in a dry ice/acetone bath. t -BuLi 2M in pentane (4 mL, 8.0 mmol, 2.74 eq) was carefully added with a syringe to the THF obtaining a bright yellow solution. 2-bromopyridine (665.5 mg, 4.21 mmol, 1.45 eq) was slowly added with an Eppendorf to the solution that becomes dark brown rapidly. After 30 min keeping the temperature around -78 °C anhydrous $ZnCl_2$ was added (1.68 g, 12.3 mmol, 4.2 eq) and the mixture was slowly warmed up to room temperature (approx 3 h).

Meanwhile in a another flask the $[Pd(PPh_3)_4]$ was prepared following a patented procedure.⁴⁰⁵ $[Pd(OAc)_2]$ (29.3 mg, 0.13 mmol, 0.04 equiv) and PPh_3 (148.9 mg, 0.57 mmol, 0.20 equiv) were added to 2 mL of degassed dry toluene and the yellow solution obtained was heated for 20 min at 70 °C.

The $[Pd(PPh_3)_4]$, LiCl (262.5 mg, 6.19 mmol, 2.1 equiv) and 2-bromo-5-methylpyridine (500.2 mg, 2.91 mmol, 1 equiv) were added to the pyridylzinc solution that became rapidly orange-yellowish, two vacuum/ N_2 cycles were carried out and the the mixture was heated to 90 °C and let to react for 24 h during this time no changes in the aspect were noted. Reaction was then cooled down to room temperature and treated with an aqueous solution of EDTA and saturated aqueous $NaHCO_3$ until the pH of the solution is 8. Solution was extracted with CH_2Cl_2 (4 × 50 mL), the combined organic phases were treated with Na_2SO_4 for 30 min then filtered and evaporated to dryness obtaining a yellowish oil. Purification by flash chromatography on silica gel eluting with hexanes:EtOAc=4:1 led to the desired product. NMR signals as in literature.

5-trifluoromethyl-2,2'-bipyridine, bpy^{5CF₃}

2-bromo-5-trifluoromethylpyridine (878.6 mg, 3.89 mmol, 1 eq) and 2-pyridineboronic acid N-phenyldiethanolamine ester (1.35 g, 5.02 mmol, 1.3 eq) were dissolved in a 5:1 toluene:MeOH mixture (10+2 mL) in inert atmosphere. K₂CO₃ (1.07 g, 7.75 mmol, 2.0 eq) and CuI (297.9 mg, 1.56 mmol, 0.4 eq) were dissolved in the same amount of the same mixture and then added to the former solution that changes colour from whitish to pale green. [Pd(PPh₃)₄] (449.9 mg, 0.39 mmol, 0.1 eq) and 5+1 mL of solvent were finally added. The mixture was then heated to reflux and vigorously stirred for 24 h. Reaction is then quenched with 50 mL of saturated aqueous solution of EDTA (as sodic salt) and extracted with CH₂Cl₂. Organic phase is treated with Na₂SO₄ filtered and evaporated to dryness. The product is purified by column chromatography on silica gel (2-3 cm diameter, 20 cm height) eluting with petroleum ether:ethyl acetate 10:1 + 5% NEt₃ mixture. The fraction containing the product is then evaporated to dryness yielding the product as a white solid. Yield: 30%. Melting point: 160 °C. Brute formula: C₁₁H₇N₂F₃. FW: 224.1853. ¹H NMR (400 MHz, CDCl₃, 298 K, ppm): 8.94 (m, 1H, H₆); 8.72 (ddd, 1H, J_{H-H} = 4.8, 1.8, 0.9 Hz, H_{6'}); 8.57 (d br, 1H, J_{H-H} = 8.3 Hz, H₃); 8.47 (dt, 1H, J_{H-H} = 8.0, 1.0, H_{3'}); 8.06 (dd, 1H, J_{H-H} = 8.4, 2.4 Hz, H₄); 7.87 (td, 1H, J_{H-H} = 7.6, 1.8 Hz, H_{4'}); 7.38 (ddd, 1H, J_{H-H} = 7.5, 4.8, 1.2 Hz, H₅). ¹⁹F NMR (376.4 MHz, CDCl₃, 298 K, ppm): -62.3 (s, CF₃).

2-(2'-pyridyl)quinoline, pyq

Method A. 2-(2'-pyridyl)quinoline was prepared according to literature methods from quinoline-N-oxide.^{86,87} The first step of the synthesis requires the isolation of 2-cyanoquinoline, which was prepared by the reaction, at 0 °C, of quinoline-N-oxide (4.00 g, 27.5 mmol), (CH₃)₂NCOCl (3.17 g, d = 1.168 g/mL, 29.0 mmol) and (CH₃)₃SiCN (3.9 mL, 2.92 g, d = 0.744, 29.0 mmol) in CH₂Cl₂ (Yield 65%). 2-(2'-pyridyl)-quinoline was obtained from 2-cyanoquinoline through co-cyclotrimerization of acetylene in the presence of Bönemann catalyst [Co(cp)COD], in toluene at 120 °C, with a 30% yield.

Method B. 2-(2'-pyridyl)quinoline was prepared by cyclization between *o*-aminobenzaldehyde and 2-acetylpyridine, according to Harris *et al.*⁵⁵ and Smith and Opie.^{89,90} Yield

45%. ^1H NMR (300 MHz, CDCl_3 , 298 K, ppm): 7.36 (ddd, 1H, $J_{\text{H-H}} = 7.5, 4.8, 1.2$ Hz, $\text{H}_{5'}$); 7.55 (ddd, 1H, $J_{\text{H-H}} = 8.4, 6.7$ Hz, H_6); 7.75 (ddd, 1H, $J_{\text{H-H}} = 8.2, 6.7$ Hz, H_7); 7.84÷7.90 (m, 2H, $\text{H}_{3'}+\text{H}_{4'}$); 8.18 (d, 1H, $J_{\text{H-H}} = 8.5$ Hz, H_5); 8.28 (d, 1H, $J_{\text{H-H}} = 8.6$ Hz, H_4); 8.56 (d, 1H, $J_{\text{H-H}} = 8.6$ Hz, H_3); 8.65 (d, 1H, $J_{\text{H-H}} = 8.2$ Hz, H_8); 8.74 (ddd, 1H, $J_{\text{H-H}} = 5.6$ Hz, $\text{H}_{6'}$).

3'-methylphenyl-2-pyridine, $\text{ppy}^{3\text{CH}_3}$

Ligand is present in literature;^{79,113,406,407} but the procedure followed is different than those published.

All the glassware used was dried in oven for at least an hour before usage. 2-bromopyridine (508.0 mg, 3.22 mmol, 1 eq), 3-tolylboronic acid (462.3 mg, 3.40 mmol, 1.06 eq), $[\text{Pd}(\text{OAc})_2]$ (9.7 mg, 0.04 mmol, 0.01 eq) and PPh_3 (39.5 mg, 0.15 mmol, 0.05 eq) were solubilized in 4 mL of isopropyl alcohol (IPA) obtaining a yellow solution. After a couple of vacuum/ N_2 cycles in a Schlenk tube, under N_2 flow the previously prepared solution was added and degassed twice. K_2CO_3 (1107 mg, 8.01 mmol, 2.48 eq) was solubilized in 4 mL of distilled H_2O and added in the Schlenk tube and the mixture was degassed twice again. Slowly the mixture becomes a pale yellow suspension that is refluxed for 24 h under vigorous stirring.

The yellow suspension was evaporated to dryness and the yellow/white residue washed with CH_2Cl_2 (2×20 mL). The organic phase was extracted with HCl 2M (2×25 mL) and the colourless aqueous solution was neutralized with NaOH until no more bubbles develop from the solution. After stirring for 15 minutes an extraction with CH_2Cl_2 was carried out (3×20 mL), organic washings were collected together and treated with Na_2SO_4 , filtered and evaporated to dryness obtaining a orange-red oily residue (308.5 mg, 1.82 mmol). 56.6% yield. ^1H NMR (400 MHz, CDCl_3 , 298 K, ppm): 8.69 (d br, 1H, $J_{\text{H-H}} = 4.8$ Hz, H_6); 7.84 (s, 1H, H_2); 7.78÷7.70 (m, 3H); 7.36 (t, 1H, $J_{\text{H-H}} = 7.6$ Hz, $\text{H}_{5'}$); 7.25÷7.20 (m, 2H); 2.44 (s, 3H). ^1H - ^1H COSY (400 MHz, CDCl_3), 298 K, ppm): 8.69 correlates with signals at 7.22, 7.75 and 7.37.

3'-trifluoromethylphenyl-2-pyridine, ppy^{3CF₃}

This procedure is adapted following Fraser et al.^{85,404} For a successful synthesis it is extremely important to operate in inert atmosphere and all the glassware used need to be dried in oven for at least an hour before usage. 5 mL of dry THF were placed in a two neck round bottomed flask under N₂ flow and degassed twice with a vacuum/N₂ cycle, then was cooled down in a dry ice/acetone bath. 6 mL of *t*-BuLi 2M in pentane (12.0 mmol, 2.70 eq) were carefully added with a syringe to the THF obtaining a bright yellow solution. 520 μ L of 2-bromopyridine ($d=1.625$ g mL⁻¹, 5.35 mmol, 1.20 eq) were slowly added with an Eppendorf to the solution that becomes dark brown rapidly. After 30 min keeping the temperature around -78 °C anhydrous ZnCl₂ was added (1788.4 mg, 13.1 mmol, 2.95 eq) and the mixture was slowly warmed up to room temperature (approx 2 h). Meanwhile in a another flask the [Pd(PPh₃)₄] was prepared following a patented procedure.⁴⁰⁵ [Pd(OAc)₂] (43.6 mg, 0.19 mmol, 0.04 eq) and PPh₃ (253.2 mg, 0.96 mmol, 0.22 eq) were added to 2 mL of degassed dry toluene and the yellow solution obtained was heated for 20 min at 70 °C.

The [Pd(PPh₃)₄], LiCl (437.5 mg, 10.3 mmol, 2.32 eq) and 3-bromobenzotrifluoride (620 μ L, $d=1.613$ g mL⁻¹, 4.44 mmol, 1 eq) were added to the pyridylzinc solution, two vacuum/N₂ cycles were carried out and the the mixture was heated to 90 °C and let to react for 24 h. Reaction was then cooled down to room temperature and treted with an aqueous solution of EDTA (4652.2 mg, 15.9 mmol, 3.58 eq) and saturated aqueous NaHCO₃ until no more gas develops from the solution. Solution was extracted with CH₂Cl₂ (3 $\times$ 30 mL), the combined organic phases were treted with Na₂SO₄ for 20 min then filtered and evaporated to dryness obtaining a dark brown oil. Product was obtained after flash chromatography on silica gel eluting with hexane:Et₂O=2:3.

¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 8.73 (d br, 1H, J_{H-H} = 4.8 Hz, H₆); 8.29 (s, 1H, H₂); 8.18 (d br, 1H, J_{H-H} = 7.7 Hz); 7.81 (td, 1H, J_{H-H} = 8.0, 1.7 Hz, H₄); 7.79÷7.75 (m, 1H); 7.68 (d br, 1H, J_{H-H} = 7.8 Hz); 7.60 (t br, 1H, J_{H-H} = 7.7 Hz, H₅); 7.30 (ddd, 1H, J_{H-H} = 6.8, 4.8, 1.9 Hz, H₅). ¹H-¹H COSY (300 MHz, CDCl₃, 298 K, ppm): 8.71 correlates with signals at 7.76, 7.28; 8.29 correlates with signals at 7.60, 7.68. ¹⁹F NMR (282 MHz, CCl₃F, 298 K, ppm): -63.2 (s, CF₃).

3'-fluorophenyl-2-pyridine, ppy^{3F}

Ligand is present in literature^{408–410} but the procedure followed is different than those published.

All the glassware used was dried in oven for at least an hour before usage. 2-bromopyridine (509.0 mg, 3.22 mmol, 1 eq), 3-fluoroboronic acid (465.7 mg, 3.33 mmol, 1.04 eq), [Pd(OAc)₂] (9.9 mg, 0.04 mmol, 0.01 eq) and PPh₃ (41.8 mg, 0.16 mmol, 0.05 eq) were solubilized in 6 mL of isopropyl alcohol (IPA) obtaining a yellow solution. After a couple of vacuum/N₂ cycles in a Schlenk tube, under N₂ flow the previously prepared solution was added and degassed twice. K₂CO₃ (1095.7 mg, 7.93 mmol, 2.46 eq) was solubilized in 5 mL of distilled H₂O and added in the Schlenk tube and mixture was degassed twice again. Slowly the mixture becomes a pale yellow suspension that is refluxed for 24 h under vigorous stirring.

The yellow suspension was evaporated to dryness and the yellow/white residue washed with CH₂Cl₂ (3 × 15 mL). The organic phase was extracted with HCl 2M (2 × 25 mL) and the colourless aqueous solution was neutralized with NaOH until no more bubbles develop from the solution, in a couple of minutes the solution becomes an orange/pink suspension. After stirring for 15 minutes an extraction with CH₂Cl₂ was carried out (3 × 15 mL), organic washings were collected together and treated with Na₂SO₄, filtered and evaporated to dryness obtaining a yellow oily residue (449.7 mg, 2.60 mmol). 80.6% yield. ¹H NMR (400 MHz, CDCl₃, 298 K, ppm): 8.69 (d br, 1H, J_{H-H} = 4.8 Hz, H₆); 7.84 (s br, 1H); 7.77÷7.71 (m, 3H); 7.36 (t, 1H, J_{H-H} = 7.6 Hz, H₅); 7.24÷7.20 (m, 2H). ¹H-¹H COSY (300 MHz, CDCl₃, 298 K, ppm): 8.68 correlates with signals at 7.25, 7.74, 7.42; 7.44 correlates with signals at 7.09, 7.75. ¹⁹F NMR (282 MHz, CCl₃F, 298 K, ppm): -112.98 (s).

[Pt(bpy^{6CH₃})(CH₃)₂], 1b

The species was detected and characterized in solution because its isolation in pure form is difficult to achieve due to the contemporary presence in the solution of the cyclometalated [Pt(bpy^{6CH₃}-H)(CH₃)(DMSO)]. NMR signals are in agreement with those in literature.²⁰ ¹H NMR (700 MHz, acetone-*d*₆, 298 K, ppm): 9.14 (d sat, 1H, ³J_{Pt-H} = 22.6 Hz, J_{H-H} =

5.4 Hz, H_{6'}); 8.35 (d, 1H, J_{H-H} = 8.1 Hz, H_{3'}); 8.26 (d, 1H, J_{H-H} = 7.6 Hz, H₃); 8.10 (t, 1H, J_{H-H} = 7.8 Hz, H_{4'}); 7.62 (ddd, 1H, J_{H-H} = 7.4, 5.6, 1.0 Hz, H_{5'}); 7.58 (d, 1H, J_{H-H} = 7.6 Hz, H₄); 7.21 (d, 1H, J_{H-H} = 9.1 Hz, H₅); 2.84 (s, 3H, CH₃); 1.04 (s sat, 3H, ³J_{Pt-H} = 87.3 Hz, Pt-CH₃); 1.03 (s sat, 3H, ³J_{Pt-H} = 89.5 Hz, Pt-CH₃). ¹⁹⁵Pt-¹H HMQC (500 MHz, acetone-*d*₆, 298 K, ppm): -3334 (s) correlates with signals at 9.14, 1.04 and 1.03.

[Pt(bpy^{5CH₃})(CH₃)₂], **1d**

To an acetone solution of bpy^{5CH₃} (183.8 mg, 1.08 mmol, 1.11 eq) at room temperature *cis*-[Pt(CH₃)₂(DMSO)₂] was added (372.1 mg, 0.97 mmol, 1 eq) and the mixture was left stirring for 1 h. The colour quickly turned red and a precipitate formed. Brute formula: C₁₃H₁₆N₂Pt. FW: 395.3635. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 9.24 (d sat, 1H, ³J_{Pt-H} = 21.6 Hz, J_{H-H} = 6.0 Hz, H_{6'}); 9.06 (s sat, 1H, ³J_{Pt-H} = 22.0 Hz, H₆); 8.07 (td, 1H, J_{H-H} = 8.9, 1.6 Hz, H_{4'}); 7.95 (d, 1H, J_{H-H} = 7.8 Hz H_{3'}); 7.89 (m, 2H, H₃ + H₄); 7.49 (dd, 1H, J_{H-H} = 7.1, 1.3 Hz, H_{5'}); 2.52 (s, 3H, CH₃(bpy)); 1.12 (s sat, 3H, ²J_{Pt-H} = 85.5 Hz, Pt-CH₃); 1.11 (s sat, 3H, ²J_{Pt-H} = 85.4 Hz, Pt-CH₃).

[Pt(bpy^{5CF₃})(CH₃)₂], **1e**

To an acetone solution of bpy^{5CF₃} (22.5 mg, 0.1 mmol, 1.7 eq) at room temperature *cis*-[Pt(CH₃)₂(DMSO)₂] was added (22.3 mg, 0.0585 mmol, 1 eq) and the mixture was left stirring for 24 h. The colour quickly turned red and didn't change for the whole period. Yield 50%. Brute formula: C₁₃H₁₃N₂F₃Pt. FW: 449.3349. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 9.58 (s sat, 1H, ³J_{Pt-H} = 23.5 Hz, H₆); 9.35 (d sat, 1H, ³J_{Pt-H} = n.r. Hz, J_{H-H} = 5.0 Hz H_{6'}); 8.39 (d, 1H, J_{H-H} = 6.8 Hz, H_{3'}); 8.19 (td, 1H, J_{H-H} = 7.9, 1.5 Hz, H_{4'}); 8.10 (m, 2H, H₃ + H₄); 7.64 (m, 1H, H_{5'}); 1.24 (s sat, 3H, ²J_{Pt-H} = 85.7 Hz, Pt-CH₃); 1.20 (s sat, 3H, ²J_{Pt-H} = 86.5 Hz, Pt-CH₃). ¹H NMR (700 MHz, acetone-*d*₆, 298 K, ppm): 9.49 (s sat, 1H, ³J_{Pt-H} = 21.6 Hz, H₆); 9.30 (d sat, 1H, ³J_{Pt-H} = 21.3 Hz, J_{H-H} = 5.3 Hz, H_{6'}); 8.75 (dd, 1H, J_{H-H} = 8.5, 1.8 Hz, H₄); 8.66 (d, 1H, J_{H-H} = 8.5 Hz, H₃); 8.58 (d, 1H, J_{H-H} = 8.1 Hz, H_{3'}); 8.41 (td, 1H, J_{H-H} = 7.8, 1.5 Hz, H_{4'}); 7.82 (ddd, 1H, J_{H-H} = 7.5, 5.4, 1.1 Hz, H_{5'}); 1.08 (s sat, 3H, ²J_{Pt-H} = 87.2 Hz, Pt-CH₃); 1.02 (s sat, 3H, ³J_{Pt-H} = 86.2 Hz, Pt-CH₃). ¹H-¹H COSY (400 MHz, acetone-*d*₆, 298 K, ppm): Signal at 9.30 correlates with 7.82,

8.41 and 8.58; 8.75 correlates with 8.66 (they also show roof effect); 9.49 doesn't have any correlations.

[Pt(bpy-H)(CH₃)(DMSO)], 2a

To a solution of *cis*-[Pt(CH₃)₂(DMSO)₂] (390.5 mg, 1.02 mmol, 1 eq) in anhydrous toluene (8 mL) bpy was added (486.5 mg, 3.11 mmol, 3.1 eq). The mixture is heated to reflux for 2 h and a colour change is observed: the colourless solution of the starting complex became suddenly red upon addition of the bpy and then slowly turns yellow. The volume of the mixture is then reduced to ca. 3 mL and *n*-pentane is added until complete precipitation of the product which is then filtered, washed with *n*-pentane and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 92%. Melting point: 95 °C. Brute formula: C₁₃H₁₆N₂OSPt. FW: 443.4290. Elemental analysis % calculated for C₁₃H₁₆N₂OSPt: C 35.12, H 3.64, N 6.32; found C 35.49, H 3.20, N 6.42. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 9.71 (d sat, 1H, ³J_{Pt-H} = 14 Hz, J_{H-H} = 6.3 Hz, H₆); 8.36 (dd, 1H, J_{H-H} = 4.2, 1.2 Hz, H₆); 8.29 (d, 1H, J_{H-H} = 8.1 Hz, H₃); 8.01 (dd sat, 1H, ³J_{Pt-H} = 56.0 Hz, J_{H-H} = 7.8, 1.5 Hz, H₄); 7.95 (td, 1H, J_{H-H} = 7.5 Hz, H₄); 7.36 (dd, 1H, J_{H-H} = 3.9, 1.5 Hz, H₅); 7.17 (dd, 1H, J_{H-H} = 7.8, 4.5 Hz, H₅); 3.25 (s sat, 6H, ³J_{Pt-H} = 18.3 Hz, CH₃(DMSO)); 0.70 (s sat, 3H, ²J_{Pt-H} = 82 Hz, Pt-CH₃). ¹³C NMR (75.4 MHz, CDCl₃, 298 K, ppm): 164.8 (s sat, ²J_{Pt-C} = 24 Hz, C₂); 162.5 (s sat, ²J_{Pt-C} = 55 Hz, C₂); 150.3 (s, CH); 145.8 (s, CH); 145.1 (s sat, J_{Pt-C} = 1090 Hz, C₃); 140.3 (s, CH); 138.5 (s, CH); 124.5 (s, CH); 123.9 (s, CH); 121.2 (s, CH); 43.7 (s sat, ²J_{Pt-C} = 42 Hz, CH₃(DMSO)); -13.4 (s sat, J_{Pt-C} = 760 Hz, Pt-CH₃).

[Pt(bpy⁶CH₃-H)(CH₃)(DMSO)], 2b

To a solution of *cis*-[Pt(CH₃)₂(DMSO)₂] (301.2 mg, 0.790 mmol, 1 eq) in acetone (15 mL) bpy⁶CH₃ was added (174.0 mg, 1.01 mmol, 1.28 eq). The mixture is heated to reflux for 4 h and a colour change is observed: the colourless solution of the starting complex became suddenly red upon addition of the bpy and then slowly turns yellow. The volume of the mixture is then reduced to ca. 3 mL and *n*-pentane is added until complete precipitation of the product which is then filtered, washed with *n*-pentane and vacuum-pumped to give

the analytical sample as a yellow solid. Yield 81%. Melting point: 180 °C. Brute formula: $C_{14}H_{18}N_2OSPt$ FW: 457.4558. ^1H NMR (300 MHz, $CDCl_3$, 298 K, ppm): 9.67 (d sat, 1H, $^3J_{Pt-H} \approx 14$ Hz, $J_{H-H} = 5.9$ Hz, H_6); 8.31 (d, 1H, $J_{H-H} = 7.6$ Hz, H_3); 7.91 (m, 1H, H_4); 7.88 (d sat, 1H, $^3J_{Pt-H} = 53.0$ Hz, $J_{H-H} = 8.0$ Hz, H_4); 7.31 (m, 1H, H_5); 7.04 (d sat, 1H, $^3J_{Pt-H} = 18.6$ Hz, $J_{H-H} = 7.9$ Hz, H_5); 3.24 (s sat, 6H, $^3J_{Pt-H} = 18.3$ Hz, $CH_3(DMSO)$); 2.52 (s, 3H, $CH_3(bpy)$); 0.69 (s sat, 3H, $^2J_{Pt-H} = 82.1$ Hz, $Pt-CH_3$). $^{195}Pt-^1H$ HMQC (300 MHz, acetone- d_6 , 298 K, ppm): -4072 (s) correlates with signals at 9.79, 7.84, 7.05, 3.23 and 0.67.

[Pt(bpy^{6CF_3} -H)(CH_3)(DMSO)], 2c

To a solution of *cis*-[Pt(CH_3)₂(DMSO)₂] (101.9 mg, 0.267 mmol, 1 eq) in acetone (6 mL) bpy^{6CF_3} was added (104.4 mg, 0.466 mmol, 1.7 eq). The mixture is heated to reflux for 5 h and a colour change is observed: the colourless solution of the starting complex became quickly yellow upon addition of the bpy^{6CF_3} . The volume of the mixture is then reduced to ca. 3 mL and *n*-hexane is added until complete precipitation of the product which is then filtered, washed with *n*-hexane and vacuum-pumped to give the analytical sample as a yellow solid. Yield 66%.

The same reaction was carried out in anhydrous toluene refluxing for 3 h and elaborating in the same way. Yield 82%. Melting point: 150 °C. Brute formula: $C_{14}H_{15}N_2OF_3SPt$. FW: 511.4272. ^1H NMR (400 MHz, $CDCl_3$, 298 K, ppm): 9.73 (d sat, 1H, $^3J_{Pt-H} \approx 20$ Hz, $J_{H-H} = 7.2$ Hz, H_6); 8.40 (d, 1H, $J_{H-H} = 7.8$ Hz, H_3); 8.15 (d sat, 1H, $^3J_{Pt-H} = 55.7$ Hz, $J_{H-H} = 8.2$ Hz, H_4); 7.98 (m, 1H, H_4); 7.48 (d, 1H, $J_{H-H} = 8.1$ Hz, H_5); 7.40 (m, 1H, H_5); 3.26 (s sat, 6H, $^3J_{Pt-H} = 19.2$ Hz, $CH_3(DMSO)$); 0.73 (s sat, 3H, $^3J_{Pt-H} = 81.6$ Hz, $Pt-CH_3$). ^1H NMR (700 MHz, acetone- d_6 , 298 K, ppm): 9.85 (d sat, 1H, $^3J_{Pt-H} = 18.8$ Hz, $J_{H-H} = 5.8$ Hz, H_6); 8.36 (d, 1H, $J_{H-H} = 7.6$ Hz, H_3); 8.22 (d sat, 1H, $^3J_{Pt-H} = 55.1$ Hz, $J_{H-H} = 7.8$ Hz, H_4); 8.22 (td, 1H, $J_{H-H} = 7.6$, 1.4 Hz, H_4 or H_5); 7.62 (ddd, 1H, $J_{H-H} = 7.4$, 5.6, 1.5 Hz, H_5 or H_4); 7.59 (d sat, 1H, $^4J_{Pt-H} = 16.4$ Hz, H_5); 3.29 (s sat, 6H, $^3J_{Pt-H} = 18.6$ Hz, $CH_3(DMSO)$); 0.73 (s sat, 3H, $^3J_{Pt-H} = 83.1$ Hz, $Pt-CH_3$). $^1H-^1H$ COSY (700 MHz, acetone- d_6 , 298 K, ppm): Signal at 9.85 correlates with 7.62, 8.21 and 8.36; signal at 8.22 correlates with 7.59. ^{13}C NMR (100.6 MHz, $CDCl_3$, 298 K, ppm): 165.1 (s sat, $^2J_{Pt-C} = 29.0$ Hz, C_2); 161.3 (s sat, $^2J_{Pt-C} = 55.0$ Hz, C_2); 150.2 (s sat, $^2J_{Pt-C} \approx 7$ Hz, C_6);

149.5 (s sat, $J_{\text{Pt-C}} = 1100$ Hz, C_3); 144.2 (s sat, $^4J_{\text{Pt-C}} = 34.0$ Hz, C_6); 141.2 (s sat, $^2J_{\text{Pt-C}} = 88.4$ Hz, C_4); 138.8 (s, C_4); 125.2 (s sat, $^2J_{\text{Pt-C}} \approx 10$ Hz, C_5); 122.2 (q, $J_{\text{F-C}} = 273.4$ Hz, CF_3); 122.0 (s sat, $^3J_{\text{Pt-C}} = 22.6$ Hz, C_3); 119.7 (q sat, $^3J_{\text{Pt-C}} \approx 65$ Hz, $^3J_{\text{F-C}} = 3.0$ Hz, C_5); 43.8 (s sat, $^2J_{\text{Pt-C}} = 43.4$ Hz, $\text{CH}_3(\text{DMSO})$); -13.4 (s sat, $J_{\text{Pt-C}} = 761$ Hz, Pt-CH_3). $^{195}\text{Pt-}^1\text{H}$ HMQC (700 MHz, acetone- d_6 , 298 K, ppm): -4059 (s) correlates with signals at 9.85, 8.22, 7.59, 3.29 and 0.73.

[Pt(bpy $^{5\text{CH}_3}$ -H)(CH $_3$)(DMSO)], 2d

To a solution of $[\text{Pt}(\text{bpy}^{5\text{CH}_3})(\text{CH}_3)_2]$ (**1d**, 80 mg, 0.202 mmol, 1 eq) in 3 mL of anhydrous toluene anhydrous DMSO was added (30 μL , $d = 1.101$ g·mL $^{-1}$, 0.420 mmol, 2.08 eq). The mixture is refluxed for 3 h, during this time changed colour from red to yellow. The volume of the mixture is then reduced and *n*-pentane is added until complete precipitation of the product which is then filtered, washed with *n*-pentane and vacuum-pumped to give the analytical sample as a yellow solid. Brute formula: $\text{C}_{14}\text{H}_{18}\text{N}_2\text{OSPt}$. FW: 457.4558. ^1H NMR (300 MHz, CDCl_3 , 298 K, ppm): Selected data for the two isomers 9.54 (s sat, 1H, $^2J_{\text{Pt-H}} = 15.0$ Hz, $J_{\text{H-H}} = 6.0$ Hz, Pt-H_6 (substituted bpy activated)); 9.42 (s sat, 1H, $^2J_{\text{Pt-H}} = 15.0$ Hz, Pt-H_6 (unsubstituted bpy activated)); 3.08 (s sat, 12H, $^3J_{\text{Pt-H}} = 17.7$ Hz, $\text{CH}_3(\text{DMSO})$ both isomers); 2.25 (s, 3H, $\text{CH}_3(\text{bpy})$); 2.21 (s, 3H, $\text{CH}_3(\text{bpy})$); 0.55 (s sat, 3H, $^2J_{\text{Pt-H}} = 82.2$ Hz, Pt-CH_3); 0.54 (s sat, 3H, $^2J_{\text{Pt-H}} = 81.4$ Hz, Pt-CH_3).

[Pt(bpy $^{5\text{CF}_3}$ -H)(CH $_3$)(DMSO)], 2e

To a solution of *cis*- $[\text{Pt}(\text{CH}_3)_2(\text{DMSO})_2]$ (89.4 mg, 0.234 mmol, 1 eq) in anhydrous toluene (6 mL) $\text{bpy}^{5\text{CF}_3}$ was added (89.8 mg, 0.40 mmol, 1.7 eq). The mixture is heated to reflux for 3 h and a colour change is observed: the colourless solution of the starting complex became suddenly red upon addition of the $\text{bpy}^{5\text{CF}_3}$ and then slowly turns yellow. The volume of the mixture is then reduced to ca. 3 mL and *n*-hexane is added until complete precipitation of the product which is then filtered, washed with *n*-hexane and vacuum-pumped to give the analytical sample as a yellow solid. Yield 75%. Melting point: decompose at 200 °C. Brute formula: $\text{C}_{14}\text{H}_{15}\text{N}_2\text{OF}_3\text{SPt}$ FW: 511.4272. ^1H NMR (300 MHz, CDCl_3 , 298 K, ppm): Major species. 9.76 (m sat, 1H, $^3J_{\text{Pt-H}} = \text{n.r.}$, H_6); 8.59

(s, 1H, H₆); 8.36 (d, 1H, J_{H-H} = 7.9 Hz H₃); 8.21 (s sat, 1H, ³J_{Pt-H} = 55.2 Hz, H₄); 8.00 (m, 1H, H₄); 7.44 (m, 1H, H₅); 3.27 (s sat, 6H, ³J_{Pt-H} = 19.0 Hz, CH₃(DMSO)); 0.73 (s sat, 3H, ²J_{Pt-H} = 81.2 Hz, Pt-CH₃). Minor species. 3.23 (s sat, 6H, ³J_{Pt-H} = n.r., CH₃(DMSO)); 0.75 (s sat, 3H, ²J_{Pt-H} = 78.0 Hz, Pt-CH₃).

[Pt(pyq-H)(CH₃)(DMSO)], **2f**

To a solution of *cis*-[Pt(CH₃)₂(DMSO)₂] (100 mg, 0.262 mmol, 1 eq) in acetone (30 mL), pyq (54 mg, 0.262 mmol, 1 eq) was added under vigorous stirring. The solution was heated to reflux for 4 h, then it was evaporated to a small volume and treated with *n*-hexane. The precipitate formed was filtered off, washed with *n*-hexane and vacuum pumped to give the analytical sample as a yellow solid. Yield 90%. Melting point: decompose at 150 °C. Brute formula: C₁₇H₁₈N₂OSPt. FW: 493.4888. Elemental analysis % calculated for C₁₇H₁₈N₂OSPt: C 41.38, H 3.68, N 5.68; found C 41.27, H 3.43, N 5.56. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 9.82 (ddd sat, 1H, ³J_{Pt-H} = 14.2 Hz, J_{H-H} = 5.6, 1.6, 0.8 Hz, H₆); 8.62 (d, 1H, J_{H-H} = 7.9 Hz, H₃); 8.41 (s sat, 1H, ³J_{Pt-H} = 60.4 Hz, H₄); 8.03 (d, 1H, J_{H-H} = 8.3 Hz, H₈); 8.01 (td, 1H, J_{H-H} = 7.8 Hz, H₄); 7.79 (d, 1H, J_{H-H} = 8.3 Hz, H₅); 7.60 (td, 1H, J_{H-H} = 8.3, 6.8, 1.5 Hz, H₇); 7.47 (ddd, 1H, J_{H-H} = 8.3, 6.8, 1.3 Hz, H₆); 7.43 (ddd, 1H, J_{H-H} = 7.2, 5.5, 1.4 Hz, H₅); 3.29 (s sat, 6H, ³J_{Pt-H} = 18.3 Hz, CH₃(DMSO)); 0.82 (s sat, 3H, ²J_{Pt-H} = 82.0 Hz, Pt-CH₃). ¹³C NMR (75.4 MHz, CDCl₃, 298 K, ppm): 166.09 (²J_{Pt-C} = 27.9 Hz, C₂); 161.75 (²J_{Pt-C} = 52.4 Hz, C₂); 150.45; 146.32; 140.80 (J_{Pt-C} = 1090 Hz, Pt-C₃); 139.26 (J_{Pt-C} = 89.0 Hz); 138.36; 129.23 (J_{Pt-C} = 64.5 Hz); 129.20; 127.88; 127.42; 126.37; 125.19 (J_{Pt-C} = 10.7 Hz); 122.46 (J_{Pt-C} = 23.2 Hz); 43.77 (²J_{Pt-C} = 41.9 Hz, CH₃(DMSO)); -13.07 (J_{Pt-C} = 766.1 Hz, Pt-CH₃). When the reaction is followed at room temperature in acetone-*d*₆, a mixture of complexes [Pt(pyq)(CH₃)₂] (**1f**) and **2f** is observed in solution by means of ¹H NMR. Selected data for **1f**: 8.90 (dd sat, 1H, ³J_{Pt-H} = 24.4 Hz, H₆); 1.23 (s sat, 3H, ²J_{Pt-H} = 86.7 Hz, Pt-CH₃); 1.16 (s sat, 3H, ²J_{Pt-H} = 88.9 Hz, Pt-CH₃).

[Pt(vpy-H)(CH₃)(DMSO)], 2g

In inert atmosphere 34 μ L of vpy ($d = 0.977 \text{ g}\cdot\text{mL}^{-1}$, 0.316 mmol, 1.2 eq) were added to a 13 mL anhydrous toluene solution of *cis*-[Pt(CH₃)₂(DMSO)₂] (100.0 mg, 0.264 mmol, 1 eq). The mixture is heated to 80 °C for 2 h then it is evaporated to dryness obtaining an orangish oil. Brute formula: C₁₀H₁₅NOSPt. FW: 392.3812. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 9.24 (d sat, 1H, ³J_{Pt-H} = 11.4 Hz, J_{H-H} = 5.5 Hz, H₆); 7.63 (td, 1H, J_{H-H} = 7.5, 1.6 Hz, H₄); 7.42 (d sat, 1H, ²J_{Pt-H} = 171 Hz, J_{H-H} = 8.7 Hz, H_β); 7.08 (d, 1H, J_{H-H} = 7.5 Hz, H₃); 7.00 (m, 1H, H₅); 6.94 (d sat, 1H, ³J_{Pt-H} = 108 Hz, J_{H-H} = 8.7 Hz, H_α); 3.07 (s sat, 6H, ³J_{Pt-H} = 16.8 Hz, CH₃(DMSO)); 0.69 (s sat, 3H, ²J_{Pt-H} = 82.5 Hz, Pt-CH₃). ¹³C NMR (75.4 MHz, CDCl₃, 298 K, ppm): 166.9 (s sat, J_{Pt-C} = 115 Hz, C₂); 163.2 (s sat, J_{Pt-C} = 1035 Hz, C_β); 150.5 (s sat, J_{Pt-C} = 16 Hz, C₆); 139.3 (s sat, C); 138.4 (s sat, J_{Pt-C} = 4 Hz, C); 121.2 (s sat, J_{Pt-C} = 5 Hz, C₅ or C₃); 119.5 (s sat, J_{Pt-C} = 19 Hz, C₃ or C₅); 43.5 (s sat, ²J_{Pt-C} = 40 Hz, CH₃(DMSO)); -19.9 (s sat, J_{Pt-C} = 756 Hz, Pt-CH₃).

[Pt(ppy^{4F}-H)(CH₃)(DMSO)], 2k

To an acetone solution of *cis*-[Pt(CH₃)₂(DMSO)₂] (9.4 mg, 0.025 mmol, 1 eq) was added the ppy^{4F} (5.0 mg, 0.029 mmol, 1.2 eq). No immediate change was observed but after 10 min the solution became yellow and didn't change for 5 h. The reaction mixture was evaporated to dryness, the residue was dissolved in distilled H₂O and extracted with CH₂Cl₂ (3 × 5 mL) before being treated with Na₂SO₄ filtered and evaporated to dryness. Brute formula: C₁₄H₁₆NOFSPt FW: 460.4316. ¹H NMR (250 MHz, CDCl₃, 298 K, ppm): 9.69 (d br sat, 1H, ³J_{Pt-H} = 13.6 Hz, J_{H-H} = 6.0 Hz, H₆); 7.82 (td, 1H, J_{H-H} = 7.7, 1.7 Hz, H₄); 7.69 (d br, 1H, J_{H-H} = 8.3 Hz, H₃); 7.63 (dd, 1H, J_{F-H} = 8.6 Hz, J_{H-H} = 5.5 Hz, H₆ or H₅); 7.40 (dd sat, 1H, ³J_{Pt-H} = 68.2 Hz, ³J_{F-H} = 10.2 Hz, J_{H-H} = 2.4 Hz, H₃); 7.19 (ddd, 1H, J_{H-H} = 7.2, 5.6, 1.6 Hz, H₅); 6.82 (td, 1H, J_{H-H} = 8.5, 2.6 Hz, H₅ or H₆); 3.22 (s sat, 6H, ³J_{Pt-H} = 17.9 Hz, CH₃(DMSO)); 0.67 (s sat, 3H, ²J_{Pt-H} = 81.6 Hz, Pt-CH₃). ¹H-¹H COSY (250 MHz, CDCl₃, 298 K, ppm): 9.69 correlates with signals at 7.82, 7.19, 7.69; 7.40 correlates with signals at 6.82, 7.63. ¹⁹F NMR (282 MHz, CCl₃F, 298 K, ppm): -111.5 (s sat, ⁴J_{Pt-F} = 71.5 Hz).

Single crystals of [Pt(ppy^{4F}-H)(Ph)(DMSO)], C₁₉H₁₈NOFSPt, were grown from a CH₂Cl₂

solution. A suitable crystal was selected and mounted on a glass fibre using Fromblin oil on an Oxford Diffraction Xcalibur Gemini diffractometer with a Ruby CCD detector. The crystal was kept at 150(2) K. The data collection nominally covered over a hemisphere of reciprocal space, by a combination of seven sets of exposures with different ω angles for the crystal; each 12 s exposure covered 1.0% in ω . The crystal-to-detector distance was 5.5 cm. Crystal decay was found to be negligible by repeating the initial frames at the end of data collection and analyzing the duplicate reflections.

Hydrogen atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameter equal to 1.2 (or 1.5 for methyl H-atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached.

Systematic absences indicated space group C2/c and shown to be correct by successful refinement.

The structure was solved by direct methods using SHELXS (TREF)⁴¹¹ with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups.

The Oxford Diffraction Gemini XRD system was obtained through the Science City Advanced Materials project: Creating and Characterising Next Generation Advanced Materials, with support from Advantage West Midlands (AWM) and part funded by the European Regional Development Fund (ERDF). Full details in Table 5.1.

[Pt(bpy^{6CF₃}-H)(Ph)(DMSO)], 4c

To a solution of *cis*-[Pt(Ph)₂(DMSO)₂] (59.3 mg, 0.117 mmol, 1 eq) in acetone (6 mL) bpy^{6CF₃} was added (31.4 mg, 0.140 mmol, 1.2 eq). The mixture is stirred at room temperature for 4 h and a colour change is observed: the colourless solution of the starting complex became suddenly orange upon addition of the bpy^{6CF₃}. The volume of the mixture is then reduced to ca. 3 mL and *n*-hexane is added until complete precipitation of the product which is then filtered, washed with *n*-hexane and vacuum-pumped to give the analytical sample. Yield: 66%. Brute formula: C₁₉H₁₇N₂OF₃SPt. FW: 573.4981. ¹H NMR (400 MHz, CDCl₃, 298 K, ppm): 9.70 (d sat, 1H, ³J_{Pt-H} = 10.2 Hz, J_{H-H} = 5.1 Hz,

H₆); 8.40 (d, 1H, J_{H-H} = 7.1 Hz, H₃); 8.00 (td, 1H, J_{H-H} = 7.7, 0.9 Hz, H₄); 7.6÷7.00 (m, 8H, H₅ + H₄ + H₅ + H_o(Ph) + H_m(Ph) + H_p(Ph)); 2.98 (s sat, 1H, ³J_{Pt-H} = 18.4 Hz, CH₃(DMSO)).

[Pt(pyq-H)(Ph)(DMSO)], 4f

In inert atmosphere *cis*-[Pt(Ph)₂(DMSO)₂] (101.2 mg, 0.225 mmol, 1 eq) was added to a toluene solution (20 mL) of pyq (46.0 mg, 0.223 mmol, 0.99 eq). The initial colourless solution became red after the complex addition and was heated to reflux for 24 h. The mixture turned orange-yellow and was concentrated to a small volume after cooling to room temperature, then treatment with Et₂O afforded the product. Yield 68%. Melting point: decompose at 240 °C. Brute formula: C₂₂H₂₀N₂OSPt. FW: 555.5997. Elemental analysis % calculated for C₂₂H₂₀N₂OSPt: C 47.56, H 3.63, N 5.04; found C 48.45, H 3.61, N 5.56. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 9.75 (d sat, 1H, ³J_{Pt-H} = 16.2 Hz, J_{H-H} = 5.7 Hz, H₆); 8.62 (d, 1H, J_{H-H} = 7.8 Hz, H₃); 8.06÷7.69 (m, 2H, H₄ + H₈); 7.66÷7.00 (m, 10H, aromatics+Ph); 2.99 (s sat, 6H, ³J_{Pt-H} = 17.5 Hz, CH₃(DMSO)).

[Pt(vpy-H)(Ph)(DMSO)], 4g

In inert atmosphere 11.7 µL of vpy (*d* = 0.977 g·mL⁻¹, 0.109 mmol, 0.5 eq) were added to a 8 mL anhydrous toluene solution of *cis*-[Pt(Ph)₂(DMSO)₂] (101.0 mg, 0.200 mmol, 1 eq). The mixture is heated to 80 °C for 3 h then it is concentrated to small volume and treated with Et₂O. Yield 48%. Melting point: 133 °C. Brute formula: C₁₅H₁₇NOSPt. FW: 454.4521. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 9.28 (d sat, 1H, ³J_{Pt-H} = 12.8 Hz, J_{H-H} = 5.5 Hz, H₆); 7.72 (dd, 1H, J_{H-H} = 7.6, 1.7 Hz, H₄); 7.38 (d sat, 1H, ²J_{Pt-H} ≈ 162 Hz, ³J_{H-H} = 8.7 Hz, H_β); 7.38 (m sat, 2H, ³J_{Pt-H} = 69.7 Hz, H_o); 7.19 (d, 1H, J_{H-H} = 7.9 Hz, H₃); 7.12 (m, 1H, H₅); 7.06 (t, 2H, J_{H-H} = 7.1 Hz, H_m); 6.96 (m, 1H, H_p); 6.90 (d sat, 1H, ³J_{Pt-H} = 118 Hz, ³J_{H-H} = 8.7 Hz, H_α); 2.89 (s sat, 6H, ³J_{Pt-H} = 16 Hz, CH₃(DMSO)).

[Pt(vpy-H)(Ph)(DMS)], 4g'

In inert atmosphere a 3-fold excess of vpy was added to an anhydrous toluene solution of *cis*-[Pt(Ph)₂(DMS)₂]. The mixture is heated to 80 °C for 4 h then it is evaporated to

dryness. Brute formula: $C_{15}H_{17}NSPt$. FW: 438.4527. ^1H NMR (300 MHz, $CDCl_3$, 298 K, ppm): 9.31 (d sat, 1H, $^3J_{Pt-H} = 30.4$ Hz, $J_{H-H} = 5.6$ Hz, H_6); 8.00÷6.80 (m, 9H, $H_3 + H_4 + H_5 + H_\alpha + Ph$); 6.70 (d sat, 1H, $^3J_{Pt-H} = 145.0$ Hz, $J_{H-H} = 7.6$ Hz, H_β); 2.69 (s sat, 6H, $^3J_{Pt-H} = 54.2$ Hz, $CH_3(DMS)$).

[Pt(bpy-H)(CH₃)(PMe₃)], 7a

Under an N_2 atmosphere *cis*-[Pt(CH₃)₂(DMSO)₂] (47.6 mg, 0.1248 mmol, 1 eq) was dissolved in 2 mL of distilled toluene and then, to the colourless solution, an excess of bpy was added (50.5 mg, 0.3233 mmol, 2.6 equiv), yielding a red solution that was degassed twice and then heated to reflux for 3 h. A few drops of PMe₃ were added (excess) under N_2 flow, giving a yellow solution that was left to react for 30 min. The reaction mixture was then evaporated to dryness and purified by chromatography on silica gel, with Et₂O as eluent, and evaporating to dryness the coloured fraction (32.9 mg, 0.0745 mmol). Yield: 60%. Brute formula: $C_{14}H_{19}N_2PPt$. FW: 441.3721. ^1H NMR (500 MHz, acetone-*d*₆, 298 K, ppm): 8.86 (d sat, 1H, $^3J_{Pt-H} = 22.0$ Hz, $J_{H-H} = 5.6$ Hz, H_6); 8.33 (ddd, $J_{H-H} = 7.9$, 1.5, 0.7 Hz, H_3); 8.28 (ddd, 1H, $J_{H-H} = 4.6$, 1.8, 0.9 Hz, H_6); 8.10 (td, 1H, $J_{H-H} = 7.9$, 1.5 Hz, H_4); 8.09 (ddd sat, 1H, $^3J_{Pt-H} = 44.4$ Hz, $J_{H-H} = 5.6$, 3.6, 1.7 Hz, H_4); 7.44 (ddd, 1H, $J_{H-H} = 7.4$, 5.5, 1.5 Hz, H_5); 7.16 (ddd sat, 1H, $^4J_{Pt-H} = 15.2$ Hz, $J_{H-H} = 7.4$, 4.5, 1.9 Hz, H_5); 1.57 (d sat, 9H, $^3J_{Pt-H} = 21.0$ Hz, $^2J_{P-H} = 8.1$ Hz, $P(CH_3)_3$); 0.85 (d sat, 3H, $^2J_{Pt-H} = 84.0$ Hz, $^3J_{P-H} = 8.0$ Hz, Pt-CH₃). ^{13}C NMR (100.6 MHz, acetone-*d*₆, 298 K, ppm): 151.8 (s sat, $^3J_{Pt-C} = 4$ Hz, C_6); 145.0 (s sat, $^4J_{Pt-C} = 15$ Hz, C_6); 141.2 (s, C_4); 139.9 (s sat, $^2J_{Pt-C} = 78$ Hz, C_4); 138.7 (br); 125.7 (s sat, $^3J_{Pt-C} = 13$ Hz, C_5); 124.7 (d sat, $^3J_{Pt-C} = 49$ Hz, $^4J_{P-C} = 6$ Hz, C_5); 122.4 (s sat, $^3J_{Pt-C} = 20$ Hz, C_3); 15.0 (d sat, $^2J_{Pt-C} = n.r.$, $J_{P-C} = 29$ Hz, $P(CH_3)_3$); -17.0 (d sat, $J_{Pt-C} = n.r.$, $^2J_{P-C} = 7$ Hz, Pt-CH₃). ^{31}P NMR (202.4 MHz, acetone-*d*₆, 298 K, ppm): -18.6 (s sat, $J_{Pt-P} = 2112$ Hz, $P(CH_3)_3$). ^{195}Pt - ^1H HMQC (500 MHz, acetone-*d*₆, 298 K, ppm): -4107 (d, $J_{Pt-P} = 2112$ Hz, $P(CH_3)_3$). ESI-MS (*m/z*): found 442.1008, calcd for $C_{14}H_{20}N_2P^{196}Pt$ 442.0935.

[Pt(bpy-H)(CH₃)(PPh₃)], 8a

Method A. For the reaction of [Pt(bpy-H)(CH₃)(DMSO)] (**2a**) with PPh₃, yield 67%.¹⁶

Method B. To a solution of *cis*-[Pt(CH₃)₂(DMSO)₂] (50.1 mg, 0.131 mmol, 1 eq) in anhydrous toluene an excess of bpy (63.5 mg, 0.406 mmol, 3.1 eq) was added under a nitrogen atmosphere. The solution became suddenly red and was heated to reflux for 3 h. At the end of the reaction PPh₃ (37.8 mg, 0.144 mmol, 1.1 eq) was added to the hot solution and left to react for about 30 min; then the solution was concentrated to a small volume and treated with *n*-hexane to form a precipitate. The solid was filtered off, washed with *n*-hexane, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 87%. Melting point: 215 °C. Brute formula: C₂₉H₂₅N₂Pt. FW: 627.5847. Elemental analysis % calculated for C₂₉H₂₅N₂Pt·½H₂O: C 54.72, H 4.12, N 4.40; found C 54.67, H 3.79, N 4.51. ¹H NMR (600 MHz, acetone-*d*₆, 298 K, ppm): 8.34 (d br, 1H, J_{H-H} = 4.3 Hz, H₆); 8.32 (d br, 1H, J_{H-H} = 7.9 Hz, H₃); 8.12 (ddd sat, 1H, ³J_{Pt-H} = 48.1 Hz, J_{H-H} = 7.4, 5.5, 1.7 Hz, H₄); 7.95 (td, 1H, J_{H-H} = 7.6, 1.5 Hz, H₄); 7.81÷7.75 (m, 7H, H₆ + H_o(PPh₃) or H_m(PPh₃)); 7.53÷7.47 (m, 9H, H_p(PPh₃) + H_m(PPh₃) or H_o(PPh₃)); 7.21 (ddd sat, 1H, ⁴J_{Pt-H} = n.r. Hz, J_{H-H} = 7.4, 4.7, 1.7 Hz, H₅); 6.85 (ddd, 1H, J_{H-H} = 7.4, 5.6, 1.4 Hz, H₅); 0.66 (d sat, 1H, ²J_{Pt-H} = 84.6 Hz, ³J_{P-H} = 7.7 Hz, Pt-CH₃). ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 8.40 (m, 1H, H₆); 8.31 (dd, 1H, J_{H-H} = 8.0, 1.5 Hz, H₃); 8.24 (ddd sat, 1H, ³J_{Pt-H} = 48.0 Hz, J_{H-H} = 7.5, 5.4, 1.8 Hz, H₄); 7.79÷7.72 (m, 7H, H₄ + H_o(PPh₃)); 7.46÷7.35 (m, 10H, H₆ + H_m(PPh₃) + H_p(PPh₃)); 7.22 (ddd, 1H, J_{H-H} = 7.8, 7.5, 1.7, H₅); 6.67 (td, 1H, J_{H-H} = 5.4, 1.5 Hz, H₅); 0.74 (s sat, 3H, ²J_{Pt-H} = 83 Hz, ³J_{Pt-H} = 7.7 Hz, Pt-CH₃). ¹³C NMR (75.4 MHz, CDCl₃, 298 K, ppm): 165.7 (s sat, ²J_{Pt-C} = 19.6 Hz, C₂); 164.7 (d sat, ²J_{Pt-C} = 48.3 Hz, ³J_{P-C} = 3.5 Hz, C₂); 155.4 (d sat, J_{Pt-C} = 970.3 Hz, ²J_{P-C} = 119.6 Hz, C₃); 150.5 (d sat, ³J_{Pt-C} = 13.7 Hz, ⁴J_{P-C} = 3.8 Hz, C₆); 145.0 (s, C₄); 140.0 (s sat, ²J_{Pt-C} = 82.4 Hz, C₄); 137.5 (s, C₆); 135.0 (d sat, ³J_{Pt-C} = 17.1 Hz, ²J_{P-C} = 11.9 Hz, C_o(PPh₃)); 132.1 (d sat, ²J_{Pt-C} = 17.0 Hz, J_{P-C} = 44.0 Hz, H_{ipso}(PPh₃)); 130.3 (d, ⁴J_{P-C} = 1.7 Hz, H_p(PPh₃)); 126.3 (d, ³J_{P-C} = 9.8 Hz, H_m(PPh₃)); 124.5 (d sat, ²J_{Pt-C} = 53.4 Hz, ³J_{P-C} = 5.6 Hz, C₅); 123.7 (s sat, ³J_{Pt-C} = 11.1 Hz, C₅); 121.4 (s sat, ³J_{Pt-C} = 20.1 Hz, C₃); -12.4 (d sat, J_{Pt-C} = 725.3 Hz, ²J_{P-C} = 4.7 Hz, Pt-CH₃). ³¹P NMR (121.4 MHz, CDCl₃, 298 K, ppm): 33.6 (s sat, J_{Pt-P} = 2229 Hz, PPh₃).

Single crystals of $[\text{Pt}(\text{bpy}-\text{H})(\text{CH}_3)(\text{PPh}_3)]$, $\text{C}_{29}\text{H}_{25}\text{N}_2\text{PPt}$, were grown from a CH_2Cl_2 solution.

The crystals were mounted in oil and the temperature of the crystal was controlled using the Oxford Cryosystem Cryostream Cobra. The data collection nominally covered over a hemisphere of reciprocal space, by a combination of nine sets of exposures with different θ angles for the crystal and each 20 s exposure covered 1.0% in ω . The crystal-to-detector distance was 5.5 cm. Crystal decay was found to be negligible by repeating the initial frames at the end of data collection and analyzing the duplicate reflections.

Hydrogen atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameter equal to 1.2 (or 1.5 for methyl H-atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached.

The assignment of nitrogen or carbon on the bpy ring was relatively straightforward by considering the thermal parameters of all the atoms concerned modelled as carbon. The atoms with much smaller thermal parameters were assigned as nitrogens. There was no hydrogen located on N12 so it is not protonated.

The structure was solved by direct methods using SHELXS (TREF)⁴¹¹ with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups.

X-ray crystallographic data in CIF format have been deposited at the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 963378. Full details in Table 5.2.

$[\text{Pt}(\text{bpy}^{6\text{CH}_3}-\text{H})(\text{CH}_3)(\text{PPh}_3)]$, 8b

To a solution of *cis*- $[\text{Pt}(\text{CH}_3)_2(\text{DMSO})_2]$ (320.7 mg, 0.841 mmol, 1 eq) in acetone (15 mL) an excess of $\text{bpy}^{6\text{CH}_3}$ (146.3 mg, 0.849 mmol, 1 eq) was added under a nitrogen atmosphere. The solution became suddenly red and was heated to reflux for 5 h. At the end of the reaction PPh_3 (441.8 mg, 1.68 mmol, 2 eq) was added to the hot solution and left to react for 1 h; then the solution was concentrated to a small volume and treated with *n*-pentane to form a precipitate. The solid was filtered off, washed with *n*-pentane,

and vacuum-pumped to give the analytical sample as a yellow solid. Yield 85%. Melting point: 200 °C. Brute formula: $C_{30}H_{27}N_2Pt$ FW: 641.6116. ^1H NMR (600 MHz, $CDCl_3$, 298 K, ppm): 8.36 (d, 1H, $J_{H-H} = 7.9$ Hz, H_3); 8.13 (dd sat, 1H, $^3J_{Pt-H} = 46.0$ Hz, $J_{H-H} = 7.7, 5.3$ Hz, H_4); 7.79÷7.73 (m, 8H, H_4 + H_6 + $H_o(PPh_3)$ or $H_m(PPh_3)$); 7.46÷7.42 (m, 3H, $H_p(PPh_3)$); 7.42÷7.37 (m, 6H, $H_m(PPh_3)$ or $H_o(PPh_3)$); 7.11 (dd sat, 1H, $^3J_{Pt-H} = 14.8$ Hz, $^5J_{P-H} = 1.0$ Hz, $J_{H-H} = 7.7$ Hz, H_5); 6.65 (ddd, 1H, $J_{H-H} = 7.2, 5.8, 1.5$ Hz, H_5); 2.52 (s, 3H, $CH_3(bpy)$); 0.74 (d sat, 1H, $^3J_{Pt-H} = 83.0$ Hz, $^3J_{P-H} = 8.1$ Hz, Pt- CH_3). ^1H - ^1H COSY (600 MHz, $CDCl_3$, 298 K, ppm): 8.36 correlates with signals at 7.75, 6.65; 8.13 correlates with signal at 7.11. ^{31}P NMR (242.9 MHz, $CDCl_3$, 298 K, ppm): 32.6 (s sat, $J_{Pt-P} = 2226$ Hz, PPh_3). ^{195}Pt - ^1H HMQC (600 MHz, $CDCl_3$, 298 K, ppm): -4218 (d, $J_{Pt-P} \approx 2356$) correlates with signals at 8.13, 7.74, 0.74.

[Pt(bpy^{6CF_3-H})(CH_3)(PPh_3)], **8c**

To a solution of [Pt(bpy^{6CF_3-H})(CH_3)(DMSO)] (**2c**, 114.9 mg, 0.225 mmol, 1 eq) in acetone (10 mL) PPh_3 was added (89.3 mg, 0.340 mmol, 1.5 eq). After 3 h the mixture was concentrated to small volume and treated with *n*-hexane yielding the product as a yellow solid. Yield 74%. Melting point: decompose 200÷205 °C. Brute formula: $C_{30}H_{24}N_2F_3Pt$. FW: 695.5830. ^1H NMR (600 MHz, $CDCl_3$, 298 K, ppm): 8.44 (d, 1H, $J_{H-H} = 7.7$ Hz, H_3); 8.39 (dd sat, 1H, $^3J_{Pt-H} = 47.8$ Hz, $J_{H-H} = 7.7, 5.4$ Hz, H_4); 7.83 (td, 1H, $J_{H-H} = 7.7, 1.4$ Hz, H_4); 7.76 (m, 7H, H_6 + $H_m(PPh_3)$ or $H_o(PPh_3)$); 7.56 (dd sat, 1H, $^3J_{Pt-H} = 14.3$ Hz, $^4J_{P-H} = 1.5$ Hz, $J_{H-H} = 7.9$ Hz, H_5); 7.46 (m, 3H, $H_p(PPh_3)$); 7.42 (m, 6H, $H_o(PPh_3)$ or $H_m(PPh_3)$); 6.75 (ddd, 1H, $J_{H-H} = 7.5, 5.5, 1.5$ Hz, H_5); 0.79 (d sat, 3H, $^2J_{Pt-H} = 83.0$ Hz, $^3J_{P-H} = 7.9$ Hz, Pt- CH_3). ^1H - ^1H COSY (600 MHz, $CDCl_3$, 298 K, ppm): 8.44 correlates with signals at 7.83, 6.75, 7.76; 8.39 correlates with signal at 7.56. ^{31}P NMR (242.9 MHz, $CDCl_3$, 298 K, ppm): 32.1 (s sat, $J_{Pt-P} = 2279$ Hz, PPh_3). ^{195}Pt - ^1H HMQC (600 MHz, $CDCl_3$, 298 K, ppm): -4202 (d, $J_{Pt-P} \approx 2395$) correlates with signals at 8.39, 7.77, 7.56, 0.79.

[Pt(bpy^{5CH₃}-H)(CH₃)(DMSO)], 8d

To a solution of [Pt(bpy^{5CH₃}-H)(CH₃)(DMSO)] (**2d**, 38.1 mg, 0.090 mmol, 1 eq) in acetone (10 mL) PPh₃ was added (35.0 mg, 0.133 mmol, 1.48 eq). After 3 h the mixture was concentrated to small volume and treated with *n*-hexane yielding the product as a yellow solid. Yield 63%. Brute formula: C₃₀H₂₇N₂PPt. FW: 641.6116. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): Selected data for the two isomers 2.35 (s, 6H, CH₃(bpy) both isomers); 0.76 (s sat, 3H, ²J_{Pt-H} = n.r., Pt-CH₃); 0.73 (s sat, 3H, ²J_{Pt-H} = n.r., Pt-CH₃). ³¹P NMR (121.4 MHz, CDCl₃, 298 K, ppm): 33.8 (s sat, J_{Pt-P} = 2216 Hz, PPh₃); 33.6 (s sat, J_{Pt-P} = 2224 Hz, PPh₃).

[Pt(bpy^{5CF₃}-H)(CH₃)(PPh₃)], 8e

To a solution of [Pt(bpy^{5CF₃}-H)(CH₃)(DMSO)] (**2e**, 39.1 mg, 0.076 mmol, 1 eq) in acetone (10 mL) PPh₃ was added (29.6 mg, 0.113 mmol, 1.49 eq). After 3 h the mixture was concentrated to small volume and treated with *n*-hexane yielding the product as a yellow solid. Yield 81%. Melting point: decompose at 200 °C. Brute formula: C₃₀H₂₄N₂F₃PPt. FW: 695.5830. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 8.63 (m, 1H, H₆); 8.46 (d sat, 1H, ³J_{Pt-H} = 39.0 Hz, ⁴J_{P-H} = 4.0 Hz, H₄); 8.38 (d, 1H, J_{H-H} = 8.1 Hz, H₃); 7.85÷7.38 (m, 17H, H₆ + H₄ + H₀(PPh₃) + H_m(PPh₃) + H_p(PPh₃)); 6.76 (m, 1H, H₅); 0.77 (d sat, 3H, ²J_{Pt-H} = 85.6 Hz, ³J_{P-H} = 7.7 Hz, Pt-CH₃). ³¹P NMR (121.4 MHz, CDCl₃, 298 K, ppm): 33.2 (s sat, J_{Pt-P} = 2312 Hz, PPh₃).

[Pt(pyq-H)(CH₃)(PPh₃)], 8f

To a solution of [Pt(pyq-H)(CH₃)(DMSO)] (**2f**, 95.7 mg, 0.121 mmol, 1 eq) in CH₂Cl₂ (25 mL), PPh₃ (32.0 mg, 0.121 mmol, 1 eq) was added under vigorous stirring. The solution was stirred for 1 h, then concentrated to a small volume and treated with *n*-hexane. The precipitate formed was filtered off and washed with *n*-pentane to give the analytical sample as a yellow solid. Yield 95%. Melting point: 201÷205 °C. Brute formula: C₃₃H₂₇N₂PPt. FW: 677.6446. ¹H NMR (600 MHz, CDCl₃, 298 K, ppm): 8.66 (m sat, 2H, ³J_{Pt-H} = 52.3 Hz, H₄+H₃); 8.05 (d br, 1H, J_{H-H} = 8.8 Hz, H₈); 7.88÷7.84 (m, 2H); 7.84÷7.78 (m, 7H); 7.60 (ddd, 1H, J_{H-H} = 8.5, 6.8, 1.3 Hz, H₅); 7.49÷7.40 (m, 10H); 6.75

(ddd, 1H, $J_{H-H} = 7.3, 5.5, 1.5$ Hz, H_5); 0.89 (d sat, 3H, $^2J_{Pt-H} = 82.7$ Hz, $^3J_{P-H} = 7.8$ Hz, Pt-CH₃). ^1H - ^1H COSY (600 MHz, CDCl₃, 298 K, ppm): 8.66 correlates with signals at 7.86, 6.75; 8.05 correlates with signals at 7.60, 7.45. ^{31}P NMR (242.9 MHz, CDCl₃, 298 K, ppm): 32.4 (s sat, $J_{Pt-P} = 2235$ Hz, PPh₃). ^{195}Pt - ^1H HMQC (600 MHz, CDCl₃, 298 K, ppm): -4177 correlates with signals at 8.66 and 0.89.

[Pt(vpy-H)(CH₃)(PPh₃)], **8g**

The cyclometalation was carried out following the synthesis of [Pt(vpy-H)(CH₃)(DMSO)], **2g**. Then a stoichiometric amount of PPh₃ was added after the solution was cooled to room temperature and left stirring for 1 h. The mixture was then concentrated and treated with *n*-hexane obtaining an orange solid which was filtered, washed with *n*-hexane and vacuum pumped to give the analytical sample. Yield 92%. Melting point: 162 °C. Brute formula: C₂₆H₂₄NPt. FW: 576.5371. ^1H NMR (300 MHz, CDCl₃, 298 K, ppm): 7.90 (t sat, 1H, $^3J_{Pt-H} = 164$ Hz, $J_{H-H} = 8.9$ Hz, H_β); 7.65÷7.32 (m, 19H, $H_4 + H_5 + H_6 + PPh_3 + H_\alpha$); 7.14 (d, 1H, $J_{H-H} = 7.8$ Hz, H_3); 0.80 (d sat, 3H, $^2J_{Pt-H} = 83.9$ Hz, $^3J_{P-H} = 8.1$ Hz Pt-CH₃). ^{31}P NMR (121.4 MHz, CDCl₃, 298 K, ppm): 28.5 (s sat, $J_{Pt-P} = 2020$ Hz, PPh₃). Single crystals of [Pt(vpy-H)(CH₃)(PPh₃)], C₂₆H₂₄NPt, obtained by concentrating the mother liquor, adding Et₂O and storing the solution in freezer for 48 h. A suitable crystal was selected and mounted on a glass fibre using Fromblin oil on an Oxford Diffraction Xcalibur Gemini diffractometer with a Ruby CCD detector. The crystal was kept at 150(2) K. The temperature of the crystal was controlled using the Oxford Cryosystem Cryostream Cobra. The data collection nominally covered over a hemisphere of reciprocal space, by a combination of six sets of exposures with different ϕ angles for the crystal; each 30 s exposure covered 1.0% in ω . The crystal-to-detector distance was 5.5 cm. Crystal decay was found to be negligible by repeating the initial frames at the end of data collection and analyzing the duplicate reflections.

Hydrogen atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameter equal to 1.2 (or 1.5 for methyl H-atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached.

The structure was solved by direct methods using SHELXS (TREF)⁴¹¹ with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Full details in Table 5.4.

[Pt(ppy-H)(CH₃)(PPh₃)], **8I**

Complex **8I** was obtained as **8a** following *Method B*. NMR data were in agreement with those in literature.²⁷³

Single crystals of [Pt(ppy-H)(CH₃)(PPh₃)], C₃₀H₂₆NPt, were grown from a CH₂Cl₂ solution. A suitable crystal was selected and mounted on a glass fibre using Fromblin oil on an Oxford Diffraction Xcalibur Gemini diffractometer with a Ruby CCD detector. The crystal was kept at 150.15 K. The temperature of the crystal was controlled using the Oxford Cryosystem Cobra. The data collection nominally covered over a hemisphere of reciprocal space, by a combination of six sets of exposures with different ω angles for the crystal; each 30 s exposure covered 1.0% in ω . The crystal-to-detector distance was 5.5 cm. Crystal decay was found to be negligible by repeating the initial frames at the end of data collection and analyzing the duplicate reflections.

Hydrogen atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameter equal to 1.2 (or 1.5 for methyl H-atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached.

Using Olex2,⁴¹² the structure was solved with the XS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation.⁴¹³ Full details in Table 5.3.

[Pt(bpy-H)(CH₃)(PCy₃)], **9a**

Method A. To a solution of *cis*-[Pt(CH₃)₂(DMSO)₂] (209.1 mg, 0.548 mmol, 1 eq) in anhydrous toluene was added an excess of bpy (267.4 mg, 1.71 mmol, 3.1 eq) under a nitrogen atmosphere. The solution became suddenly red and was heated to reflux for 3 h.

At the end of the reaction was added 268.3 mg (0.956 mmol, 1.74 eq) of PCy₃ to the hot solution, and the mixture was left to react for about 30 min. The resulting solution was concentrated to a small volume and treated with *n*-pentane. The precipitate that formed was filtered off, washed with *n*-hexane, and vacuum-pumped to give the analytical sample, a vivid yellow solid. Yield: 76%.

Method B. To a solution of [Pt(bpy-H)(CH₃)(DMSO)] (**2a**, 200.0 mg, 0.450 mmol, 1 eq) in acetone (15 mL) were added 141.5 mg of PCy₃ (0.504 mmol, 1.12 eq) under an inert atmosphere. The solution was refluxed for 3 h then concentrated to a small volume and treated with *n*-pentane, the precipitate that formed was filtered off, washed with *n*-hexane, and vacuum-pumped to give the analytical sample. Yield: 51%. Melting point: 229 °C. Brute formula: C₂₉H₄₃N₂PPt. FW: 645.7276. Elemental analysis % calculated for C₂₉H₂₅N₂PPt: C 53.94, H 6.71, N 4.34; found C 54.38, H 6.32, N 4.90. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 8.75 (d sat, 1H, ³J_{Pt-H} = 12.4 Hz, J_{H-H} = 5.6 Hz, H₆); 8.40÷8.33 (m ov, 2H, H₃ + H₆); 8.20 (ddd sat, 1H, ³J_{Pt-H} = 45.2 Hz, ⁴J_{P-H} = 5.1 Hz, J_{H-H} = 7.6, 1.7 Hz, H₄); 7.91 (ddd, 1H, J_{H-H} = 8.4, 5.6, 1.3 Hz, H₄); 7.26÷7.13 (m, 2H, H₅ + H₅); 2.40÷1.20 (m, 33H, PCy₃); 1.00 (d sat, 3H, ²J_{Pt-H} = 84.3 Hz, ³J_{P-H} = 5.5 Hz, Pt-CH₃). ³¹P NMR (121.4 MHz, CDCl₃, 298 K, ppm): 19.3 (s sat, J_{Pt-P} = 2083 Hz, PCy₃).

[Pt(bpy^{6CF₃}-H)(CH₃)(PCy₃)], **9c**

In an NMR tube [Pt(bpy^{6CF₃}-H)(CH₃)(DMSO)] (**2c**) was dissolved in acetone-*d*₆ (1 mL) and an excess of PCy₃ was added. The reaction was followed by ¹H, ¹⁹F and ³¹P NMR. Quantitative yield by NMR criteria. Brute formula: C₃₀H₄₂N₂F₃PPt. FW: 713.7259. ¹H NMR (400 MHz, acetone-*d*₆, 298 K, ppm): 9.03 (d sat, 1H, ³J_{Pt-H} = 14.4 Hz, J_{H-H} = 5.9 Hz, H₆); 8.39 (d, 1H, J_{H-H} = 7.7 Hz, H₃); 8.34 (dd sat, 1H, ³J_{Pt-H} = 44.9 Hz, J_{H-H} = 7.8 Hz, H₄); 8.18 (t, 1H, J_{H-H} = 7.7 Hz, H₄); 7.61 (t, 1H, J_{H-H} = 5.9 Hz, H₅); 7.57 (d sat, 1H, ⁴J_{Pt-H} = 15.0 Hz, J_{H-H} = 7.7 Hz, H₅); 1.93÷1.19 (m, 33H, PCy₃); 0.98 (d sat, 3H, ²J_{Pt-H} = 84.9 Hz, ³J_{P-H} = 5.4 Hz, Pt-CH₃). ³¹P NMR (161.9 MHz, acetone-*d*₆, 298 K, ppm): 28.8 (s sat, J_{Pt-P} = 2164 Hz, PCy₃). ¹⁹F NMR (376.4 MHz, acetone-*d*₆, 298 K, ppm): -67.8 (s, CF₃).

[Pt(pyq-H)(CH₃)(PCy₃)], 9f

In inert atmosphere to a solution of *cis*-[Pt(CH₃)₂(DMSO)₂] (220.1 mg, 0.577 mmol, 1 eq) in acetone (15 mL), pyq (119.2 mg, 0.578 mmol, 1 eq) was added under vigorous stirring. The solution was heated to reflux and stirred for 4 h, then under inert gas flow were added 173 mg of PCy₃ (0.616 mmol, 1.07 eq). The mixture was concentrated to a small volume and treated with Et₂O. The precipitate formed was filtered off and washed with Et₂O to give the analytical sample as a yellow solid. Yield 92%. Melting point: 225 °C. Brute formula: C₃₃H₄₅N₂Pt. FW: 695.7875. Elemental analysis % calculated for C₃₃H₄₅N₂Pt: C 56.97, H 6.52, N 4.03; found C 56.95, H 5.94, N 4.04. ¹H NMR (600 MHz, acetone-*d*₆, 298 K, ppm): 9.08 (d sat, 1H, ³J_{Pt-H} = 12.8 Hz, J_{H-H} = 5.6 Hz, H₆); 8.67 (dd, 1H, J_{H-H} = 8.0, 1.3 Hz, H₃); 8.53 (d sat, 1H, ³J_{Pt-H} = 48.4 Hz, ⁴J_{P-H} = 5.6 Hz, H₄); 8.20 (td, 1H, J_{H-H} = 7.9, 1.4 Hz, H₄); 7.96 (d, 1H, J_{H-H} = 8.3 Hz, H₅ or H₈); 7.84 (d, 1H, J_{H-H} = 8.3 Hz, H₈ or H₅); 7.62÷7.56 (m, 2H, H₅ + H₆ or H₇); 7.46 (ddd, 1H, J_{H-H} = 8.0, 6.8, 1.0 Hz, H₇ or H₆); 2.55÷1.25 (m, 33H, Cy); 1.06 (d sat, 3H, ²J_{Pt-H} = 85.7 Hz, ³J_{P-H} = 5.6 Hz, Pt-CH₃). ¹H-¹H COSY (600 MHz, acetone-*d*₆, 298 K, ppm): 9.08 correlates with signals at 7.61, 8.20, 8.67; 7.46 correlates with signal at 7.84; 7.58 with signal at 7.96; signal at 8.53 doesn't show any correlation. ³¹P NMR (242.9 MHz, acetone-*d*₆, 298 K, ppm): 23.9 (s sat, J_{Pt-P} = 2126 Hz, PCy₃). ¹⁹⁵Pt-¹H HMQC (600 MHz, acetone-*d*₆, 298 K, ppm): -4036 (d, J_{Pt-P} ≈ 2320) correlates with signals at 9.08, 8.53 and 1.06.

[Pt(vpy-H)(CH₃)(PCy₃)], 9g

To a solution of *cis*-[Pt(CH₃)₂(DMSO)₂] (106.0 mg, 0.278 mmol, 1 eq) in anhydrous toluene was added an excess of vpy (90 μL, 0.836 mmol, 3 eq) under a nitrogen atmosphere. The solution became suddenly red and was heated to 80 °C for 2 h. At the end of the reaction the mixture was cooled to room temperature and was added a stoichiometric amount of PCy₃; the mixture was left to react for about 30 min. The resulting solution was evaporated to dryness. Brute formula: C₂₆H₄₂NP₂Pt. FW: 594.6800. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 8.46 (d sat, 1H, ³J_{Pt-H} = 17.1 Hz, J_{H-H} = 5.2 Hz, H₆); 7.62 (m, 1H, H₄); 7.11 (t sat, 1H, ²J_{Pt-H} = 105 Hz, ³J_{P-H} = 7.9 Hz, H_α); 6.90 (m, 1H, H₅); 2.00÷1.00 (m, 33H, PCy₃); 1.04 (d sat, 3H, ²J_{Pt-H} = 84.9 Hz, ³J_{P-H} = 6.0 Hz, Pt-CH₃). ³¹P

NMR (121.4 MHz, CDCl₃, 298 K, ppm): 26.2 (s sat, $J_{\text{Pt-P}} = 1875$ Hz, PCy₃).

[Pt(bpy-H)(CH₃)(P(OPh)₃)], 10a

To a solution of *cis*-[Pt(CH₃)₂(DMSO)₂] (103.0 mg, 0.270 mmol, 1 eq) in anhydrous toluene was added an excess of bpy (123.5 mg, 0.791 mmol, 2.93 eq) under a nitrogen atmosphere. The solution became suddenly red and was heated to reflux for 3 h. At the end of the reaction was added to the hot solution 92 µL (0.351 mmol, 1.3 eq) of P(OPh)₃, and the mixture was left to react for about 30 min. The resulting solution was evaporated to dryness and treated with *n*-pentane to obtain a pale yellow solid, which was filtered on a Hirsch funnel, washed with *n*-pentane, and vacuum-pumped to give the analytical sample. Yield: 78%. Melting point: 90÷95 °C. Brute formula: C₂₉H₂₅N₂O₃PPt. FW: 675.5829. Elemental analysis % calculated for C₂₉H₂₅N₂PPt: C 51.56, H 3.73, N 4.15; found C 52.02, H 3.49, N 3.62. ¹H NMR (600 MHz, CDCl₃, 298 K, ppm): 9.41 (d br sat, 1H, $^3J_{\text{Pt-H}} = 15.9$ Hz, $J_{\text{H-H}} = 5.6$ Hz, H₆); 8.32 (m, 1H, H₃); 8.31 (m, 1H, H₆); 8.13 (td, 1H, $J_{\text{H-H}} = 7.6, 1.6$ Hz, H₄); 7.93 (ddd sat, 1H, $^3J_{\text{Pt-H}} = 42.3$ Hz, $J_{\text{H-H}} = 7.3, 5.6, 1.6$ Hz, H₄); 7.52 (ddd, 1H, $J_{\text{H-H}} = 7.3, 5.6, 1.6$ Hz, H₅); 7.45 (m, 6H, H_o(PPh₃)); 7.35 (m, 6H, H_m(PPh₃)); 7.19÷7.15 (m, 4H, H₅ + H_p(PPh₃)); 0.83 (d sat, 3H, $^2J_{\text{Pt-H}} = 84.4$ Hz, $^3J_{\text{H-H}} = 7.2$ Hz, Pt-CH₃). ¹H-¹H COSY (600 MHz, CDCl₃, 298 K, ppm): 9.41 correlates with signals at 7.52, 8.13, 8.32; 7.93 correlates with signals at 7.17, 8.31. ³¹P NMR (121.4 MHz, CDCl₃, 298 K, ppm): 118.0 (s sat, $J_{\text{Pt-P}} = 3848$ Hz, P(OPh)₃). ¹⁹⁵Pt-¹H HMQC (600 MHz, CDCl₃, 298 K, ppm): -4233 (d, $J_{\text{Pt-P}} \approx 3995$) correlates with signals at 9.41, 7.93, 0.83.

[Pt(bpy-H)(CH₃)(P(*p*-tol)₃)], 11a

To a solution of *cis*-[Pt(CH₃)₂(DMSO)₂] (66.2 mg, 0.174 mmol, 1 eq) in anhydrous toluene was added an excess of bpy (57.3 mg, 0.367 mmol, 2.1 eq) under a nitrogen atmosphere. The solution became suddenly red and was heated to reflux for 3 h; then 69.0 mg (0.227 mmol, 1.3 eq) of P(*p*-tol)₃ was added to the hot solution and left to react for about 1 h. Complex was extracted with water (3 × 10 mL), and the aqueous phase was back-extracted with CH₂Cl₂ (2 × 5 mL). All the organic phases were then mixed together

and treated with Na_2SO_4 for 15 min with stirring, filtered, concentrated to a small volume, and then treated with *n*-hexane to give a vivid yellow precipitate that was filtered off and vacuum-dried. Yield: 50%. Brute formula: $\text{C}_{32}\text{H}_{31}\text{N}_2\text{Pt}$. FW: 669.6654. Elemental analysis % calculated for $\text{C}_{32}\text{H}_{31}\text{N}_2\text{Pt}$: C 57.39, H 4.66, N 4.18; found C 57.22, H 4.85, N 4.03. ^1H NMR (400 MHz, CD_2Cl_2 , 298 K, ppm): 8.38 (d br, 1H, $J_{\text{H-H}} = 4.9$ Hz, H_6); 8.33 (dd, 1H, $J_{\text{H-H}} = 8.2, 1.3$ Hz, H_3); 8.18 (ddd sat, 1H, $^3J_{\text{Pt-H}} = 48$ Hz, $^4J_{\text{P-H}} = 5.4$ Hz, $J_{\text{H-H}} = 7.6, 1.6$ Hz, H_4); 7.86–7.79 (m, 2H, $\text{H}_4 + \text{H}_5$); 7.64 (dd, 6H, $^3J_{\text{P-H}} = 10.2$ Hz, $J_{\text{H-H}} = 8.1$ Hz, $\text{H}_6(\text{P}(p\text{-tol})_3)$); 7.24 (d br, 7H, $J_{\text{H-H}} = 8.3$ Hz, $\text{H}_6 + \text{H}_m(\text{P}(p\text{-tol})_3)$); 6.73 (ddd, 1H, $J_{\text{H-H}} = 7.2, 5.8, 1.5$ Hz, H_5); 2.41 (s, 9H, $\text{CH}_3(\text{P}(p\text{-tol})_3)$); 0.66 (d sat, 3H, $^2J_{\text{Pt-H}} = 84$ Hz, $^3J_{\text{P-H}} = 7.7$ Hz, Pt-CH_3). ^{31}P NMR (161.9 MHz, CD_2Cl_2 , 298 K, ppm): 30.0 (s sat, $J_{\text{Pt-P}} = 2245$ Hz, $\text{P}(p\text{-tol})_3$).

[Pt(ppy-H)(CH₃)(P(*p*-tol)₃)], **11l**

Complex **11l** was obtained as **11a**. Single crystals of [Pt(ppy-H)(CH₃)(P(*p*-tol)₃)], $\text{C}_{33}\text{H}_{32}\text{N}_2\text{Pt}$, were grown from a CH_2Cl_2 solution. A suitable crystal was selected and mounted on a glass fibre using Fromblin oil on an Oxford Diffraction Xcalibur Gemini diffractometer with a Ruby CCD detector. The crystal was kept at 150(1) K during data collection. Using Olex2,⁴¹² the structure was solved with the XS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation.⁴¹³ Full details in Table 5.5.

[Pt(bpy-H)(CH₃)(κ¹-dppm)], **12a**

Method A. To a solution of [Pt(bpy-H)(CH₃)(DMSO)] (**2a**, 61.0 mg, 0.138 mmol, 1 eq) in CH_2Cl_2 (10 mL) was added 65.8 mg of dppm (0.171 mmol, 1.24 eq) under a nitrogen atmosphere. The solution was stirred for 2 h then was concentrated to a small volume and treated with Et_2O obtaining a yellow solid. Yield: 54%.

Method B. To a solution of *cis*-[Pt(CH₃)₂(DMSO)₂] (212.3 mg, 0.557 mmol, 1 eq) in anhydrous toluene an excess of bpy (171.6 mg, 1.099 mmol, 1.97 eq) was added under a nitrogen atmosphere. The solution became suddenly red and was heated to reflux for 3 h. At the end of the reaction dppm (237.8 mg, 0.619 mmol, 1.11 eq) was added after cooling

the solution to room temperature and left to react for about 1 hour; then the solution was concentrated to a small volume and treated with Et₂O to form a precipitate. The solid was filtered off, washed with Et₂O, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 60%. Melting point: 174÷180 °C. Brute formula: C₃₆H₃₂N₂P₂Pt. FW: 749.6911. Elemental analysis % calculated for C₃₆H₃₂N₂P₂Pt·½H₂O: C 56.99, H 4.38, N 3.69; found C 57.16, H 4.24, N 3.77. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 8.39 (d br, 1H, H₆); 8.24 (d, 1H, J_{H-H} = 7.8 Hz, H₃); 8.16 (m sat, 1H, ³J_{Pt-H} = 48 Hz, H₄); 7.84 (m, 4H, H_o(Ph-P-Pt)); 7.74 (td, 1H, H₄); 7.62 (d sat, 1H, ³J_{Pt-H} = n.r., J_{H-H} = 5.5 Hz, H₆); 7.42÷7.10 (m, 17H, PPh₂ + H₅); 6.65 (ddd, 1H, J_{H-H} = 7.1, 5.6, 1.5 Hz, H₅); 3.42 (m, 2H, CH₂); 0.79 (d sat, 3H, ²J_{Pt-H} = 83.4 Hz, ³J_{PA-H} = 7.9 Hz, Pt-CH₃). ³¹P NMR (121.4 MHz, CDCl₃, 298 K, ppm): 19.7 (d sat, J_{Pt-PA} = 2209.5 Hz, ²J_{PA-PB} = 78.6 Hz, Pt-PPh₂); -24.8 (d sat, ³J_{Pt-PB} = 57.2 Hz, ²J_{PA-PB} = 78.6 Hz, PPh₂).

[Pt(vpy-H)(Ph)(PPh₃)], **13g**

To a solution of [Pt(vpy-H)(Ph)(DMSO)] (**4g**, 36.0 mg, 0.079 mmol, 1 eq) in 10 mL of CH₂Cl₂ a 10% excess of PPh₃ was added (23.0 mg, 0.088 mmol, 1.1 eq). The mixture was stirred for 3 h at room temperature then evaporated to dryness. Yield 67%. Melting point: 154 °C. Brute formula: C₃₁H₂₆NPt. FW: 638.6079. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 7.79 (td, 1H, J_{H-H} = 7.7, 1.5 Hz, H₄); 7.70÷7.20 (m, 21H, PPh₃ + H₃ + H₆ + H_α + H_β + H_m(Ph)); 7.01 (d sat, 1H, ³J_{Pt-H} = 70.1 Hz, J_{H-H} = 6.3 Hz, H_o(Ph)); 6.60 (m, 2H); 6.43 (td, 1H, J_{H-H} = 5.7, 1.5 Hz, H₅). ³¹P NMR (121.4 MHz, CDCl₃, 298 K, ppm): 31.5 (s sat, J_{Pt-P} = 1990 Hz, PPh₃).

[Pt(pyq-H)(Ph)(PCy₃)], **14f**

In inert atmosphere 90.0 mg (0.321 mmol, 1.15 eq) of PCy₃ were solubilized in refluxing acetone then added to an acetone solution (20 mL) of [Pt(pyq-H)(Ph)(DMSO)] (**4f**, 146.6 mg, 0.278 mmol, 1 eq) and the reflux was kept for 3 h. The mixture was concentrated to a small volume after cooling to room temperature, then treatment with *n*-hexane afforded the product. Yield 41%. Melting point: 200÷210 °C. Brute formula: C₃₈H₄₇N₂PPt. FW: 757.8584. Elemental analysis % calculated for C₃₈H₄₇N₂PPt: C 60.22, H 6.25, N 3.70;

found C 60.00, H 6.15, N 3.50. ^1H NMR (300 MHz, CDCl_3 , 298 K, ppm): 8.79 (d, 1H, $J_{\text{H-H}} = 5.8$ Hz, H_6); 8.72 (d, 1H, $J_{\text{H-H}} = 7.9$ Hz); 8.00 (dd, 1H, $J_{\text{H-H}} = 7.9, 7.5$ Hz, H_4); 7.93 (d, 1H, $J_{\text{H-H}} = 7.9$ Hz, H_8); 7.53–7.29 (m, 6H); 7.17 (d, 1H, $J_{\text{H-H}} = 5.9$ Hz); 7.05–6.91 (m, 3H); 2.17–0.90 (m, 33H, Cy). ^{31}P NMR (121.4 MHz, CDCl_3 , 298 K, ppm): 22.9 (s, $J_{\text{Pt-P}} = 1995$ Hz, PCy_3).

[Pt(vpy-H)(Ph)(PCy₃)], **14g**

The cyclometalation was carried out following the synthesis of [Pt(vpy-H)(Ph)(DMSO)], **4g**. Then a 10% excess of PCy_3 was added after the solution was cooled to room temperature and left stirring for 2 h. The solution was then evaporated to dryness. Yield 75%. Melting point: 147 °C. Brute formula: $\text{C}_{31}\text{H}_{44}\text{NPt}$. FW: 656.7509. ^1H NMR (300 MHz, CDCl_3 , 298 K, ppm): 8.43 (d sat, 1H, $^3J_{\text{Pt-H}} = 17$ Hz, $J_{\text{H-H}} = 5.4$ Hz, H_6); 7.59 (td, 1H, $J_{\text{H-H}} = 7.6, 1.3$ Hz, H_4); 7.33 (m, 1H, H_α); 7.01 (d, 1H, $J_{\text{H-H}} = 7.6$ Hz, H_3); 6.90 (m, 1H, H_5); 6.71 (m, 1H, H_β); 2.00–0.90 (m, 33H, PCy_3). ^{31}P NMR (121.4 MHz, CDCl_3 , 298 K, ppm): 24.1 (s sat, $J_{\text{Pt-P}} = 1843$ Hz, PCy_3).

Single crystals of [Pt(vpy-H)(Ph)(PCy₃)], $\text{C}_{31}\text{H}_{44}\text{NPt}$, were grown from a CH_2Cl_2 solution. A suitable crystal was selected and mounted on a glass fibre using Fromblin oil on an Oxford Diffraction Xcalibur Gemini diffractometer with a Ruby CCD detector. The crystal was kept at 150(2) K. The temperature of the crystal was controlled using the Oxford Cryosystem Cryostream Cobra. The data collection nominally covered over a hemisphere of reciprocal space, by a combination of twelve sets of exposures with different θ angles for the crystal; each 12 s exposure at low angle and 48 s exposure at high angle covered 1.0% in

ω. The crystal-to-detector distance was 5.5 cm. Crystal decay was found to be negligible by repeating the initial frames at the end of data collection and analyzing the duplicate reflections.

Hydrogen atoms were added at calculated positions and refined using a riding model except the H_β on the vinyl which was located in a difference map. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of the atom to which they are attached.

H_β was located in a difference map. Its position was allowed to refine freely but was given an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of the atom to which it was attached.

The structure was solved by direct methods using SHELXS (TREF)⁴¹¹ with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Full details in Table 5.6.

[Pt(bpy-H)(CH₃)(κ^2 -dppe)], **15a**

To a solution of [Pt(bpy-H)(CH₃)(DMSO)] (**2a**, 46.1 mg, 0.106 mmol, 1 eq) in CH₂Cl₂ (15 mL) was added 51.3 mg of dppe (0.129 mmol, 1.22 eq). The solution was stirred for 2 h then was concentrated to a small volume and treated with Et₂O obtaining a yellow solid. Yield: 43%. Melting point: 198 °C. Brute formula: C₃₇H₃₄N₂P₂Pt. FW: 763.7180. Elemental analysis % calculated for C₃₇H₃₄N₂P₂Pt: C 58.19, H 4.49, N 3.67; found C 58.34, H 4.43, N 2.86. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 8.35 (m, 1H); 8.22 (m, 1H); 7.95 (m, 1H); 7.84÷7.76 (m, 2H); 7.62÷7.28 (m, 17 H); 7.18 (m, 1 H); 7.06÷6.96 (m, 2H); 6.84÷6.68 (m, 2H); 2.50÷1.90 (m, 4H, CH₂(dppe)); 0.47 (dd sat, 3H, ²J_{Pt-H} = 70.6 Hz, ³J_{H-H} = 7.0 Hz, Pt-CH₃). ³¹P NMR (121.4 MHz, CDCl₃, 298 K, ppm): 44.7 (s sat, J_{Pt-P_A} = 1953 Hz, P_A); 43.3 (s sat, J_{Pt-P_B} = 1814 Hz, P_B).

[Pt(bpy-H)(Cl)(DMSO)], **16a**

Method A. To a solution of [Pt(bpy-H)(CH₃)(DMSO)] (**2a**, 200.0 mg, 0.451 mmol, 1 eq) in acetone (20 mL) aqueous HCl 0.1 M was added (4.5 mL, 0.451 mmol, 1 eq) and 2 mL of DMSO. After 8 h the mixture was concentrated to a small volume, extracted with CH₂Cl₂ (3 × 8 mL) and the organic phase treated with Na₂SO₄ and filtered. Reduction to a small volume and treatment with *n*-hexane led to the product as a yellow solid. Yield 70%.

Method B. To a solution of [Pt(bpy-H)(CH₃)(DMSO)] (**2a**, 73.2 mg, 0.165 mmol, 1 eq) in acetone (20 mL) LiCl was added (23.4 mg, 0.552 mmol, 3.34 eq) and 68.1 mg of [H₃O · 18-crown-6][BF₄] (0.184 mmol, 1.12 eq). The mixture changes colour from yel-

low to red and then back to yellow. After 1 h the mixture is concentrated to a small volume and treated with Et₂O to obtain a yellow solid which is filtered. Yield 87%.

Method C. To a solution of [Pt(bpy-H)(CH₃)(DMSO)] (**2a**, 63.7 mg, 0.144 mmol, 1 eq) in acetone (20 mL) NH₄Cl was added (13.5 mg, 0.252 mmol, 1.75 eq). The mixture was left stirring for 14 h at room temperature then it was concentrated to a small volume and treated with Et₂O and the yellow solid obtained was filtered. Yield 71%. Melting point: 142 °C. Brute formula: C₁₂H₁₃N₂OSClPt. FW: 463.8468. Elemental analysis % calculated for C₁₃H₁₆N₂OSPt: C 31.05, H 3.14, N 5.66; found C 31.41, H 2.89, N 5.86. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 9.59 (dd, 1H, ³J_{Pt-H} = 36 Hz, J_{H-H} = 5.8, 1.6, 0.8 Hz, H_{6'}); 8.60 (dd, 1H, ³J_{Pt-H} = 42 Hz, J_{H-H} = 8.0, 1.5 Hz, H₄); 8.37 (dd, 1H, J_{H-H} = 4.5, 1.5 Hz, H₆); 8.22 (d br, 1H, J_{H-H} = 7.7 Hz, H_{3'}); 7.98 (td, 1H, J_{H-H} = 7.7, 1.6 Hz, H_{4'}); 7.40 (ddd, 1H, J_{H-H} = 7.7, 5.8, 1.6 Hz, H₅); 7.08 (dd, 1H, ⁴J_{Pt-H} = 16.5 Hz, J_{extH-H} = 4.5, 8.0 Hz, H₅); 3.65 (s, 6H, ³J_{Pt-H} = 24.2 Hz, CH₃(DMSO)).

[Pt(pyq-H)(Cl)(DMSO)], **16f**

To a solution of complex [Pt(pyq-H)(CH₃)(DMSO)] (**2f**, 100 mg, 0.203 mmol, 1 eq) in acetone (25 mL), 2.0 mL of HCl 0.1 M (0.203 mmol, 1 eq) and 0.2 mL of DMSO (2.8 mmol, 13.8 eq) were added under vigorous stirring. The mixture was stirred for 8 h, then was extracted with CH₂Cl₂ (3 × 10 mL), dried with Na₂SO₄, filtered, and concentrated to a small volume. Addition of *n*-pentane produced a precipitate that was filtered off, washed with *n*-pentane and vacuum pumped to give the analytical sample as a yellow solid. Yield 65%. Melting point: decompose at 150 °C. Brute formula: C₁₆H₁₅N₂OSClPt. FW: 493.4888. Elemental analysis % calculated for C₁₆H₁₅N₂OSClPt: C 37.39, H 2.94, N 5.45; found C 37.03, H 2.71, N 5.07. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 9.71 (d sat, 1H, J_{H-H} = 4.8 Hz, ³J_{Pt-H} = 33.3 Hz, H_{6'}); 9.02 (s sat, 1H, ³J_{Pt-H} = 46.3 Hz, H₄); 8.55 (d, 1H, J_{H-H} = 8.3 Hz, H_{3'}); 8.05 (t, 1H, J_{H-H} = 7.8 Hz, H_{4'}); 8.00 (d, 1H, J_{H-H} = 7.8 Hz, H₈); 7.81 (d, 1H, J_{H-H} = 8.3 Hz, H₅); 7.63 (m, 1H, H₇); 7.48 (m, 2H, H₅+H₆); 3.71 (s sat, 6H, ³J_{Pt-H} = 24.0 Hz, CH₃(DMSO)).

[Pt(vpy-H)(Cl)(DMSO)], 16g

Method A. The cyclometalation was carried out following the synthesis of [Pt(vpy-H)-(CH₃)(DMSO)], **2g**. Then a stoichiometric amount of aqueous HCl 0.1 M dissolved in acetone was added after the solution was cooled to room temperature and left stirring for 1 h. The mixture was then concentrated and extracted with CH₂Cl₂ (3 × 10 mL), the organic phase was treated with Na₂SO₄, filtered and concentrated to a small volume. Treatment with *n*-hexane gave an orange solid which was filtered, washed with *n*-hexane and vacuum pumped to give the analytical sample. Yield 90%.

Method B. 300 µL (2.85 mmol, 1.2 eq) of vpy were added, under N₂, to a solution of *cis*-[Pt(Cl)₂(DMSO)₂] (980 mg, 2.32 mmol, 1 eq) in anhydrous toluene. The mixture was heated to 80 °C for 2 h then concentrated and treated with *n*-hexane.

Method C. 49 µL (0.456 mmol, 1.1 eq) of vpy were added, under N₂, to a solution of *trans*-[Pt(CH₃)(Cl)(DMSO)₂] (165 mg, 0.411 mmol, 1 eq) in distilled acetone. The yellow solution is heated to reflux for 6 h, during this period the colour changes to orange. The mixture is concentrated to small volume and upon treatment with *n*-hexane a precipitate is obtained which is filtered and washed with Et₂O. Yield 90%. Melting point: 124 °C. Brute formula: C₉H₁₂NOSClPt. FW: 412.7991. Elemental analysis: expected C 26.19%, H 2.93%, N 3.39%; found C 26.32%, H 2.68%, N 3.29%. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 9.10 (d sat, 1H, ³J_{Pt-H} = 35 Hz, J_{H-H} = 5.8 Hz, H₆); 7.75 (t, 1H, J_{H-H} = 7.7 Hz, H₄); 7.26 (d sat, 1H, ³J_{Pt-H} = 84 Hz, J_{H-H} = 7.5 Hz, H_α); 7.16 (m, 2H, H₅ + H₃); 6.65 (d sat, 1H, ³J_{Pt-H} = 97.2 Hz, J_{H-H} = 7.5 Hz, H_β); 3.54 (s sat, 6H, ³J_{Pt-H} = 25.6 Hz, CH₃(DMSO)).

[Pt(bpy-H)(κ²-dppe)][BF₄], 17a

Method A. To a solution of [Pt(bpy*)(CH₃)(DMSO)][BF₄] (**34a**, 39.4 mg, 0.074 mmol, 1 eq) in CH₂Cl₂ (15 mL) was added 29.4 mg of dppe (0.074 mmol, 1 eq). The solution was stirred for 80 min then was concentrated to a small volume and treated with Et₂O obtaining a white solid. Yield: 37%.

Method B. To a solution of [Pt(bpy-H)(CH₃)(dppe)] (**15a**, 32.0 mg, 0.042 mmol, 1 eq) in acetone (15 mL) was added 20.6 mg of [H₃O · 18-crown-6][BF₄] (0.052 mmol, 1.24

eq). The solution was stirred for 80 min and two colour changes were observed from yellow to red and back to yellow. The mixture was concentrated to a small volume and treated with Et₂O obtaining a white solid. Yield: 80%. Melting point: 162 °C. Brute formula: C₃₆H₃₁BN₂F₄P₂Pt. FW: 835.4878. Elemental analysis % calculated for C₃₆H₃₁BN₂F₄P₂Pt: C 51.75, H 3.74, N 3.35; found C 48.05, H 3.19, N 2.57. ¹H NMR (300 MHz, CD₂Cl₂, 298 K, ppm): 8.39 (br, 1H); 8.34 (br, 1H); 8.17 (br, 1H); 7.98 (br, 1H); 7.82 (br, 6H); 7.58 (br, 10H); 7.30 (br, 1H); 7.08 (br, 1H); 6.73 (br, 1H); 2.57 (br, 1H). ³¹P NMR (121.4 MHz, CDCl₃, 298 K, ppm): 51.8 (s sat, J_{Pt-PA} = 1949 Hz, P_A); 42.6 (s sat, J_{Pt-PB} = 3691 Hz, P_B).

[Pt(ppy^{4F}-H)(κ²-dppe)][BF₄], 17k

To a solution of *cis*-[Pt(Cl)₂(DMSO)₂] (15.4 mg, 0.036 mmol, 1 eq) in acetic acid (8 mL) was added the ppy^{4F} (11.0 mg, 0.064 mmol, 1.7 eq) obtaining a suspension that was heated at 80°C overnight. After 2 h the reaction mixture became a yellow solution. The solution cooled down to room temperature and dppe was added (31.8 mg, 0.080 mmol, 2.2 eq) under stirring. After 1 h the reaction mixture was evaporated to dryness and the yellow residue was dissolved in CH₂Cl₂, washed with aqueous HCl 0.1 M (2 × 10 mL) and distilled water (2 × 10 mL). Aqueous washings were back-extracted with CH₂Cl₂ (2 × 10 mL) and all the organic fractions collected and treated with Na₂SO₄ under vigorous stirring. Filtration and evaporation to dryness yield a very pale yellow solid that was solubilized in acetone and treated with AgBF₄ under stirring and in the dark for 2 h. The solution was then concentrated to small volume and CH₂Cl₂ was added. The mixture was then washed with distilled H₂O, concentrated and treated with Et₂O obtaining a pale yellow solid. Brute formula: C₃₇H₃₁BNF₅P₂Pt. FW: 852.4904. Selected NMR signals: ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 8.16 (t br sat, 1H, ³J_{Pt-H} = 30 Hz, J_{H-H} = 4.3 Hz, H₆); 6.87 (t, 1H, J_{H-H} = 5.9 Hz); 6.79 (td, 1H, J_{H-H} = 8.5, 2.4 Hz); 6.64 (m sat, 1H, ³J_{Pt-H} = 47 Hz, H_{3'}); 2.77÷2.36 (m, 4H, CH₂CH₂). ³¹P NMR (121.4 MHz, 298 K, ppm): 50.2 (d sat, 1P, J_{Pt-P} = 1894 Hz, ⁵J_{P-F} = 5.2 Hz, PPh₂ *trans* C); 40.7 (s sat, 1P, J_{Pt-P} = 3706 Hz, PPh₂ *trans* N); ¹⁹F NMR (282.3 MHz, CCl₃F, 298 K, ppm): -108.9 (d sat, 1F, ⁴J_{Pt-F} = 40.3 Hz, ⁵J_{P-F} = 5.1 Hz, ppy^{4F}); -154.0 (s, 4F, BF₄⁻). ESI-MS (*m/z*): found 765.1559 (M-BF₄)⁺, calcd for C₃₇H₃₁NFP₂Pt 765.6858.

[Pt(ppy-H)(κ^2 -dppe)][BF₄], 17I

To a solution of *cis*-[Pt(Cl)₂(DMSO)₂] (13.4 mg, 0.032 mmol, 1 eq) in acetic acid (8 mL) was added the ppy (10.4 mg, 0.067 mmol, 2.1 eq) obtaining a suspension that was heated at 80°C overnight. After 2 h the reaction mixture became a yellow solution. The solution cooled down to room temperature and dppe was added (25.9 mg, 0.065 mmol, 2.0 eq) under stirring. After 1 h the reaction mixture was evaporated to dryness and the yellow residue was dissolved in CH₂Cl₂, washed with aqueous HCl 0.1 M (2 × 10 mL) and distilled water (2 × 10 mL). Aqueous washings were back-extracted with CH₂Cl₂ (2 × 10 mL) and all the organic fractions collected and treated with Na₂SO₄ under vigorous stirring. Filtration and evaporation to dryness yield a very pale yellow solid that was solubilized in acetone and treated with AgBF₄ under stirring and in the dark for 2 h. The solution was then concentrated to small volume and CH₂Cl₂ was added. The mixture was then washed with distilled H₂O, concentrated and treated with Et₂O obtaining a pale yellow solid. Brute formula: C₃₇H₃₂BNF₄P₂Pt. FW: 834.5000. Selected NMR signals: ¹H NMR (400 MHz, CDCl₃, 298 K, ppm): 8.21 (t br sat, 1H, ³J_{Pt-H} = 27 Hz, J_{H-H} = 5.5 Hz, H₆); 7.13 (t, 1H, J_{H-H} = 7.5 Hz); 7.03 (td sat, 1H, J_{H-H} = 6.8, 3.3 Hz, ³J_{Pt-H} = 43 Hz, H_{3'}); 6.91 (t br, 1H, J_{H-H} = 6.4 Hz); 6.81 (t br, 1H, J_{H-H} = 7.4 Hz); 2.76÷2.38 (m, 4H, CH₂CH₂). ³¹P NMR (121.4 MHz, 298 K, ppm): 50.5 (s sat, 1P, J_{Pt-P} = 1832 Hz, PPh₂ *trans* C); 40.8 (s sat, 1P, J_{Pt-P} = 3766 Hz, PPh₂ *trans* N). ESI-MS (*m/z*): found 747.1661 (M-BF₄)⁺, calcd for C₃₇H₃₂NP₂Pt 747.6953.

[Pt(bpy-H)(dppm)][BF₄], 18a

Method A. To a solution of [Pt(bpy-H)(CH₃)(dppm)] (**12a**, 104.8 mg, 0.140 mmol, 1 eq) in acetone (15 mL) was added 101.3 mg of [H₃O · 18-crown-6][BF₄] (0.274 mmol, 1.96 eq). The solution was stirred for 1 h then was concentrated to a small volume and treated with Et₂O obtaining a white solid. Yield: 95%.

Method B. To a solution of [Pt(bpy*)(CH₃)(DMSO)][BF₄] (**34a**, 219.8 mg, 0.414 mmol, 1 eq) in acetone (15 mL) was added 150.7 mg of dppm (0.392 mmol, 0.95 eq). The solution was stirred for 1 h then was concentrated to a small volume and treated with Et₂O obtaining a white solid. Yield: 89%. Brute formula: C₃₅H₂₉BN₂F₄P₂Pt. FW:

821.4609. ^1H NMR (300 MHz, CDCl_3 , 298 K, ppm): 8.59 (m, 2H); 8.44 (t, 1H); 8.27 (t, 1H); 7.88÷7.72 (m, 9H); 7.62÷7.48 (m, 13H); 7.36 (t, 1H); 4.91 (t, 2H, $^2J_{\text{P-H}} = 10.8$ Hz, $^3J_{\text{P-H}} = \text{n.r.}$, CH_2). ^{31}P NMR (121.4 MHz, CDCl_3 , 298 K, ppm): -30.4 (d sat, $J_{\text{Pt-P}_A} = 1582$ Hz, $^2J_{\text{P}_A-\text{P}_B} = 50.7$ Hz, P_A); -36.9 (d sat, $J_{\text{Pt-P}_B} = 3186$ Hz, $^2J_{\text{P}_A-\text{P}_B} = 51.1$ Hz, P_B).

[Pt(ppy^{4F}-H)(κ^2 -dppm)][BF₄], 18k

To a solution of *cis*-[Pt(Cl)₂(DMSO)₂] (23.9 mg, 0.057 mmol, 1 eq) in acetic acid (8 mL) was added the ppy^{4F} (16.2 mg, 0.093 mmol, 1.6 eq) obtaining a suspension that was heated at 80°C overnight. After 2 h the reaction mixture became a yellow solution. The solution cooled down to room temperature and dppm was added (41.9 mg, 0.109 mmol, 1.9 eq) under stirring. After 1 h the reaction mixture was evaporated to dryness and the yellow residue was dissolved in CH_2Cl_2 , washed with aqueous HCl 0.1 M (2×10 mL) and distilled water (2×10 mL). Aqueous washings were back-extracted with CH_2Cl_2 (2×10 mL) and all the organic fractions collected and treated with Na_2SO_4 under vigorous stirring. Filtration and evaporation to dryness yield a very pale yellow solid that was solubilized in acetone and treated with AgBF_4 under stirring and in the dark for 2 h. The solution was then concentrated to small volume and CH_2Cl_2 was added. The mixture was then washed with distilled H_2O , concentrated and treated with Et_2O obtaining a pale yellow solid. Brute formula: $\text{C}_{36}\text{H}_{29}\text{BNF}_5\text{P}_2\text{Pt}$. FW: 824.4568. Selected NMR signals: ^1H NMR (400 MHz, CDCl_3 , 298 K, ppm): 8.33 (m sat, 1H, $^3J_{\text{Pt-H}} = \text{n.r.}$, H_6); 8.08 (td, 1H, $J_{\text{H-H}} = 8.2, 1.3$ Hz); 7.94 (d br, 1H, $J_{\text{H-H}} = 8.4$ Hz); 6.84 (td, 1H, $J_{\text{H-H}} = 8.7, 2.5$ Hz); 6.65 (tdd sat, 1H, $^3J_{\text{Pt-H}} = 52$ Hz, $J_{\text{H-H}} = 8.7, 4.0, 2.6$ Hz, $\text{H}_{3'}$); 4.76 (t sat, 2H, $^3J_{\text{Pt-H}} = \text{n.r.}$, $^2J_{\text{P-H}} = 10.7$ Hz, CH_2). ^{31}P NMR (121.4 MHz, 298 K, ppm): -28.4 (dd sat, 1P, $J_{\text{Pt-P}} = 1461$ Hz, $^2J_{\text{P-P}} = 41.3$ Hz, $^5J_{\text{P-F}} = 5.7$ Hz, PPh_2 *trans* C); -35.9 (d sat, 1P, $J_{\text{Pt-P}} = 3318$ Hz, $^2J_{\text{P-P}} = 41.3$ Hz, PPh_2 *trans* N); ^{19}F NMR (282.3 MHz, CCl_3F , 298 K, ppm): -108.5 (d sat, 1F, $^4J_{\text{Pt-F}} \approx 36$ Hz, $^5J_{\text{P-F}} = 5.7$ Hz, ppy^{4F}) -152.3 (s, 4F, BF_4^-). ESI-MS (m/z): found 751.1403 (M-BF_4)⁺, calcd for $\text{C}_{36}\text{H}_{29}\text{NFP}_2\text{Pt}$ 751.6589.

[Pt(ppy-H)(κ^2 -dppm)][BF₄], 18l

To a solution of *cis*-[Pt(Cl)₂(DMSO)₂] (23.1 mg, 0.055 mmol, 1 eq) in acetic acid (8 mL) was added the ppy (17.6 mg, 0.113 mmol, 2.1 eq) obtaining a suspension that was heated at 80°C overnight. After 2 h the reaction mixture became a yellow solution. The solution cooled down to room temperature and dppm was added (42.4 mg, 0.110 mmol, 2.0 eq) under stirring. After 1 h the reaction mixture was evaporated to dryness and the yellow residue was dissolved in CH₂Cl₂, washed with aqueous HCl 0.1 M (2 × 10 mL) and distilled water (2 × 10 mL). Aqueous washings were back-extracted with CH₂Cl₂ (2 × 10 mL) and all the organic fractions collected and treated with Na₂SO₄ under vigorous stirring. Filtration and evaporation to dryness yield a very pale yellow solid that was solubilized in acetone and treated with AgBF₄ under stirring and in the dark for 2 h. The solution was then concentrated to small volume and CH₂Cl₂ was added. The mixture was then washed with distilled H₂O, concentrated and treated with Et₂O obtaining a pale yellow solid. Brute formula: C₃₆H₃₀BNF₄P₂Pt. FW: 820.4731. Selected NMR signals: ¹H NMR (400 MHz, CDCl₃, 298 K, ppm): 8.37 (m sat, 1H, ³J_{Pt-H} = n.r., H₆); 8.08 (td, 1H, J_{H-H} = 8.4, 1.6 Hz); 7.98 (d br, 1H, J_{H-H} = 7.9 Hz); 4.73 (t sat, 2H, ³J_{Pt-H} = n.r., ²J_{P-H} = 10.7 Hz, CH₂). ³¹P NMR (121.4 MHz, 298 K, ppm): -26.7 (d sat, 1P, J_{Pt-P} = 1403 Hz, ²J_{P-P} = 40.4 Hz, PPh₂ *trans* C); -34.5 (d sat, 1P, J_{Pt-P} = 3388 Hz, ²J_{P-P} = 40.4 Hz, PPh₂ *trans* N); ESI-MS (*m/z*): found 733.1494 (M-BF₄)⁺, calcd for C₃₆H₃₀NP₂Pt 733.6684.

[(μ -dppm){Pt(bpy-H)(CH₃)₂}]₂, 19a

To a solution of *cis*-[Pt(CH₃)₂(DMSO)₂] (54.1 mg, 0.142 mmol, 1 eq) in anhydrous toluene an excess of bpy (72.4 mg, 0.464 mmol, 3.27 eq) was added under a nitrogen atmosphere. The solution became suddenly red and was heated to reflux for 3 h. At the end of the reaction dppm (28.1 mg, 0.073 mmol, 0.52 eq) was added to the hot solution and left to react for about 1 h; then the mixture was concentrated to a small volume and treated with *n*-pentane to form a precipitate. The solid was filtered off, washed with *n*-pentane, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 73%. Melting point: > 265 °C. Brute formula: C₄₇H₄₂N₄P₂Pt₂. FW: 1114.9850. Elemental analysis % calculated for C₄₇H₄₂N₄P₂Pt₂: C 49.82, H 3.91, N 4.94; found C 47.35, H

2.86, N 4.21. ^1H NMR (300 MHz, CDCl_3 , 298 K, ppm): 8.24 (dd, 2H, $J_{\text{H-H}} = 4.3$ Hz, H_6); 7.94÷7.84 (m, 10H, H_3 , + $\text{H}_0(\text{Ph})$); 7.77 (m sat, 2H, $^3J_{\text{Pt-H}} = 46.2$ Hz, H_4); 7.54 (d sat, 2H, $^3J_{\text{Pt-H}} = 21$ Hz, H_6); 7.42 (td, 2H, $J_{\text{H-H}} = 15.3, 1.5$ Hz, H_4); 7.32÷7.18 (m, 12H, $\text{H}_m(\text{Ph}) + \text{H}_p(\text{Ph})$); 7.00 (ddd, 2H, H_5); 6.28 (ddd, 2H, $J_{\text{H-H}} = 7.1, 5.6, 1.6$ Hz, H_5); 4.09 (m, 2H, CH_2); 0.74 (m sat, $^2J_{\text{Pt-H}} = 82.0$ Hz, $^3J_{\text{P-H}} = 7.1$ Hz, Pt-CH_3). ^{31}P NMR (121.4 MHz, CDCl_3 , 298 K, ppm): 21.9 (s sat, $J_{\text{Pt-P}} = 1085$ Hz, $^2J_{\text{P-P}} = 39$ Hz, Pt-PPh_2).

$[(\mu\text{-dppm})\{\text{Pt}(\text{bpy-H})(\text{Cl})\}_2]$, 21a

To a solution of $[\text{Pt}(\text{bpy-H})(\text{Cl})(\text{DMSO})]$ (**16a**, 50.0 mg, 0.108 mmol, 1 eq) in CH_2Cl_2 (15 mL) was added 20.5 mg of dppm (0.053 mmol, 0.5 eq) and the solution was stirred for 3 h at room temperature. The mixture was concentrated to a small volume and treated with *n*-pentane to form a precipitate. The solid was filtered off, washed with *n*-pentane, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 82%. Melting point: > 250 °C. Brute formula: $\text{C}_{45}\text{H}_{36}\text{N}_4\text{P}_2\text{Cl}_2\text{Pt}_2$. FW: 1155.8207. Elemental analysis % calculated for $\text{C}_{45}\text{H}_{36}\text{N}_4\text{P}_2\text{Cl}_2\text{Pt}_2 \cdot \text{H}_2\text{O}$: C 46.04, H 3.26, N 4.77; found C 45.77, H 3.60, N 4.49. ^1H NMR (300 MHz, CDCl_3 , 298 K, ppm): 9.57 (m, 2H, H_6); 8.16 (d, 2H, $J_{\text{H-H}} = 7.8$ Hz, H_3); 8.08 (m, 12H, $\text{H}_0(\text{PPh}_3)$); 7.97 (t, 2H, $J_{\text{H-H}} = 7.5$ Hz, H_4); 7.50 (m, 2H); 7.42 (t, 2H, $J_{\text{H-H}} = 7$ Hz); 7.16 (m, 18H, $\text{H}_m(\text{PPh}_3) + \text{H}_p(\text{PPh}_3)$); 6.45 (d, 2H, $^3J_{\text{Pt-H}} = 50$ Hz, $J_{\text{H-H}} = 8.1$ Hz, H_4); 6.34 (dd, 2H, $J_{\text{H-H}} = 7.8, 4.5$ Hz); 5.02 (t, 2H, $J_{\text{H-H}} = 12.9$ Hz, $\text{CH}_2(\text{dppm})$). ^{31}P NMR (121.4 MHz, CDCl_3 , 298 K, ppm): 10.4 (s sat, $J_{\text{Pt-P}} = 4286$ Hz, $^3J_{\text{Pt-P}} = 41.9$ Hz, Pt-PPh_2).

$[\text{Pt}(\text{bpy-H})(\text{Cl})(\text{PPh}_3)]$, 22a

Method A. To a solution of $[\text{Pt}(\text{bpy-H})(\text{Cl})(\text{DMSO})]$ (**16a**, 140.0 mg, 0.304 mmol, 1 eq) in CH_2Cl_2 (20 mL) PPh_3 was added (79.6 mg, 0.304 mmol, 1 eq). After 2 h the mixture was concentrated to small volume and treated with *n*-hexane yielding the product as a yellow solid. Yield 88%.

Method B. To a solution of *cis*- $[\text{Pt}(\text{CH}_3)_2(\text{DMSO})_2]$ (145.2 mg, 0.381 mmol, 1 eq) in anhydrous toluene (20 mL) bpy was added (122.3 mg, 0.783 mmol, 2.06 eq). The mixture was heated to reflux for 3 h and is cooled to room temperature before the addition of

[H₃O · 18-crown-6][BF₄] (168.0 mg, 0.454 mmol, 1.2 eq) and 27.5 mg of LiCl (0.649 mmol, 1.7 eq) and 10 mL of acetone in order to solubilize everything. An orange precipitate formed and after 1 hour 164.8 mg of PPh₃ (0.628 mmol, 1.65 eq) were added. The precipitate dissolved and the solution became yellow, after 1 h the mixture was filtered, concentrated to a small volume and treated with Et₂O and the yellow solid obtained filtered. Yield 52%.

Method C. To a solution of *cis*-[Pt(CH₃)₂(DMSO)₂] (20.3 mg, 0.053 mmol, 1 eq) in anhydrous toluene (4 mL) were added 13.0 mg of bpy (0.083 mmol, 1.6 eq). The mixture is heated to reflux for 2 h and is concentrated to approximately 2 mL before the addition of 530 µL of aqueous HCl 0.1 M (0.053 mmol, 1 eq) dissolved in 4 mL of acetone. Upon addition the yellow solution became rapidly brownish and was left stirring overnight. The solution was extracted with CH₂Cl₂ (2 × 10 mL) and the chlorinated phase treated with Na₂SO₄, filtered and concentrated. Addition of 16.4 mg of PPh₃ (0.062 mmol, 1.2 eq) made the solution paler, evaporation of the solvent and treatment with Et₂O gave the product. Melting point: >250 °C. Brute formula: C₂₈H₂₂N₂PClPt. FW: 648.0026. Elemental analysis % calculated for C₂₈H₂₂N₂PClPt: C 51.90, H 3.49, N 4.32; found C 49.21, H 3.20, N 4.77. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 9.85 (m sat, 1H, ³J_{Pt-H} = 31 Hz, H_{6'}); 8.26 (d, 1H, J_{H-H} = 8.2 Hz, H_{3'}); 8.17 (d, 1H, J_{H-H} = 3.1 Hz, H₆); 8.0 (td, 1H, J_{H-H} = 7.6, 6.6 Hz, H_{4'}); 7.82÷7.62 (m, 6H, H_o(PPh₃)); 7.46÷7.36 (m, 10H, H_{5'} + H_m(PPh₃) + H_p(PPh₃)); 6.85 (d sat, 1H, ³J_{Pt-H} = 49 Hz, J_{H-H} = 5.1 Hz, H₄); 6.42 (dd, 1H, J_{H-H} = 8.4, 4.5 Hz, H₅). ³¹P NMR (121.4 MHz, CDCl₃, 298 K, ppm): 23.6 (s sat, J_{Pt-P} = 4285 Hz, PPh₃)

[Pt(bpy^{6CF₃}-H)(Cl)(PPh₃)], **22c**

Obtained leaving a CDCl₃ solution [Pt(bpy^{6CF₃}-H)(CH₃)(PPh₃)] (**8c**) at room temperature for some hours. Quantitative yield by NMR criteria. Brute formula: C₂₉H₂₁N₂F₃PClPt. FW: 716.0009. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 9.87 (m sat, 1H, ³J_{Pt-H} = n.r. Hz, H_{6'}); 8.38 (d, 1H, J_{H-H} = 7.3 Hz, H_{3'}); 8.02 (t, 1H, J_{H-H} = 7.7 Hz, H_{4'}); 7.81÷7.37 (m, 16H, H_{5'} + H_o(PPh₃) + H_m(PPh₃) + H_p(PPh₃)); 6.98 (d sat, 1H, ³J_{Pt-H} = 41.1 Hz, J_{H-H} = 7.5 Hz, H₄); 6.76 (d, 1H, J_{H-H} = 8.3 Hz, H₅). ³¹P NMR (121.4 MHz, CDCl₃, 298 K, ppm): 22.8 (s sat, J_{Pt-P} = 4238 Hz, PPh₃).

[Pt(ppy-H)(Cl)(PPh₃)], **22l**

Single crystals of [Pt(ppy-H)(Cl)(PPh₃)], C₂₉H₂₃NPClPt, were grown from a CH₂Cl₂ solution. A suitable crystal was selected and mounted on a glass fibre using Fromblin oil on a Xcalibur Gemini diffractometer with a Ruby CCD area detector. The crystal was kept at 150.15 K during data collection. Using Olex2,⁴¹² the structure was solved with the XS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation.⁴¹³ Full details in Table 5.8.

[Pt(pyq-H)(CH₃)(CO)], **24f**

CO was bubbled into a solution of [Pt(pyq-H)(CH₃)(DMSO)] (**2f**, 86.0 mg, 0.178 mmol, 1 eq) in CH₂Cl₂ (20 mL) at room temperature for 2 h. The solution was concentrated to a small volume and treated with *n*-pentane. The precipitate formed was filtered off, washed with *n*-pentane, and vacuum pumped to give the analytical sample as a dark-yellow solid. Yield 85%. Melting point: 180 °C. Brute formula: C₁₆H₁₂N₂OPt. FW: 443.3642. Elemental analysis % calculated for C₁₆H₁₂N₂OPt: C 43.34, H 2.73, N 6.32; found C 43.37, H 2.67, N 5.94. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 8.71 (d sat, 1H, J_{H-H} = 5.4 Hz, ³J_{Pt-H} = 18 Hz, H₆); 8.61 (d, 1H, J_{H-H} = 7.7 Hz, H₃); 8.46 (s sat, 1H, ³J_{Pt-H} = 53.7 Hz, H₄); 8.03 (dt, 1H, J_{H-H} = 7.7, 1.6 Hz, H₄); 8.01 (m, 1H, H₈); 7.79 (d, 1H, J_{H-H} = 8.2 Hz, H₅); 7.61 (dd, 1H, J_{H-H} = 8.2, 1.5 Hz, H₇); 7.50 (d, 1H, J_{H-H} = 8.1 Hz, H₆); 7.37 (ddd, 1H, J_{H-H} = 7.2, 5.4, 1.5 Hz, H₅); 1.29 (s sat, 3H, ²J_{Pt-H} = 85.9 Hz, Pt-CH₃). IR (CH₂Cl₂, ν_{max}/cm⁻¹): 2057 s (CO); (Nujol, ν_{max}/cm⁻¹): 2053 s (CO).

[(DMSO)(Cl)Pt(μ-bpy-2H)Pd(μ-OAc)]₂, **27**

To a solution of [Pt(bpy-H)(Cl)(DMSO)] (**16a**; 131 mg, 0.39 mmol, 1 eq) in 30 mL of benzene was added 91.8 mg of [Pd(OAc)₂] (0.41 mmol, 1 eq). The solution was heated to 80 °C for 12 h and then filtered and concentrated to dryness under reduced pressure. The solid residue was dissolved in CH₂Cl₂, filtered over Celite, concentrated to a small volume, and treated with diethyl ether. The precipitate that formed was filtered, washed with diethyl ether, and vacuum-pumped to give the analytical sample as an orange-yellow solid. Yield: 60%. Brute formula: C₂₈H₃₀N₄O₆S₂Cl₂Pd₂Pt₂. FW: 1256.6070. Elemental

analysis % calculated for $C_{28}H_{30}N_4O_6S_2Cl_2Pd_2Pt_2$: C 26.76, H 2.41, N 4.46; found: C 26.48, H 2.45, N 4.49. The ^1H NMR spectrum shows the presence of two species in a 4:1 molar ratio. ^1H NMR ($CDCl_3$; main species, **27trans**): 8.53 (dd, 2H, $J_{H-H} = 5.6, 1.2$ Hz, $^3J_{Pt-H} = 30$ Hz, $H_{6'}$); 8.26 (dd, 2H, $J_{H-H} = 7.9, 1.2$ Hz, $^3J_{Pt-H} = ca. 26$ Hz, H_4); 7.55 (dd, 2H, $J_{H-H} = 5.5, 1.1$ Hz, H_6); 7.04 (dd, 2H, $J_{H-H} = 7.6, 1.2$ Hz, $H_{4'}$); 6.67 (dd, 2H, $J_{H-H} = 7.9, 5.5$ Hz, H_5); 6.38 (dd, 2H, $J_{H-H} = 7.6, 5.6$ Hz, $H_{5'}$); 3.83 (s, 6H, $^3J_{Pt-H} = ca. 17$ Hz, $CH_3(DMSO)$); 3.49 (s, 6H, $^3J_{Pt-H} = ca. 19$ Hz, $CH_3(DMSO)$); 2.22 (s, 6H, $CH_3(OAc)$). ^{195}Pt NMR ($CDCl_3$): -3562. ^1H NMR ($CDCl_3$; minor species, **27cis**): 8.63 (dd, 2H, $J_{H-H} = 5.6, 1.2$ Hz, $^3J_{Pt-H}$ n.r., $H_{6'}$); 8.35 (dd, 2H, $J_{H-H} = 7.8, 1.2$ Hz, $^3J_{Pt-H}$ n.r., H_4); 7.47 (dd, 2H, $J_{H-H} = 5.5, 1.1$ Hz, H_6); 6.94 (dd, 2H, $J_{H-H} = 7.6, 1.2$ Hz, $H_{4'}$); 6.57 (dd, 2H, $J_{H-H} = 7.8, 5.5$ Hz, $H_{5'}$ or H_5); 6.51 (dd, 2H, $J_{H-H} = 7.6, 5.6$ Hz, H_5 or $H_{5'}$); 3.79 (s, 6H, $^3J_{Pt-H} = n.r.$, $CH_3(DMSO)$); 3.49 (s, ov, 6H, $^3J_{Pt-H}$ n.r., $CH_3(DMSO)$); 2.64 (s, 3H, $CH_3(OAc)$); 2.17 (s, 3H, $CH_3(OAc)$). ^{195}Pt NMR ($CDCl_3$): -3568.

[(DMSO)(Cl)Pt(μ -bpy-2H)Pd(μ -Cl)]₂, 28

To a solution of [Pt(bpy-H)(Cl)(DMSO)] (**16a**; 131 mg, 0.39 mmol, 1 eq) in 30 mL of benzene was added 91.8 mg of [Pd(OAc)₂] (0.41 mmol, 1 eq). The solution was stirred for 8 h at 80 °C and then filtered through Celite and evaporated to dryness under reduced pressure. The solid residue was treated with a 3/1 water/acetone mixture and an excess of LiCl. The mixture was stirred for 12 h: the precipitate that formed was filtered, washed with diethyl ether, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 70%. Brute formula: $C_{12}H_{12}N_2OCl_2SPdPt$. FW: 604.7116. Elemental analysis % calculated for $C_{12}H_{12}N_2OCl_2SPdPt$: C 23.83, H 2.00, N 4.63; found: C 23.87, H 1.65, N 4.68. ^1H NMR (acetone- d_6): 8.83 (d, 1H, $J_{H-H} = 5.4$ Hz, H_6); 8.75 (d sat, 1H, $^3J_{Pt-H} = 36$ Hz, $J_{H-H} = 5.4$ Hz, $H_{6'}$); 8.51 (d sat, 1H, $^3J_{Pt-H} = 42$ Hz, $J_{H-H} = 7.6$ Hz, H_4); 8.24 (d, 1H, $J_{H-H} = 7.6$ Hz, $H_{4'}$); 7.04 (dd, 1H, $J_{H-H} = 5.5, 7.6$ Hz, $H_{5'}$ or H_5); 7.00 (dd, 1H, $J_{H-H} = 5.5, 7.6$ Hz, H_5 or $H_{5'}$); 3.61 (s, 6H, $^3J_{Pt-H} = 25.2$ Hz, $CH_3(DMSO)$).

[(PPh₃)(Cl)Pt(μ-bpy-2H)Pd(μ-Cl)]₂, 29

Complex **29** was synthesized as for complex **28**, starting from [Pt(bpy-H)(Cl)(PPh₃)] (**22a**) instead of [Pt(bpy-H)(Cl)(DMSO)] (**16a**). Yield: 85% (yellow solid). Brute formula: C₂₈H₂₁Cl₂N₂PPdPt · 0 · 5 H₂O. FW: 797.8750. Elemental analysis % calculated for C₂₈H₂₁Cl₂N₂PPdPt · 0 · 5 H₂O: C 42.15, H 2.78, N 3.51; found: C 42.04, H 2.83, N 3.44. ¹H NMR (CDCl₃): 9.03 (m, 1H, H_{6'}); 7.99 (d, 1H, J_{H-H} = 5.3 Hz, H₆); 7.78–7.72 (m, 6H, H_o(PPh₃)); 7.47–7.37 (m, 10H, H_m(PPh₃) + H_p(PPh₃), H_{4'}); 6.97 (m br, 1H, H₅ or H_{5'}); 6.69 (d, 1H, ³J_{Pt-H} = n.r., J_{H-H} = 7.5 Hz, H₄); 6.33 (m br, 1H, H_{5'} or H₅). ³¹P NMR (CDCl₃): 18.15 (s, J_{Pt-P} = 4154 Hz, PPh₃).

[(PPh₃)(Cl)Pt(μ-bpy-2H)Pd(3,5-lut)(Cl)], 32

To a solution of **29** (51.7 mg, 0.066 mmol) in CHCl₃ (30 mL) was added 0.66 mmol of 3,5-dimethylpyridine. The solution was stirred at room temperature for 8 h, concentrated to a small volume, filtered, and treated with diethyl ether. The precipitate that formed was filtered, washed with diethyl ether, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 75%. Melting point: >260 °C. Brute formula: C₃₅H₃₀Cl₂N₃PPdPt₂ · H₂O. FW: 932.0531. Elemental analysis % calculated for C₃₅H₃₀Cl₂N₃PPdPt₂ · H₂O: C 45.10, H 3.68, N 4.51; found: C 44.82, H 3.62, N 4.42. ¹H NMR (CDCl₃): 9.07 (m sat, 1H, ³J_{Pt-H} = 30 Hz, H_{6'}); 8.66 (d, 1H, J_{H-H} = 5.4 Hz, H₆); 8.54 (s, 2H, H_o(py)); 7.79÷7.73 (m, 6H, H_o(PPh₃)); 7.50÷7.38 (m, 10H, H_m(PPh₃) + H_p(PPh₃) + H_p(py)); 6.89 (d, 1H, J_{H-H} = 7.5 Hz, H_{5'} or H₅); 6.68 (m sat, 2H, ³J_{Pt-H} = ca. 45 Hz, H_{4'} + H₄ ov); 6.34 (dd, 1H, J_{H-H} = 5.4, 7.5 Hz, H₅ or H_{5'}); 2.38 (s, 6H, CH₃(py)). ³¹P NMR (CDCl₃): 18.87 (s, J_{Pt-P} = 4155 Hz, PPh₃). ¹⁹⁵Pt NMR (CDCl₃): -4034 ppm (d). ESI-MS (*m/z*): 859.0557, calculated for C₃₅H₃₀ClN₃P¹⁰⁶Pd¹⁹⁵Pt (M - Cl)⁺ 859.0553.

The temperature of the crystal was controlled using the Oxford Cryosystem Cobra. The data collection nominally covered over a hemisphere of reciprocal space, by a combination of nine sets of exposures with different

φ angles for the crystal; each 85 s exposure covered 1.0% in

ω. The crystal-to-detector distance was 5.5 cm. Crystal decay was found to be negligible by repeating the initial frames at the end of data collection and analyzing the duplicate

reflections.

Hydrogen atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameter equal to 1.2 (or 1.5 for methyl H-atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached.

The asymmetric unit contains two mixed metal complexes. These are crystallographically independent but chemically identical (4 complexes in the unit cell). There was also other electron density in the cell modelled as two chloroforms at 50% occupancy, two waters at 50% occupancy and a molecule of acetonitrile at 50% occupancy. The two waters were modelled as disordered over the same position as chloroform C1-Cl3. The occupancies were fixed at 50% so that region of the crystal is either occupied by the chloroform or the two waters.

Additionally, both the partially occupied chloroforms were modelled as disordered over two positions related by rotation about the CH bond. The two positions were fixed at 50:50 for C1-Cl3 but tied to a free variable for chloroform C2-Cl6 and refined to an occupancy of 60:40.

No hydrogens were found for the two partially occupied water molecules O100 and O200 but these were included in the formula so as to calculate the correct density. DFIX and SIMU restraints were used to give both disordered chloroform molecules chemically reasonable bond lengths and thermal parameters. SIMU restraints were used to give both 3,5-dimethylpyridine molecules and one of the phenyls (C119-C124) of the PPh₃ reasonable thermal parameters. Full details in Table 5.7.

[Pt(bpy*)(CH₃)(DMSO)][BF₄], 34a

To a solution of [Pt(bpy-H)(CH₃)(DMSO)] (**2a**, 55.5 mg, 0.125 mmol) in acetone was added with stirring [H₃O · 18-crown-6][BF₄] in a 1:1 molar ratio. The solution was stirred for 3 h and then concentrated to a small volume and treated with diethyl ether. The precipitate that formed was filtered and washed with diethyl ether to give the analytical sample in almost quantitative yield. Mp: 110 °C dec. Elemental analysis % calculated for C₁₃H₁₇BN₂OF₄SPt: C 29.39, H 3.23, N 5.27; found: C 29.28, H 3.09, N 4.98. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 13.8 (broad, 1H, NH); 9.95 (dd, 1H, ³J_{Pt-H} ≈ 15 Hz, J_{H-H}

= 4.8 Hz, $H_{6'}$); 8.75 (dd, 1H, $J_{H-H} = 8.1$ Hz); 8.68 (dd, 1H, $J_{H-H} = 5.4$ Hz); 8.51 (d, 1H, $J_{H-H} = 8.1$ Hz); 8.24 (td, 1H, 7.4 Hz); 7.72–7.60 (m, 2H); 3.30 (s, 6H, $^3J_{Pt-H} = 20.5$ Hz, $CH_3(DMSO)$); 0.78 (s, 3H, $^3J_{Pt-H} = 81$ Hz, Pt- CH_3). IR (Nujol, ν_{max}/cm^{-1}): 3295 m, 3190 m, 1087 s br.

[Pt(pyq*)(CH₃)(DMSO)][BF₄], 34f

To a solution of [Pt(pyq-H)(CH₃)(DMSO)] (**2f**, 50 mg, 0.101 mmol, 1 eq) in CH_2Cl_2 (25 mL), $[H_3O \cdot 18\text{-crown-6}][BF_4]$ (41.3 mg, 0.111 mmol, 1.1 eq) was added under vigorous stirring. After 1 h the solution was filtered, concentrated to a small volume and treated with Et_2O . The precipitate formed was filtered off, washed with Et_2O , and vacuum pumped to give the analytical sample as a green-yellow solid. Yield 80%. Melting point: decompose at 140 °C. Brute formula: $C_{17}H_{19}BN_2OF_4SPt$. FW: 581.3014. Elemental analysis % calculated for $C_{17}H_{19}BN_2OF_4SPt$: C 35.15, H 3.29, N 4.82; found C 35.02, H 3.58, N 4.63. ^1H NMR (300 MHz, $CDCl_3$, 298 K, ppm): 13.9 (s br, 1H, N–H); 10.0 (d sat, 1H, $J_{H-H} = 5.2$ Hz, $^3J_{Pt-H} = 13.2$ Hz, $H_{6'}$); 9.02 (s sat, 1H, $^3J_{Pt-H} = 63$ Hz, H_4); 8.95 (d, 1H, $J_{H-H} = 7.9$ Hz, H_8); 8.53 (d, 1H, $J_{H-H} = 8.1$ Hz); 8.31 (m, 1H); 8.02–7.95 (m, 2H, aromatics); 7.76 (m, 1H); 7.69 (m, 1H); 3.33 (s sat, 6H, $^3J_{Pt-H} = 20.3$ Hz, $CH_3(DMSO)$); 0.85 (s sat, 3H, $^2J_{Pt-H} = 81.3$ Hz, Pt- CH_3). IR (Nujol, ν_{max}/cm^{-1}): 3280, 1058, s br (BF_4^-).

[Pt(bpy*)(CH₃)(PPh₃)][BF₄], 35a

Method A. To a stirred pale yellow solution of [Pt(bpy-H)(CH₃)(PPh₃)] (**8a**, 50.3 mg, 0.080 mmol, 1 eq) in 10 mL of CH_2Cl_2 was added $[H_3O \cdot 18\text{-crown-6}][BF_4]$ (29.5 mg, 0.081 mmol, 1.01 eq) at room temperature, under a nitrogen atmosphere. The solution was stirred for 30 min; then it was concentrated to a small volume and treated with diethyl ether. The precipitate that formed was filtered off, washed with diethyl ether, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 86%.

Method B. To a solution of [Pt(bpy*)(CH₃)(DMSO)][BF₄] (**34a**, 65.1 mg, 0.122 mmol, 1 eq) in CH_2Cl_2 (30 mL) PPh_3 (32.3 mg, 0.123 mmol, 1.04 eq) was added under a nitrogen atmosphere. The solution was stirred for 90 min; then it was concentrated to a small volume and treated with diethyl ether. The precipitate that formed was filtered off, washed

with Et₂O, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 85%. Melting point: 183 °C. Brute formula: C₂₉H₂₈BN₂F₄PPt. FW: 733.5402. Elemental analysis % calculated for C₂₉H₂₈BN₂F₄PPt·2H₂O: C 47.49, H 3.85, N 3.82; found C 47.88, H 3.98, N 3.87. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 13.5 (s br, 1H, N–H); 8.97 (ddd sat, 1H, ³J_{Pt-H} = 50 Hz, ⁴J_{P-H} = 6.3 Hz, J_{H-H} = 7.5, 1.2 Hz, H₄); 8.69 (dd, 1H, J_{H-H} = 5.4, 1.2 Hz, H₆); 8.48 (d, 1H, J_{H-H} = 8.2 Hz, H₃); 8.16 (t, 1H, J_{H-H} = 7.9 Hz, H₄); 7.88 (dd sat, 1H, ³J_{Pt-H} = 10 Hz, J_{H-H} = 5.3 Hz, H₆); 7.78 (m, 1H, J_{H-H} = 7.2, 5.4 Hz, H₅); 7.71÷7.64 (m, 6H, H_m(PPh₃)); 7.50÷7.42 (m, 9H, H_o(PPh₃) + H_p(PPh₃)); 6.96 (d, 1H, J_{H-H} = 7.6 Hz, H₅); 0.83 (d sat, 3H, ²J_{Pt-H} = 82 Hz, ³J_{P-H} = 7.1 Hz, Pt-CH₃). ¹³C NMR (75.4 MHz, CDCl₃, 298 K, ppm): 163.4 (d sat, J_{Pt-C} = 997 Hz, ²J_{P-C} = 122.6 Hz, C₃); 156.8 (s sat, ²J_{Pt-C} = 24 Hz, C₂ or C₂); 155.4 (d sat, ²J_{Pt-C} = 49 Hz, ³J_{P-C} = 4.0 Hz, C₂ or C₂); 151.8 (d sat, ²J_{Pt-C} = 12 Hz, ³J_{P-C} = 3.5 Hz, C₆); 149.8 (s sat, ²J_{Pt-C} = 75.8 Hz, C₄); 139.8 (s, C₄); 136.8 (s, C₆); 134.8 (d sat, ³J_{Pt-C} = 17.4 Hz, ²J_{P-C} = 11.9 Hz, C_o(PPh₃)); 130.9 (d, ⁴J_{P-C} = 2.4 Hz, C_p(PPh₃)); 130.7 (d sat, ²J_{Pt-C} = 19 Hz, J_{P-C} = 48.0 Hz, C_i(PPh₃)); 128.6 (d, ³J_{P-C} = 9.9 Hz, C_m(PPh₃)); 127.4 (s sat, ³J_{Pt-C} = 5.1 Hz, C₅); 125.6 (d sat, ³J_{Pt-C} = 54.7 Hz, ³J_{P-C} = 5.6 Hz, C₅); 121.8 (s sat, ³J_{Pt-C} = 15.5 Hz, C₃); -11.6 (d sat, J_{Pt-C} = 716 Hz, ²J_{P-C} = 5.5 Hz, Pt-CH₃). ³¹P NMR (121.4 MHz, CD₂Cl₂, 298 K, ppm): 32.1 (s sat, J_{Pt-P} = 2500 Hz, PPh₃). IR (Nujol, ν_{max}/cm⁻¹): 3563 N–H.; 1060 (broad) BF₄⁻.

[Pt(pyq*)(CH₃)(PPh₃)] [BF₄], **35f**

To a solution of [Pt(pyq-H)(CH₃)(PPh₃)] (**8f**, 24.4 mg, 0.36 mmol, 1 eq) in CH₂Cl₂ (15 mL) [H₃O · 18-crown-6][BF₄] (13.4 mg, 0.036 mmol, 1 eq) was added. After 2 h, the mixture was concentrated to a small volume and treated with Et₂O to form a precipitate. The solid was filtered off, washed with Et₂O and vacuum-pumped to give the analytical sample as a yellow solid. Yield 90%. Brute formula: C₃₃H₂₈BN₂F₄PPt. FW: 765.4572. Elemental analysis % calculated for C₃₃H₂₈BN₂F₄PPt: C 51.78, H 3.69, N 3.66; found C 51.96, H 3.57, N 3.49. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 13.79 (s br, 1H, N–H); 9.91 (d, 1H, J_{H-H} = 8.1 Hz, H₈); 9.35 (d sat, 1H, ⁴J_{P-H} = 5.6 Hz, ³J_{Pt-H} = 55.2 Hz, H₄); 8.53 (d, 1H, J_{H-H} = 8.7 Hz, H₃); 8.21 (td, J_{H-H} = 9.0, 1.2 Hz, H₄); 8.11÷7.92 (m, 3H); 7.84÷7.70 (m, 7H); 7.56÷7.40 (m, 9H); 7.04 (t, 1H, J_{H-H} = 6.4 Hz, H₅); 0.91 (s sat, 3H, ³J_{P-H} = 7.2 Hz, ²J_{Pt-H} = 82 Hz, Pt-CH₃). ³¹P NMR (121.4 MHz, CDCl₃, 298 K, ppm):

32.0 (s sat, $J_{\text{Pt-P}} = 2507$ Hz, PPh_3).

[Pt(bpy*)(CH₃)(PCy₃)] [BF₄], 36a

To a stirred solution of [Pt(bpy-H)(CH₃)(PCy₃)] (**9a**, 0.116 mmol, 1 eq) in 10 mL of distilled CH₂Cl₂ was added at room temperature, under a nitrogen atmosphere, 43.5 mg (0.118 mmol, 1.02 eq) of [H₃O · 18-crown-6][BF₄]. After 15 min of reaction at room temperature the dark solution was concentrated to give an oil: treatment with Et₂O gave, after stirring, a pale yellow solid, which was filtered off and washed with Et₂O. ¹H and ³¹P NMR spectra show a mixture of two species, **9a** and [Pt(bpy)(CH₃)(PCy₃)] [BF₄] (**41a**), in a 2:1 molar ratio. Brute formula: C₂₉H₄₄BN₂F₄PPt. FW: 733.5402. Selected NMR data for **9a** are as follows. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 13.6 (br, 1H, N-H); 9.06÷8.90 (m, 2H, H₆ + H_{6'}); 8.62 (m, 1H, H₄); 8.49 (d, $J_{\text{H-H}} = 8.1$ Hz, H_{3'}); 8.25 (t br, $J_{\text{H-H}} = 7.14$ Hz, H_{4'}); 7.71 (ov, H₅ or H_{5'}); 7.57 (t br, $J_{\text{H-H}} = 6.22$ Hz, H₅ or H_{5'}); 2.45÷1.20 (m, 33H, Cy); 1.09 (d sat, 3H, $^2J_{\text{Pt-H}} = 83.1$ Hz, $^3J_{\text{P-H}} = 4.9$ Hz, Pt-CH₃). ³¹P NMR (121.4 MHz, CD₂Cl₂, 298 K, ppm): 19.3 (s sat, $J_{\text{Pt-P}} = 2337$ Hz, PCy₃).

[Pt(bpy*)(CH₃)(P(OPh)₃)] [BF₄], 37a

In an NMR tube [Pt(bpy-H)(CH₃)(P(OPh)₃)] (**10a**, 13.3 mg, 0.020 mmol, 1 eq) was dissolved in ca. 1 mL of CD₂Cl₂, giving a light yellow solution. A 7.4 mg portion (0.020 mmol, 1 eq) of [H₃O · 18-crown-6][BF₄] was added at room temperature, and the solution became slightly darker. The reaction was followed by means of NMR spectroscopy. After a few minutes complex [Pt(bpy*)(CH₃)(P(OPh)₃)] [BF₄] was formed in an almost quantitative yield (¹H and ³¹P NMR criteria). Brute formula: C₂₉H₂₆BN₂O₃F₄PPt. FW: 763.3955. ¹H NMR (600 MHz, CDCl₃, 298 K, ppm): 14.5 (s br, 0.5H); 11.5 (s br, 0.5H); 9.75 (d br sat, 1H, $^3J_{\text{Pt-H}} = 14.9$ Hz, $J_{\text{H-H}} = 5.5$ Hz, H₆); 8.83 (d, 1H, $J_{\text{H-H}} = 5.5$ Hz, H_{3'}); 8.80 (td br, 1H, $J_{\text{H-H}} = 8.1, 1.1$ Hz, H_{4'}); 8.52÷8.48 (m, 2H); 8.01 (ddd sat, 1H, $^3J_{\text{Pt-H}} = \text{n.r.}$, $J_{\text{H-H}} = 7.9, 5.7, 2.4$ Hz, H₄); 7.94 (td, 1H, $J_{\text{H-H}} = 5.9, 3.1$ Hz, H₅); 7.46 (m, 6H, H_o(P(OPh)₃)); 7.39 (m, 6H, H_m(P(OPh)₃)); 7.22 (m, 3H, H_p(P(OPh)₃)); 0.92 (d sat, 3H, $^2J_{\text{Pt-H}} = 81.8$ Hz, $^3J_{\text{P-H}} = 6.4$ Hz, Pt-CH₃). ¹H NMR (300 MHz, CD₂Cl₂, 298 K, ppm): 9.58 (d sat, 1H, $^3J_{\text{Pt-H}} \approx 15$ Hz, $J_{\text{H-H}} = 5.4$ Hz, H₆); 8.73 (d sat, 1H, $^3J_{\text{Pt-H}} = 49$ Hz, $J_{\text{H-H}}$

= 7.8 Hz, H_4); 8.56 (d, 1H, $J_{H-H} = 5.0$ Hz, H_6); 8.45 (d, 1H, $J_{H-H} = 7.4$ Hz, H_3); 8.24 (t, 1H, $J_{H-H} = 7.4$ Hz, H_4); 7.75 (m, 1H, H_5); 7.63 (m, 1H, H_5); 7.36÷7.09 (m, 15H, $H_o(P(OPh)_3) + H_m(P(OPh)_3) + H_p(P(OPh)_3)$); 0.90 (d sat, 3H, $^2J_{Pt-H} = 82.0$ Hz, $^3J_{P-H} = 6.3$ Hz, Pt-CH₃). ^{31}P NMR (121.4 MHz, CD₂Cl₂, 298 K, ppm): 111.6 (s sat, $J_{Pt-P} = 4255$ Hz, P(OPh)₃). ^{195}Pt - ^1H HMQC (600 MHz, CDCl₃, 298 K, ppm): -4255 (d, $J_{Pt-P} \approx 4207$) correlates with signals at 9.75, 8.80, 0.92.

[Pt(bpy*)(CH₃)(P(*p*-tol)₃)] [BF₄], **38a**

At room temperature, in an NMR tube, [Pt(bpy-H)(CH₃)(P(*p*-tol)₃)] (**11a**, 6.7 mg, 0.01 mmol, 1 eq) was dissolved in 1.0 mL of CD₂Cl₂ and [H₃O · 18-crown-6-H₃O][BF₄] (5.3 mg, 0.014 mmol, 1 eq) was added. The solution instantly changed colour, becoming bright yellow and remaining clear. The reaction was then followed by NMR spectroscopy. Brute formula: C₃₂H₃₂BN₂F₄PPt. FW: 757.4779. ^1H NMR (400 MHz, CD₂Cl₂, 298 K, ppm): 8.99 (ddd sat, 1H, $^3J_{Pt-H} = 50$ Hz, $^4J_{P-H} = 5.1$ Hz, $J_{H-H} = 7.8, 1.5$ Hz, H_4); 8.66 (d br, 1H, $J_{H-H} = 5.7$ Hz, H_6); 8.41 (d, 1H, $J_{H-H} = 8.0$ Hz, H_3); 8.12 (td, 1H, $J_{H-H} = 7.8, 1.4$ Hz, H_4); 8.00 (m sat, 1H, $^3J_{Pt-H} = 14$ Hz, H_6); 7.81 (ddd, 1H, $^5J_{P-H} = 1.7$ Hz, $J_{H-H} = 7.8, 5.8$ Hz, H_5); 7.60 (dd, 4H, $^3J_{P-H} = 10.6$ Hz, $J_{H-H} = 8.1$ Hz, $H_o(p\text{-tol})$); 7.27 (dd, 4H, $^4J_{P-H} = 1.5$ Hz, $J_{H-H} = 7.9$ Hz, $H_m(p\text{-tol})$); 7.02 (ddd, 1H, $J_{H-H} = 7.6, 5.6, 1.0$ Hz, H_5); 2.42 (s, 9H, CH₃(*p*-tol)); 0.82 (d sat, 3H, $^2J_{Pt-H} = 83$ Hz, $^3J_{P-H} = 7.0$ Hz, Pt-CH₃). ^{31}P NMR (161.9 MHz, CD₂Cl₂, 298 K, ppm): 28.7 (s sat, $J_{Pt-P} = 2502$ Hz, P(*p*-tol)₃).

[Pt(pyq*)(CH₃)(CO)] [BF₄], **39f**

To a solution of [Pt(pyq-H)(CH₃)(CO)] (**24f**, 17.7 mg, 0.040 mmol, 1 eq) in CH₂Cl₂ (15 mL) [H₃O · 18-crown-6][BF₄] (14.7 mg, 0.040 mmol, 1 eq) was added. After 2 h, the mixture was concentrated to a small volume and treated with Et₂O to form a precipitate. The solid was filtered off, washed with Et₂O and vacuum-pumped to give the analytical sample as a yellow solid. Yield 85%. Brute formula: C₁₆H₁₃BN₂OF₄Pt. FW: 531.1767. Elemental analysis % calculated for C₁₆H₁₃BN₂OF₄Pt: C 36.18, H 2.47, N 5.27; found C 36.04, H 2.58, N 5.11. ^1H NMR (300 MHz, CDCl₃, 298 K, ppm): 9.17 (s, 1H, H_4); 9.10 (d, 1H, $J_{H-H} = 9.0$ Hz); 8.98 (d, 1H, $J_{H-H} = 4.8$ Hz, H_6); 8.60 (d, 2H, $J_{H-H} = 7.9$ Hz);

8.47 (m, 1H); 8.06 (m, 2H); 7.85 (m, 1H); 7.75 (m, 1H); 1.36 (s sat, 3H, $^2J_{\text{Pt-H}} = 84.0$ Hz, Pt-CH₃). IR (Nujol, $\nu_{\text{max}}/\text{cm}^{-1}$): 3340 m (N-H), 2079 vs (CO), 1074 vs, br (BF₄⁻).

[Pt(bpy)(CH₃)(PPh₃)] [BF₄], 40a

Method A. To a solution of [Pt(bpy-H)(CH₃)(PPh₃)] (**8a**, 57.9 mg, 0.090 mmol, 1 eq) in 10 mL of CH₂Cl₂ was added, under a nitrogen atmosphere, 47.0 mg (0.127 mmol, 1.4 eq) of [H₃O · 18-crown-6][BF₄]. The reaction mixture was stirred under nitrogen at 30 °C for 1 week. The resulting solution was concentrated to a small volume and treated with diethyl ether. The precipitate that formed was filtered off, washed with diethyl ether, and vacuum-pumped to give the analytical sample as a pale yellow solid. Yield: 76%.

Method B. To a solution of [Pt(bpy*)(CH₃)(DMSO)][BF₄] (**34a**, 48.0 mg, 0.0904 mmol, 1 eq) in CH₂Cl₂ was added with stirring 24.0 mg of PPh₃ (0.0916 mmol, 1 eq) and 3 drops of DMSO. The solution was stirred under a nitrogen atmosphere at room temperature for 5 h; then it was concentrated to a small volume, and pentane was added. The precipitate that formed was filtered off and washed with pentane to give the analytical sample as a yellow solid. Yield: 70%. Melting point: 187 °C. Brute formula: C₂₉H₂₈BN₂F₄PPt. FW: 733.5402. Elemental analysis % calculated for C₂₉H₂₈BN₂F₄PPt: C 48.77, H 3.50, N 3.92; found: C 49.05, H 3.58, N 3.59. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 8.95 (m sat, 1H, $^3J_{\text{Pt-H}} = \text{ca. } 32$ Hz, H₆); 8.75 (d, 1H, $J_{\text{H-H}}$ 8.0 Hz, H_{3'} or H₃); 8.66 (d, 1H, $J_{\text{H-H}}$ 8.0 Hz, H₃ or H_{3'}); 8.42 (m, 1H, $J_{\text{H-H}}$ 8.0 Hz, 7.6 Hz, H_{4'} or H₄); 8.20 (m, 1H, $J_{\text{H-H}}$ 8.0 Hz, 7.6 Hz, H₄ or H_{4'}); 7.83 (m, 1H, H₅); 7.71÷7.89 (m, 6H, H₀(PPh₃)); 7.58÷7.40 (m, 10H, H_{6'} + H_m + H_p(PPh₃)); 7.03 (m, 1H, H_{5'}); 0.78 (d sat, 3H, $^2J_{\text{Pt-H}} = 69.0$ Hz, $^3J_{\text{P-H}} = 3.4$ Hz, Pt-CH₃). ³¹P NMR (121.4 MHz, CDCl₃, 298 K, ppm): 20.36 (s sat, $J_{\text{Pt-P}} = 4351$ Hz, PPh₃). IR (Nujol, $\nu_{\text{max}}/\text{cm}^{-1}$): 1058 s br, BF₄⁻.

[Pt(pyq)(CH₃)(PPh₃)] [BF₄], 40f

To a solution of [Pt(pyq-H)(CH₃)(PPh₃)] (**8f**, 6.8 mg, 0.01 mmol, 1 eq) in CD₂Cl₂ (1.0 mL) 3.6 mg of [H₃O · 18-crown-6][BF₄] (0.01 mmol, 1 eq) were added. The reaction was followed through ¹H and ³¹P NMR spectroscopy. After 2 days, the conversion into the adducts **40f** was complete (almost 100% conversion). Selected NMR data (CDCl₃, 298

K, ppm): P *cis* to N(quinoline) (minor species, ca. 44%) ^1H (400 MHz): 8.85 and 8.76 (AB system, 2H, H_3+H_4 , $J_{\text{A-B}} = 8.5$ Hz); 7.65 (d, 1H, $J_{\text{H-H}} = 5.6$ Hz, H_6); 0.96 (d sat, 3H, $^3J_{\text{P-H}} = 3.2$ Hz, $^2J_{\text{Pt-H}} = 70$ Hz, Pt- CH_3). ^{31}P (161.9 MHz): 17.1 ($J_{\text{Pt-P}} = 4410$ Hz). P *trans* to N(quinoline) (main species, ca. 56%) ^1H (400 MHz): 8.94 (m broad, 1H, $^4J_{\text{P-H}} \approx J_{\text{H-H}} \approx 4.5\text{--}5.0$ Hz, $^3J_{\text{Pt-H}} = 34$ Hz, $\text{H}_{6'}$); 8.72 and 8.69 (AB system, 2H, H_3+H_4 , $J_{\text{A-B}} = 8.5$ Hz); 0.72 (d sat, 3H, $^3J_{\text{P-H}} = 4.7$ Hz, $^2J_{\text{Pt-H}} = 74$ Hz, Pt- CH_3). ^{31}P (161.9 MHz): 15.2 ($J_{\text{Pt-P}} = 4449$ Hz). Other ^1H NMR signals: 8.91 (d, 1H, $J_{\text{H-H}} = 8.5$ Hz); 8.80 (d, 1H, $J_{\text{H-H}} = 7.9$ Hz); 8.47 (m, 1H); 8.42 (t, 1H, $J_{\text{H-H}} = 8.7$ Hz); 8.22 (d, 1H, $J_{\text{H-H}} = 7.8$ Hz); 8.09 (d, 1H, $J_{\text{H-H}} = 8.1$ Hz); 7.84÷7.21 (m, PPh_3); 7.01 (m, 1H); 6.83 (m, 1H).

[Pt(bpy)(CH₃)(PCy₃)] [BF₄], 41a

Under an N₂ atmosphere 71.0 mg (0.11 mmol, 1 eq) of [Pt(bpy-H)(CH₃)(PCy₃)] (**9a**) was dissolved in 10 mL of CH₂Cl₂, and 44.4 mg (0.12 mmol, 1.1 eq) of [H₃O · 18-crown-6][BF₄] was added. The solution was stirred under a nitrogen atmosphere at 30 °C for 48 h. Afterward the solution was evaporated to dryness and diethyl ether was added. The suspension was filtered off and washed with diethyl ether to give the analytical sample. Yield: 76%. Melting point: 254÷256 °C. Brute formula: C₂₉H₄₄BN₂F₄PPt. FW: 733.5402. Elemental analysis % calculated for C₂₉H₄₄BN₂F₄PPt · H₂O: C 46.35, H 6.17, N 3.73; found: C 46.32, H 5.73, N 3.85. ^1H NMR (300 MHz, CDCl₃, 298 K, ppm): 8.84 (m, 2H); 8.74 (m, 2H); 8.73 (m, 2H); 8.38 (m, 2H); 2.42÷1.18 (m, 33H, Cy); 1.00 (d sat, 3H, $^2J_{\text{Pt-H}} = 71.6$ Hz, $^3J_{\text{P-H}} = 1.5$ Hz, Pt- CH_3). ^{31}P NMR (121.4 MHz, CDCl₃, 298 K, ppm): 16.41 (s sat, $J_{\text{Pt-P}} = 4068$ Hz, PCy₃).

[Pt(bpy)(CH₃)(P(OPh)₃)] [BF₄], 42a

Obtained leaving an NMR tube with [Pt(bpy*)(CH₃)(P(OPh)₃)] [BF₄] (**37a**) in solution after ca. 3 months. Quantitative yield by NMR criteria. Brute formula: C₂₉H₂₆BN₂O₃F₄PPt. FW: 763.3955. ^1H NMR (300 MHz, CDCl₃, 298 K, ppm): 9.47 (d sat, 1H, $J_{\text{H-H}} = 5.2$ Hz, $^3J_{\text{Pt-H}} = \text{n.r.}$, $\text{H}_{6'}$); 8.68 (m sat, 1H, $^3J_{\text{Pt-H}} = \text{n.r.}$); 8.52 (m, 2H); 8.35 (m, 2H); 7.74 (m, 2H); 7.41÷7.10 (m, 14H); 6.83 (m, 1H); 0.84 (s sat, 3H, $^2J_{\text{Pt-H}} = 66.3$ Hz, $^3J_{\text{P-H}} = \text{n.r.}$, Pt- CH_3). ^{31}P NMR (121.4 MHz, CDCl₃, 298 K, ppm): 69.72 (s sat, $J_{\text{Pt-P}} = 7164.9$ Hz, P(OPh)₃).

[Pt(bpy)(CH₃)(P(*p*-tol)₃)] [BF₄], 43a

Complex [Pt(bpy*)(CH₃)(P(*p*-tol)₃)] [BF₄] (**38a**) slowly converts to the adduct **43a** (ca. 90% of conversion after 6 days, almost complete conversion after two weeks). Quantitative yield by NMR criteria. Brute formula: C₃₂H₃₂BN₂F₄Ppt. FW: 757.4779. ¹H NMR (300 MHz, CD₂Cl₂, 298 K, ppm): 9.02 (dm sat, 1H, ³J_{Pt-H} ≈ 34 Hz, H_{6'}); 8.56 (d, 1H, J_{H-H} = 8.0 Hz); 8.46 (d, 1H, J_{H-H} = 8.0 Hz); 8.41 (t, 1H, J_{H-H} = 7.6 Hz); 8.18 (t, 1H, J_{H-H} = 7.6 Hz); 7.84 (t, 1H, J_{H-H} = 6.0 Hz); 7.64 (dd, 6H, J_{H-H} = 7.8 Hz, J_{P-H} = 11.2 Hz, H_o(P(*p*-tol)₃)); 7.31 (d, 6H, J_{H-H} = 7.8 Hz, H_m(P(*p*-tol)₃)); 7.26 (d, 1H, J_{H-H} = 7.8 Hz); 7.08 (m, 1H, J_{H-H} = 6.8 Hz); 2.44 (s, 9H, CH₃(P(*p*-tol)₃)); 0.80 (d sat, 3H, ²J_{Pt-H} = 72 Hz, ³J_{P-H} = 3.3 Hz, Pt-CH₃). ³¹P NMR (121.4 MHz, CDCl₃, 298 K, ppm): 16.76 (s sat, J_{Pt-P} = 4343 Hz, P(*p*-tol)₃).

[Pt(bpy-H)(PPh₃)₂] [BF₄], 47

To a solution of [Pt(bpy-H)(CH₃)(DMSO)] [BF₄] (**34a**, 36.2 mg; 0.0683 mmol) in CH₂Cl₂ was added at room temperature 36.0 mg of PPh₃ (0.137 mmol). The mixture was stirred under an inert atmosphere for 4 h; then it was concentrated and treated with diethyl ether. The precipitate that formed was filtered off, washed with diethyl ether, and vacuum-pumped to give the analytical sample as a yellow solid in almost quantitative yield. Melting point: 183 °C. Brute formula: C₄₆H₃₇BN₂F₄P₂Pt. FW: 961.6454. Elemental analysis % calculated for C₄₆H₃₇BN₂F₄P₂Pt: C 57.45, H 3.88, N 2.91; found: C 57.22, H 3.96, N 3.29. ¹H NMR (CDCl₃): 8.35 (m, 1H); 7.94 (m, 1H); 7.26÷7.62 (m, 18H); 6.84 (m, 1H); 6.67 (m, 1H). ³¹P NMR (CDCl₃): 17.68 (d, J_{Pt-P} = 2104.6 Hz, ²J_{P-P} = 19 Hz, P *trans* C); 24.63 (d, J_{Pt-P} = 3937.6 Hz, ²J_{P-P} = 19 Hz, P *trans* N).

[Pt(bpy-H)(bpy)] [BF₄], 48

Method A. To a solution of [Pt(bpy*)(CH₃)(DMSO)] [BF₄] (**34a**, 54.1 mg, 0.102 mmol, 1 eq) in CH₂Cl₂ was added 16.1 mg of bpy (0.103 mmol, 1 eq). The solution was stirred for 3 h at 35 °C under a nitrogen atmosphere. The resulting orange solution was concentrated to a small volume and treated with *n*-pentane; the precipitate that formed was filtered off, washed with *n*-pentane, and vacuum-pumped to give the analytical sample as an orange

solid. Yield: 65%.

Method B. To a solution of [Pt(bpy-H)(CH₃)(DMSO)] (**2a**, 81.3 mg, 0.183 mmol, 1 eq) in CH₂Cl₂ was added 44.4 mg of bpy (0.283 mmol, 1.55 eq) and 68.3 mg of [H₃O · 18-crown-6][BF₄] (0.184 mmol, 1 eq). The solution was stirred for 2 h 30 min at room temperature; then it was concentrated to a small volume and treated with *n*-pentane. The precipitate that formed was filtered off, washed with *n*-pentane, and vacuum-pumped to give the analytical sample as an orange solid. Yield: 55%. Brute formula: C₂₀H₁₅BN₄F₄Pt. FW: 593.2507. Elemental analysis % calculated for C₂₀H₁₅BN₄F₄Pt: C 40.49, H 2.55, N 9.44; found C 39.63, H 2.39, N 9.46. ¹H NMR (300 MHz, CD₂Cl₂, 298 K, ppm): 9.35 (d, 1H); 9.20÷9.10 (m, 1H); 9.08÷8.96 (m, 1H); 8.77÷8.71 (m, 2H); 8.51÷8.39 (m, 3H); 8.38÷8.26 (m, 1H); 8.25÷8.17 (m, 1H); 8.17÷7.95 (m, 1H); 7.88÷7.86 (m, 1H); 7.84÷7.78 (m, 1H); 7.66÷7.62 (m, 1H); 7.25÷7.21 (m, 1H).

[Pt(bpy-H)(CH₃)₂(I)(PMe₃)], **49aA**

At room temperature, in an NMR tube, 10 mg of [Pt(bpy-H)(CH₃)(PMe₃)] (**7a**) was dissolved in acetone-*d*₆ and 3 drops (excess) of CH₃I were added to the solution. The reaction was followed by NMR and was complete in ca. 10 min; during this time the solution became paler and almost colourless. The reaction is completely clean by NMR criteria. Brute formula: C₁₅H₂₂N₂PIPt. FW: 583.3114. ¹H NMR (500 MHz, acetone-*d*₆, 298 K, ppm): 8.91 (d sat, 1H, ³J_{Pt-H} = 10.0 Hz, J_{H-H} = 5.5 Hz, H_{6'}); 8.51 (d br, 1H, J_{H-H} = 8.1 Hz, H_{3'}); 8.32 (d br, 1H, J_{H-H} = 4.4 Hz, H₆); 8.11 (t br, 1H, J_{H-H} = 7.8 Hz, H_{4'}); 7.99 (t br sat, 1H, ³J_{Pt-H} = 30.3 Hz, J_{H-H} = 7.9 Hz, H₄); 7.52 (t br, 1H, J_{H-H} = 6.7 Hz, H_{5'}); 7.24 (ddd sat, 1H, ⁴J_{Pt-H} = 10 Hz, J_{H-H} = 7.7, 4.7, 2.4 Hz, H₅); 1.84 (d sat, 9H, ³J_{Pt-H} = 12.2 Hz, ²J_{P-H} = 9.6 Hz, P(CH₃)₃); 1.40 (d sat, 3H, ²J_{Pt-H} = 69.2 Hz, ³J_{P-H} = 7.4 Hz, Pt-CH₃(eq)); 0.82 (d sat, 3H, ²J_{Pt-H} = 69.4 Hz, ³J_{P-H} = 7.4 Hz, Pt-CH₃(ax)). ¹³C NMR (100.6 MHz, acetone-*d*₆, 298 K, ppm): 150.4; 145.0; 138.7; 137.4 (J_{Pt-C} = 38 Hz); 124.8 (J_{Pt-C} = 12 Hz); 122.9 (J_{Pt-C} = 15 Hz); 11.8 (J_{P-C} = 32 Hz, J_{Pt-C} = 13 Hz); 2.88 (J_{P-C} = 3, J_{Pt-C} = 593 Hz); -6.45 (J_{P-C} = 4 Hz). ³¹P NMR (202.4 MHz, acetone-*d*₆, 298 K, ppm): -46.4 (s sat, J_{Pt-P} = 1467 Hz, P(CH₃)₃). ¹⁹⁵Pt-¹H HMQC (500 MHz, acetone-*d*₆, 298 K, ppm): -3429 (d, J_{Pt-P} = 1467 Hz, P(CH₃)₃). ESI-MS (*m/z*): found 455.1146, calcd for C₁₅H₂₂N₂P¹⁹⁴Pt 455.1142.

Single crystals of $[\text{Pt}(\text{bpy-H})(\text{CH}_3)_2(\text{I})(\text{PMe}_3)]$, $\text{C}_{15}\text{H}_{22}\text{N}_2\text{PIPt}$, were grown from slow evaporation of an acetone solution.

The crystals were mounted in oil and the temperature of the crystal was controlled using the Oxford Cryosystem Cryostream Cobra. The data collection nominally covered over a hemisphere of reciprocal space, by a combination of four sets of exposures with different ω angles for the crystal; each 5 s exposure covered 1.0% in ω . The crystal-to-detector distance was 5.5 cm. Crystal decay was found to be negligible by repeating the initial frames at the end of data collection and analyzing the duplicate reflections.

Hydrogen atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameter equal to 1.2 (or 1.5 for methyl H-atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached.

From the cell metric, one angle appeared to be 90.05° . The structure was eventually solved in monoclinic P_2 and Platon used to convert to the higher symmetry orthorhombic $Pca2_1$ and shown to be correct by successful refinement.

The structure was solved by direct methods using SHELXS (TREF)⁴¹¹ with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups.

The flack parameter was 0.001(6) (Shelxl). The Hooft y parameter was 0.008(4) (Olex2). X-ray crystallographic data in CIF format have been deposited at the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 933129. Full details in Table 5.9.

$[\text{Pt}(\text{bpy-H})(\text{CH}_3)_2(\text{I})(\text{PMe}_3)]$, **49aE**

Method A. An acetone- d_6 solution of $[\text{Pt}(\text{bpy-H})(\text{CH}_3)_2(\text{I})(\text{PMe}_3)]$ (**49aA**) was heated to 60°C and the progress of the reaction was monitored by ^1H and ^{31}P NMR spectroscopy. The reaction looks complete after 10 days. Quantitative yield by NMR criteria.

Method B. An acetone- d_6 solution of $[\text{Pt}(\text{bpy-H})(\text{CH}_3)_2(\text{I})(\text{PMe}_3)]$ (**49aA**) was treated with excess of AgBF_4 , removal of the precipitate by filtration and subsequent treatment with excess KI gave the product. The characterization was carried out after filtration of the

solid in the NMR tube. Quantitative yield. Brute formula: $C_{15}H_{22}N_2PIPt$. FW: 583.3114. ^1H NMR (600 MHz, acetone- d_6 , 298 K, ppm): 9.82 (d sat, 1H, $^3J_{Pt-H} = 11.5$ Hz, $J_{H-H} = 5.6$ Hz, H_6); 8.50 (d br, 1H, $J_{H-H} = 8.0$ Hz, H_3); 8.41 (dt, 1H, $J_{H-H} = 4.4, 1.2$ Hz, H_6); 8.18 (td, 1H, $J_{H-H} = 7.8, 1.2$ Hz, H_4); 7.69 (dt sat, 1H, $^3J_{Pt-H} = 44.0$ Hz, $J_{H-H} = 7.8, 1.2$ Hz, H_4); 7.60 (ddd, 1H, $J_{H-H} = 7.3, 5.6, 1.4$ Hz, H_5); 7.28 (dd sat, 1H, $^4J_{Pt-H} = 14.4$ Hz, $J_{H-H} = 7.8, 4.5$ Hz, H_5); 1.40 (d sat, 3H, $^2J_{Pt-H} = 70.6$ Hz, $^3J_{P-H} = 8.6$ Hz, Pt-CH₃(eq)); 1.14 (d sat, 9H, $^3J_{Pt-H} = 12.3$ Hz, $^2J_{P-H} = 10.0$ Hz, P(CH₃)₃); 0.76 (d sat, 3H, $^2J_{Pt-H} = 55.6$ Hz, $^3J_{P-H} = 8.1$ Hz, Pt-CH₃(ax)). ^{31}P NMR (242.9 MHz, acetone- d_6 , 298 K, ppm): -42.9 (s sat, $J_{Pt-P} = 1239$ Hz, P(CH₃)₃). ^{195}Pt - ^1H HMQC (600 MHz, acetone- d_6 , 298 K, ppm): -3411 (d, $J_{Pt-P} = 1250$ Hz) correlates with signals at 9.82, 7.69, 1.40, 1.14, 0.76.

[Pt(bpy-H)(CH₃)₂(I)(PPh₃)], 50a

In inert atmosphere 317.3 mg of PPh₃ (1.21 mmol, 2 eq) were added to an acetone solution (15 mL) of [Pt(bpy-H)(CH₃)(DMSO)] (**2a**, 268.1 mg, 0.605 mmol, 1 eq), the mixture is then heated to reflux for 3 h. After cooling to room temperature 188 μ L of CH₃I (3.02 mmol, 5 eq) were added and the solution became paler. Upon treatment with Et₂O the product is obtained. Yield 64%. Melting point: 169 °C. Brute formula: $C_{30}H_{28}N_2PIPt$. FW: 769.5240. ESI-MS (m/z): 769 (M^+); 642.1642 ($M-I^+$). Elemental analysis % calculated for $C_{30}H_{28}N_2PIPt$: C 46.82, H 3.67, N 3.64; found C 46.95, H 3.73, N 3.66. ^1H NMR (300 MHz, CDCl₃, 298 K, ppm): 9.58 (d sat, 1H, $^3J_{Pt-H} = 10.1$ Hz, $J_{H-H} = 5.5$ Hz, H_6); 8.25 (d, 1H, $J_{H-H} = 4.1$ Hz, H_6); 8.20 (d, 1H, $J_{H-H} = 7.4$ Hz, H_3); 7.75 (t, 1H, $J_{H-H} = 7.5$ Hz, H_4); 7.26÷7.11 (m, 16H, H_5 + $H_o(PPh_3)$ + $H_m(PPh_3)$ + $H_p(PPh_3)$); 7.05 (d sat, 1H, $^3J_{Pt-H} = 46.9$ Hz, $J_{H-H} = 7.9$ Hz, H_4); 6.82 (dd sat, 1H, $^3J_{Pt-H} = 15$ Hz, $J_{H-H} = 7.9, 4.6$ Hz, H_5); 1.66 (d sat, 3H, $^2J_{Pt-H} = 70.9$ Hz, $^3J_{P-H} = 7.6$ Hz, Pt-CH₃(eq)); 1.20 (d sat, 3H, $^2J_{Pt-H} = 59.8$ Hz, $^3J_{P-H} = 7.5$ Hz, Pt-CH₃(ax)). ^{31}P NMR (121.4 MHz, CDCl₃, 298 K, ppm): -9.33 (s sat, $J_{Pt-P} = 970$ Hz, PPh₃).

[Pt(bpy^{6CH₃}-H)(CH₃)₂(I)(PPh₃)], 50b

In an inert atmosphere to a solution of [Pt(bpy^{6CH₃}-H)(CH₃)(PPh₃)] (**8b**, 201.6 mmol, 0.312 mmol, 1 eq) in acetone (15 mL) was added an excess of CH₃I (92 μ L, 1.55 mmol, 5

eq). The solution was stirred for 3 h at room temperature then was treated with *n*-hexane to obtain a precipitate that was filtered and washed with *n*-hexane. Yield 70%. Melting point: 165÷170 °C. Brute formula: C₃₁H₃₀N₂PIPt FW: 783.5509. Elemental analysis % calculated for C₃₁H₃₀N₂PIPt: C 47.52, H 3.86, N 3.58; found C 47.37, H 3.43, N 3.30. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 9.55 (ddd sat, 1H, ³J_{Pt-H} = 17 Hz, J_{H-H} = 5.6, 1.6, 0.8 Hz, H₆); 8.22 (dd, 1H, J_{H-H} = 8.0, 0.8 Hz, H₃); 7.69-7.82 (m, 2H, H₄ + H₅); 7.05-7.26 (m, 15H, PPh₃); 6.88 (dd sat, 1H, ³J_{Pt-H} = 44.7 Hz, ⁴J_{P-H} = 1.2 Hz, J_{H-H} = 8.0 Hz, H₄); 6.69 (d sat, 1H, ⁴J_{Pt-H} = 13.8 Hz, J_{H-H} = 8.0 Hz, H₅); 2.51 (s, 3H, CH₃-bipy); 1.65 (d sat, 3H, ²J_{Pt-H} = 70.8 Hz, ³J_{P-H} = 7.6 Hz, Pt-CH₃); 1.19 (d sat, 3H, ²J_{Pt-H} = 60.0 Hz, ³J_{P-H} = 7.6 Hz, Pt-CH₃). ³¹P NMR (121.4 MHz, CDCl₃, 298 K, ppm): -9.71 (s sat, J_{Pt-P} = 967 Hz, PPh₃).

[Pt(bpy^{6CF₃}-H)(CH₃)₂(I)(PPh₃)], 50c

In an NMR tube the complex [Pt(bpy^{6CF₃}-H)(CH₃)(PPh₃)] (**8c**) was dissolved in acetone-*d*₆ and was added a 5-fold excess of CH₃I. The reaction is followed by ¹H and ³¹P NMR. Quantitative yield by NMR criteria. Brute formula: C₃₁H₂₇N₂F₃PIPt. FW: 837.5223. ¹H NMR (300 MHz, acetone-*d*₆, 298 K, ppm): 9.65 (d sat, 1H, ³J_{Pt-H} = 13.4 Hz, J_{H-H} = 5.5 Hz, H₆); 8.32 (d, 1H, J_{H-H} = 7.8 Hz, H₃); 8.09 (td, 1H, J_{H-H} = 7.9, 1.4 Hz, H₄); 7.51 (m, 1H, H₅); 7.38÷7.21 (m, 17H, H₄ + H₅ + H_o(PPh₃) + H_m(PPh₃) + H_p(PPh₃)); 1.68 (s sat, 3H, ²J_{Pt-H} = 70.8 Hz, ³J_{P-H} = 7.6 Hz, Pt-CH₃(ax)); 1.12 (s sat, 3H, ²J_{Pt-H} = 60.3 Hz, ³J_{P-H} = 7.4 Hz, Pt-CH₃(eq)). ³¹P NMR (121.4 MHz, acetone-*d*₆, 298 K, ppm): -10.6 (s sat, J_{Pt-P} = 988 Hz, PPh₃).

[Pt(pyq-H)(CH₃)₂(I)(PPh₃)], 50f

To a solution of [Pt(pyq-H)(CH₃)(PPh₃)] (**8f**, 142.0 mg, 0.219 mmol, 1 eq) in acetone (15 mL), 68.0 µL of CH₃I (1.09 mmol, 5 eq) were added at room temperature. The solution was stirred for 3 h, during this time the mixture became paler. Solution was then concentrated to a small volume and treated with *n*-pentane. The precipitate formed was filtered off and washed with *n*-pentane to give the analytical sample as a yellow solid. Yield 74%. Melting point: 150÷155 °C. Brute formula: C₃₄H₃₀N₂PIPt. FW: 819.5839.

Elemental analysis % calculated for $C_{34}H_{30}N_2Pt \cdot 2H_2O$: C 49.83, H 3.69, N 3.42; found C 47.78, H 3.67, N 2.96. ESI-MS (m/z): 843.1 ($M+Na^+$); 819.1 (M^+); 692.1798 ($M-I^+$). ^1H NMR (600 MHz, $CDCl_3$, 298 K, ppm): 9.73 (d sat, 1H, $^3J_{Pt-H} = 11.3$ Hz, $J_{H-H} = 5.5$ Hz, H_6); 8.55 (d, 1H, $J_{H-H} = 8.0$ Hz, H_3); 8.10 (td, 1H $J_{H-H} = 7.7, 1.4$ Hz, H_4); 8.01 (d, 1H, $J_{H-H} = 8.4$ Hz, H_8); 7.69 (ddd, 1H, $J_{H-H} = 8.3, 6.8, 1.3$ Hz, H_7 or H_6); 7.61 (d, 1H, $J_{H-H} = 8.0$ Hz, H_5); 7.53 (ddd, 1H, $J_{H-H} = 8.2, 6.7, 0.9$ Hz, H_6 or H_7); 7.50 (ddd, 1H, $J_{H-H} = 7.5, 5.5, 1.3$ Hz, H_5); 7.43 (d sat, 1H, $^3J_{Pt-H} = 49.6$ Hz, $J_{H-H} = 1.3$ Hz, H_4); 7.27 (dd, 6H, $J_{H-H} = 9.6, 1.3$ Hz, $H_o(PPh_3)$); 7.20 (td, 3H, $J_{H-H} = 7.3, 1.5$ Hz, $H_p(PPh_3)$); 7.09 (td, 6H, $J_{H-H} = 7.8, 2.2$ Hz, $H_m(PPh_3)$); 1.75 (d sat, 3H, $^2J_{Pt-H} = 71.3$ Hz, $^3J_{P-H} = 7.5$ Hz, $PtCH_3(eq)$); 1.22 (d sat, 3H, $^2J_{Pt-H} = 60.8$ Hz, $^3J_{P-H} = 7.8$ Hz, $PtCH_3(ax)$). ^1H - ^1H COSY (600 MHz, $CDCl_3$, 298 K, ppm): 9.72 correlates with signals at 7.50, 8.10, 8.55; 8.01 correlates with signals at 7.69, 7.53, 7.61; signal at 7.43 doesn't have any correlation. ^{31}P NMR (242.9 MHz, $CDCl_3$, 298 K, ppm): -10.7 (s sat, $J_{Pt-P} = 973$ Hz, PPh_3). ^{195}Pt - ^1H HMQC (600 MHz, $CDCl_3$, 298 K, ppm): -3345 (d, $J_{Pt-P} \approx 1009$ Hz, PPh_3) correlates with signals at 9.73, 7.43, 1.75, 1.22.

[Pt(vpy-H)(CH₃)₂(I)(PPh₃)], 50g

In an inert atmosphere to a solution of [Pt(vpy-H)(CH₃)(PPh₃)] (**8g**, 33.0 mg, 0.058 mmol, 1 eq) in acetone (15 mL) was added an excess of CH₃I (17 μ L, 0.274 mmol, 4.7 eq). The solution was stirred for 3 h at room temperature then was treated with *n*-hexane to obtain a precipitate that was filtered and washed with *n*-hexane. Yield 73%. Melting point: 130 °C. Brute formula: $C_{27}H_{27}NPIPt$. FW: 718.4764. ^1H NMR (300 MHz, $CDCl_3$, 298 K, ppm): 9.06 (d sat, 1H, $^3J_{Pt-H} = 10.7$ Hz, $J_{H-H} = 5.4$ Hz, H_6); 7.48 (m, 1H, H_4); 7.42÷7.19 (m, 16H, $H_\beta + PPh_3$); 7.09 (m, 1H, H_3); 6.74 (m, H_5); 6.54 (d sat, 1H, $^3J_{Pt-H} = 86$ Hz, $J_{H-H} = 8.7$ Hz, H_α); 1.80 (d sat, 3H, $^2J_{Pt-H} = 69.4$ Hz, $^3J_{P-H} = 7.9$ Hz, $Pt-CH_3(eq)$); 1.10 (d sat, 3H, $^2J_{Pt-H} = 60.0$ Hz, $^3J_{P-H} = 7.8$ Hz, $Pt-CH_3(ax)$). ^{31}P NMR (121.4 MHz, $CDCl_3$, 298 K, ppm): -5.98 (s sat, $J_{Pt-P} = 1018$ Hz, PPh_3).

[Pt(bpy-H)(CH₃)₂(I)(PCy₃)], 51a

In inert atmosphere PCy₃ (280.1 mg, 0.998 mmol, 2.1 eq) was added to an acetone solution (15 mL) of [Pt(bpy-H)(CH₃)(DMSO)] (**2a**, 215.1 mg, 0.484 mmol, 1 eq), the mixture is then heated to reflux for 3 h. After cooling to room temperature CH₃I (204 µL, 3.27 mmol, 6.8 eq) was added and the solution became paler. Upon treatment with Et₂O the product is obtained. Yield 56%. Melting point: 203÷204 °C. Brute formula: C₃₀H₄₆N₂PIPt. FW: 787.6670. Elemental analysis % calculated for C₃₀H₂₈N₂PIPt: C 45.75, H 5.89, N 3.56; found C 46.47, H 5.71, N 3.62. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 9.98 (d, 1H, J_{H-H} = 5.2 Hz, H_{6'}); 8.41 (m, 2H, H_{3'} + H₆); 7.94 (td, 1H, J_{H-H} = 7.9, 6.8 Hz, H_{4'}); 7.77 (d sat, 1H, ³J_{Pt-H} = 46.9 Hz, J_{H-H} = 7.8 Hz, H₄); 7.40 (dd, 1H, J_{H-H} = 6.2, 6.0 Hz, H₅); 7.21 (dd, 1H, J_{H-H} = 7.6, 4.6 Hz, H_{5'}); 2.0÷0.9 (m, 33H, PCy₃); 1.73 (d sat, 3H, ²J_{Pt-H} = 71.8 Hz, ³J_{P-H} = 6.4 Hz, Pt-CH₃(eq)); 0.96 (d sat, 3H, ²J_{Pt-H} = 57.2 Hz, ³J_{P-H} = 7 Hz, Pt-CH₃(ax)). ³¹P NMR (121.4 MHz, CDCl₃, 298 K, ppm): -17.9 (s sat, J_{Pt-P} = 957 Hz, PCy₃).

[Pt(bpy^{6CF₃}-H)(CH₃)₂(I)(PCy₃)], 51c

In an NMR tube the complex [Pt(bpy^{6CF₃}-H)(CH₃)(PCy₃)] (**9c**) was dissolved in acetone-*d*₆ and was added a 5-fold excess of CH₃I. The reaction is followed by ¹H and ³¹P NMR. Quantitative yield by NMR criteria. Brute formula: C₃₁H₄₅N₂F₃PIPt. FW: 860.6175. ¹H NMR (400 MHz, acetone-*d*₆, 298 K, ppm): 9.95 (d sat, 1H, ³J_{Pt-H} = 10.4 Hz, J_{H-H} = 5.6 Hz, H_{6'}); 8.55 (d, 1H, J_{H-H} = 8.1 Hz, H_{3'}); 8.27 (t, 1H, J_{H-H} = 7.7 Hz, H_{4'}); 8.14 (d sat, 1H, ³J_{Pt-H} = 46.1 Hz, J_{H-H} = 8.1 Hz, H₄); 7.82÷7.76 (m, 2H, H₅ + H_{5'}); 1.99÷0.97 (m, 36H, Pt-CH₃ + PCy₃); 0.89 (d sat, 3H, ²J_{Pt-H} = 57.7 Hz, ³J_{P-H} = 7.0 Hz, Pt-CH₃(ax)). ³¹P NMR (161.9 MHz, acetone-*d*₆, 298 K, ppm): -18.5 (s sat, J_{Pt-P} = 972 Hz, PCy₃). ¹⁹F NMR (376.4 MHz, acetone-*d*₆, 298 K, ppm): 109.7 (s, CF₃).

[Pt(pyq-H)(CH₃)₂(I)(PCy₃)], 51f

In an NMR tube [Pt(pyq-H)(CH₃)(PCy₃)] (**9f**, 1 eq) was solubilized and two drops of CH₃I were added (excess). Solution became rapidly paler and quantitative yield was assessed by NMR criteria. Brute formula: C₃₄H₄₈N₂PIPt. FW: 837.7268. ¹H NMR (600

MHz, acetone- d_6 , 298 K, ppm): 10.06 (d sat, 1H, $^3J_{\text{Pt-H}} = 11.6$ Hz, $J_{\text{H-H}} = 5.5$ Hz, $\text{H}_{6'}$); 8.79 (d, 1H, $J_{\text{H-H}} = 7.9$ Hz, $\text{H}_{3'}$); 8.29 (td, 1H, $J_{\text{H-H}} = 7.8, 1.6$ Hz, $\text{H}_{4'}$); 8.22 (s sat, 1H, $^3J_{\text{Pt-H}} = 51.2$ Hz, H_4); 8.11 (d, 1H, $J_{\text{H-H}} = 8.5$ Hz, H_8); 8.00 (d, 1H, $J_{\text{H-H}} = 8.1$ Hz, H_5); 7.79 (ddd, 1H, $J_{\text{H-H}} = 7.2, 5.6, 1.3$ Hz, $\text{H}_{5'}$); 7.74 (ddd, 1H, $J_{\text{H-H}} = 8.5, 6.7, 1.1$ Hz, H_7); 7.63 (ddd, 1H, $J_{\text{H-H}} = 7.7, 6.9, 1.0$ Hz, H_6); 2.04÷0.88 (different m, 33H, Cy); 1.85 (d sat, 3H, $^2J_{\text{Pt-H}} = 71.9$ Hz, $^3J_{\text{P-H}} = 6.3$ Hz, Pt- $\text{CH}_3(\text{eq})$); 0.97 (d sat, 3H, $^2J_{\text{Pt-H}} = 58.1$ Hz, $^3J_{\text{P-H}} = 7.1$ Hz, Pt- $\text{CH}_3(\text{ax})$). ^1H - ^1H COSY (600 MHz, acetone- d_6 , 298 K, ppm): 10.06 correlates with signals at 7.79, 8.29, 8.79; 8.11 correlates with signal at 7.73; 8.00 with signal at 7.63; signal at 8.21 doesn't show any correlation. ^{31}P NMR (242.9 MHz, acetone- d_6 , 298 K, ppm): -19.6 (s sat, $J_{\text{Pt-P}} = 965$ Hz, PCy_3). ^{195}Pt - ^1H HMQC (600 MHz, acetone- d_6 , 298 K, ppm): -3195 (d, $J_{\text{Pt-P}} \approx 978$, PCy_3).

[Pt(bpy $^{3\text{CH}_3}$)(CH $_3$)(PPh $_3$)] [BF $_4$], **52a**

To a solution of [Pt(bpy-H)(CH $_3$) $_2$ (I)(PPh $_3$)] (**50a**, 0.20 mmol) in acetone (15 ml) was added under stirring a 10% excess of AgBF $_4$ (0.22 mmol): the mixture was stirred for 3 h at room temperature, then filtered through Celite to remove the AgI formed and washed with acetone. The filtered solution was concentrated to small volume and treated with Et $_2$ O. The precipitate formed was filtered, washed with Et $_2$ O, and vacuum-dried to give the analytical sample as a pale yellow solid. Yield 70 %. Selected ^1H NMR data, **52a'**: 9.07 (m, 1H, $\text{H}_{6'}$); 8.59 (d, 1H, H_3); 8.43 (d, 1H, $\text{H}_{4'}$); 7.93 (dd, 1H, H_4); 7.88 (m, 6H, $\text{H}_6(\text{PPh}_3)$); 2.98 (s, 3H, $\text{CH}_3(\text{bpy})$); 0.78 (d sat, 3H, $^2J_{\text{Pt-H}} = 71.1$ Hz, $^3J_{\text{P-H}} = 3.4$ Hz, Pt-Me). **52a''**: 9.19 (m, 1H, H_6); 8.69 (dd, 1H, $\text{H}_{3'}$); 8.58 (dd 1H, H_4); 8.17 (dd, 1H, $\text{H}_{4'}$); 8.03 m, 1H, H_5); 7.88 (m, 6H, $\text{H}_6(\text{PPh}_3)$); 2.94 (s, 3H, $\text{CH}_3(\text{bpy})$); 0.81 (d sat, 3H, $^2J_{\text{Pt-H}} = 72.3$ Hz, $^3J_{\text{P-H}} = 3.5$ Hz, Pt-Me). ^{31}P NMR: 19.2 ppm (s sat, $J_{\text{Pt-P}} = 4294$ Hz); 18.9 ppm (s sat, $J_{\text{Pt-P}} = 4318$ Hz).

[Pt(bpy $^{3\text{CH}_3}$)(CH $_3$)(PCy $_3$)] [BF $_4$]

Method A. In inert atmosphere 233.7 mg of PCy $_3$ (0.833 mmol, 2.0 eq) are added to an acetone solution (15 mL) of [Pt(bpy-H)(CH $_3$)(DMSO)] (**2a**, 184.0 mg, 0.414 mmol, 1 eq), the mixture is then heated to reflux for 3 h. After cooling to room temperature 130 μL

of CH₃I (2.07 mmol, 5 eq) were added and the solution became paler. After 90 min 118 µL of DMSO (1.66 mmol, 4 eq) and 86 mg of AgBF₄ (0.442 mmol, 1.1 eq) were added and the mixture was kept stirring for 2 h. Filtration, concentration to a small volume and treatment with Et₂O gave the product in 85% yield. The same product is obtained in absence of DMSO.

Method B. AgBF₄ (38 mg, 0.19 mmol, 1.1 eq) was added to an acetone solution (15 mL) of [Pt(bpy-H)(CH₃)₂(I)(PCy₃)] (**51a**, 139.7 mg, 0.178 mmol, 1 eq) and the mixture was stirred for 3 h at room temperature. Filtration, concentration to small volume and treatment with Et₂O gave the product in 98% yield. The product is obtained as two isomers interconverting on the NMR time scale. Conductivity: $\Lambda_M=124 \frac{\text{cm}^2}{\text{ohm}\cdot\text{mol}}$ (initial value); $\Lambda_M=170 \frac{\text{cm}^2}{\text{ohm}\cdot\text{mol}}$ (after 10 minutes). Melting point: 160÷165 °C. Brute formula: C₃₀H₄₆BN₂F₄PPt. FW: 747.5671. Elemental analysis % calculated for C₃₀H₄₆BN₂F₄PPt: C 48.20, H 6.20, N 3.75; found C 43.70, H 5.61, N 3.43. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): CHECK 8.95 (d sat, 1H, ³J_{Pt-H} = n.r., J_{H-H} = 6.2 Hz, H_{6'}); 8.80 (d sat, 1H, ³J_{Pt-H} = n.r., J_{H-H} = 5.0 Hz, H₆); 8.49-8.36 (m, 2H, H_{3'} + H_{4'}); 8.16 (t, 1H, J_{H-H} = 8.5 Hz, H₄); 7.85-7.68 (m, 2H, H₅ + H_{5'}); 2.90 (s+s, 3H+3H, CH₃(bpy) both isomers); 2.45÷1.19 (m, 33H, PCy₃); 1.01 (d sat, ²J_{Pt-H} = 71.7 Hz, ³J_{P-H} = 1.9 Hz, Pt-CH₃); 0.94 (d sat, ²J_{Pt-H} = 52.8 Hz, ³J_{P-H} = 1.8 Hz, Pt-CH₃). ³¹P NMR (121.4 MHz, CDCl₃, 298 K, ppm): 16.8 (s sat, J_{Pt-P} = 4074 Hz, PCy₃); 16.1 (s sat, J_{Pt-P} = 4034 Hz, PCy₃);.

[Pt(bpy^{3,6}CH₃)(CH₃)(PPh₃)] [BF₄], **52b**

AgBF₄ (31 mg, 0.159 mmol, 1.2 eq) was added to an acetone solution (15 mL) of [Pt(bpy⁶CH₃-H)(CH₃)₂(I)(PPh₃)] (**50b**, 103 mg, 0.131 mmol, 1 eq) and the mixture was stirred for 3 hours at room temperature. Filtration, contraction to a small volume and treatment with Et₂O give the product in 98% yield.

The product is obtained as two isomers interconverting on the NMR time scale. Melting point: 160÷165 °C. Brute formula: C₃₁H₃₀BN₂F₄PPt. FW: 743.4510. Elemental analysis % calculated for C₃₁H₃₀BN₂F₄PPt: C 50.08, H 4.07, N 3.77; found C 49.57, H 4.32, N 3.36. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 8.85 (m sat, 1H, ³J_{Pt-H} = 38 Hz, H_{6'}); 8.50÷7.20 (m aromatics); 6.90 (m, 2H); 2.95 (s, 3H, Me-bpy); 2.92 (s, 3H, Me-bpy); 2.84 (s, 3H, Me-bpy); 1.94 (s, 3H, Me-bpy (cis-Pt-PPh₃)); 0.81 (d sat, 3H, ²J_{Pt-H} = 70 Hz, ³J_{P-H}

= 3.5 Hz, Pt-Me); 0.46 (d sat, 3H, $^2J_{\text{Pt-H}} = 70$ Hz, $^3J_{\text{P-H}} = 4.3$ Hz, Pt-Me). ^{31}P NMR (121.4 MHz, CDCl_3 , 298 K, ppm): 18.2 (s sat, $J_{\text{Pt-P}} = 4463$ Hz, PPh_3); 15.3 (s sat, $J_{\text{Pt-P}} = 4463$ Hz, PPh_3).

[Pt(pyq^{3CH₃})(CH₃)(PPh₃)] [BF₄], 52f

30 mg of AgBF_4 (0.154 mmol, 1.22 eq) were added to an acetone solution (15 mL) of [Pt(pyq-H)(CH₃)₂(I)(PPh₃)] (**50f**, 100 mg, 0.126 mmol, 1 eq) and the mixture was stirred for 3 h at room temperature. Filtration, concentration to a small volume and treatment with Et_2O gave the product in 68% yield. The product is obtained as two isomers in 4:3 ratio interconverting on the NMR time scale. Brute formula: $\text{C}_{34}\text{H}_{30}\text{BN}_2\text{F}_4\text{PPt}$. FW: 779.4840. ^1H NMR (300 MHz, CDCl_3 , 298 K, ppm): 9.05 (d, 1H); 8.97 (m sat, 1H, $^3J_{\text{Pt-H}} = \text{n.r.}$, H_6); 8.85÷6.75 (m, aromatics); 3.17 (s, 3H, $\text{CH}_3(\text{pyq})$, species B); 3.16 (s, 3H, $\text{CH}_3(\text{pyq})$, species A); 0.95 (d sat, 3H, $^2J_{\text{Pt-H}} \approx 73$ Hz, Pt-CH₃ (species B)); 0.47 (d sat, 3H, $^2J_{\text{Pt-H}} \approx 72$ Hz, Pt-CH₃ (species A)). ^{31}P NMR (242.9 MHz, CDCl_3 , 298 K, ppm): 18.5 (s sat, $J_{\text{Pt-P}} = 4470$ Hz, PPh_3 (species A)); 16.7 (s sat, $J_{\text{Pt-P}} = 4325$ Hz, PPh_3 (species B)). It is also visible a third species accounting for the 40% which gives a singlet with satellites at 31.9 ppm ($J_{\text{Pt-P}} = 3144$ Hz).

[Pt(pyq^{3CH₃})(CH₃)(PCy₃)] [BF₄]

32 mg of AgBF_4 (0.164 mmol, 1.17 eq) were added to an acetone solution (15 mL) of [Pt-(pyq-H)(CH₃)₂(I)(PCy₃)] (**51f**, 113.4 mg, 0.140 mmol, 1 eq) and the mixture was stirred for 3 h at room temperature. Filtration, concentration to a small volume and treatment with *n*-pentane gave the product in 68% yield. Brute formula: $\text{C}_{34}\text{H}_{48}\text{BN}_2\text{F}_4\text{PPt}$. FW: 797.6270. ^1H NMR (300 MHz, CDCl_3 , 298 K, ppm): 9.00÷7.76 (m, 9H, broad signals); 3.11 (s, 3H, $\text{CH}_3\text{-bipy}$); 2.45÷0.75 (m, 33H+3H, $^3J_{\text{Pt-H}} = 74.1$ Hz, Cy + Pt-CH₃). ^{31}P NMR (242.9 MHz, CDCl_3 , 298 K, ppm): 15.3 (s sat, $J_{\text{Pt-P}} = 4157$ Hz, PCy₃).

[Pt(bpy-H)(CH₃)₂(PMe₃)(OH₂)] [BF₄], 53

An acetone-*d*₆ solution of [Pt(bpy-H)(CH₃)₂(I)(PMe₃)] (**49a(eq)**) was treated with excess of AgBF_4 . The characterization was carried out after filtration of the solid in the NMR

tube. Quantitative yield.

The same synthesis works starting from the complex $[\text{Pt}(\text{bpy-H})(\text{CH}_3)_2(\text{I})(\text{PMe}_3)]$ (**49a(ax)**).

Brute formula: $\text{C}_{15}\text{H}_{24}\text{BN}_2\text{OF}_4\text{PPt}$. FW: 561.2268. ^1H NMR (600 MHz, acetone- d_6 , 298 K, ppm): 8.99 (d br sat, 1H, $^3J_{\text{Pt-H}} = 8.8$ Hz, $J_{\text{H-H}} = 5.0$ Hz, H_6); 8.61 (d br, 1H, $J_{\text{H-H}} = 7.8$ Hz, H_3); 8.47 (d br, 1H, $J_{\text{H-H}} = 4.2$ Hz, H_6); 8.33 (t br, 1H, $J_{\text{H-H}} = 7.8$ Hz, H_4); 7.84 (ddd, 1H, $J_{\text{H-H}} = 7.4, 5.6, 1.5$ Hz, H_5); 7.78 (d sat, 1H, $^3J_{\text{Pt-H}} = 54.1$ Hz, $J_{\text{H-H}} = 7.9$ Hz, H_4); 7.31 (dd sat, 1H, $^4J_{\text{Pt-H}} = 15.1$ Hz, $J_{\text{H-H}} = 7.8, 4.8$ Hz, H_5); 7.10 (d, 2H, $^3J_{\text{P-H}} = 1.5$, Pt-OH₂); 1.35 (d sat, 3H, $^2J_{\text{Pt-H}} = 66.3$ Hz, $^3J_{\text{P-H}} = 8.2$ Hz, Pt-CH₃(eq)); 1.16 (d sat, 9H, $^3J_{\text{Pt-H}} = 11.9$ Hz, $^2J_{\text{P-H}} = 10.3$ Hz, P(CH₃)₃); 0.57 (d sat, 3H, $^2J_{\text{Pt-H}} = 50.4$ Hz, $^3J_{\text{P-H}} = 7.8$ Hz, Pt-CH₃(ax)). ^{31}P NMR (242.9 MHz, acetone- d_6 , 298 K, ppm): -25.6 (s sat, $J_{\text{Pt-P}} = 1243$ Hz, P(CH₃)₃). ^{195}Pt - ^1H HMQC (600 MHz, acetone- d_6 , 298 K, ppm): -2676 (d, $J_{\text{Pt-P}} \approx 1511$ Hz) correlates with signals at 8.99, 7.78, 7.31, 7.10, 1.35, 1.16, 0.57. ^{31}P - ^1H HMQC (600 MHz, acetone- d_6 , 298 K, ppm): Signal at -25.6 correlates with 8.99, 7.78, 7.10, 1.35, 1.16, 0.57.

3-methyl-2,2'-bipyridine, $\text{bpy}^{3\text{CH}_3}$, **55**

To a solution of $[\text{Pt}(\text{bpy}^{3\text{CH}_3})(\text{CH}_3)(\text{L})][\text{BF}_4]$ (L = PPh₃, PCy₃, 1 eq) in CH₂Cl₂ (15 mL) dppe was added (38.1 mg, 0.0956 mmol, 1 eq) and the initially yellow solution was left stirring for 15 min at room temperature. During this time the solution became colourless. Evaporation of the solvent and purification by column chromatography eluting with Et₂O on silica gel led to the pure product. Brute formula: $\text{C}_{11}\text{H}_{10}\text{N}_2$. FW: 170.2139. ^1H NMR (300 MHz, CDCl₃, 298 K, ppm): 8.69 (ddd, 1H, $J_{\text{H-H}} = 4.8, 1.6, 0.9$ Hz, H_6); 8.54 (d, 1H, $J_{\text{H-H}} = 4.8$ Hz, H_6); 7.83 (m, 1H, H_4); 7.78 (m, 1H, H_3); 7.62 (d, 1H, $J_{\text{H-H}} = 7.8$ Hz, H_4); 7.30 (ddd, 1H, $J_{\text{H-H}} = 7.6, 4.8, 1.8$ Hz, H_5); 7.25 (dd, 1H, $J_{\text{H-H}} = 7.7, 4.8$ Hz, H_5); 2.51 (s, 3H, CH₃(bpy)). ^{13}C NMR (75.4 MHz, CDCl₃, 298 K, ppm): 158.9 (s); 156.3 (s); 148.5 (s); 146.7 (s); 139.2 (s); 136.5 (s); 132.3 (s); 124.2 (s); 123.0 (s); 122.6 (s); 19.9 (s, CH₃(bpy)).

3,6-dimethyl-2,2'-bipyridine, bpy^{3,6CH₃}, **56**

To a solution of [Pt(bpy^{3,6CH₃})(CH₃)(PPh₃)] [BF₄] (**52b**, 51.0 mg, 0.0659 mmol, 1 eq) in CH₂Cl₂ (15 mL) dppe was added (26.0 mg, 0.0660 mmol, 1 eq) and the initially yellow solution was left stirring for 15 min at room temperature. During this time the solution became colourless. The mixture is concentrated to a small volume and treated with Et₂O, the product was filtered and vacuum pumped. Brute formula: C₁₂H₁₂N₂. FW: 184.2408. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 8.69 (d, 1H, J_{H-H} = 4.8 Hz, H_{6'}); 7.81 (dd, 1H, J_{H-H} = 7.8, 7.5 Hz, H_{4'}); 7.73 (d, 1H, J_{H-H} = 7.8 Hz, H_{3'}); 7.51 (d, 1H, J_{H-H} = 7.9 Hz, H₄); 7.10 (d, 1H, J_{H-H} = 7.9 Hz, H₅); 2.58 (s, 3H, CH₃(bpy)); 2.41 (s, 3H, CH₃(bpy)).

3-methyl-2-(2'-pyridyl)quinoline, pyq^{3CH₃}, **57**

To a solution of [Pt(pyq^{3CH₃})(CH₃)(PPh₃)] [BF₄] (**52f**, 35.0 mg, 0.0149 mmol, 1 eq) in CH₂Cl₂ (15 mL) dppe was added (20.0 mg, 0.0502 mmol, 3.4 eq) and the initially yellow solution was left stirring for 15 min at room temperature. During this time the solution became colourless. Evaporation of the solvent and purification by column chromatography eluting with Et₂O on silica gel led to the pure product. Brute formula: C₁₅H₁₂N₂. FW: 220.2738. ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 8.72 (d, 1H, J_{H-H} = 4.8 Hz, H_{6'}); 8.13 (d, 1H, J_{H-H} = 8.5 Hz, H₈); 8.05 (s, 1H, H₄); 7.84-7.89 (m, 2H, H_{3'} + H_{4'}); 7.80 (d, 1H, J_{H-H} = 8.2 Hz, H₅); 7.67 (m, 1H, H₆ or H₇); 7.54 (m, 1H, H₇ or H₆); 7.30 (m, 1H, H₅); 2.62 (s, 3H, CH₃(pyq)).

5.5 Structure refinements and DFT data

Table 5.1: Crystal data and structure refinement for [Pt(ppy^{4F}-H)(Ph)(DMSO)].

Empirical formula	C ₁₉ H ₁₈ NOFSPt
Formula weight	522.49
Temperature/K	150(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	10.53367(15)
b/Å	16.5764(2)
c/Å	19.8389(3)
α/°	90
β/°	99.6488(13)
γ/°	90
Volume/Å ³	3415.07(8)
Z	8
ρ _{calc} /mg·mm ⁻³	2.032
μ(Mo K _α)/mm ⁻¹	8.355
F(000)	2000
Crystal size/mm ³	0.3 × 0.2 × 0.2
2θ range for data collection	2.88 to 31.39°
Index ranges	-14 ≤ h ≤ 15, -22 ≤ k ≤ 23, -24 ≤ l ≤ 28
Reflections collected	20446
Independent reflections	5258 [R(int) = 0.0279]
Data/restraints/parameters	5258/0/219
Goodness-of-fit on F ²	1.067
Final R indexes [<i>I</i> ≥ 2σ(<i>I</i>)]	R ₁ = 0.0192, wR ₂ = 0.0435
Final R indexes [all data]	R ₁ = 0.0430, wR ₂ = 0.0695
Largest diff. peak/hole / e·Å ⁻³	0.973/-1.018

Table 5.2: Crystal data and structure refinement for [Pt(bpy-H)(CH₃)(PPh₃)].

Empirical formula	C ₂₉ H ₂₅ N ₂ PPt
Formula weight	627.57
Temperature/K	150(2)
Crystal system	triclinic
Space group	P -1
a/Å	10.1446(3)
b/Å	10.7123(3)
c/Å	12.8321(4)
$\alpha/^\circ$	77.820(2)
$\beta/^\circ$	74.559(2)
$\gamma/^\circ$	63.643(3)
Volume/Å ³	1197.46(6)
Z	2
$\rho_{\text{calc}}/\text{mg}\cdot\text{mm}^{-3}$	1.741
$\mu(\text{Mo K}\alpha)/\text{mm}^{-1}$	5.946
F(000)	612
Crystal size/mm ³	0.16 × 0.16 × 0.10
2 θ range for data collection	2.84 to 30.22°
Index ranges	-14 ≤ h ≤ 13, -15 ≤ k ≤ 14, -17 ≤ l ≤ 18
Reflections collected	21612
Independent reflections	6424
Data/restraints/parameters	6424/0/299
Goodness-of-fit on F ²	1.056
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0249, wR ₂ = 0.0495
Final R indexes [all data]	R ₁ = 0.0278, wR ₂ = 0.0288

Table 5.3: Crystal data and structure refinement for [Pt(ppy-H)(CH₃)(PPh₃)].

Empirical formula	C ₃₀ H ₂₆ NPt
Formula weight	626.58
Temperature/K	150.15
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	9.52531(20)
b/Å	13.0441(3)
c/Å	19.4043(4)
α/°	90
β/°	100.161(2)
γ/°	90
Volume/Å ³	2373.16(9)
Z	4
ρ _{calc} / mg·mm ⁻³	1.754
μ(Mo K _α)/mm ⁻¹	5.999
F(000)	1224.0
Crystal size/mm ³	0.2 × 0.08 × 0.06
2θ range for data collection	5.286 to 61.782°
Index ranges	-13 ≤ h ≤ 13, -17 ≤ k ≤ 18, -26 ≤ l ≤ 27
Reflections collected	61963
Independent reflections	7159 [R(int) = 0.0613]
Data/restraints/parameters	7159/0/299
Goodness-of-fit on F ²	1.075
Final R indexes [<i>I</i> ≥ 2σ(<i>I</i>)]	R ₁ = 0.0322, wR ₂ = 0.0658
Final R indexes [all data]	R ₁ = 0.0430, wR ₂ = 0.0695
Largest diff. peak/hole / e·Å ⁻³	1.90/-1.16

Table 5.4: Crystal data and structure refinement for [Pt(vpy-H)(CH₃)(PPh₃)].

Empirical formula	C ₂₆ H ₂₄ NPt
Formula weight	576.52
Temperature/K	298(2)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	9.33290(13)
b/Å	19.1459(2)
c/Å	12.87984(19)
$\alpha/^\circ$	90
$\beta/^\circ$	101.3736(14)
$\gamma/^\circ$	90
Volume/Å ³	2256.26(5)
Z	4
$\rho_{\text{calc}}/\text{mg}\cdot\text{mm}^{-3}$	1.697
$\mu(\text{Mo K}\alpha)/\text{mm}^{-1}$	6.301
F(000)	1120
Crystal size/mm ³	0.30 × 0.30 × 0.22
2 θ range for data collection	3.08 to 31.45°
Index ranges	-13 ≤ h ≤ 8, -28 ≤ k ≤ 27, -18 ≤ l ≤ 18
Reflections collected	13006
Independent reflections	6885 [R(int) = 0.0370]
Data/restraints/parameters	6885/0/263
Goodness-of-fit on F ²	1.054
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0262, wR ₂ = 0.0487
Final R indexes [all data]	R ₁ = 0.0370, wR ₂ = 0.0514
Largest diff. peak/hole / e·Å ⁻³	0.670/-0.476

Table 5.5: Crystal data and structure refinement for [Pt(ppy-H)(CH₃)(P(*p*-tol)₃)].

Empirical formula	C ₃₃ H ₃₂ NPt
Formula weight	668.65
Temperature/K	150.15
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	12.14654(15)
b/Å	10.85040(15)
c/Å	21.2519(3)
α/°	90
β/°	99.9916(13)
γ/°	90
Volume/Å ³	2758.41(6)
Z	4
ρ _{calc} / mg·mm ⁻³	1.610
μ(Mo K _α)/mm ⁻¹	5.167
F(000)	1320.0
Crystal size/mm ³	0.35 × 0.3 × 0.3
2θ range for data collection	5.6 to 64.73°
Index ranges	-18 ≤ h ≤ 17, -15 ≤ k ≤ 16, -31 ≤ l ≤ 31
Reflections collected	43740
Independent reflections	9253 [R(int) = 0.0347]
Data/restraints/parameters	9253/0/329
Goodness-of-fit on F ²	1.059
Final R indexes [<i>I</i> ≥ 2σ(<i>I</i>)]	R ₁ = 0.0220, wR ₂ = 0.0460
Final R indexes [all data]	R ₁ = 0.0280, wR ₂ = 0.0484
Largest diff. peak/hole / e·Å ⁻³	0.89/-0.72

Table 5.6: Crystal data and structure refinement for [Pt(vpy-H)(Ph)(PCy₃)].

Empirical formula	C ₃₁ H ₄₄ NPt
Formula weight	656.73
Temperature/K	150(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	8.64617(12)
b/Å	18.0240(2)
c/Å	35.5920(5)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å ³	5546.62(13)
Z	8
$\rho_{\text{calc}}/\text{mg}\cdot\text{mm}^{-3}$	1.573
$\mu(\text{Mo K}\alpha)/\text{mm}^{-1}$	10.135
F(000)	2640
Crystal size/mm ³	0.20 × 0.04 × 0.02
2 θ range for data collection	4.91 to 77.56°
Index ranges	-10 ≤ h ≤ 7, -15 ≤ k ≤ 22, -44 ≤ l ≤ 41
Reflections collected	20284
Independent reflections	5794 [R(int) = 0.0342]
Data/restraints/parameters	5794/0/310
Goodness-of-fit on F ²	1.127
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0306, wR ₂ = 0.0669
Final R indexes [all data]	R ₁ = 0.0342, wR ₂ = 0.0685
Largest diff. peak/hole / e·Å ⁻³	0.925/-1.064

Table 5.7: Crystal data and structure refinement for [(PPh₃)(Cl)Pt(μ -bpy-2H)Pd(Cl)(3,5-lut)].

Empirical formula	C ₃₆ H _{32.25} N _{3.25} O _{0.50} PCl _{3.50} PdPt
Formula weight	974.94
Temperature/K	150(2)
Crystal system	triclinic
Space group	P -1
a/Å	9.8002(2)
b/Å	19.5809(5)
c/Å	20.0382(5)
α /°	94.331(2)
β /°	94.5328(19)
γ /°	93.6782(19)
Volume/Å ³	3812.77(16)
Z	4
$\rho_{\text{calc}}/\text{mg}\cdot\text{mm}^{-3}$	1.698
$\mu(\text{Mo K}\alpha)/\text{mm}^{-1}$	4.454
F(000)	1894
Crystal size/mm ³	0.16 $\times$ 0.14 $\times$ 0.12
2 θ range for data collection	3.06 to 27.50°
Index ranges	-12 $\leq$ h $\leq$ 12, -25 $\leq$ k $\leq$ 25, -25 $\leq$ l $\leq$ 26
Reflections collected	19833
Independent reflections	17410
Data/restraints/parameters	17410/153/856
Goodness-of-fit on F ²	1.166
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0895, wR ₂ = 0.1900
Final R indexes [all data]	R ₁ = 0.1064, wR ₂ = 0.1980

Table 5.8: Crystal data and structure refinement for [Pt(ppy-H)(Cl)(PPh₃)].

Empirical formula	C ₂₉ H ₂₃ NPClPt
Formula weight	646.99
Temperature/K	150.15
Crystal system	triclinic
Space group	P -1
a/Å	9.89983(12)
b/Å	10.22220(14)
c/Å	13.5605(2)
α /°	79.0363(12)
β /°	70.6117(12)
γ /°	67.7385(12)
Volume/Å ³	1194.72(3)
Z	2
$\rho_{\text{calc}}/\text{mg}\cdot\text{mm}^{-3}$	1.799
$\mu(\text{Mo K}\alpha)/\text{mm}^{-1}$	6.069
F(000)	628.0
Crystal size/mm ³	0.34 × 0.32 × 0.24
2 θ range for data collection	5.556 to 30.58°
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 14, -20 ≤ l ≤ 20
Reflections collected	73315
Independent reflections	8197[R(int)=0.0315]
Data/restraints/parameters	6197/0/298
Goodness-of-fit on F ²	1.096
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0141, wR ₂ = 0.0319
Final R indexes [all data]	R ₁ = 0.0151, wR ₂ = 0.0321
Largest diff. peak/hole/ e·Å ⁻³	0.64/-0.91

Table 5.9: Crystal data and structure refinement for [Pt(bpy-H)(CH₃)₂(I)(PMe₃)].

Empirical formula	C ₁₅ H ₂₂ N ₂ PIPt
Formula weight	583.31
Temperature/K	150(2)
Crystal system	orthorhombic
Space group	Pca2 ₁
a/Å	11.0642(2)
b/Å	9.9079(2)
c/Å	16.0189(4)
α/°	90
β/°	90
γ/°	90
Volume ^a /Å ³	1756.04(6)
Z	4
ρ _{calc} / mg·mm ⁻³	2.206
μ(Mo K _α)/mm ⁻¹	9.832
F(000)	1088
Crystal size/mm ³	0.2 × 0.2 × 0.2
2θ range for data collection	3.03 to 29.67°
Index ranges	-15 ≤ h ≤ 15, -12 ≤ k ≤ 12, -16 ≤ l ≤ 21
Reflections collected	10177
Independent reflections	4056 [R(int) =]
Data/restraints/parameters	4056/1/186
Final R indexes [<i>I</i> ≥ 2σ(<i>I</i>)]	R ₁ = 0.0337, wR ₂ = 0.0906
Largest diff. peak/hole / e·Å ⁻³	1.494/-1.246

^a By least square refinement on 6057 reflection positions.

Table 5.10: Atom In Molecules (AIM) analysis for the optimized complexes of general formula $[\text{Pt}(\kappa^2\text{-N,N})(\text{CH}_3)_2]$. Geometries obtained at PBE0/def2-SVP level using ZORA formalism with RI-J approximation.

		$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	$G(\mathbf{r})$	ε	$\frac{\lambda_1}{\lambda_3}$	$\frac{G(\mathbf{r})}{\rho(\mathbf{r})}$	Γ_{cov}
Pt-N_1	bpy	0.10396	0.45775	0.14472	0.03616	0.15366	1.39205	23.2
	bpy ⁵ CF ₃	0.10460	0.45874	0.14551	0.05536	0.15750	1.39114	23.5
	bpy ⁵ CH ₃	0.10359	0.44988	0.14274	0.05794	0.15855	1.37788	23.6
	bpy ⁶ CF ₃	0.08664	0.37001	0.11334	0.13921	0.16262	1.30810	23.4
	bpy ⁶ CH ₃	0.08844	0.36797	0.11387	0.13108	0.16638	1.28757	23.9
	pyq	0.09305	0.39008	0.12195	0.11395	0.16546	1.31069	23.9
$\text{Pt-N}_1'$	bpy	0.10150	0.43658	0.13816	0.08830	0.16262	1.36124	23.8
	bpy ⁵ CF ₃	0.10340	0.44899	0.14243	0.06123	0.15903	1.37748	23.6
	bpy ⁵ CH ₃	0.10356	0.45004	0.14274	0.05746	0.15837	1.37835	23.6
	bpy ⁶ CF ₃	0.10736	0.45983	0.14798	0.07405	0.16315	1.37838	24.0
	bpy ⁶ CH ₃	0.10568	0.45365	0.14513	0.05809	0.16055	1.37334	23.8
	pyq	0.10638	0.45183	0.14530	0.05930	0.16340	1.36591	24.1
Pt-CH_3^a	bpy	0.14862	0.04727	0.09881	0.06384	0.45330	0.66485	46.8
	bpy ⁵ CF ₃	0.14966	0.04575	0.09941	0.06559	0.45616	0.66425	46.9
	bpy ⁵ CH ₃	0.14920	0.05004	0.09993	0.06369	0.45038	0.66975	46.6
	bpy ⁶ CF ₃	0.15100	0.02853	0.09671	0.04065	0.47227	0.64049	48.1
	bpy ⁶ CH ₃	0.15028	0.03764	0.09806	0.04295	0.46115	0.65250	47.5
	pyq	0.14976	0.03840	0.09783	0.04595	0.46073	0.65325	47.4
Pt-CH_3	bpy	0.14941	0.04865	0.09977	0.05561	0.45071	0.66774	46.7
	bpy ⁵ CF ₃	0.14956	0.04606	0.09938	0.06321	0.45515	0.66452	46.9
	bpy ⁵ CH ₃	0.14918	0.05042	0.09999	0.06416	0.45003	0.67025	46.6
	bpy ⁶ CF ₃	0.14874	0.03160	0.09547	0.04664	0.46930	0.64186	47.9
	bpy ⁶ CH ₃	0.14712	0.04530	0.09695	0.05458	0.45346	0.65897	46.9
	pyq	0.14748	0.04363	0.09690	0.05125	0.45497	0.65705	47.0
$\text{N}_1\text{-C}_2$	bpy	0.33040	-0.97522	0.28936	0.12404	1.87676	0.87580	78.0
	bpy ⁵ CF ₃	0.33004	-0.98032	0.28643	0.11649	1.89474	0.86789	78.2
	bpy ⁵ CH ₃	0.33073	-0.95863	0.29670	0.13328	1.81132	0.89710	77.3
	bpy ⁶ CF ₃	0.32610	-0.96940	0.27734	0.11400	1.92583	0.85048	78.5
	bpy ⁶ CH ₃	0.32839	-0.99970	0.27141	0.11850	2.04333	0.82648	79.5
	pyq	0.34023	-0.94169	0.33157	0.15392	1.62741	0.97456	75.2
$\text{C}_2\text{-C}_2'$	bpy	0.27333	-0.67744	0.06380	0.13052	1.56114	0.23342	74.6
	bpy ⁵ CF ₃	0.27335	-0.67758	0.06379	0.13042	1.56098	0.23334	74.6
	bpy ⁵ CH ₃	0.27314	-0.67595	0.06391	0.13284	1.56184	0.23397	74.6
	bpy ⁶ CF ₃	0.27224	-0.67274	0.06343	0.13296	1.55818	0.23298	74.6
	bpy ⁶ CH ₃	0.27216	-0.67323	0.06316	0.12903	1.55628	0.23205	74.6
	pyq	0.27348	-0.67678	0.06423	0.13379	1.56088	0.23485	74.6
$\text{C}_2\text{-N}_1'$	bpy	0.32973	-0.98001	0.28499	0.12319	1.91421	0.86433	78.3
	bpy ⁵ CF ₃	0.33007	-0.97906	0.28643	0.12656	1.90745	0.86776	78.3
	bpy ⁵ CH ₃	0.32998	-0.97795	0.28691	0.12192	1.89550	0.86947	78.2
	bpy ⁶ CF ₃	0.33124	-0.97967	0.29065	0.12732	1.87943	0.87747	78.0
	bpy ⁶ CH ₃	0.33102	-0.97318	0.29279	0.12240	1.84677	0.88450	77.7
	pyq	0.32971	-0.97381	0.28822	0.11981	1.87216	0.87415	78.0

^a Methyl group *trans* to the substituted nitrogen.

Table 5.11: Atom In Molecules (AIM) analysis for the optimized complexes of general formula $[\text{Pt}(\kappa^2\text{-N,C})(\text{CH}_3)(\text{DMSO})]$. Geometries obtained at PBE0/def2-SVP level using ZORA formalism with RI-J approximation.

		$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	$G(\mathbf{r})$	ε	$\frac{\lambda_1}{\lambda_3}$	$\frac{G(\mathbf{r})}{\rho(\mathbf{r})}$	Γ_{cov}
Pt-N ₁	bpy	0.09838	0.38365	0.12358	0.06337	0.17183	1.25613	25.0
	bpy ^{6CF₃}	0.09793	0.38199	0.12291	0.06274	0.17146	1.25503	25.0
	bpy ^{6CH₃}	0.09831	0.38339	0.12347	0.06477	0.17203	1.25591	25.0
	pyq	0.09863	0.38650	0.12441	0.06100	0.17102	1.26130	24.9
	vpy	0.09863	0.37983	0.12295	0.08743	0.17750	1.24658	25.4
Pt-C ₃	bpy	0.15198	0.10054	0.11324	0.01468	0.39251	0.74508	43.8
	bpy ^{6CF₃}	0.15255	0.10818	0.11548	0.01471	0.38612	0.75700	43.4
	bpy ^{6CH₃}	0.15201	0.09877	0.11288	0.01470	0.39414	0.74255	43.9
	pyq	0.15199	0.10069	0.11326	0.01360	0.39211	0.74522	43.8
	vpy	0.15985	0.09521	0.11975	0.03364	0.40682	0.74911	44.5
Pt-CH ₃	bpy	0.14248	0.05228	0.09445	0.02492	0.43525	0.66294	46.2
	bpy ^{6CF₃}	0.14270	0.05017	0.09419	0.02481	0.43786	0.66005	46.4
	bpy ^{6CH₃}	0.14249	0.05228	0.09446	0.02464	0.43521	0.66294	46.2
	pyq	0.14225	0.05113	0.09398	0.02509	0.43654	0.66072	46.3
	vpy	0.14351	0.05103	0.09510	0.01812	0.43610	0.66270	46.4
Pt-S	bpy	0.10799	0.30525	0.11902	0.11727	0.18830	1.10213	26.3
	bpy ^{6CF₃}	0.10815	0.30289	0.11860	0.12258	0.19064	1.09656	26.5
	bpy ^{6CH₃}	0.10824	0.30695	0.11962	0.11425	0.18740	1.10513	26.2
	pyq	0.10816	0.30549	0.11922	0.11249	0.18806	1.10228	26.3
	vpy	0.10682	0.30645	0.11840	0.14802	0.18834	1.10839	26.1
N ₁ ⁺ -C ₂ ⁻	bpy	0.32948	-0.90998	0.31340	0.08382	1.56438	0.95120	75.0
	bpy ^{6CF₃}	0.32988	-0.91258	0.31350	0.08904	1.57397	0.95034	75.1
	bpy ^{6CH₃}	0.32932	-0.91005	0.31290	0.08329	1.56626	0.95015	75.1
	pyq	0.32995	-0.90709	0.31571	0.08668	1.55230	0.95684	74.9
	vpy	0.32388	-0.94533	0.28307	0.07295	1.77424	0.87399	77.4
C ₂ ⁻ -C ₂ ⁻	bpy	0.27708	-0.69997	0.06561	0.12393	1.58562	0.23678	75.0
	bpy ^{6CF₃}	0.27715	-0.70046	0.06505	0.12212	1.58131	0.23472	74.9
	bpy ^{6CH₃}	0.27682	-0.69894	0.06557	0.12310	1.58368	0.23686	75.0
	pyq	0.27598	-0.69654	0.06457	0.11602	1.57287	0.23395	74.9
	vpy	0.28100	-0.70474	0.07413	0.13653	1.63485	0.26382	75.4
C ₂ -C ₃	bpy	0.29922	-0.73703	0.09515	0.15921	1.64848	0.31800	75.4
	bpy ^{6CF₃}	0.29861	-0.73702	0.09411	0.15002	1.64095	0.31515	75.4
	bpy ^{6CH₃}	0.29982	-0.73958	0.09585	0.16165	1.65467	0.31968	75.5
	pyq	0.28805	-0.69969	0.08601	0.11985	1.57633	0.29859	74.9
	vpy	0.32804	-0.84428	0.12553	0.29455	1.98863	0.38268	77.9

Table 5.12: DFT-calculated bond distances (pm) and angles (deg) around the metal centre for complexes [Pt(pyq-H)(CH₃)(L)] and the corresponding protonated species.

L	DMSO		CO		PPh ₃	
	2f	34f	24f	39f	8f	35f
Pt-L	233.0	233.1	190.3	190.9	235.0	235.8
Pt-CH ₃	205.5	204.6	205.9	205.3	205.8	204.9
Pt-N _{1'}	215.6	217.3	216.5	217.9	217.5	219.1
Pt-C ₃	201.5	201.4	205.3	205.3	203.8	203.7
N _{1'} -C _{2'}	134.9	133.5	134.8	135.2	135.0	135.4
C _{2'} -C ₂	147.3	146.7	147.6	147.2	147.3	146.8
C ₂ -C ₃	143.5	139.1	143.5	141.3	143.4	141.4
N _{1'} -Pt-C ₃	80.3	79.5	79.7	79.0	79.6	78.8
C ₃ -Pt-CH ₃	91.0	91.5	90.8	91.4	89.9	90.5
CH ₃ -Pt-L	90.4	90.4	89.7	88.7	86.0	85.7
L-Pt-N _{1'}	98.2	98.5	99.8	100.9	104.6	105.0
N _{1'} -Pt-CH ₃	171.3	171.1	170.5	170.4	169.3	169.2
C ₃ -Pt-L	178.5	178.0	179.5	179.9	175.6	176.0

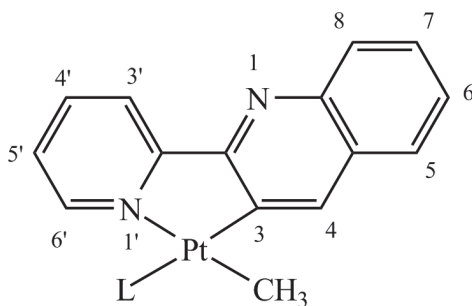
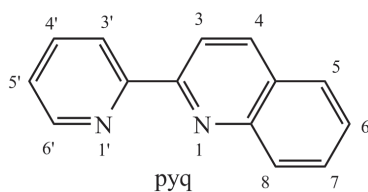


Table 5.13: DFT-calculated bond distances (pm) of the cyclometalated ligand in complexes [Pt-(pyq-H)(CH₃)(L)] and in relative protonates.

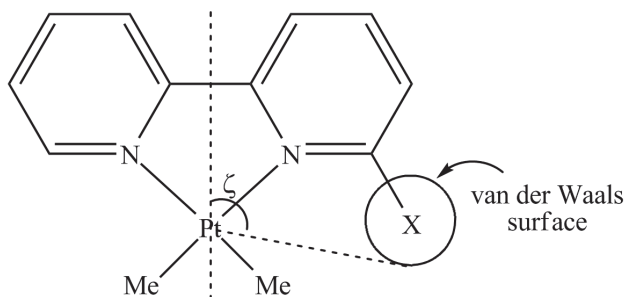
L	DMSO		CO		PPh ₃	
	2f	34f	24f	39f	8f	35f
N _{1'} -C _{2'}	134.9	133.5	134.8	135.2	135.0	135.4
C _{2'} -C _{3'}	139.5	139.6	139.7	139.5	139.7	139.6
C _{3'} -C _{4'}	138.8	138.8	138.7	139.2	138.7	139.2
C _{4'} -C _{5'}	139.4	139.3	139.6	139.0	139.4	138.9
C _{5'} -C _{6'}	139.1	139.4	138.8	139.3	139.0	139.4
C _{6'} -N _{1'}	134.0	135.3	133.8	133.3	133.8	133.4
C _{2'} -C ₂	147.3	146.7	147.6	147.2	147.3	146.8
C ₂ -N ₁	131.4	141.6	131.5	134.2	131.6	134.3
C ₂ -C ₃	143.5	139.1	143.5	141.3	143.4	141.4
C ₃ -C ₄	138.0	141.4	138.0	139.0	138.1	139.3
C ₄ -C ₅	141.8	142.1	141.8	141.4	141.8	141.4
C ₅ -C ₆	141.8	136.5	141.8	141.9	141.9	141.9
C ₆ -C ₇	137.6	134.1	137.6	137.5	137.6	137.5
C ₇ -C ₈	141.6	141.9	141.6	141.5	141.6	141.5
C ₈ -C ₉	137.5	137.5	137.5	137.8	137.5	137.7
C ₉ -C ₁₀	142.0	141.5	142.0	140.8	142.0	140.8
C ₁₀ -N ₁	135.1	137.8	135.1	136.6	135.0	136.4
C ₁₀ -C ₅	142.9	140.8	143.0	142.2	142.9	142.1



Evaluating steric hindrance

Using a geometrical approach it is possible to roughly evaluate the steric hindrance of a substituent in position 6 on the 2,2'-bipyridine when κ^2 -N,N chelated on metal fragment.

What we need to do is calculate the angle ζ as defined in Scheme A.1, *i.e.* the angle



Scheme A.1

between the line that bisect the N-Pt-N angle and the one tangent to the outermost van der Waals surface of the substituent. For simplicity we put the origin of the reference system at the position of the metal centre, in doing this we also have that one line coincides with the y-axis, and we define the nuclear position of the substituent X with the coordinates (J, K) .

The equation of a circle with radius $R = r_{\text{vdW}}$ centered in X is

$$(x - J)^2 + (y - K)^2 = R^2 \quad (\text{A.1})$$

the equation of the line passing through the origin is $y = m \cdot x$ and substitution for y in Equation A.1 leads to

$$x^2 + (mx)^2 - 2xJ - 2mxK + J^2 + K^2 - R^2 = 0 \quad (\text{A.2})$$

we rewrite as a quadratic equation

$$x^2 \cdot (1 + m^2) - x \cdot (2J + 2mK) + J^2 + K^2 - R^2 = 0 \quad (\text{A.3})$$

the two roots can be obtained by application of the formula

$$\frac{-B \pm \sqrt{B^2 - 4AC}}{2A} \quad (\text{A.4})$$

where $A = 1 + m^2$, $B = 2J + 2mK$ and $C = J^2 + K^2 - R^2$. In order to satisfy the desired condition, *i.e.* tangency, we need to impose $\Delta = 0$ therefore we have

$$\begin{aligned} \Delta &= (2J + 2mK)^2 - 4 \cdot (1 + m^2) \cdot (J^2 + K^2 - R^2) = \\ &= m^2 \cdot (4R^2 - 4J^2) + m \cdot (-8JK) + 4R^2 - 4K^2 = 0 \end{aligned} \quad (\text{A.5})$$

that can be solved in order to obtain the two roots m_1 and m_2 , that corresponds to the angular coefficients of the two tangents to the circle, using the formula

$$\frac{-E \pm \sqrt{E^2 - 4DF}}{2D} \quad (\text{A.6})$$

where $D = 4R^2 - 4J^2$, $E = -8JK$ and $F = 4R^2 - 4K^2$.

Once obtained the two roots, the value of the ζ angle can be obtained using the formula

$$\zeta = 90 + \frac{180}{\pi} \cdot \arctan m \quad (\text{A.7})$$

where ζ is the desired angle, $\frac{180}{\pi}$ is the conversion from radian to degree units and m is the root that has the negative sign (Scheme A.1).

The position of the centre of the circle, (J, K) , was evaluated starting from the diagrams in Figure A.1. The angle α used has been taken as half of the average between those reported from X-ray crystals^{174,175} and is equal to 38.95° , notably the average is 77.9° differing only 0.3° from the value obtained with the DFT calculations in this work. The angles at the sp^2 hybridized atoms were taken as 120° and those at $C(sp^3)$ as 109.5° , thus

$$\beta = 120 - 90 = 30 \quad \text{and} \quad \gamma = 109.5 - 60 = 49.5$$

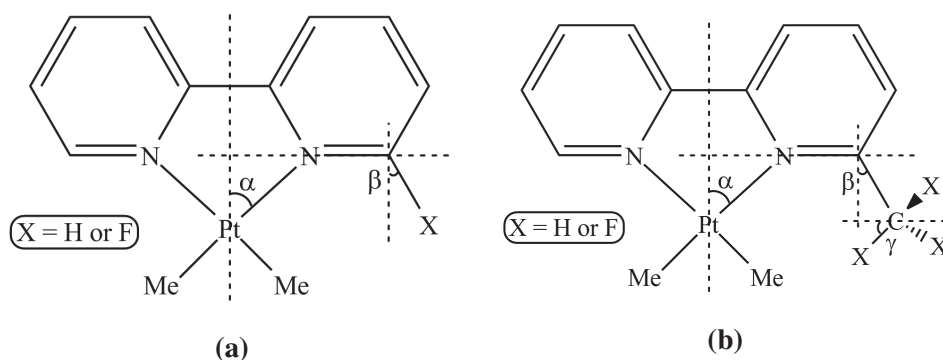


Figure A.1: Schematic representations of the geometries used to calculate the angle ζ .

Bond distances were calculated using the covalent radii published by Cordero *et al.*⁴¹⁴ while as van der Waals radii we used those published by Bondi.¹⁸⁴ All of them are summarized in Table A.1. With all these data in hand we can derive all the quantities reported in Table A.2.

Table A.1: Covalent and van der Waals radii, in pm, used in the calculation of the angle ζ .

Atom	r_{cov}	r_{vdW}
H	31	120
C(sp^2)	73	170
C(sp^3)	76	
N	71	155
F	57	147
Pt	136	175

Table A.2: Values for ζ , roots m_1 and m_2 , in degrees, coordinates of the centre (J, K) in pm obtained with the procedure described.

	ζ	m_1	m_2	J	K
bpy	98.80	-8.804692	33.340483	326.128886	70.916192
bpy ^F	107.29	-17.289188	33.533679	339.128886	48.399532
bpy ^{CH₃}	125.08	-35.083458	15.004302	279.137945	-49.418389
bpy ^{CF₃}	137.60	-47.598155	18.039453	262.252296	-69.188944

Bader's AIM analysis

The theory of Atoms in Molecules (AIM) was initially developed in late 1960s by Bader⁴¹⁵ and reviewed by himself first in 1985 and later in 1991.^{416,417} Using this approach it is possible to define the structure of a many-body system, *i.e.* a molecule, as a sum of proper open systems, *i.e.* the atoms, which can share energy and electron density.

The cornerstone of Bader's theory is that given a molecular system defined by its electron density $\rho(\mathbf{r})$ it is possible to divide it in only one way in a sum of different regions Ω_i , each one bounded by a surface $S(\Omega_i, \mathbf{r})$, such that the total flux of $\nabla\rho(\mathbf{r})$ through each surface is zero, *i.e.*

$$\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0 \quad \forall \mathbf{r} \in S(\Omega_i, \mathbf{r}) \text{ and } \forall \Omega_i$$

Every Ω_i constitutes an atomic volume and integrating the appropriate operator on this volume it is possible to calculate the atomic properties.^{416,418} Analyzing the topology of the electron density $\rho(\mathbf{r})$ it is therefore possible to gain informations on the molecular system under investigation.

The points $\mathbf{r}_c$ where the gradient of the electron density vanishes, *i.e.* where $\nabla\rho(\mathbf{r}) = 0$, are called *critical points* and are identified on the basis of the eigenvalues, λ_i , of the Hessian of $\rho(\mathbf{r}_c)$. The notation used is (σ, s) where σ indicates the number of non zero eigenvalues (the *rank*) and s is the difference between the number of positive and negative eigenvalues (the *signature*).

As we operate in a tridimensional space there are only four possible signatures for rank three critical points: $s = +3$ refers to a situation where $\rho(\mathbf{r})$ is a local minimum and is identified with a cage critical point (CCP); when $s = +1$ the electron density is a minimum

in the plane where the two positive curvatures lie and a maximum in the perpendicular direction, this a ring critical point (RCP); $s = -1$ describes a situation where $\rho(\mathbf{r})$ has a minimum along one direction (bond path) and maxima along the other two and is associated to bond critical points (BCP); $s = -3$ indicates nuclear attractors (NA) which are local maxima for $\rho(\mathbf{r})$ and corresponds to the position of the nuclei.^{416,419,420}

Analysis of the sign of Laplacian of the electron density, $\nabla^2\rho(\mathbf{r})$, gives information on the charge distribution and can help to identify those region with concentration of charge ($\nabla^2\rho(\mathbf{r}) < 0$) and those subjected to depletion ($\nabla^2\rho(\mathbf{r}) > 0$). If one considers the Laplacian at a BCP $\mathbf{r}_c$ holds the relationship

$$\nabla^2\rho(\mathbf{r}_c) = \lambda_1 + \lambda_2 + \lambda_3$$

and, if we assume $\lambda_1 < \lambda_2 < 0 < \lambda_3$, it is possible to define another useful descriptor known as the *ellipticity* of the bond, ε , as

$$\varepsilon = \frac{\lambda_1}{\lambda_2} - 1$$

this formula represents well the deformation of the electronic cloud at the BCP for the hydrocarbons.¹⁸¹

According to Bader three kind of interactions can exist between atomic volumes that share a common surface and present a critical point on this surface: (a) *shared interactions* are characterized by $\nabla^2\rho(\mathbf{r}_c) < 0$, $\rho(\mathbf{r}_c) > 0$ and relatively large, $\left|\frac{\lambda_1}{\lambda_3}\right| > 1$ and the ratio between the kinetic energy density $G(\mathbf{r}_c)$ and the electron density evaluated at the BCP is smaller than 1, *i.e.* $\frac{G(\mathbf{r}_c)}{\rho(\mathbf{r}_c)} < 1$; (b) *closed interactions* are instead characterized by $\nabla^2\rho(\mathbf{r}_c) > 0$, $\rho(\mathbf{r}_c) > 0$ and small, $\left|\frac{\lambda_1}{\lambda_3}\right| < 1$ and $\frac{G(\mathbf{r}_c)}{\rho(\mathbf{r}_c)} > 1$; and finally (c) *intermediate interactions* are those that present $\nabla^2\rho(\mathbf{r}_c) > 0$, $\rho(\mathbf{r}_c) > 0$ relatively large and intermediate values of $\left|\frac{\lambda_1}{\lambda_3}\right|$ and $\frac{G(\mathbf{r}_c)}{\rho(\mathbf{r}_c)}$.¹⁸⁰

Another interesting parameter that can be used to roughly evaluate the type of bond involved was proposed by Sierralta and Ruette in 1994 and it is the *degree of covalency*, Γ_{cov} , that was defined as

$$\Gamma_{\text{cov}} = \frac{|\lambda_1 + \lambda_2|}{|\lambda_1 + \lambda_2| + \lambda_3}$$

the corresponding *degree of ionicity*, Γ_{ion} , was defined as $\Gamma_{\text{ion}} = 1 - \Gamma_{\text{cov}}$.¹⁷⁹

Assessing the NICS methodology

In their first contribution to the Nucleus Independent Chemical Shift (NICS) approach Schleyer and co-workers stated that the obtained values are "only somewhat sensitive to the basis set" and suggested to use the 6-31G with polarization and diffuse functions.¹⁸⁶ Given this advice we carried out a series of benchmark calculations to check the reliability of our approach using as reference data those reported by Schleyer *et al.* in their review.¹⁸⁵

All the calculations were performed with ORCA 2.9.1 package⁹⁸ which uses the Valeev's libint2 library to evaluate the integrals,⁴²¹ input and output files were managed with Avogadro^{422,423} and Gabedit.⁴²⁴

The procedure for calculation of the NICS values was possible according to the following steps:

1. optimization of the molecule using the hybrid PBE0 functional⁹⁴⁻⁹⁶ with ZORA approximation^{91-93,425} using the SV-ZORA or TZV-ZORA basis sets^{99,100} along with the RI-JONX approximation as implemented in ORCA 2.9.1;
2. evaluation of the centroid using Mercury;⁴²⁶
3. search for the ring critical point (RCP) using MultiWFN program package;⁴²⁷
4. evaluation of the NICS using the PBE functional^{95,96} with the def2-TZVP basis set developed by Ahlrichs and co-workers^{97,428} using the IGLO method (Individual Gauge for Localized Orbitals).

NICS value were calculated in four different positions that are indicated as follows:

NICS(0) centroid of the ring;

NICS(1) 1 Å above the centroid, this position was calculated from the centroid in the direction normal to the mean plane calculated through the atoms that constitute the ring;

NICS_{RCP}(0) ring critical point;

NICS_{RCP}(1) 1 Å above the ring critical point evaluated using the same approach used for NICS(1).

Table C.1: Comparison of the literature reported NICS values with those calculated in this work.

	NICS(0) ¹⁸⁵	NICS(0)	NICS _{RCP} (0)	NICS(1) ¹⁸⁵	NICS(1)	NICS _{RCP} (1)
Benzene	-8.03	-8.0	-8.1	-10.2	-10.2	-10.3
Fluorene ^a	-7.31	-6.9	-7.0	-9.54	-9.2	-9.3
Fluorene ^b	1.25	1.3	1.1	-2.33	-2.4	-2.5
Furan	-11.88	-12.2	-12.3	-9.38	-9.9	-9.9
Indene ^a	-8.11	-7.8	-7.9	-10.17	-9.9	-9.9
Indene ^b	-0.5	-0.7	-0.8	-3.37	-3.7	-3.7
Naphtalene	-8.55	-8.3	-8.4	-10.71	-10.6	-10.6
Pyridine	-6.82	-6.7	-6.8	-10.17	-10.2	-10.2
Pyrrole	-13.62	-14.1	-14.2	-10.09	-10.7	-10.7
Quinoline ^c	-7.47	-7.3	-7.3	-10.52	-10.5	-10.5
Quinoline ^d	-8.81	-8.4	-8.5	-10.85	-10.7	-10.7
Thiophene	-12.87	-14.3	-15.0	-10.24	-11.3	-11.4
Toluene	-8.01	-7.9	-8.0	-10.07	-10.0	-10.0

^a 6-membered ring. ^b 5-membered ring. ^c Pyridinic ring. ^d Benzenic ring.

The data obtained using the aforementioned procedures are collected in Table C.1. What emerges is that our methodology nicely reproduces the value reported by Schleyer *et al.* using GIAO^a method at the B3LYP/6-311+G** level, the agreement is highlighted by a mean absolute error (MAE) of ca. 0.3 ppm that is reasonably acceptable taking in account the differences in the methodology mainly due to the IGLO vs GIAO difference.⁴²⁹

^aThe Gauge-Including Atomic Orbital method (GIAO) is not yet available in ORCA package.

A remarkable deviation is found for thiophene (more than 1 ppm) but the reason behind this are currently unclear.

Software used

This work has been carried out using the following software.

The thesis has been written with L^AT_EX document preparation system and the bibliography has been produced with B_IB_TE_X reference management software as provided in TeX Live 2012/SUSE Linux version on openSUSE 12.3 (kernel 3.7.10-1.16) with KDE 4.10.5.

The chemical diagrams were produced with ChemDraw 12.0.

ORTEP diagrams were prepared with Ortep-3 for Windows,⁴³⁰ and exported as pov files which then have been rendered with POV-Ray 3.6.2 for Windows.

NMR spectra were analysed with ACD/NMR Processor Academic Edition or with Bruker's TopSpinTM software package for NMR data analysis and the acquisition and processing of NMR spectra.

NMR were simulated with gNMR.²⁷⁰

DFT calculations were carried out with the Firefly QC package,⁴³¹ which is partially based on the GAMESS (US)⁴³² source code or with ORCA 2.9.1 package.⁹⁸

Input files were prepared using Avogadro^{422,423} and output file were managed with Gabe-dit.⁴²⁴

Plots were made with Gnuplot version 4.6 (patchlevel 1).

Analysis of the wavefunction was made using the package MultiWFN.⁴²⁷

Compositions of molecular orbitals, overlap populations between molecular fragments, bond orders and density-of-states spectra were calculated using the AOMix program.^{433,434}

Bibliography

- [1] DePasquale, J.; Nieto, I.; Reuther, L. E.; Herbst-Gervasoni, C. J.; Paul, J. J.; Mochalin, V.; Zeller, M.; Thomas, C. M.; Addison, A. W.; Papish, E. T. *Inorganic Chemistry* **2013**, *52*, 9175–9183.
- [2] Hashiguchi, B. G.; Young, K. J. H.; Yousufuddin, M.; Goddard, W. A.; Periana, R. A. *J. Am. Chem. Soc.* **2010**, *132*, 12542–5.
- [3] Crabtree, R. H. *Science* **2010**, *330*, 455–456.
- [4] Koo, C.-K.; Wong, K.-L.; Lau, K.-C.; Wong, W.-Y.; Lam, M. H.-W. *Chemistry* **2009**, *15*, 7689–97.
- [5] Koo, C.-K.; Lam, B.; Leung, S.-K.; Lam, M. H.-W.; Wong, W.-Y. *Journal of the American Chemical Society* **2006**, *128*, 16434–5.
- [6] Li, K.; Chen, Y.; Lu, W.; Zhu, N.; Che, C.-M. *Chemistry – A European Journal* **2011**, *17*, 4109–4112.
- [7] Kaes, C.; Katz, A.; Hosseini, M. W. *Chemical Reviews* **2000**, *100*, 3553–3590; PMID: 11749322.
- [8] Cinellu, M. A.; Zucca, A.; Stoccoro, S.; Minghetti, G.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1996**, 4217–4225.
- [9] Brown, A. R.; Guo, Z.; Mosselmans, F. W. J.; Parsons, S.; Schröder, M.; Yellowlees, L. J. *Journal of the American Chemical Society* **1998**, *120*, 8805–8811.
- [10] Usón, R.; Forniés, J.; Tomás, M.; Martínez, F.; Casas, J.; Fortuño, C. *Inorganica Chimica Acta* **1995**, *235*, 51–60.
- [11] Fornies, J.; Navarro, R.; Sicilia, V.; Tomas, M. *Inorganic Chemistry* **1993**, *32*, 3675–3681.
- [12] Creaven, B. S.; Long, C.; Howie, R.; McQuillan, G. P.; Low, J. *Inorganica Chimica Acta* **1989**, *157*, 151–152.
- [13] Uson, R.; Fornies, J.; Tomas, M.; Casas, J. M.; Fortuño, C. *Polyhedron* **1989**, *8*, 2209–2211.
- [14] Petretto, G. L.; Rourke, J. P.; Maidich, L.; Stoccoro, S.; Cinellu, M. A.; Minghetti, G.; Clarkson, G. J.; Zucca, A. *Organometallics* **2012**, *31*, 2971–2977.

-
- [15] Cocco, F.; Cinellu, M. A.; Minghetti, G.; Zucca, A.; Stoccoro, S.; Maiore, L.; Manassero, M. *Organometallics* **2010**, *29*, 1064–1066.
- [16] Zucca, A.; Petretto, G. L.; Stoccoro, S.; Cinellu, M. A.; Manassero, M.; Manassero, C.; Minghetti, G. *Organometallics* **2009**, *28*, 2150–2159.
- [17] Zhao, J.-W.; Wang, C.-M.; Zhang, J.; Zheng, S.-T.; Yang, G.-Y. *Chemistry – A European Journal* **2008**, *14*, 9223–9239.
- [18] Zucca, A.; Petretto, G. L.; Stoccoro, S.; Cinellu, M. A.; Minghetti, G.; Manassero, M.; Manassero, C.; Male, L.; Albinati, A. *Organometallics* **2006**, *25*, 2253–2265.
- [19] Zucca, A.; Cinellu, M. A.; Minghetti, G.; Stoccoro, S.; Manassero, M. *European Journal of Inorganic Chemistry* **2004**, *2004*, 4484–4490.
- [20] Minghetti, G.; Stoccoro, S.; Cinellu, M. A.; Soro, B.; Zucca, A. *Organometallics* **2003**, *22*, 4770–4777.
- [21] Zucca, A.; Doppiu, A.; Cinellu, M. A.; Stoccoro, S.; Minghetti, G.; Manassero, M. *Organometallics* **2002**, *21*, 783–785.
- [22] Doppiu, A.; Minghetti, G.; Cinellu, M. A.; Stoccoro, S.; Zucca, A.; Manassero, M. *Organometallics* **2001**, *20*, 1148–1152.
- [23] Skapski, A. C.; Sutcliffe, V. F.; Young, G. B. *J. Chem. Soc., Chem. Commun.* **1985**, 609–611.
- [24] Butschke, B.; Schwarz, H. *Chemical Science* **2012**, *3*, 308–326.
- [25] Canty, A. J.; Honeyman, R. *Journal of Organometallic Chemistry* **1990**, *387*, 247–263.
- [26] Zhao, S.-B.; Wang, R.-Y.; Wang, S. *Journal of the American Chemical Society* **2007**, *129*, 3092–3093; PMID: 17323955.
- [27] Farsadpour, S.; Ghoochany, L. T.; Sun, Y.; Thiel, W. R. *European Journal of Inorganic Chemistry* **2011**, *2011*, 4603–4609.
- [28] Taghizadeh Ghoochany, L.; Kerner, C.; Farsadpour, S.; Menges, F.; Sun, Y.; Niedner-Schatteburg, G.; Thiel, W. R. *European Journal of Inorganic Chemistry* **2013**, *2013*, 4305–4317.
- [29] Crosby, S. H.; Clarkson, G. J.; Rourke, J. P. *Organometallics* **2011**, *30*, 3603–3609.
- [30] Takayama, A.; Suzuki, T.; Ikeda, M.; Sunatsuki, Y.; Kojima, M. *Dalton Trans.* **2013**, *42*, 14556–14567.
- [31] Crosby, S. H.; Clarkson, G. J.; Deeth, R. J.; Rourke, J. P. *Organometallics* **2010**, *29*, 1966–1976.
- [32] Crosby, S. H.; Clarkson, G. J.; Rourke, J. P. *Journal of the American Chemical Society* **2009**, *131*, 14142–14143; PMID: 19764750.

-
- [33] Mamtora, J.; Crosby, S. H.; Newman, C. P.; Clarkson, G. J.; Rourke, J. P. *Organometallics* **2008**, *27*, 5559–5565.
- [34] Newman, C. P.; Casey-Green, K.; Clarkson, G. J.; Cave, G. W. V.; Errington, W.; Rourke, J. P. *Dalton Trans.* **2007**, 3170–3182.
- [35] Mdleleni, M. M.; Bridgewater, J. S.; Watts, R. J.; Ford, P. C. *Inorganic Chemistry* **1995**, *34*, 2334–2342.
- [36] Butschke, B.; Schwarz, H. *Organometallics* **2010**, *29*, 6002–6011.
- [37] Butschke, B.; Schlangen, M.; Schröder, D.; Schwarz, H. *Chemistry – A European Journal* **2008**, *14*, 11050–11060.
- [38] Parshall, G. W. *Accounts of Chemical Research* **1970**, *3*, 139–144.
- [39] Ryabov, A. D. *Chemical Reviews* **1990**, *90*, 403–424.
- [40] Canty, A. J.; van Koten, G. *Accounts of Chemical Research* **1995**, *28*, 406–413.
- [41] Lersch, M.; Tilset, M. *Chemical Reviews* **2005**, *105*, 2471–2526; PMID: 15941220.
- [42] Boutadla, Y.; Davies, D. L.; Macgregor, S. A.; Poblador-Bahamonde, A. I. *Dalton Trans.* **2009**, 5820–5831.
- [43] Albrecht, M. *Chemical Reviews* **2010**, *110*, 576–623; PMID: 20017477.
- [44] Balcells, D.; Clot, E.; Eisenstein, O. *Chemical Reviews* **2010**, *110*, 749–823; PMID: 20067255.
- [45] Lin, Z. *Coordination Chemistry Reviews* **2007**, *251*, 2280–2291.
- [46] Perutz, R. N.; Sabo-Etienne, S. *Angewandte Chemie International Edition* **2007**, *46*, 2578–2592.
- [47] Butschke, B.; Schlangen, M.; Schröder, D.; Schwarz, H. *Helvetica Chimica Acta* **2008**, *91*, 1902–1915.
- [48] Butschke, B.; Schröder, D.; Schwarz, H. *Organometallics* **2009**, *28*, 4340–4349.
- [49] Butschke, B.; Tabrizi, S. G.; Schwarz, H. *International Journal of Mass Spectrometry* **2010**, *291*, 125–132.
- [50] Butschke, B.; Ghassemi Tabrizi, S.; Schwarz, H. *Chemistry – A European Journal* **2010**, *16*, 3962–3969.
- [51] Zuber, M.; Pruchnik, F. *Polyhedron* **2006**, *25*, 2773–2777.
- [52] Constable, E. C.; Hannon, M. J. *Inorganica Chimica Acta* **1993**, *211*, 101–110.
- [53] Constable, E. C. *J. Chem. Soc., Dalton Trans.* **1985**, 2687–2689.
- [54] Hill, G. S.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 1478–1486.
-

-
- [55] Harris, C.; Kokot, S.; Patil, H.; Sinn, E.; Wong, H. *Australian Journal of Chemistry* **1972**, *25*, 1631–1643.
- [56] Qaseer, H. A. *Croatica Chemica Acta* **2005**, *78*, 79–84.
- [57] Zaghal, M. H.; Qaseer, H. A. *Inorganica Chimica Acta* **1989**, *163*, 193–200.
- [58] O'Connor, C. J.; Sinn, E. *Inorganic Chemistry* **1978**, *17*, 2067–2071.
- [59] Castro-Rodrigo, R.; Esteruelas, M. A.; Fuertes, S.; López, A. M.; Mozo, S.; Oñate, E. *Organometallics* **2009**, *28*, 5941–5951.
- [60] Esteruelas, M. A.; Fernández, I.; Fuertes, S.; López, A. M.; Oñate, E.; Sierra, M. A. *Organometallics* **2009**, *28*, 4876–4879.
- [61] Arikawa, Y.; Asayama, T.; Itatani, K.; Onishi, M. *Journal of the American Chemical Society* **2008**, *130*, 10508–10509.
- [62] Azam, K. A.; Bennett, D. W.; Hassan, M. R.; Haworth, D. T.; Hogarth, G.; Kabir, S. E.; Lindeman, S. V.; Salassa, L.; Simi, S. R.; Siddiquee, T. A. *Organometallics* **2008**, *27*, 5163–5166.
- [63] Zhang, L.; Dang, L.; Wen, T. B.; Sung, H. H.-Y.; Williams, I. D.; Lin, Z.; Jia, G. *Organometallics* **2007**, *26*, 2849–2860.
- [64] Buil, M. L.; Esteruelas, M. A.; Goni, E.; Oliván, M.; Oñate, E. *Organometallics* **2006**, *25*, 3076–3083.
- [65] Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Oñate, E. *Organometallics* **2005**, *24*, 1428–1438.
- [66] Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 3627–3639.
- [67] Coalter, J. N.; Streib, W. E.; Caulton, K. G. *Inorganic Chemistry* **2000**, *39*, 3749–3756.
- [68] Klein, H.-F.; Camadanli, S.; Beck, R.; Leukel, D.; Flörke, U. *Angewandte Chemie International Edition* **2005**, *44*, 975–977.
- [69] Kasahara, A.; Tanaka, K.; Izumi, T. *Bulletin of the Chemical Society of Japan* **1969**, *42*, 1702–1704.
- [70] Navarro, J.; Sola, E.; Martín, M.; Dobrinovitch, I. T.; Lahoz, F. J.; Oro, L. A. *Organometallics* **2004**, *23*, 1908–1917.
- [71] Wong-Foy, A. G.; Henling, L. M.; Day, M.; Labinger, J. A.; Bercaw, J. E. *Journal of Molecular Catalysis A: Chemical* **2002**, *189*, 3–16.
- [72] Cinellu, M. A.; Cocco, F.; Minghetti, G.; Stoccoro, S.; Zucca, A.; Manassero, M. *Journal of Organometallic Chemistry* **2009**, *694*, 2949–2955.
- [73] Ozerov, O. V.; Pink, M.; Watson, L. A.; Caulton, K. G. *Journal of the American Chemical Society* **2004**, *126*, 2105–2113; PMID: 14971945.
-

- [74] Lim, Y.-G.; Kang, J.-B.; Hae Kim, Y. *J. Chem. Soc., Perkin Trans. 1* **1998**, 699–708.
- [75] Schubert, U. S.; Eschbaumer, C.; Heller, M. *Organic Letters* **2000**, 2, 3373–3376; PMID: 11029214.
- [76] Fang, Y.-Q.; Hanan, G. S. *Synlett* **2003**, 2003, 852–854.
- [77] Lützen, A.; Hapke, M. *European Journal of Organic Chemistry* **2002**, 2002, 2292–2297.
- [78] Savage, S. A.; Smith, A. P.; Fraser, C. L. *The Journal of Organic Chemistry* **1998**, 63, 10048–10051.
- [79] Blakemore, D. C.; Marples, L. A. *Tetrahedron Letters* **2011**, 52, 4192–4195.
- [80] Christoph, G.; Lützen, A. *Synthesis* **2010**, 2010, 85–90.
- [81] van Esch, J. H.; Hoffmann, M. A. M.; Nolte, R. J. M. *The Journal of Organic Chemistry* **1995**, 60, 1599–1610.
- [82] Huang, T. L. J.; Brewer, D. G. *Canadian Journal of Chemistry* **1981**, 59, 1689–1700.
- [83] Garber, T.; Van Wallendaël, S.; Rillema, D. P.; Kirk, M.; Hatfield, W. E.; Welch, J. H.; Singh, P. *Inorganic Chemistry* **1990**, 29, 2863–2868.
- [84] Smith, A. P.; Savage, S. A.; Love, J. C.; Fraser, C. L. *Organic Syntheses, Collective Volume* **2004**, 10, 517.
- [85] Smith, A. P.; Savage, S. A.; Love, J. C.; Fraser, C. L. *Organic Syntheses* **2002**, 78, 51.
- [86] Botteghi, C.; Chelucci, C.; Chessa, G.; Delogu, G.; Gladiali, S.; Soccolini, F. *Journal of Organometallic Chemistry* **1986**, 304, 217–225.
- [87] Azzena, U.; Chelucci, G.; Delogu, G.; Gladiali, S.; Marchetti, M.; Soccolini, F.; Botteghi, C. *Gazzetta Chimica Italiana* **1986**, 116, 307.
- [88] Bönnemann, H. *Angewandte Chemie International Edition in English* **1978**, 17, 505–515.
- [89] Smith, L. I.; Opie, J. W. *Organic Syntheses, Collective Volume* **1955**, 3, 56.
- [90] Smith, L. I.; Opie, J. W. *Organic Syntheses* **1948**, 28, 11.
- [91] van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *The Journal of Chemical Physics* **1993**, 99, 4597–4610.
- [92] Chang, C.; Pelissier, M.; Durand, P. *Physica Scripta* **1986**, 34, 394.
- [93] Heully, J. L.; Lindgren, I.; Lindroth, E.; Lundqvist, S.; Martensson-Pendrill, A. M. *Journal of Physics B: Atomic and Molecular Physics* **1986**, 19, 2799.
- [94] Adamo, C.; Barone, V. *The Journal of Chemical Physics* **1999**, 110, 6158–6170.
- [95] Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, 77, 3865–3868.
- [96] Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, 78, 1396–1396.

- [97] Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
- [98] Neese, F. *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2012**, *2*, 73–78.
- [99] Pantazis, D. A.; Neese, F. *Journal of Chemical Theory and Computation* **2009**, *5*, 2229–2238.
- [100] Pantazis, D. A.; Chen, X.-Y.; Landis, C. R.; Neese, F. *Journal of Chemical Theory and Computation* **2008**, *4*, 908–919.
- [101] Göller, A. H.; Grummt, U.-W. *Chemical Physics Letters* **2002**, *354*, 233–242.
- [102] Göller, A.; Grummt, U.-W. *Chemical Physics Letters* **2000**, *321*, 399–405.
- [103] Zahn, S.; Reckien, W.; Kirchner, B.; Staats, H.; Matthey, J.; Lützen, A. *Chemistry – A European Journal* **2009**, *15*, 2572–2580.
- [104] Kalyani, D.; Sanford, M. S. *Organic Letters* **2005**, *7*, 4149–4152; PMID: 16146374.
- [105] Kuzmina, O. M.; Steib, A. K.; Flubacher, D.; Knochel, P. *Organic Letters* **2012**, *14*, 4818–4821.
- [106] Ackermann, L.; Potukuchi, H. K.; Kapdi, A. R.; Schulzke, C. *Chemistry – A European Journal* **2010**, *16*, 3300–3303.
- [107] Kayushina, E.; Levin, D.; Mortikov, E.; Promonenkov, V. *Bulletin of the Academy of Sciences of the USSR, Division of chemical science* **1986**, *35*, 1474–1477.
- [108] Meek, J. S.; Merrow, R. T.; Cristol, S. J. *Journal of the American Chemical Society* **1952**, *74*, 2667–2668.
- [109] Abbiati, G.; Arcadi, A.; Bianchi, G.; Di Giuseppe, S.; Marinelli, F.; Rossi, E. *The Journal of Organic Chemistry* **2003**, *68*, 6959–6966; PMID: 12946136.
- [110] Zhou, B.; Chen, H.; Wang, C. *Journal of the American Chemical Society* **2013**, *135*, 1264–1267.
- [111] US 20020064681 A1 - Luminescence device, display apparatus and metal coordination compound; 2002.
- [112] Reddy, V. P.; Qiu, R.; Iwasaki, T.; Kambe, N. *Organic Letters* **2013**, *15*, 1290–1293.
- [113] Liu, C.; Yang, W. *Chem. Commun.* **2009**, 6267–6269.
- [114] Shavaleev, N. M.; Monti, F.; Scopelliti, R.; Armaroli, N.; Grätzel, M.; Nazeeruddin, M. K. *Organometallics* **2012**, *31*, 6288–6296.
- [115] Muller, P. *Pure and Applied Chemistry* **1994**, *66*, 1077–1184.
- [116] Mikami, K.; Itoh, Y.; Yamanaka, M. *Chemical Reviews* **2004**, *104*, 1–16; PMID: 14719970.
- [117] Müller, K.; Faeh, C.; Diederich, F. *Science* **2007**, *317*, 1881–1886.
- [118] Leroux, F. *ChemBioChem* **2004**, *5*, 644–649.

- [119] Alongi, K. S.; Shields, G. C. In *Annual Reports in Computational Chemistry*; Wheeler, R. A., Ed.; Annual Reports in Computational Chemistry, Vol. 6; Elsevier, 2010; pp 113–138.
- [120] Mujika, J. I.; Mercero, J. M.; Lopez, X. *The Journal of Physical Chemistry A* **2003**, *107*, 6099–6107.
- [121] Jang, Y. H.; Goddard, W. A.; Noyes, K. T.; Sowers, L. C.; Hwang, S.; Chung, D. S. *The Journal of Physical Chemistry B* **2003**, *107*, 344–357.
- [122] Lopez, X.; Schaefer, M.; Dejaegere, A.; Karplus, M. *Journal of the American Chemical Society* **2002**, *124*, 5010–5018; PMID: 11982365.
- [123] Hunter, E. P. L.; Lias, S. G. *Journal of Physical and Chemical Reference Data* **1998**, *27*, 413–656.
- [124] Oresmaa, L.; Haukka, M.; Vainiotalo, P.; Pakkanen, T. A. *The Journal of Organic Chemistry* **2002**, *67*, 8216–8219; PMID: 12423154.
- [125] David R. Lide, e. *CRC Handbook of Chemistry and Physics, 89th Edition (Internet Version 2009)*, 89th ed.; CRC Press/Taylor and Francis, Boca Raton, FL, 2009.
- [126] Aue, D. H.; Webb, H. M.; Davidson, W. R.; Toure, P.; Hopkins, H. P.; Moulik, S. P.; Jahagirdar, D. V. *Journal of the American Chemical Society* **1991**, *113*, 1770–1780.
- [127] Timperley, C. M.; Bird, M.; Heard, S. C.; Notman, S.; Read, R. W.; Tattersall, J. E.; Turner, S. R. *Journal of Fluorine Chemistry* **2005**, *126*, 1160–1165.
- [128] Hoefelmeyer, J. D.; Schulte, M.; Tschinkl, M.; Gabbaï, F. P. *Coordination Chemistry Reviews* **2002**, *235*, 93–103.
- [129] Hosmane, R. S.; Liebman, J. F. *Structural Chemistry* **2009**, *20*, 693–697.
- [130] Romeo, R.; Scolaro, L. M.; Catalano, V.; Achar, S.; John Wiley & Sons, Inc., 1998; pp 153–158.
- [131] Eaborn, C.; Kundu, K.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1981**, 933–938.
- [132] Hill, G. S.; Irwin, M. J.; Levy, C. J.; Rendina, L. M.; Puddephatt, R. J.; Andersen, R. A.; Mclean, L.; John Wiley & Sons, Inc., 1998; pp 149–153.
- [133] Rashidi, M.; Fakhroieian, Z.; Puddephatt, R. J. *Journal of Organometallic Chemistry* **1991**, *406*, 261–267.
- [134] Hadj-Bagheri, N.; Puddephatt, R. J. *Polyhedron* **1988**, *7*, 2695–2702.
- [135] Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643–1648.
- [136] Minghetti, G.; Doppiu, A.; Zucca, A.; Stoccoro, S.; Cinellu, M.; Manassero, M.; Sansoni, M. *Chemistry of Heterocyclic Compounds* **1999**, *35*, 992–1000.
- [137] Owen, J. S.; Labinger, J. A.; Bercaw, J. E. *Journal of the American Chemical Society* **2004**, *126*, 8247–8255; PMID: 15225067.

- [138] Battan, L.; Fantasia, S.; Manassero, M.; Pasini, A.; Sansoni, M. *Inorganica Chimica Acta* **2005**, *358*, 555–564.
- [139] Pearson, R. G. *Inorganic Chemistry* **1973**, *12*, 712–713.
- [140] Jorgensen, C. K. *Inorganic Chemistry* **1964**, *3*, 1201–1202.
- [141] Cuevas, J. V.; García-Herbosa, G.; Miguel, D.; Muñoz, A. *Inorganic Chemistry Communications* **2002**, *5*, 340–343.
- [142] Vicente, J.; Abad, J.-A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chemistry – A European Journal* **1999**, *5*, 3066–3075.
- [143] Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, *16*, 2127–2138.
- [144] Jagodzinska, M.; Huguenot, F.; Candiani, G.; Zanda, M. *ChemMedChem* **2009**, *4*, 49–51.
- [145] Petretto, G. L.; Ph.D. thesis; Scuola di Dottorato in Scienze Chimiche; 2009.
- [146] Zucca, A.; Cordeschi, D.; Maidich, L.; Pilo, M. I.; Masolo, E.; Stoccoro, S.; Cinellu, M. A.; Galli, S. *Inorganic Chemistry* **2013**, *52*, 7717–7731.
- [147] Yagyu, T.; Ohashi, J.-i.; Maeda, M. *Organometallics* **2007**, *26*, 2383–2391.
- [148] Begantsova, Y. E.; Bochkarev, L. N.; Ketkov, S. Y.; Baranov, E. V.; Bochkarev, M. N.; Yakhvarov, D. G. *Journal of Organometallic Chemistry* **2013**, *733*, 1–8.
- [149] Jenkins, D. M.; Bernhard, S. *Inorganic Chemistry* **2010**, *49*, 11297–11308.
- [150] Godbert, N.; Pugliese, T.; Aiello, I.; Bellusci, A.; Crispini, A.; Ghedini, M. *European Journal of Inorganic Chemistry* **2007**, *2007*, 5105–5111.
- [151] Cho, J.-Y.; Domercq, B.; Barlow, S.; Suponitsky, K. Y.; Li, J.; Timofeeva, T. V.; Jones, S. C.; Hayden, L. E.; Kimyonok, A.; South, C. R.; Weck, M.; Kippelen, B.; Marder, S. R. *Organometallics* **2007**, *26*, 4816–4829.
- [152] Niedermair, F.; Waich, K.; Kappaun, S.; Mayr, T.; Trimmel, G.; Mereiter, K.; Slugovc, C. *Inorganica Chimica Acta* **2007**, *360*, 2767–2777.
- [153] Cho, J.-Y.; Suponitsky, K. Y.; Li, J.; Timofeeva, T. V.; Barlow, S.; Marder, S. R. *Journal of Organometallic Chemistry* **2005**, *690*, 4090–4093.
- [154] Brookhart, M.; Green, M. L. H.; Parkin, G. *Proceedings of the National Academy of Sciences* **2007**, *104*, 6908–6914.
- [155] Blanksby, S. J.; Ellison, G. B. *Accounts of Chemical Research* **2003**, *36*, 255–263.
- [156] Ervin, K. M.; DeTuri, V. F. *The Journal of Physical Chemistry A* **2002**, *106*, 9947–9956.

- [157] Ghedini, M.; Aiello, I.; Crispini, A.; Golemme, A.; La Deda, M.; Pucci, D. *Coordination Chemistry Reviews* **2006**, *250*, 1373–1390.
- [158] Slater, J. W.; Rourke, J. P. *Journal of Organometallic Chemistry* **2003**, *688*, 112–120.
- [159] Crispini, A.; Ghedini, M. *J. Chem. Soc., Dalton Trans.* **1997**, 75–80.
- [160] Navarro-Ranninger, C.; Lopez-Solera, I.; Alvarez-Valdes, A.; Rodriguez-Ramos, J. H.; Masaguer, J. R.; Garcia-Ruano, J. L.; Solans, X. *Organometallics* **1993**, *12*, 4104–4111.
- [161] Rodríguez, J.; Zafrilla, J.; Albert, J.; Crespo, M.; Granell, J.; Calvet, T.; Font-Bardía, M. *Journal of Organometallic Chemistry* **2009**, *694*, 2467–2475.
- [162] Crespo, M.; Martinez, M.; Sales, J.; Solans, X.; Font-Bardía, M. *Organometallics* **1992**, *11*, 1288–1295.
- [163] Crespo, M.; Solans, X.; Font-Bardía, M. *Journal of Organometallic Chemistry* **1996**, *518*, 105–113.
- [164] Crespo, M.; Solans, X.; Font-Bardía, M. *Organometallics* **1995**, *14*, 355–364.
- [165] Crespo, M.; Martinez, M.; Sales, J. *Organometallics* **1993**, *12*, 4297–4304.
- [166] Crespo, M.; Solans, X.; Font-Bardía, M. *Polyhedron* **1998**, *17*, 1651–1657.
- [167] Crespo, M.; Font-Bardía, M.; Solans, X. *Polyhedron* **2002**, *21*, 105–113.
- [168] Anderson, C.; Crespo, M.; Rochon, F. D. *Journal of Organometallic Chemistry* **2001**, *631*, 164–174.
- [169] Anderson, C.; Crespo, M.; Font-Bardía, M.; Klein, A.; Solans, X. *Journal of Organometallic Chemistry* **2000**, *601*, 22–33.
- [170] Crespo, M.; Grande, C.; Klein, A.; Font-Bardía, M.; Solans, X. *Journal of Organometallic Chemistry* **1998**, *563*, 179–190.
- [171] Baar, C. R.; Jenkins, H. A.; Vittal, J. J.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 2805–2818.
- [172] López, O.; Crespo, M.; Font-Bardía, M.; Solans, X. *Organometallics* **1997**, *16*, 1233–1240.
- [173] Allen, F. H. *Acta Crystallographica Section B* **2002**, *58*, 380–388.
- [174] Klein, A.; Slageren, J. v.; Zális, S. *European Journal of Inorganic Chemistry* **2003**, *2003*, 1917–1938.
- [175] Achar, S.; Catalano, V. J. *Polyhedron* **1997**, *16*, 1555–1561.
- [176] Britovsek, G. J. P.; Taylor, R. A.; Sunley, G. J.; Law, D. J.; White, A. J. P. *Organometallics* **2006**, *25*, 2074–2079.
- [177] Thomas, C. M.; Peters, J. C. *Organometallics* **2005**, *24*, 5858–5867.
- [178] Bader, R. F. W. *Atoms in Molecules - A Quantum Theory*; Oxford University Press, 1990.

-
- [179] Sierraalta, A.; Ruetter, F. *Journal of Computational Chemistry* **1994**, *15*, 313–321.
- [180] Bader, R. F. W.; Essén, H. *The Journal of Chemical Physics* **1984**, *80*, 1943–1960.
- [181] Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *Journal of the American Chemical Society* **1983**, *105*, 5061–5068.
- [182] Su, P.; Li, H. *The Journal of Chemical Physics* **2009**, *131*, 014102.
- [183] Fox, M. A.; Whitesell, J. K. *Organische Chemie: Grundlagen, Mechanismen, Bioorganische Anwendungen*; Springer, 1995.
- [184] Bondi, A. *The Journal of Physical Chemistry* **1964**, *68*, 441–451.
- [185] Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chemical Reviews* **2005**, *105*, 3842–3888.
- [186] Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *Journal of the American Chemical Society* **1996**, *118*, 6317–6318.
- [187] Barquera-Lozada, J. E.; Obenhuber, A.; Hauf, C.; Scherer, W. *The Journal of Physical Chemistry A* **2013**, *117*, 4304–4315.
- [188] Omae, I. *Coordination Chemistry Reviews* **2004**, *248*, 995–1023.
- [189] Butschke, B.; Schwarz, H. *International Journal of Mass Spectrometry* **2011**, *306*, 108–113.
- [190] Petretto, G. L.; Zucca, A.; Stoccoro, S.; Cinellu, M. A.; Minghetti, G. *Journal of Organometallic Chemistry* **2010**, *695*, 256–259.
- [191] Butschke, B.; Schlangen, M.; Schröder, D.; Schwarz, H. *International Journal of Mass Spectrometry* **2009**, *283*, 3–8.
- [192] Kwak, J.; Ohk, Y.; Jung, Y.; Chang, S. *Journal of the American Chemical Society* **2012**, *134*, 17778–17788.
- [193] Shibata, T.; Takayasu, S.; Yuzawa, S.; Otani, T. *Organic Letters* **2012**, *14*, 5106–5109.
- [194] Bojan, R. V.; Czerwieniec, R.; Laguna, A.; Lasanta, T.; Lopez-de Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Yersin, H. *Dalton Trans.* **2013**, *42*, 4267–4277.
- [195] Rachford, A. A.; Castellano, F. N. *Inorganic Chemistry* **2009**, *48*, 10865–10867; PMID: 19852485.
- [196] Sun, W.; Zhu, H.; Barron, P. M. *Chemistry of Materials* **2006**, *18*, 2602–2610.
- [197] Chen, J.-L.; Zhang, L.-Y.; Chen, Z.-N.; Gao, L.-B.; Abe, M.; Sasaki, Y. *Inorganic Chemistry* **2004**, *43*, 1481–1490; PMID: 14966986.
- [198] Frezza, M.; Dou, Q. P.; Xiao, Y.; Samouei, H.; Rashidi, M.; Samari, F.; Hemmateenejad, B. *Journal of Medicinal Chemistry* **2011**, *54*, 6166–6176.

- [199] Dulai, A.; de Bod, H.; Hanton, M. J.; Smith, D. M.; Downing, S.; Mansell, S. M.; Wass, D. F. *Organometallics* **2009**, *28*, 4613–4616.
- [200] Adam, F. I.; Hogarth, G.; Kabir, S. E.; Richards, I. *Comptes Rendus Chimie* **2008**, *11*, 890 – 905.
- [201] Gao, W.; Ekström, J.; Liu, J.; Chen, C.; Eriksson, L.; Weng, L.; Åkermark, B.; Sun, L. *Inorganic Chemistry* **2007**, *46*, 1981–1991; PMID: 17295467.
- [202] Huynh, H. V.; Fröhlich, R.; Hahn, F. E. *Zeitschrift für Naturforschung B* **2003**, *58B*, 359–361.
- [203] Díaz, C.; Araya, E. *Polyhedron* **1997**, *16*, 1775 – 1781.
- [204] Song, L.; Lin, P.; Li, Z.-H.; Li, J.-R.; Du, S.-W.; Wu, X.-T. *Polyhedron* **2007**, *26*, 1199 – 1204.
- [205] Castro, R.; Romero, J.; Garcia-Vazquez, J.; Sousa, A.; Chang, Y.; Zubieta, J. *Inorganica Chimica Acta* **1996**, *245*, 119 – 122.
- [206] Li, J.-J.; Duan, T.; Zhang, Q.-F.; Leung, W.-H. *Chemistry Letters* **2009**, *38*, 506–507.
- [207] Hossain, M. K.; Rajbangshi, S.; Rahaman, A.; Chowdhury, M. A. H.; Siddiquee, T. A.; Ghosh, S.; Richmond, M. G.; Nordlander, E.; Hogarth, G.; Kabir, S. E. *Journal of Organometallic Chemistry* **2013**, –.
- [208] Chaplin, A. B.; Scopelliti, R.; Dyson, P. J. *European Journal of Inorganic Chemistry* **2005**, *2005*, 4762–4774.
- [209] Moura, E. M.; Dickman, M. H.; Siebald, H. G.; Gama, G. J. *Polyhedron* **1999**, *18*, 2899 – 2906.
- [210] Xiao, J.; Cowie, M. *Canadian Journal of Chemistry* **1993**, *71*, 726–737.
- [211] Martínez, J.; Adrio, L. A.; Antelo, J. M.; Ortigueira, J. M.; Pereira, M. T.; Fernández, J. J.; Fernández, A.; Vila, J. M. *Journal of Organometallic Chemistry* **2006**, *691*, 2721 – 2733.
- [212] Zhuravel, M. A.; Glueck, D. S.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **1999**, *18*, 4673–4676.
- [213] Liu, C.; Sarkar, B.; Liaw, B.-J.; Lin, Y.-W.; Lobana, T. S.; Wang, J.-C. *Journal of Organometallic Chemistry* **2009**, *694*, 2134 – 2141.
- [214] Effendy; Marchetti, F.; Pettinari, C.; Pettinari, R.; Skelton, B. W.; White, A. H. *Inorganica Chimica Acta* **2007**, *360*, 1388 – 1413.
- [215] Blitz, J. P.; Lucas, N. T.; Humphrey, M. G. *Journal of Organometallic Chemistry* **2002**, *650*, 133 – 140.
- [216] Low, P. M. N.; Yong, Y. L.; Yan, Y. K.; Hor, T. S. A.; Lam, S.-L.; Chan, K. K.; Wu, C.; Au-Yeung, S. C. F.; Wen, Y.-S.; Liu, L.-K. *Organometallics* **1996**, *15*, 1369–1375.
- [217] Meyer, K. E.; Root, D. R.; Fanwick, P. E.; Walton, R. A. *Inorganic Chemistry* **1992**, *31*, 3067–3076.

- [218] Jaafar, M. H.; Al-Ohaly, A. A. *Asian Journal of Chemistry* **2013**, *25*, 642–644.
- [219] Battisti, A.; Bellina, O.; Diversi, P.; Losi, S.; Marchetti, F.; Zanello, P. *European Journal of Inorganic Chemistry* **2007**, *2007*, 865–875.
- [220] Artigas, M.; Crespo, O.; Gimeno, M.; Jones, P. G.; Laguna, A.; Villacampa, M. *Journal of Organometallic Chemistry* **1998**, *561*, 1 – 6.
- [221] Tang, S. S.; Chang, C.-P.; Lin, I. J. B.; Liou, L.-S.; Wang, J.-C. *Inorganic Chemistry* **1997**, *36*, 2294–2300.
- [222] Irwin, M. J.; Vittal, J. J.; Yap, G. P. A.; Puddephatt, R. J. *Journal of the American Chemical Society* **1996**, *118*, 13101–13102.
- [223] Raoof, F.; Esmailbeig, A. R.; Nabavizadeh, S. M.; Niroomand Hosseini, F.; Kubicki, M. *Organometallics* **2013**, *32*, 3850–3858.
- [224] Nabavizadeh, S. M.; Sepehrpour, H.; Kia, R.; Rheingold, A. L. *Journal of Organometallic Chemistry* **2013**, *745–746*, 148 – 157.
- [225] Samouei, H.; Rashidi, M.; Heinemann, F. W. *Journal of Organometallic Chemistry* **2011**, *696*, 3764 – 3771.
- [226] Jamali, S.; Czerwieniec, R.; Kia, R.; Jamshidi, Z.; Zabel, M. *Dalton Trans.* **2011**, *40*, 9123–9130.
- [227] Nabavizadeh, S. M.; Amini, H.; Shahsavari, H. R.; Namdar, M.; Rashidi, M.; Kia, R.; Hemmateenejad, B.; Nekoeinia, M.; Ariaftard, A.; Hosseini, F. N.; Gharavi, A.; Khalafi-Nezhad, A.; Sharbati, M. T.; Panahi, F. *Organometallics* **2011**, *30*, 1466–1477.
- [228] Haghighi, M. G.; Rashidi, M.; Nabavizadeh, S. M.; Jamali, S.; Puddephatt, R. J. *Dalton Trans.* **2010**, *39*, 11396–11402.
- [229] Nabavizadeh, S. M.; Haghighi, M. G.; Esmailbeig, A. R.; Raoof, F.; Mandegani, Z.; Jamali, S.; Rashidi, M.; Puddephatt, R. J. *Organometallics* **2010**, *29*, 4893–4899.
- [230] Ghavale, N.; Wadawale, A.; Dey, S.; Jain, V. K. *Journal of Organometallic Chemistry* **2010**, *695*, 1237 – 1245.
- [231] Jamali, S.; Nabavizadeh, S. M.; Rashidi, M. *Inorganic Chemistry* **2008**, *47*, 5441–5452; PMID: 18484719.
- [232] Adrio, L.; Antelo, J. M.; Ortigueira, J. M.; Lata, D.; Pereira, T.; López-Torres, M.; Vila, J. M. *Zeitschrift für anorganische und allgemeine Chemie* **2007**, *633*, 1875–1882.
- [233] Zucca, A.; Stoccoro, S.; Cinellu, M. A.; Minghetti, G.; Manassero, M.; Sansoni, M. *European Journal of Inorganic Chemistry* **2002**, *2002*, 3336–3346.
- [234] Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99–127.

- [235] Steffen, W. L.; Palenik, G. J. *Inorganic Chemistry* **1976**, *15*, 2432–2439.
- [236] Flener Lovitt, C.; Frenking, G.; Girolami, G. S. *Organometallics* **2012**, *31*, 4122–4132.
- [237] Hoseini, S. J.; Nabavizadeh, S. M.; Jamali, S.; Rashidi, M. *Journal of Organometallic Chemistry* **2007**, *692*, 1990–1996.
- [238] Rashidi, M.; Jamali, S.; Hashemi, M. *Journal of Organometallic Chemistry* **2001**, *633*, 105–113.
- [239] Yahav-Levi, A.; Goldberg, I.; Vigalok, A.; Vedernikov, A. N. *Journal of the American Chemical Society* **2008**, *130*, 724–731.
- [240] Peters, R. G.; White, S.; Roddick, D. M. *Organometallics* **1998**, *17*, 4493–4499.
- [241] Leung, S. Y.-L.; Lam, W. H.; Zhu, N.; Yam, V. W.-W. *Organometallics* **2010**, *29*, 5558–5569.
- [242] Nocera, D. G.; Maverick, A. W.; Winkler, J. R.; Che, C.-M.; Gray, H. B. *Oxidation-Reduction Photochemistry of Polynuclear Complexes in Solution*, 1983; Chapter 3, pp 21–33.
- [243] Lu, W.; Chan, M. C. W.; Zhu, N.; Che, C.-M.; Li, C.; Hui, Z. *Journal of the American Chemical Society* **2004**, *126*, 7639–7651; PMID: 15198612.
- [244] Lu, W.; Chan, M. C. W.; Cheung, K.-K.; Che, C.-M. *Organometallics* **2001**, *20*, 2477–2486.
- [245] Lai, S.-W.; Chan, M. C.-W.; Cheung, T.-C.; Peng, S.-M.; Che, C.-M. *Inorganic Chemistry* **1999**, *38*, 4046–4055.
- [246] Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.; Hwang, W. S.; Lin, I. J. B. *Chemical Reviews* **2009**, *109*, 3561–3598; PMID: 19361198.
- [247] Maidich, L.; Zuri, G.; Stoccoro, S.; Cinellu, M. A.; Masia, M.; Zucca, A. *Organometallics* **2013**, *32*, 438–448.
- [248] Pregosin, P. S.; Kunz, R. W. *³¹P and ¹³C NMR of Transition Metal Phosphine Complexes*; Springer Berlin-Heidelberg, 1979.
- [249] Tolman, C. A. *Chemical Reviews* **1977**, *77*, 313–348.
- [250] Waddell, P. G.; Slawin, A. M. Z.; Woollins, J. D. *Dalton Trans.* **2010**, *39*, 8620–8625.
- [251] Rigamonti, L.; Manassero, C.; Rusconi, M.; Manassero, M.; Pasini, A. *Dalton Trans.* **2009**, 1206–1213.
- [252] Haar, C. M.; Nolan, S. P.; Marshall, W. J.; Moloy, K. G.; Prock, A.; Giering, W. P. *Organometallics* **1999**, *18*, 474–479.
- [253] Romeo, R.; Alibrandi, G. *Inorganic Chemistry* **1997**, *36*, 4822–4830.
- [254] Romeo, R.; Plutino, M. R.; Scolaro, L. M.; Stoccoro, S. *Inorganica Chimica Acta* **1997**, *265*, 225–233.

- [255] Cobley, C. J.; Pringle, P. G. *Inorganica Chimica Acta* **1997**, *265*, 107–115.
- [256] Passmore, J.; Taylor, P.; Whidden, T.; White, P. S. *Canadian Journal of Chemistry* **1979**, *57*, 968–973.
- [257] Guido, E.; D'Amico, G.; Russo, N.; Sicilia, E.; Rizzato, S.; Albinati, A.; Romeo, A.; Plutino, M. R.; Romeo, R. *Inorganic Chemistry* **2011**, *50*, 2224–2239.
- [258] Smith, M. B. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 7th ed.; John Wiley & Sons, Inc., Hoboken, New Jersey, 2013.
- [259] Hammett, L. P. *Journal of the American Chemical Society* **1937**, *59*, 96–103.
- [260] Al-Jibori, S. A.; Al-Zaubai, A. S.; Mohammed, M. Y.; Al-Allaf, T. A. *Transition Metal Chemistry* **2007**, *32*, 281–286.
- [261] Crespo, M.; Granell, J.; Solans, X.; Font-Bardà, M. *Journal of Organometallic Chemistry* **2003**, *681*, 143–149.
- [262] Heise, J. D.; Nash, J. J.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1996**, *15*, 1690–1696.
- [263] Chaudret, B.; Commenges, G.; Poilblanc, R. *J. Chem. Soc., Dalton Trans.* **1984**, 1635–1639.
- [264] Vicente, J.; Abad, J.-A.; Martínez-Viviente, E.; Jones, P. G. *Organometallics* **2002**, *21*, 4454–4467.
- [265] Eguillor, B.; Caldwell, P. J.; Cockett, M. C. R.; Duckett, S. B.; John, R. O.; Lynam, J. M.; Sleight, C. J.; Wilson, I. *Journal of the American Chemical Society* **2012**, *134*, 18257–18265.
- [266] Byabartta, P.; Laguna, M. *Transition Metal Chemistry* **2007**, *32*, 187–192.
- [267] Garrou, P. E. *Chemical Reviews* **1981**, *81*, 229–266.
- [268] Günther, H. *Angewandte Chemie International Edition in English* **1972**, *11*, 861–874.
- [269] Garbisch, E. W. *Journal of Chemical Education* **1968**, *45*, 480.
- [270] Budzelaar, P. H. M.; *gNMR - NMR Simulation Program - Version 5.0.6.0*; 2006.
- [271] Kaeser, A.; Mohankumar, M.; Mohanraj, J.; Monti, F.; Holler, M.; Cid, J.-J.; Moudam, O.; Nierengarten, I.; Karmazin-Brelot, L.; Duhayon, C.; Delavaux-Nicot, B.; Armaroli, N.; Nierengarten, J.-F. *Inorganic Chemistry* **2013**, *52*, 12140–12151.
- [272] Masui, H. *Coordination Chemistry Reviews* **2001**, *219–221*, 957–992.
- [273] Edwards, G. L.; Black, D. S.; Deacon, G. B.; Wakelin, L. P. *Canadian Journal of Chemistry* **2005**, *83*, 980–989.
- [274] Otto, S.; Roodt, A. *Inorganica Chimica Acta* **2004**, *357*, 1–10.
- [275] Buchner, W.; Schenk, W. A. *Inorganic Chemistry* **1984**, *23*, 132–137.
- [276] Burdett, J. K.; Albright, T. A. *Inorganic Chemistry* **1979**, *18*, 2112–2120.

- [277] Cotton, F. A. *Inorganic Chemistry* **1964**, 3, 702–711.
- [278] Minkin, V. I. *Pure and Applied Chemistry* **1999**, 71, 1919–1981.
- [279] Pearson, R. G. *Journal of Chemical Education* **1999**, 76, 267.
- [280] Pearson, R. G. *Accounts of Chemical Research* **1993**, 26, 250–255.
- [281] Kaim, W.; Klein, A.; Glöckle, M. *Accounts of Chemical Research* **2000**, 33, 755–763; PMID: 11087312.
- [282] Evans, P. G.; Brown, N. A.; Clarkson, G. J.; Newman, C. P.; Rourke, J. P. *Journal of Organometallic Chemistry* **2006**, 691, 1251–1256.
- [283] Espinet, P.; Perez, J.; Marcos, M.; Ros, M. B.; Serrano, J. L.; Barbera, J.; Levelut, A. M. *Organometallics* **1990**, 9, 2028–2033.
- [284] Stonehouse, J.; Adell, P.; Keeler, J.; Shaka, A. J. *Journal of the American Chemical Society* **1994**, 116, 6037–6038.
- [285] Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986.
- [286] Minghetti, G.; Zucca, A.; Stoccoro, S.; Cinellu, M. A.; Manassero, M.; Sansoni, M. *Journal of Organometallic Chemistry* **1994**, 481, 195–204.
- [287] Minghetti, G.; Cinellu, M. A.; Stoccoro, S.; Zucca, A. *Gazzetta Chimica Italiana* **1992**, 122, 455–459.
- [288] Chisholm, M. H.; Huffman, J. C.; Rothwell, I. P.; Bradley, P. G.; Kress, N.; Woodruff, W. H. *Journal of the American Chemical Society* **1981**, 103, 4945–4947.
- [289] Pregosin, P. *Coordination Chemistry Reviews* **1982**, 44, 247–291.
- [290] Davies, H. M. L.; Manning, J. R. *Nature* **2008**, 451, 417–424.
- [291] Godula, K.; Sames, D. *Science* **2006**, 312, 67–72.
- [292] Bercaw, J. E.; Chen, G. S.; Labinger, J. A.; Lin, B.-L. *Organometallics* **2010**, 29, 4354–4359.
- [293] Wik, B. J.; Lersch, M.; Tilset, M. *Journal of the American Chemical Society* **2002**, 124, 12116–12117; PMID: 12371850.
- [294] Heiberg, H.; Johansson, L.; Gropen, O.; Ryan, O. B.; Swang, O.; Tilset, M. *Journal of the American Chemical Society* **2000**, 122, 10831–10845.
- [295] Holtcamp, M. W.; Henling, L. M.; Day, M. W.; Labinger, J. A.; Bercaw, J. E. *Inorganica Chimica Acta* **1998**, 270, 467–478.
- [296] Wick, D. D.; Goldberg, K. I. *Journal of the American Chemical Society* **1997**, 119, 10235–10236.

- [297] Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *Journal of the American Chemical Society* **1997**, *119*, 848–849.
- [298] Jenkins, H. A.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1946–1955.
- [299] Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Journal of the American Chemical Society* **1996**, *118*, 5961–5976.
- [300] Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Journal of the American Chemical Society* **1995**, *117*, 9371–9372.
- [301] Crabtree, R. H. *Coordination Chemistry Reviews* **2013**, *257*, 755–766.
- [302] Iglesias, M.; Albrecht, M. *Dalton Trans.* **2010**, *39*, 5213–5215.
- [303] Schuster, O.; Yang, L.; Raubenheimer, H. G.; Albrecht, M. *Chemical Reviews* **2009**, *109*, 3445–3478; PMID: 19331408.
- [304] Wickramasinghe, W. A.; Bird, P. H.; Serpone, N. *J. Chem. Soc., Chem. Commun.* **1981**, 1284–1286.
- [305] Stander-Grobler, E.; Schuster, O.; Heydenrych, G.; Cronje, S.; Tosh, E.; Albrecht, M.; Frenking, G.; Raubenheimer, H. G. *Organometallics* **2010**, *29*, 5821–5833.
- [306] Moorlag, C.; Wolf, M. O.; Bohne, C.; Patrick, B. O. *Journal of the American Chemical Society* **2005**, *127*, 6382–6393; PMID: 15853346.
- [307] Moorlag, C.; Clot, O.; Wolf, M. O.; Patrick, B. O. *Chem. Commun.* **2002**, 3028–3029.
- [308] Constable, E. C.; Dunne, S. J.; Rees, D. G. F.; Schmitt, C. X. *Chem. Commun.* **1996**, 1169–1170.
- [309] Zucca, A.; Cordeschi, D.; Stoccoro, S.; Cinellu, M. A.; Minghetti, G.; Chelucci, G.; Manassero, M. *Organometallics* **2011**, *30*, 3064–3074.
- [310] Benitez, D.; Shapiro, N. D.; Tkatchouk, E.; Wang, Y.; Goddard, W. A.; Toste, F. D. *Nature Chemistry* **2009**, *1*, 482–486.
- [311] Hashmi, A. S. K. *Angewandte Chemie International Edition* **2008**, *47*, 6754–6756.
- [312] Dixon, D. A.; Arduengo, A. J. *The Journal of Physical Chemistry* **1991**, *95*, 4180–4182.
- [313] Poulain, A.; Neels, A.; Albrecht, M. *European Journal of Inorganic Chemistry* **2009**, *2009*, 1871–1881.
- [314] Albrecht, M.; Stoeckli-Evans, H. *Chem. Commun.* **2005**, 4705–4707.
- [315] Crispini, A.; Harrison, K. N.; Orpen, A. G.; Pringle, P. G.; Wheatcroft, J. R. *J. Chem. Soc., Dalton Trans.* **1996**, 1069–1076.
- [316] Mather, G. G.; Pidcock, A.; Rapsey, G. J. N. *J. Chem. Soc., Dalton Trans.* **1973**, 2095–2099.
- [317] Appleton, T.; Clark, H.; Manzer, L. *Coordination Chemistry Reviews* **1973**, *10*, 335–422.

- [318] Pidcock, A. *Applications of P-31 NMR to the study of Metal-Phosphorus Bonding*; Alyea, E. C.; Meek, D. W., Eds.; Advances in Chemistry, Vol. Catalytic Aspects of Metal Phosphine Complexes, 1982; pp 1–22.
- [319] Romeo, R.; D'Amico, G.; Guido, E.; Albinati, A.; Rizzato, S. *Inorganic Chemistry* **2007**, *46*, 10681–10692; PMID: 17999491.
- [320] Romeo, R.; Carnabuci, S.; Fenech, L.; Plutino, M. R.; Albinati, A. *Angewandte Chemie International Edition* **2006**, *45*, 4494–4498.
- [321] Romeo, R.; Carnabuci, S.; Plutino, M. R.; Romeo, A.; Rizzato, S.; Albinati, A. *Inorganic Chemistry* **2005**, *44*, 1248–1262.
- [322] Romeo, R.; Fenech, L.; Carnabuci, S.; Plutino, M. R.; Romeo, A. *Inorganic Chemistry* **2002**, *41*, 2839–2847; PMID: 12033890.
- [323] Romeo, R.; Fenech, L.; Scolaro, L. M.; Albinati, A.; Macchioni, A.; Zuccaccia, C. *Inorganic Chemistry* **2001**, *40*, 3293–3302.
- [324] Owen, J. S.; Labinger, J. A.; Bercaw, J. E. *Journal of the American Chemical Society* **2006**, *128*, 2005–2016; PMID: 16464102.
- [325] Driver, T. G.; Day, M. W.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2005**, *24*, 3644–3654.
- [326] Heyduk, A. F.; Driver, T. G.; Labinger, J. A.; Bercaw, J. E. *Journal of the American Chemical Society* **2004**, *126*, 15034–15035; PMID: 15547993.
- [327] Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *Journal of the American Chemical Society* **2002**, *124*, 1378–1399; PMID: 11841307.
- [328] Johansson, L.; Ryan, O. B.; Rømming, C.; Tilset, M. *Journal of the American Chemical Society* **2001**, *123*, 6579–6590; PMID: 11439044.
- [329] Johansson, L.; Tilset, M. *Journal of the American Chemical Society* **2001**, *123*, 739–740; PMID: 11456590.
- [330] Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *Journal of the American Chemical Society* **2000**, *122*, 10846–10855.
- [331] Romeo, R.; Plutino, M. R.; Monsù Scolaro, L.; Stoccoro, S.; Minghetti, G. *Inorganic Chemistry* **2000**, *39*, 4749–4755.
- [332] Sini, A.; Ph.D. thesis; Scuola di Dottorato in Scienze Chimiche; 2010.
- [333] Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176–2179.
- [334] Hejda, M.; Dostál, L.; Jambor, R.; Růžička, A.; Jirásko, R.; Holeček, J. *European Journal of Inorganic Chemistry* **2012**, *2012*, 2578–2587.

- [335] Caubet, A.; López, C.; Solans, X.; Font-Bardía, M. *Journal of Organometallic Chemistry* **2003**, *669*, 164–171.
- [336] Ryabov, A. D.; Otto, S.; Samuleev, P. V.; Polyakov, V. A.; Alexandrova, L.; Kazankov, G. M.; Shova, S.; Revenco, M.; Lipkowski, J.; Johansson, M. H. *Inorganic Chemistry* **2002**, *41*, 4286–4294.
- [337] Riera, X.; López, C.; Caubet, A.; Moreno, V.; Solans, X.; Font-Bardía, M. *European Journal of Inorganic Chemistry* **2001**, *2001*, 2135–2141.
- [338] Riera, X.; Caubet, A.; López, C.; Moreno, V.; Solans, X.; Font-Bardía, M. *Organometallics* **2000**, *19*, 1384–1390.
- [339] Huheey, J. E.; Keiter, E. A.; Keiter, R. A. *Chimica Inorganica - Principi, strutture, reattività*, seconda edizione italiana ed.; Piccin, 1999.
- [340] Elding, L. I.; Groning, O. *Inorganic Chemistry* **1978**, *17*, 1872–1880.
- [341] Santoro, A.; Whitwood, A. C.; Williams, J. A. G.; Kozhevnikov, V. N.; Bruce, D. W. *Chemistry of Materials* **2009**, *21*, 3871–3882.
- [342] Tollari, S.; Cenini, S.; Penoni, A.; Granata, G.; Palmisano, G.; Demartin, F. *Journal of Organometallic Chemistry* **2000**, *608*, 34–41.
- [343] Crosby, S. H.; Clarkson, G. J.; Rourke, J. P. *Organometallics* **2012**, *31*, 7256–7263.
- [344] Puddephatt, R. J. *Coordination Chemistry Reviews* **2001**, *219–221*, 157–185.
- [345] Hammond, G. S. *Journal of the American Chemical Society* **1955**, *77*, 334–338.
- [346] Leffler, J. E. *Science* **1953**, *117*, 340–341.
- [347] Janzen, D. E.; VanDerveer, D. G.; Mehne, L. F.; da Silva Filho, D. A.; Bredas, J.-L.; Grant, G. J. *Dalton Trans.* **2008**, 1872–1882.
- [348] Ghedini, M.; Pugliese, T.; La Deda, M.; Godbert, N.; Aiello, I.; Amati, M.; Belviso, S.; Lelj, F.; Accorsi, G.; Barigelletti, F. *Dalton Trans.* **2008**, 4303–4318.
- [349] Hallett, A. J.; Kariuki, B. M.; Pope, S. J. A. *Dalton Trans.* **2011**, *40*, 9474–9481.
- [350] Weinberg, D. R.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2007**, *26*, 167–172.
- [351] Shilov, A.; Shul'pin, G. B. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*; Kluwer Academic Publishers, 2000.
- [352] Vedernikov, A. N. *Accounts of Chemical Research* **2012**, *45*, 803–813.
- [353] Pellarin, K. R.; McCready, M. S.; Puddephatt, R. J. *Organometallics* **2012**, *31*, 6388–6394.
- [354] Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507–514.

- [355] Rostovtsev, V. V.; Labinger, J. A.; Bercaw, J. E.; Lasseter, T. L.; Goldberg, K. I. *Organometallics* **1998**, *17*, 4530–4531.
- [356] Hartwig, J. F. *Nature* **2008**, *455*, 314–322.
- [357] Achar, S.; Scott, J. D.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1993**, *12*, 4592–4598.
- [358] Johnstone, T. C.; Wilson, J. J.; Lippard, S. J. *Inorganic Chemistry* **0**, *0*, null.
- [359] Chin, C. F.; Tian, Q.; Setyawati, M. I.; Fang, W.; Tan, E. S. Q.; Leong, D. T.; Ang, W. H. *Journal of Medicinal Chemistry* **2012**, *55*, 7571–7582.
- [360] Hoffmeister, B. R.; Adib-Razavi, M. S.; Jakupec, M. A.; Galanski, M.; Keppler, B. K. *Chemistry & Biodiversity* **2012**, *9*, 1840–1848.
- [361] Olszewski, U.; Ach, F.; Ulsperger, E.; Baumgartner, G.; Zeillinger, R.; Bednarski, P.; Gerhard, H. *Metal-Based Drugs* **2009**, *2009*, 348916.
- [362] Hall, M. D.; Mellor, H. R.; Callaghan, R.; Hambley, T. W. *Journal of Medicinal Chemistry* **2007**, *50*, 3403–3411.
- [363] Bednarski, P. J.; Mackay, F. S.; Sadler, P. J. *Anti-Cancer Agents in Medicinal Chemistry- Anti-Cancer Agents* **2007**, *7*, 75–93.
- [364] Hall, M. D.; Hambley, T. W. *Coordination Chemistry Reviews* **2002**, *232*, 49–67.
- [365] Ellis, L. T.; M., E. H.; W., H. T. *Australian Journal of Chemistry* **1995**, *48*, 793–806.
- [366] Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley & Sons, Inc., 2005.
- [367] Luedtke, A. T.; Goldberg, K. I. *Inorganic Chemistry* **2007**, *46*, 8496–8498.
- [368] Yahav-Levi, A.; Goldberg, I.; Vigalok, A.; Vedernikov, A. N. *Chem. Commun.* **2010**, *46*, 3324–3326.
- [369] Yahav-Levi, A.; Goldberg, I.; Vigalok, A. *Journal of the American Chemical Society* **2006**, *128*, 8710–8711; PMID: 16819847.
- [370] Ong, C. M.; Jennings, M. C.; Puddephatt, R. J. *Canadian Journal of Chemistry* **2003**, *81*, 1196–1205.
- [371] Canty, A. J.; Fritsche, S. D.; Jin, H.; Patel, J.; Skelton, B. W.; White, A. H. *Organometallics* **1997**, *16*, 2175–2182.
- [372] Crosby, S. H.; Thomas, H. R.; Clarkson, G. J.; Rourke, J. P. *Chem. Commun.* **2012**, *48*, 5775–5777.
- [373] Anderson, C. M.; Crespo, M.; Kfoury, N.; Weinstein, M. A.; Tanski, J. M. *Organometallics* **2013**, *32*, 4199–4207.
- [374] Crespo, M.; Anderson, C. M.; Kfoury, N.; Font-Bardia, M.; Calvet, T. *Organometallics* **2012**, *31*, 4401–4404.

- [375] Madison, B. L.; Thyme, S. B.; Keene, S.; Williams, B. S. *Journal of the American Chemical Society* **2007**, *129*, 9538–9539; PMID: 17629265.
- [376] Wang, T.; Keyes, L.; Patrick, B. O.; Love, J. A. *Organometallics* **2012**, *31*, 1397–1407.
- [377] Buckley, H. L.; Sun, A. D.; Love, J. A. *Organometallics* **2009**, *28*, 6622–6624.
- [378] Wang, T.; Love, J. A. *Organometallics* **2008**, *27*, 3290–3296.
- [379] Wang, T.; Alfonso, B. J.; Love, J. A. *Organic Letters* **2007**, *9*, 5629–5631.
- [380] Nabavizadeh, S. M.; Amini, H.; Jame, F.; Khosraviolya, S.; Shahsavari, H. R.; Hosseini, F. N.; Rashidi, M. *Journal of Organometallic Chemistry* **2012**, *698*, 53–61.
- [381] Stoccoro, S.; Zucca, A.; Petretto, G. L.; Cinellu, M. A.; Minghetti, G.; Manassero, M. *Journal of Organometallic Chemistry* **2006**, *691*, 4135–4146.
- [382] Rendina, L. M.; Puddephatt, R. J. *Chemical Reviews* **1997**, *97*, 1735–1754.
- [383] Crespo, M.; Font-Bardía, M.; Solans, X. *Journal of Organometallic Chemistry* **2006**, *691*, 444–454.
- [384] Keyes, L.; Wang, T.; Patrick, B. O.; Love, J. A. *Inorganica Chimica Acta* **2012**, *380*, 284–290.
- [385] Bernhardt, P. V.; Gallego, C.; Martinez, M.; Parella, T. *Inorganic Chemistry* **2002**, *41*, 1747–1754.
- [386] Bernhardt, P. V.; Gallego, C.; Martinez, M. *Organometallics* **2000**, *19*, 4862–4869.
- [387] Vosko, S. H.; Wilk, L.; Nusair, M. *Canadian Journal of Physics* **1980**, *58*, 1200–1211.
- [388] Cundari, T. R.; Stevens, W. J. *The Journal of Chemical Physics* **1993**, *98*, 5555–5565.
- [389] Stevens, W. J.; Krauss, M.; Basch, H.; Jasien, P. G. *Canadian Journal of Chemistry* **1992**, *70*, 612–630.
- [390] Stevens, W. J.; Basch, H.; Krauss, M. *The Journal of Chemical Physics* **1984**, *81*, 6026–6033.
- [391] Binkley, J. S.; Pople, J. A.; Hehre, W. J. *Journal of the American Chemical Society* **1980**, *102*, 939–947.
- [392] Maidich, L.; Zucca, A.; Clarkson, G. J.; Rourke, J. P. *Organometallics* **2013**, *32*, 3371–3375.
- [393] Tobe, M. L.; Burgess, J. *Inorganic Reaction Mechanisms*; Addison Wesley Longman Ltd., 1999.
- [394] Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; VCH Publishers Inc., 1997.
- [395] Stille, J. K.; Lau, K. S. Y. *Accounts of Chemical Research* **1977**, *10*, 434–442.
- [396] Crespo, M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 2548–2550.
- [397] Albright, T. A.; Burdett, J. K. *Orbital Interactions in Chemistry*; Wiley and Sons Inc., 1985.
- [398] Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bulletin of the Chemical Society of Japan* **1981**, *54*, 1857–1867.

- [399] US6504032 (B1) - Process for the production of 2-pyridylpyridine derivatives; 2003.
- [400] Hoste, J. *Analytica Chimica Acta* **1950**, 4, 23–37.
- [401] *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman Scientific: Harlow, United Kingdom, 1989.
- [402] Coelho, A. A. *Journal of Applied Crystallography* **2003**, 36, 86–95.
- [403] TOPAS, Version 3.0; Bruker AXS: Karlsruhe, Germany.; 2005.
- [404] Liu, T.; Fraser, C. L. *Organic Syntheses* **2010**, 89, 76–81.
- [405] US 20050267073 A1 - Triheterocyclic compounds, compositions, and methods for treating cancer or viral diseases; 2005.
- [406] Liu, C.; Ni, Q.; Hu, P.; Qiu, J. *Org. Biomol. Chem.* **2011**, 9, 1054–1060.
- [407] Pan, C.; Liu, M.; Zhang, L.; Wu, H.; Ding, J.; Cheng, J. *Catalysis Communications* **2008**, 9, 508–510.
- [408] Mongin, F.; Rebstock, A.-S.; Trécourt, F.; Quéguiner, G.; Marsais, F. *The Journal of Organic Chemistry* **2004**, 69, 6766–6771; PMID: 15387601.
- [409] WO2003000251 A1 - Novel idolinones and uses thereof; 2002.
- [410] Alcock, N. W.; Brown, J. M.; Hulmes, D. I. *Tetrahedron: Asymmetry* **1993**, 4, 743–756.
- [411] Sheldrick, G. M. *Acta Crystallographica Section A* **1990**, 46, 467–473.
- [412] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *Journal of Applied Crystallography* **2009**, 42, 339–341.
- [413] Sheldrick, G. M. *Acta Crystallographica Section A* **2008**, 64, 112–122.
- [414] Cordero, B.; Gomez, V.; Platero-Prats, A. E.; Reves, M.; Echeverria, J.; Cremades, E.; Barragan, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832–2838.
- [415] Bader, R. F. W.; Beddall, P. M.; Cade, P. E. *Journal of the American Chemical Society* **1971**, 93, 3095–3107.
- [416] Bader, R. F. W. *Chemical Reviews* **1991**, 91, 893–928.
- [417] Bader, R. F. W. *Accounts of Chemical Research* **1985**, 18, 9–15.
- [418] Bader, R. F. W.; Beddall, P. M. *The Journal of Chemical Physics* **1972**, 56, 3320–3329.
- [419] Lecomte, C.; Souhassou, M.; Pillet, S. *Journal of Molecular Structure* **2003**, 647, 53–64.
- [420] Bader, R. F. W. *Atoms in Molecules - A Quantum Theory*; Oxford University Press, Oxford, 1990.

-
- [421] Valeev, E. F.; *A library for the evaluation of molecular integrals of many-body operators over Gaussian functions*; <http://libint.valeev.net/>; 2013.
- [422] Avogadro: *an open-source molecular builder and visualization tool. Version 1.1.0.* <http://avogadro.openmolecules.net/>.
- [423] Hanwell, M.; Curtis, D.; Lonie, D.; Vandermeersch, T.; Zurek, E.; Hutchison, G. *Journal of Cheminformatics* **2012**, *4*, 17.
- [424] Allouche, A. *Journal of Computational Chemistry* **2011**, *32*, 174–182.
- [425] van Lenthe, E.; Ehlers, A.; Baerends, E.-J. *The Journal of Chemical Physics* **1999**, *110*, 8943–8953.
- [426] *Mercury 3.1.1 Development (Build RC7). Copyright CCDC 2001-2012. All rights reserved.* <http://www.ccdc.cam.ac.uk/mercury/>.
- [427] Lu, T.; Chen, F. *Journal of Computational Chemistry* **2012**, *33*, 580–592.
- [428] Schäfer, A.; Horn, H.; Ahlrichs, R. *The Journal of Chemical Physics* **1992**, *97*, 2571–2577.
- [429] Kaupp, M.; Malkina, O. L.; Malkin, V. G. *The Journal of Chemical Physics* **1997**, *106*, 9201–9212.
- [430] Farrugia, L. J. *Journal of Applied Crystallography* **2012**, *45*, 849–854.
- [431] Granovsky, A. A.; *Firefly version 7.1.G*; <http://classic.chem.msu.su/gran/firefly/index.html>.
- [432] Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *Journal of Computational Chemistry* **1993**, *14*, 1347–1363.
- [433] Gorelsky, S. I.; *AOMix: Program for Molecular Orbital Analysis*, <http://www.sg-chem.net/>, version 6.81.; 2013.
- [434] Gorelsky, S.; Lever, A. *Journal of Organometallic Chemistry* **2001**, *635*, 187–196.