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Cyclometalated Complexes

Rollover-Assisted C(sp^2)–C(sp^3) Bond Formation

Antonio Zucca,*[a] Luca Maidich,[a, b] Laura Canu,[a] Giacomo L. Petretto,[a] Sergio Stoccoro,[a] Maria Agostina Cinellu,[a] Guy J. Clarkson,[b] and Jonathan P. Rourke[b]

In memory of Professor Giovanni Minghetti, October 18th 1937–January 29th 2014

Abstract: Rollover cyclometalation involves bidentate heterocyclic donors, unusually acting as cyclometalated ligands. The resulting products, possessing a free donor atom, react differently from the classical cyclometalated complexes. Taking advantage of a "rollover"/"retro-rollover" reaction sequence, a succession of oxidative addition and reductive elimination in a series of platinum(II) complexes [Pt(N,C)(Me)-(PR_3)] resulted in a rare C(sp^2)–C(sp^3) bond formation to give the bidentate nitrogen ligands 3-methyl-2,2′-bipyridine, 3,6-dimethyl-2,2′-bipyridine, and 3-methyl-2-(2′-pyridyl)-quinoline, which were isolated and characterized. The nature of the phosphane PR_3 is essential to the outcome of the reaction. This route constitutes a new method for the activation and functionalization of C–H bond in the C(3) position of bidentate heterocyclic compounds, a position usually difficult to functionalize.

Introduction

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.[1] 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.[2] 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,[3] or C(sp^3)- and C(sp^2)–halide elimination.[4]

In contrast, examples of C(sp^2)–C(sp^3) reductive elimination are very scarce,[5] though they do include a catalytic process involving platinum(IV) compounds.[6]

Pt^{IV} complexes with chelated nitrogen ligands (both N,N and N,C) are often obtained through oxidative addition of C–X bonds.[7] In the case of cyclometalated species, the resulting Pt^{IV} complexes [Pt(N,C)(Me)$_2$(X)(L)] (L = neutral ligand, X = halide) usually display a *fac*-PtC_3 arrangement, due to the natural tendency of carbon-bonded ligands to avoid mutual *trans* coordination (*trans*-phobia), and are stable at room temperature both in solution and in the solid state.

[a] Dr. A. Zucca, Dr. L. Maidich, L. Canu, Dr. G. L. Petretto, Prof. S. Stoccoro, Prof. M. A. Cinellu
Dipartimento di Chimica e Farmacia
Università degli Studi di Sassari, Via Vienna 2, 07100 Sassari (Italy)
E-mail: zucca@uniss.it

[b] Dr. L. Maidich, Dr. G. J. Clarkson, Dr. J. P. Rourke
Department of Chemistry
University of Warwick, CV4 7AL Coventry (UK)

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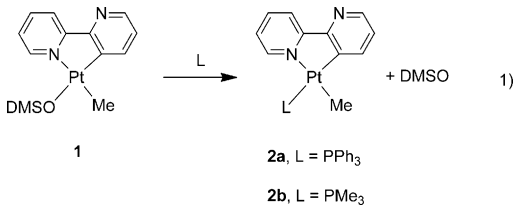
In the vast field of cyclometalated derivatives,[8] the so-called "rollover complexes" constitute an emerging class of compounds.[9] In contrast to classical cyclometalated complexes, obtained from monodentate ligands, this new class of complexes arise from bidentate heteroaromatic ligands, which, after chelation, may partially decomplex and undergo internal rotation around a suitable bond and promote the selective activation of a C–H bond previously directed away from the metal. After cyclometalation, rollover complexes contain a free donor atom able to contribute to the reactivity of the complex, this possibility is usually not accessible to classical cyclometalated species.[10] Among these possibilities we can find protonation,[11] retro-rollover reactions,[12] successive cyclometalations,[9c,13] and polymerization.[14] Recently, catalytic cycles have been designed, based on rollover and retro-rollover reactions,[15] with the ultimate aim of activating internal positions in heteroaromatic rings. Rollover complexes were also found to promote C–C bond formation in the gas phase.[16]

Results and Discussion

We have recently reported the synthesis of the rollover complex [Pt(L-H)(Me)(DMSO)], **1**, where L is κ^2-C,N-$C_{10}N_2H_7$, a C(3)-deprotonated, cyclometalated 2,2′-bipyridine. Complex **1** is the parent compound of a family of complexes [Pt(L-H)(L_X)(L_N)] where L_X and L_N are anionic and neutral ligands, respectively.[12,13]

Complex **2a**, [Pt(L-H)(Me)(PPh_3)], was obtained both from **1** by substitution of the labile DMSO ligand [Eq. (1)], or directly from [Pt(Me)$_2$(DMSO)$_2$], bipyridine and PPh_3, in a "one pot" reaction.[12] Complex **2a** is stable in air, both in solution and in the solid state, and was characterized in solution by means of NMR spectroscopy.



Our efforts in obtaining an X-ray diffraction structure were successful and we managed to obtain crystals suitable for X-ray determination by slow evaporation of an acetone solution. The structure of **2a** consists of the packing of [Pt(L-H)(Me)(PPh_3)] molecules in the triclinic space group $P\bar{1}$. The geometry around the metal center deduced from NMR spectroscopy is confirmed: a slightly distorted square planar Pt^{II} complex with a κ^2-N,C-cyclometalated unit, a PPh_3, and a methyl group (Figure 1).

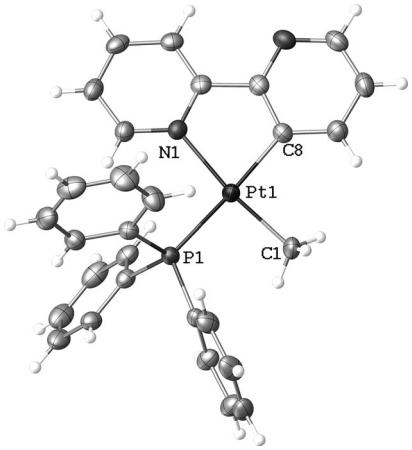


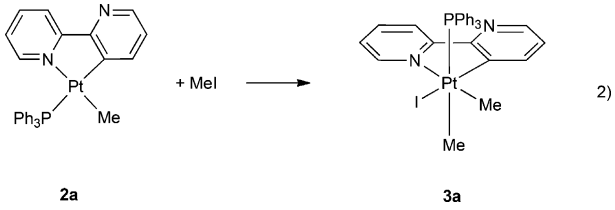
Figure 1. ORTEP view of the crystal structure of complex **2a**. Thermal ellipsoids are drawn at 50% probability.

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 N1-Pt-CH_3, 169.26°. In the crystal packing of **2a**, neighboring complexes form discrete dimers interacting via a π–π overlap between the bipy ligand (N1–N12) of one complex and a symmetry related bipy on a neighboring complex. The interacting π systems are parallel (the interaction lies across an inversion center) and the closest atomic contact is C5–C7 (3.2965 Å) (see Figure SI1 in the Supporting Information). Selected bond distances and angles are given in Table 1 along with the previously DFT calculated data.[12] All the lengths are in the expected range and no particular deviations are worth noting.

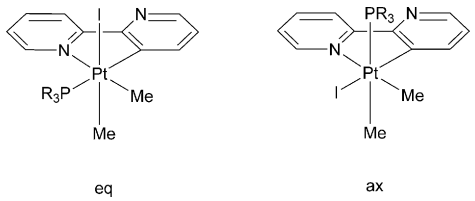
The reaction at room temperature of the electron-rich complex **2a** with MeI gives the corresponding Pt^{IV} complex [Pt(L-H)$(Me)_2$(I)(PPh_3)], **3a** [Eq. (2)], which was isolated in high yields and characterized. In the absence of an X-ray structural characterization compounds **3a** was analytically and spectroscopically characterized, in particular, through mono and bi-dimensional NMR techniques.

Table 1. Comparison of structural and DFT calculated[12] bond distances (Å), ESD in parentheses, and angles (degrees) for complex **2a**.

	Experimental	Theory
Pt–N1	2.130(2)	2.1940
Pt–C8	2.043(3)	2.0373
Pt–C1	2.077(4)	2.0445
Pt–P1	2.2904(7)	2.3492
N1–C6	1.360(3)	1.3508
C6–C7	1.468(5)	1.4705
C7–C8	1.405(4)	1.4134
N1–Pt–C8	79.61(9)	79.47
C8–Pt–C1	91.65(11)	90.12
C1–Pt1–P1	91.41(8)	92.77
P1–Pt1–N1	97.91(6)	97.68
N1–Pt1–C1	169.26(1)	169.39
P1–Pt1–C8	173.67(7)	176.84



Though the reaction may generate several isomers, due to *trans*-phobia,[12] only *fac*-PtC_3 isomers are expected and considering the cyclometalated N,C restriction, only two isomers may be reasonably formed, as indicated in Scheme 1, with the phosphane in "axial" or "equatorial" position (with respect to the bipyridine plane).



Scheme 1.

The accepted S_N2 mechanism proposed for this reaction requires the trapping of the five-coordinate intermediate formed by the nucleophilic attack of the Pt^{II} on the alkyl halide to form the kinetic equatorial product which subsequently converts into the thermodynamic axial product.[7a,18] In the chemistry of cyclometalated Pt^{IV} the isolated product of the reaction is usually the axial species, and isolation of the equatorial isomer is extremely rare.

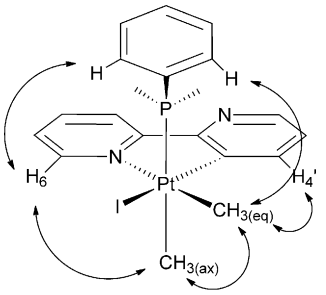
One example in which the equatorial isomer was isolated was with the analogous rollover complex [Pt(L-H)(Me)(PMe_3)], **2b**, which gives, under the same experimental conditions as here, the Pt^{IV} complex [Pt(L-H)$(Me)_2$(I)(PMe_3)], **3b(eq)**, with the small PMe_3 ligand located in the plane of the cyclometalated ligand as demonstrated by an X-ray diffraction analysis.[19]

In the absence of X-ray data, complex **3a** was characterized as the axial isomer, that is, **3a(ax)**, on the basis of analytical data and NMR spectroscopy, as detailed below. The ^{31}P NMR spectrum of **3a(ax)** shows Pt–P coupling constant values in agreement with a Pt^{IV} species ($^{1}J_{Pt-P}=992$ Hz), and the ^{1}H NMR spectrum shows two different platinum-bonded methyl groups ($\delta=1.12$ ppm, $^{3}J_{P-H}=8$ Hz, $^{2}J_{Pt-H}=61$ Hz; 1.64 ppm, $^{3}J_{P-H}=7.5$ Hz, $^{2}J_{Pt-H}=71$ Hz) as doublets with satellites due to coupling to ^{195}Pt and ^{31}P nuclei. A comparison of ^{31}P, ^{1}H, and ^{13}C NMR data of **3a(ax)** and **3b(eq)** (see Table 2) suggests coordination of PPh_3 in "axial" position in **3a(ax)** with respect to the cyclometalated plane. Accordingly, the ^{13}C NMR spectrum shows two Pt–CH_3 carbon atoms having very different P–C coupling constants, attributable to an "axial" methyl, coordinated *trans* to phosphorus (CH_3(ax): $\delta=+7.06$ ppm, $^{2}J_{P-C}=113$ Hz), and an "equatorial" methyl (CH_3(eq): $\delta=-6.87$ ppm, $^{2}J_{P-C}=4$ Hz) coordinated *cis* to phosphorus. Furthermore, a ^{13}C-^{1}H HSQC spectrum showed the following correlations: CH_3 *trans* to P, that is, CH_3(ax): $\delta_C=7.06$ ppm, $\delta_H=1.12$ ppm, CH_3 *cis* to P that is, CH_3(eq): $\delta_C=-6.87$ ppm, $\delta_H=1.64$ ppm.

Different geometries between **3a(ax)** and **3b(eq)** were supported by ^{195}Pt–^{31}P coupling constant values: whereas **2a** and **2b**, show similar $^{1}J_{Pt-P}$ values (**2a**: $\delta=33.6$ ppm, $^{1}J_{Pt-P}=2229$ Hz; **2b**: $\delta=-18.6$ ppm, $^{1}J_{Pt-P}=2112$ Hz), **3a(ax)** and **3b(eq)** have very different *J* values (**3a(ax)**: $\delta=-11.2$ ppm, $^{1}J_{Pt-P}=992$ Hz; **3b(eq)**: $\delta=-44.6$ ppm, $^{1}J_{Pt-P}=1467$ Hz). Also ^{31}P chemical shifts do not follow the same trend. Furthermore, 1D-NOE experiments on **3a(ax)** (Figure 2) clearly pointed out the geometry showing, after irradiation at 1.64 ppm ($CH_{3(eq)}$), enhancement at 7.05 ($H_{4'}$), 7.29 ($H_{5'}$) and 1.12 ppm ($CH_{3(ax)}$), and enhancements at 9.58 (H_6) and 1.64 ppm (CH_3) by irradiation at 7.21 ppm (H_{ortho}, PPh_3). Finally, irradiation at 1.12 ppm ($CH_{3(ax)}$) produces enhancement only at 1.64 ppm ($CH_{3(eq)}$). It follows that the signal at 1.12 ppm is the axial CH_3 while the signal at 1.64 is due to the equatorial one (Table 2).

On the basis of all these data we conclude that **3a** does indeed have a PPh_3 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 ($\delta=9.98$ ppm) as usual.[20] The different behavior of PPh_3 and PMe_3 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 bipyridine.

The reaction of **2a** 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 isomerization.



3a

Figure 2. NOE contacts for complex **3a**.

No intermediate species was observed, and the reaction was then performed with CD_3I in an NMR tube, in order to distinguish the previously coordinated methyl from that coming from MeI. Reaction of **2a** 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, that is, 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 **3a(ax)** should be present as a racemic mixture, with PPh_3 coordinated "above" and "below" the cyclometalated plane.

In analogy to the analysis carried out in the case of **3b**, we performed DFT calculations on the two most probable isomers of **3a**, the axial and equatorial ones. We decided to concentrate only on these two assuming that, due to *trans*-phobia, *fac* PtC_3 isomers would be more stable than the other isomers. Full optimization at PBE0/def2-SVP level led to the conclusion that the axial is more stable than the equatorial one by 25.4 kJ mol^{-1} (ΔH ZPE corrected in vacuo) showing a very similar energy difference to that for the two isomers of **3b**.[19] This result is interesting because shows that although the two

Table 2. Selected NMR data.[a]

		^{1}H (CH_3)	^{31}P	^{13}C
2a	[Pt(bipy-H)(Me)(PPh_3)]	0.74 (7.5) [83]	33.6 [2229]	−12.37 (4.5) [725]
2b	[Pt(bipy-H)(Me)(PMe_3)]	0.85 (8) [84]	−18.6 [2112]	−17.0 (7.0) [n.r.]
2c[b]	[Pt(bipy-H)(Me)(PCy_3)]	1.00 (5.5) [84]	19.3 [2083]	
2d	[Pt(L′-H)(Me)(PPh_3)]	0.74 (8) [83]	32.6 [2226]	
3a(ax)	[Pt(bipy-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]
3b(eq)	[Pt(bipy-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.]
3b(ax)	[Pt(bipy-H)(Me)$_2$(I)(PMe_3)]	1.40 (8.5) [71]	−42.9 [1239]	
		0.76 (8) [56]		
3c(ax)	[Pt(bipy-H)(Me)$_2$(I)(PCy_3)]	1.73 (6.5) [72]	−17.9 [957]	
		0.96 (7) [57]		
3d(ax)	[Pt(L′-H)(Me)$_2$(I)(PPh_3)]	1.65 (7.5) [71]	−9.71 [967]	
		1.19 (7.5) [60]		

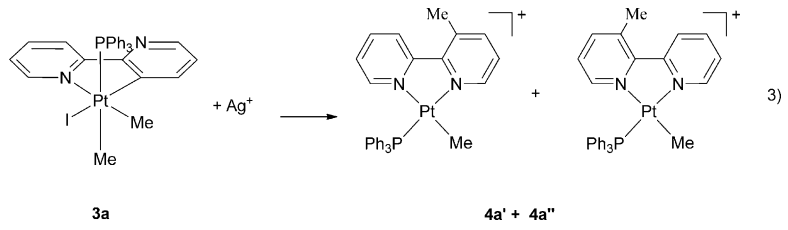
[a] Chemical shift are given in ppm, coupling constants, in parentheses (coupling with ^{31}P) and square brackets (coupling with ^{195}Pt), are given in Hz. [b] Data taken from ref. [12].

phosphanes 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.

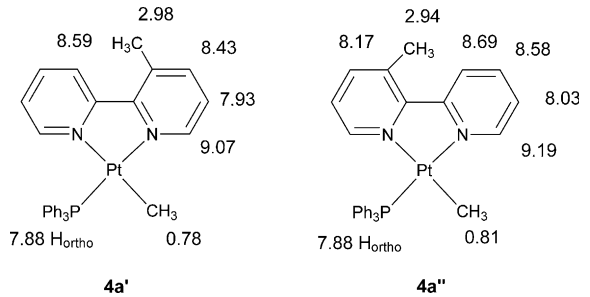
Treatment of Pt^{IV} complexes with Ag^+

Compound **3a(ax)** 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.[2] For this reason we reacted **3a(ax)** with silver salts in acetone solution in order to abstract the iodide ligand and create coordinatively unsaturated species. Unexpectedly, the reaction of **3a(ax)** with $AgBF_4$ gave the cationic Pt^{II} adduct $[Pt(\kappa^2\text{-}N,N\text{-}3\text{-Me-}2,2'\text{-bipyridine})(Me)(PPh_3)]^+$, **4a**, as indicated by analytical and NMR data, where the ligand 3-Me-2,2′-bipyridine is formed through an uncommon $C(sp^3)$–$C(sp^2)$ 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 ^{31}P NMR spectra of **4a** show two species in a 1:1 molar ratio; the analysis of the spectra allows their characterization as the geometric isomers **4a′** and **4a″**, as indicated below [Eq. (3)].



In particular, the ^{31}P spectrum of **4a** shows two singlets with satellites at 19.2 and 18.9 ppm with coupling constants ($^1J_{Pt-P}=4294$ and 4318 Hz respectively) indicative of P *trans* to N in a platinum(II) complex. Also the ^1H NMR spectra show two Pt–CH_3 groups (**4a′**: 0.78 ppm, $^3J_{P-H}=3.5$ Hz, $^2J_{Pt-H}=71$ Hz; **4a″**: 0.80 ppm, $^3J_{P-H}=3.5$ Hz, $^2J_{Pt-H}=72$ Hz) in agreement with methyl groups coordinated in *cis* to a PPh_3 and *trans* to a nitrogen. Two singlets at 2.94 and 2.98 ppm were assigned to methyls on the bipyridine in the 3-position. A ^1H-^1H NOESY spectrum helped in the characterization and assignments (Scheme 2).



Scheme 2.

This reaction has points of interest: **4a** is generated by a reductive elimination reaction involving a less common $C(sp^3)$–$C(sp^2)$ 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 bipyridine adduct, and it may be that this assists the overall process. C–C bond making and breaking by means of transition metals has been demonstrated;[21] in our case, however, we do not see any experimental evidence for a reversible process at room temperature.

Our observation is in line with that reported recently by Butschke and Schwarz,[16a] which proposed a $C(sp^3)$–$C(sp^2)$ coupling in the gas phase by means of Pt^{II} rollover complexes.

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 **3a(ax)** with Ag^+. After all, this results in the formation of a strong C–C bond in ethane with the additional favorable entropic contribution to the Gibbs free energy of the reaction that arises from the release of a molecule of gas. However, these thermodynamic factors are irrelevant in this case as they neglect to take into consideration the spatial requirements of the coupling groups at the five coordinate intermediate. If we consider the geometry of **3a(ax)** we can see that removal of the iodide results in a vacancy in the equatorial plane defined by the cyclometalated bipyridine. Orbital considerations are clear: reductive coupling of groups within this vacancy-containing plane results in the population of a nonbonding orbital, whereas coupling of groups in a four coordinate plane requires occupation of a high-energy strongly antibonding orbital.[22]

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

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; sterically this would be unfavorable for exactly the same reasons that **3a(eq)** is not observed.

The free ligand 3-Me-2,2′-bipyridine, **5**, was isolated by reaction of **4a** with dppe, 1,2-bis-diphenylphosphinoethane. The chelating diphosphine easily displaces the bipy ligand so that species **5** can be isolated in good yield and analyzed. 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 (CH_3-bipy) 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 COSY H–H spectrum allowed assignment of all ^1H NMR signals. Fur-

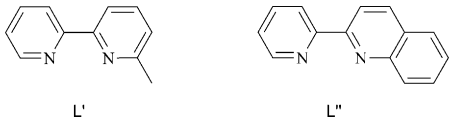
ther evidence for the characterization of **5** was provided by a high-resolution mass spectrum, which shows the $[M+H]^+$ peak with an excellent match between the calculated and experimental values (*m/z* found: 171.0915, calculated for $C_{11}H_{11}N_2$ $[M+H]^+$: 171.0917).

The synthesis of 3-methyl-2,2′-bipyridine was previously reported in the literature, through co-cyclotrimerization,[23] Negishi coupling,[24] or Suzuki–Miyaura reactions.[25] 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.

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: 6-methyl-2,2′-bipyridine, L′, and 2-(2′-pyridyl)-quinoline, L″ (Scheme 3), both able to give rollover cyclometalation.[26]

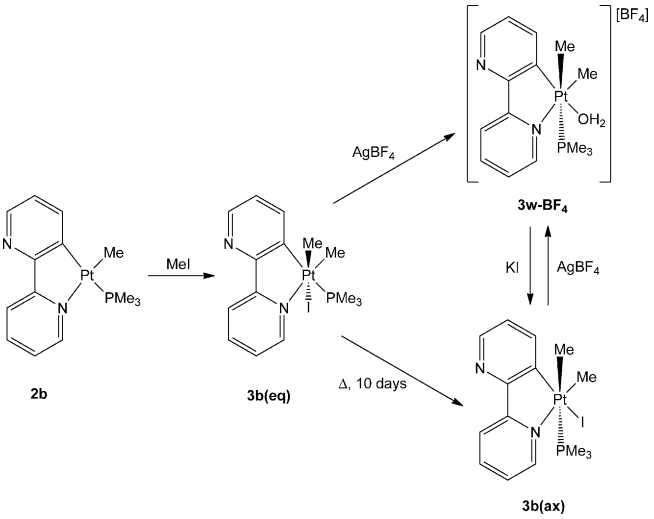


Scheme 3.

Accordingly, a series of platinum(II) complexes were prepared and characterized: [Pt(L-H)(Me)(PMe_3)], **2b**, [Pt(L-H)(Me)(PCy_3)], **2c**, [Pt(L′-H)(Me)(PPh_3)], **2d**, [Pt(L″-H)(Me)(PPh_3)], **2e**, and [Pt(L″-H)(Me)(PCy_3)], **2f**.

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

The behavior of the PMe_3 complex **2b** is different from that of the PPh_3 analogue, **2a**, as only the kinetic product **3b(eq)**, [Pt(L-H)$(Me)_2$(I)(PMe_3)], having the phosphane in "equatorial" position was obtained under mild conditions. In contrast, the PCy_3 complex **2c** behaves as the PPh_3 one, to give the axial complex **3c(ax)**, [Pt(L-H)$(Me)_2$(I)(PCy_3)]. The reaction of **2b** with MeI at room temperature was followed through NMR spectroscopy: the reaction rapidly produces the Pt^{IV} complex **3b(eq)**, which converts very slowly (ca. 10 days at 60 °C in [D_6]acetone) into the isomer having the phosphane in axial position, **3b(ax)**, that is, the thermodynamically stable species (Scheme 4). NMR data of **3b(ax)** are comparable to those of **3a(ax)**, in particular ^1H Pt-bonded methyls and ^{31}P–^{195}Pt coupling constant values (see Table 3).



Scheme 4.

In contrast to **3a(ax)**, treatment of **3b(eq)** with $AgBF_4$ does not induce reductive coupling, but produces a solvato complex, identified as the cationic species [Pt(L-H)(Me)(PMe_3)(H_2O)]$^+$, **3w**, with a coordinated water in the equatorial position and the phosphane in an axial site, as indicated by NOE measurements. Treatment of **3w** with excess iodide does not return back to the starting complex **3b(eq)** but gives the thermodynamic Pt^{IV} complex **3b(ax)**. In contrast to complex **3a(ax)**

Table 3. NMR data for PMe_3 complexes.[a]

	2b	3b(eq)	3b(ax)	3w
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
H_3	8.33	8.51	8.50	8.61
H_4	8.10	8.11	8.18	8.33
H_5	7.44	7.52	7.60	7.84
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

[a] Chemical shift are given in ppm, coupling constants in parentheses (coupling with ^{31}P) and square brackets (coupling with ^{195}Pt), are given in Hz.

the addition of $AgBF_4$ to **3b(ax)** does not result in reductive elimination but leads back to the water complex **3w**. These results indicate a strong component of steric strain in the octahedral complexes with PPh_3, relieved by reductive coupling.

The leading effect in both oxidative addition and reductive elimination processes seems to be steric rather than electronic, because the analogous PCy_3 complexes **2c** and **3c**, behave as **2a** and **3a**, 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 **3b(eq)** and **3b(ax)**, and consequently the coupling does not take place. It is worth noting that the analogous cyclometalated Pt^{IV} complex originating from 2-phenylpyridine, $[Pt(N,C)(Me)_2I(PPh_3)]$, does not show corresponding behavior, giving a complex mixture of unidentified products. NMR spectra did not give evidence for $C(sp^3)$–$C(sp^2)$ bond coupling, so this reactivity seems to be peculiar to rollover cyclometalated compounds.

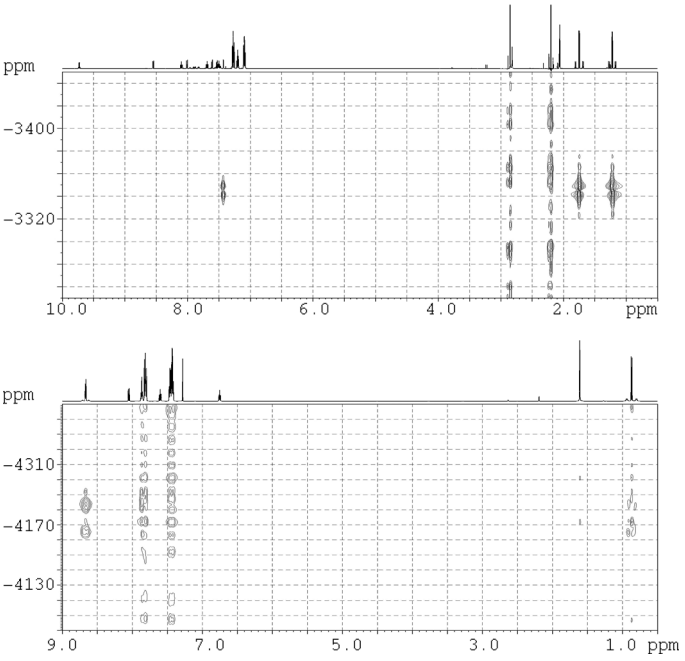
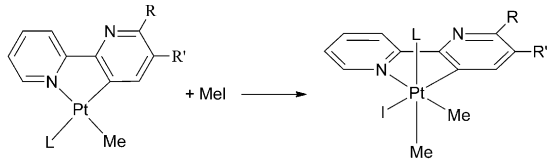


Figure 3. ^{195}Pt-^{1}H HMQC spectra of **2e** (below) and **3e** (above).

Other derivatives

In contrast to **2b**, reaction of **2d–f** with MeI rapidly gave the corresponding thermodynamic Pt^{IV} derivatives $[Pt(L'\text{-}H)(Me)_2(I)(PPh_3)]$, **3d(ax)**, $[Pt(L''\text{-}H)(Me)_2(I)(PPh_3)]$, **3e(ax)**, and $[Pt(L''\text{-}H)(Me)_2(I)(PCy_3)]$, **3f(ax)**, with high yields. ^{1}H and ^{31}P NMR data of **3d–f** are similar to those of **3a(ax)**, confirming that the PR_3 ligand is coordinated in axial position (see the Experimental Section).



2a, L = PPh_3, R = R' = H
2c, L = PCy_3, R = R' = H
2d, L = PPh_3, R = Me, R' = H
2e, L = PPh_3, R, R' = condensed Ph
2f, L = PCy_3, R, R' = condensed Ph

3a, L = PPh_3, R = R' = H
3c, L = PCy_3, R = R' = H
3d, L = PPh_3, R = Me, R' = H
3e, L = PPh_3, R, R' = condensed Ph
3f, L = PCy_3, R, R' = condensed Ph

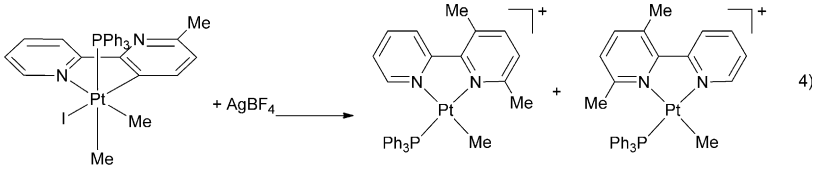
Compounds **2e** and **3e(ax)** were chosen for a thorough comparative NMR characterization (e.g., ^{1}H, ^{31}P, ^{195}Pt-^{1}H HMQC, H-H COSY, NOE-1d). ^{195}Pt-^{1}H HMQC experiments showed the expected correlations of the Pt signal with $H_{6'}$, H_4, and the methyl protons in both **2e** and **3e(ax)**. As expected,[27] the ^{195}Pt signal is strongly deshielded in the Pt^{IV} complex **3e(ax)** (−3345 ppm) when compared to the Pt^{II} complex **2e** (−4177 ppm). The same trend was observed for **2b**, **3b(eq)** and **3b(ax)** ($\delta = -4107$, −3429, and −3411 ppm, respectively, Figure 3).

A series of NOE-1d experiments of **3e(ax)** 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 ($H_{4'}$). Furthermore, irradiation at 7.44 ppm ($H_{4'}$) 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 ($H_{6'}$) gives enhancements at 7.27 (H_o, PPh_3), and 7.50 ppm ($H_{5'}$).

Confirming the generality of the reductive coupling method, reaction of **3c–f** with $AgBF_4$ gave reductive elimination with $C(sp^2)$–$C(sp^3)$ coupling, to give the adducts of the corresponding new methylated ligands, 3-Me-2,2′-bipyridine, (**5**), 3,6-Me_2-2,2′-bipyridine (**6**) and 2-pyridyl-3-Me-quinoline (**7**): $[Pt(\mathbf{5})(Me)(PCy_3)]^+$, **4c**, $[Pt(\mathbf{6})(Me)(PPh_3)]^+$, **4d**, $[Pt(\mathbf{7})(Me)(PPh_3)]^+$, **4e**, and $[Pt(\mathbf{7})(Me)(PCy_3)]^+$, **4f**.

In contrast to L, L′ and L″ have a substituent in proximity to one nitrogen, so that in the N,N′ bidentate adducts **4d–f** steric repulsions may affect the molar ratio between the geometric isomers possible for these complexes.

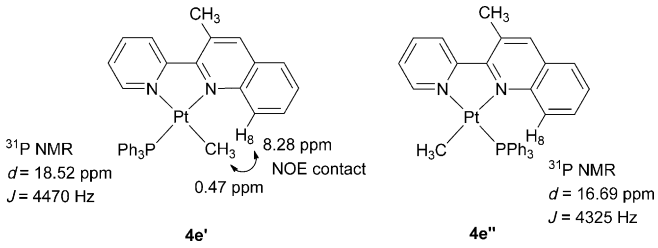
However, **4d′** and **4d″** are formed in almost 1:1 molar ratio [Eq. (4)], as demonstrated by ^{1}H NMR integrals; in one of the isomers (**4d‴**) a Me in position 6 on the bipyridine is strongly shielded in the ^{1}H NMR spectrum ($\delta = 0.47$ ppm) with respect to other one ($\delta = 0.95$ ppm) likely due to its proximity to the PPh_3 ligand.



3d **4d′ + 4d″**

In the case of the L'' ligand, the molar ratio of the isomers **4e**′ and **4e"** in solution is slightly different, around 4:3, and a third, unidentified species is also present in solution.

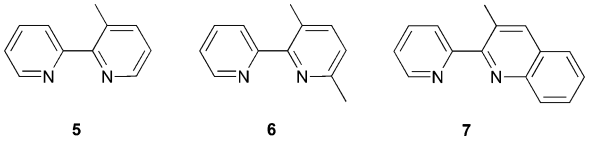
The main species, **4e**′, corresponds to the isomer having the PPh_3 ligand in *trans* to the quinoline nitrogen as may be expected by steric reasons. This is corroborated by a NOE-1d spectrum, which shows a NOE contact between the methyl at 0.47 ppm (Pt–Me, **4e**′) and the H_8 proton, a doublet at 8.28 ppm (Scheme 5). In this case the phosphorus of the two



Scheme 5.

isomers are slightly different, **4e**′: $\delta = 18.52$ ppm, $J_{Pt-P} = 4470$ Hz; **4e**′′: $\delta = 16.69$ ppm, $J_{Pt-P} = 4325$ Hz, reflecting the Pt–PPh_3 environments. The ^1H and ^{31}P NMR spectra of complex **4f** show only one a set of broad signals, indicating a fluxional behavior in solution in the NMR time scale, likely due to the bulkiness of the PCy_3 ligand.

From **4d**–**f** the corresponding free ligands 3,6-Me_2-2,2′-bipyridine, **6**, and 3-methyl-2-(2′-pyridyl)-quinoline, **7** (Scheme 6),



Scheme 6.

were isolated in the solid state and identified through high resolution mass spectrometry and NMR spectroscopy.

Also in this case high-resolution mass spectra show the $[M+H]^+$ peaks with an excellent match with the calculated values (**6**: *m/z* found: 185.1075, calculated for $C_{12}H_{13}N_2$ $[M+H]^+$: 185.1073; **7**: *m/z* found: 221.1073, calculated for $C_{15}H_{13}N_2$ $[M+H]^+$: 221.1073).

In detail, ^1H NMR of the 3,6-Me_2-2,2′-bipyridine, **6**, 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. Bipyridine **7** shows the expected signals, among these it is 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 that are diagnostic.

To the best of our knowledge there is only one synthesis of **6** in the literature, by means of co-cyclotrimerization of 2-cyanopyridine with propyne.[28] Similarly, there is only one synthesis of **7** present in the literature, that of Hoste in 1950.[29]

Conclusion

Rollover cyclometalation constitutes an uncommon way to activate the C(3) position in 2,2′-bipyridines as well as in other bidentate heteroaromatic ligands. The coupling reaction reported here constitutes a new synthetic method for the preparation of substituted heterocycles: in principle, a great array of heterocyclic bidentate donors may follow this reaction taking advantage of a rollover/retro-rollover reaction pathway. The C(3) position is often hard to activate: in the case of 2,2′-bipyridines a bibliographic research (www.reaxys.com, September 2013) showed only 57 3-substituted 2,2′-bipyridines, compared to 2226, 1101 and 462 2,2′-bipyridines monosubstituted in position 6, 5, and 4, respectively.

The reductive elimination step involves a rare $C(sp^3)$–$C(sp^2)$ coupling, in place of the more common $C(sp^3)$–$C(sp^3)$ one, and whether this reductive elimination takes place or not seems to be governed principally by steric factors, as indicated by the behavior of PPh_3, PMe_3, and PCy_3 complexes. The reaction is unique to rollover complexes; as a comparison, the analogous phenylpyridine cyclometalated complexes do not exhibit C–C coupling when treated with Ag^+.

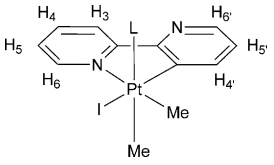
The next steps in this research will be the extension of the reaction to other bidentate heterocyclic donors and to alkylating species different from MeI. It will also be useful to understand the factors that favor the process, such as the nature of the anionic and neutral ligands on the platinum, the presence of substituents on the cyclometalated ligand, and the properties of the oxidant species.

Experimental Section

All the solvents were purified and dried according to standard procedures.[30] *cis*-$[Pt(Me)_2(DMSO)_2]$ was synthesized according to ref. [31]. Complexes **2a**, **2b**, **2c**, and **2e** were obtained as described in refs. [12], [19], and [26]. Elemental analyses were performed with a Perkin–Elmer elemental analyzer 240B.

^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded with Varian VXR 300 or Bruker Avance III 400, 500 or 600 spectrometers. Chemical shifts are given in ppm relative to internal TMS for ^1H and $^{13}C\{^1H\}$ and external 85% H_3PO_4 for $^{31}P\{^1H\}$; *J* values are given in Hz. ^1H-^1H COSY, ^1H-^{13}C HSQC, HMBC, and ^1H NOESY-1d experiments were performed by means of standard pulse sequences. ^{195}Pt–^1H correlation spectra were recorded using a variant of the HMBC pulse sequence and ^{195}Pt chemical shifts quoted are taken from here (referenced to external Na_2PtCl_6). Accurate mass spectra were run on a Bruker MaXis mass spectrometer.

Single crystals of **2a** suitable for X-ray analysis were grown from an acetone solution. X-ray diffraction data were obtained on an Oxford Diffraction Gemini four-circle system with a Ruby CCD area detector. The crystal was held at 150(2) K with the Oxford Cryosystem Cryostream Cobra. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and the remaining bond lengths and angles, deposition number CCDC 963378. Full details are given in the Supporting Information.



Synthesis of 2c–d

An equimolar amount of the ligand L′ or L′′ was added to a solution of *cis*-[Pt(Me)$_2$(DMSO)$_2$] (0.80 mmol) in acetone (40 mL) under nitrogen atmosphere. The solution was refluxed for 5 h, then the phosphane was added (PPh_3 or PCy_3, 10% excess). After 1 h the solution was evaporated to small volume and treated with *n*-pentane to give a precipitate which was filtered off, washed with *n*-pentane and vacuum-dried to give the analytical sample as a yellow solid.

[Pt(L′-H)(Me)(PPh$_3$)], 2d: Yield 85%; m.p. 200–201 °C; ^{1}H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 8.34$ (dd, J(H,H) = 8.9, 1.6 Hz, 1H; H_3); 8.11 (dd sat, 1H, ^3J(H,H) = 7.8 Hz, ^4J(H,P) = 5.5 Hz, ^3J(H,Pt) = 47 Hz, 1H; $H_{4'}$); 7.68–7.80 (m, 6H; H_m PPh_3); 7.35–7.45 (m, 11H; $H_6 + H_4 + H_o + H_p$ PPh_3); 7.10 (dd sat, J(H,H) = 7.8, 1.6 Hz, ^3J(H,Pt) = 25 Hz, 1H; $H_{5'}$); 6.63 (td, J(H,H) = 7.4, 5.5, 1.6 Hz, 1H; H_5); 2.53 (s, 3H; Me-bipy); 0.73 (d sat, ^3J(H,P) = 8 Hz, ^2J(H,Pt) = 83 Hz, 3H; Pt-Me); ^{31}P NMR ($CDCl_3$, 25 °C, 85% H_3PO_4): $\delta = 33.6$ (s sat, ^1J(P,Pt) = 2226 Hz, PPh_3); elemental analysis calcd (%) for $C_{30}H_{27}N_2PPt$: C 56.16, H 4.24, N 4.37; found: C 55.94, H 3.99, N 4.21.

[Pt(L′′-H)(Me)(PCy$_3$)], 2f: Yield 92%; m.p. 225 °C; ^{1}H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 8.85$ (d sat, J(H,H) = 5.4 Hz, ^3J(H,Pt) = 14 Hz, 1H; H_6); 8.69 (dd, J(H,H) = 7.9 Hz, 1H; H_3); 8.59 (d, ^4J(H,H) = 5.5 Hz, ^3J(H,Pt) = 50 Hz, 1H; $H_{4'}$); 7.97–8.01 (m, 2H; $H_4 + H_{8'}$); 7.79 (d, J(H,H) = 8.2 Hz, 1H; $H_{5'}$); 7.55 (dd, J(H,H) = 7.2, 6.9 Hz, 1H; $H_{7'}$ or $H_{6'}$); 7.41 (dd, J(H,H) = 8.1, 5.5 Hz, 1H; $H_{6'}$ or $H_{7'}$); 7.30 (dd, J(H,H) = 5.8 Hz, 1H; H_5); 2.46–1.18 (m, 33H; PCy_3); 1.11 (d sat, ^3J(H,P) = 6.5 Hz, ^2J(H,Pt) = 84 Hz, 3H; Pt-Me); ^{31}P NMR ($CDCl_3$, 25 °C, 85% H_3PO_4): $\delta = 24.8$ (s sat, ^1J(P,Pt) = 2090 Hz, PCy_3); elemental analysis calcd (%) for $C_{33}H_{45}N_2PPt$: C 56.97, H 6.52, N 4.03; found: C 56.95, H 6.94, N 4.04.

General Procedure for Preparation of Compounds 3

MeI (3.00 mmol) was added to a solution of **2** (0.50 mmol) in acetone (15 mL) under nitrogen atmosphere. The solution was stirred for 2 h at room temperature, then Et_2O was added to give a precipitate which was filtered, washed with Et_2O and vacuum-dried to give the analytical sample as a pale yellow solid.

[Pt(L-H)(Me)$_2$(I)(PPh$_3$)] (3a(ax)): Yield: 64%; m.p. 169 °C; ^{1}H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 9.58$ (d sat, J(H,H) = 5.5 Hz, ^3J(H,Pt) = 10 Hz, 1H; H_6), 8.25 (d, J(H,H) = 4.1 Hz, 1H; $H_{6'}$), 8.20 (d, J(H,H) = 7.4 Hz, 1H; H_3), 7.53 (t, J(H,H) = 7.5 Hz, 1H; H_4), 7.26–7.11 (m, 16H; $H_{PPh3} + H_5$), 7.05 (d sat, J(H,H) = 7.9 Hz, ^3J(H,Pt) = 47 Hz, 1H; $H_{4'}$), 6.82 (dd sat, J(H,H) = 7.9, 4.6 Hz, ^3J(H,Pt) = 15 Hz, 1H; $H_{5'}$), 1.64 (d sat, ^3J(H,P) = 8 Hz, ^2J(H,Pt) = 71 Hz, 3H; Pt-Me), 1.12 (d sat, ^3J(H,P) = 7.5 Hz, ^2J(H,Pt) = 60 Hz, 3H; Pt-Me); ^{13}C NMR ($CDCl_3$, 25 °C, TMS): $\delta = 160.2$ (s sat, J(C,Pt) = 38 Hz); 152.8 (s sat, J(C,Pt) = 6 Hz); 145.8 (d sat, J(C,P) = 2 Hz, J(C,Pt) = 4 Hz); 145.2 (d, J(C,P) = 5 Hz); 139.5 (s); 135.9 (d, J(C,P) = 2 Hz); 134.8 (d sat, J(C,P) = 8.5 Hz, J(C,Pt) = 3 Hz); 131.0 (s sat, J(C,Pt) = n.r.); 130.9 (s); 130.6 (s sat, J(C,Pt) = 11 Hz); 128.8 (d, J(C,P) = 9 Hz); 126.7 (s sat, J(C,Pt) = 10 Hz); 126.4 (d sat, J(C,P) = 2 Hz, J(C,Pt) = 25 Hz); 122.8 (s sat, J(C,Pt) = 16 Hz); 7.04 (d sat, J(C,P) = 113 Hz, J(C,Pt) = 494 Hz); −6.89 (d sat, J(C,P) = 4 Hz, J(C,Pt) = 632 Hz); ^{31}P NMR ($CDCl_3$, 25 °C, 85% H_3PO_4): $\delta = -9.3$ (s sat, ^1J(P,Pt) = 970 Hz, PPh_3); elemental analysis calcd (%) 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.

[Pt(L-H)(Me)$_2$(I)(PMe$_3$)] (3b(ax)):

Method A: A [D_6]acetone solution of **3b** was heated to 60 °C and the progress of the reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. The reaction looks complete after 10 days. Quantitative yield by NMR criteria.

Method B: A [D_6]acetone solution of **3b** 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. ^{1}H NMR (600 MHz, [D_6]acetone, 25 °C): $\delta = 9.82$ (d sat, J(H,H) = 5.6 Hz, ^3J(H,Pt) = 12 Hz, 1H; H_6); 8.50 (d br, J(H,H) = 8.0 Hz, 1H; H_3); 8.41 (dt, J(H,H) = 4.4, 1.2 Hz, 1H; $H_{6'}$); 8.18 (td, J(H,H) = 7.8, 1.2 Hz, 1H; H_4); 7.69 (dt sat, J(H,H) = 7.8, 1.2 Hz, ^3J(H,Pt) = 44 Hz, 1H; $H_{4'}$); 7.60 (ddd, J(H,H) = 7.3, 5.6, 1.4 Hz, 1H; H_5); 7.28 (dd sat, J(H,H) = 7.8, 4.5 Hz, ^4J(H,Pt) = 14 Hz, 1H; $H_{5'}$); 1.40 (d sat, ^3J(H,P) = 8.5 Hz, ^2J(H,Pt) = 71 Hz, 3H; Pt-Me(eq)); 1.14 (d sat, ^2J(H,P) = 10 Hz, ^3J(H,Pt) = 12 Hz, 9H; PMe_3); 0.76 (d sat, ^3J(H,P) = 8 Hz, ^2J(H,Pt) = 56 Hz, 3H; Pt-Me(ax)); ^{31}P{^{1}H} NMR (242.9 MHz, [D_6]acetone, 25 °C): $\delta = -42.9$ (s sat, J(P,Pt) = 1239 Hz, PMe_3); ^{195}Pt-^{1}H HMQC (600 MHz, [D_6]acetone, 25 °C): $\delta = -3411$ (d, J(Pt,P) = 1250 Hz) correlates with signals at 9.82, 7.69, 1.40, 1.14, 0.76.

[Pt(L-H)(Me)$_2$(PMe$_3$)(H$_2$O)] (3w): A [D_6]acetone solution of **3b** 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 **3b′**. ^{1}H NMR (600 MHz, [D_6]acetone, 25 °C): $\delta = 8.99$ (d br sat, J(H,H) = 5.0 Hz, ^3J(H,Pt) = 9 Hz, 1H; H_6); 8.61 (d br, J(H,H) = 7.8 Hz, 1H; H_3); 8.47 (d br, J(H,H) = 4.2 Hz, 1H; $H_{6'}$); 8.33 (t br, J(H,H) = 7.8 Hz, 1H; H_4); 7.84 (ddd, J(H,H) = 7.4, 5.6, 1.5 Hz, 1H; H_5); 7.78 (d sat, J(H,H) = 7.9 Hz, ^3J(H,Pt) = 54 Hz, 1H; $H_{4'}$); 7.31 (dd sat, J(H,H) = 7.8, 4.8 Hz, ^4J(H,Pt) = 15 Hz, 1H; $H_{5'}$); 7.10 (d, ^3J(H,P) = 1.5, 2H; Pt-OH_2); 1.35 (d sat, ^3J(H,P) = 8 Hz, ^2J(H,Pt) = 66 Hz, 3H; Pt-Me(eq)); 1.16 (d sat, ^2J(H,P) = 10.5 Hz, ^3J(H,Pt) = 12 Hz, 9H; PMe_3); 0.57 (d sat, ^3J(H,P) = 8 Hz, ^2J(H,Pt) = 50 Hz, 3H; Pt-Me(ax)); ^{31}P{^{1}H} NMR (242.9 MHz, [D_6]acetone, 25 °C): $\delta = -25.6$ (s sat, J(P,Pt) = 1243 Hz, PMe_3); ^{195}Pt-^{1}H HMQC (600 MHz, [D_6]acetone, 25 °C): $\delta = -2676$ (d, J(Pt,P) = 1511 Hz) correlates with signals at 8.99, 7.78, 7.31, 7.10, 1.35, 1.16, 0.57; ^{31}P-^{1}H HMQC (600 MHz, [D_6]acetone, 25 °C): $\delta = -25.6$ correlates with 8.99, 7.78, 7.10, 1.35, 1.16, 0.57.

[Pt(L-H)(Me)$_2$(I)(PCy$_3$)] (3c(ax)): Yield: 56%; m.p. 203–204 °C; ^{1}H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 9.98$ (d, J(H,H) = 5.2 Hz, J_{Pt-H} = 12 Hz, 1H; H_6), 8.41 (m, 2H; $H_3 + H_{6'}$), 7.94 (td, J(H,H) = 7.9, 6.8 Hz, 1H; H_4), 7.77 (d sat, $^3J_{Pt-H}$ = 47 Hz, J(H,H) = 7.8 Hz, 1H; $H_{4'}$), 7.40 (t, J(H,H) = 6.2, 6.0 Hz, 1H; $H_{5'}$), 7.21 (ddd, J(H,H) = 7.6, 4.6 Hz, 1H; H_5), 2.0–0.90 (m, 33H; PCy_3), 1.73 (d sat, ^2J(H,Pt) = 72 Hz, ^3J(H,P) = 6.5 Hz, 3H; Pt-Me), 0.96 (d sat, ^2J(H,Pt) = 57 Hz, ^3J(H,P) = 7 Hz, 3H; Pt-Me); ^{31}P NMR ($CDCl_3$, 25 °C, 85% H_3PO_4): $\delta = -17.9$ (s sat, ^1J(P,Pt) = 957 Hz, PCy_3); elemental analysis calcd (%) for $C_{30}H_{46}N_2PIPt$: C 45.75, H 5.89, N 3.56; found: C 46.47, H 5.71, N 3.62.

[Pt(L′-H)(Me)$_2$(I)(PPh$_3$)], 3d(ax): (3 h, RT, ppt with *n*-hexane). Yield 70%; m.p. 165–170 °C; ^{1}H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 9.55$ (dd sat, J(H,H) = 5.6, 1.6, 0.8 Hz, ^3J(H,Pt) = 17 Hz, 1H; H_6), 8.22 (dd, J(H,H) = 8.0, 0.8 Hz, 1H; H_3), 7.82–7.69 (m, 2H; $H_4 + H_5$), 7.05–7.26 (m, 15H; PPh_3), 6.88 (dd sat, J(H,H) = 8 Hz, ^3J(H,Pt) = 45 Hz, ^4J(H,P) = 1 Hz, 1H; $H_{4'}$), 6.69 (d sat, J(H,H) = 8 Hz, ^4J(H,Pt) = 14 Hz, 1H; $H_{5'}$), 2.51 (s, 3H; Me-bipy), 1.65 (d sat, ^2J(H,Pt) = 71 Hz, ^3J(H,P) = 7.5 Hz, 3H; Pt-Me), 1.19 (d sat, ^2J(H,Pt) = 60 Hz, ^3J(H,P) = 7.5 Hz, 3H; Pt-Me); ^{31}P NMR ($CDCl_3$, 25 °C, 85% H_3PO_4): $\delta = -9.71$ (s sat, ^1J(P,Pt) = 967 Hz, PPh_3); elemental analysis calcd (%) for $C_{31}H_{30}IN_2PPt$: C 47.52, H 3.86, N 3.58; found: C 47.37, H 3.43, N 3.30.

[Pt(L′′-H)(Me)$_2$(I)(PPh$_3$)], 3e(ax): (5 h, 35 °C, ppt with *n*-pentane). Yield 74%; m.p. 150–155 °C; ^{1}H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 9.72$ (d sat, J(H,H) = 5.5 Hz, ^3J(H,Pt) = 10 Hz, 1H; H_6); 8.50 (d, J(H,H) = 7.9 Hz, 1H; H_3); 8.02 (d, J(H,H) = 8.2 Hz, 1H; $H_{8'}$); 7.82 (t, J(H,H) = 7.9,

7.5 Hz, 1H; H_4); 7.62 (dd, J(H,H) = 7.8, 6.4 Hz, 1H; $H_{7'}$ or $H_{4'}$); 7.47–7.38 (m, 2H; $H_{6'} + H_{5'}$); 7.29–6.95 (m, 17H; $PPh_3 + H_5 + H_{7'}$ or $H_{4'}$); 1.75 (d sat, ^3J(H,P) = 7.5 Hz, ^2J(H,Pt) = 71 Hz, 3H; Pt-Me); 1.29 (d sat, ^3J(H,P) = 7.5 Hz, ^2J(H,Pt) = 60 Hz, 3H; Pt-Me); ^{31}P NMR ($CDCl_3$, 25 °C, 85% H_3PO_4): $\delta = -10.42$ (s sat, ^1J(P,Pt) = 956 Hz, PPh_3); elemental analysis calcd (%) for $C_{34}H_{30}N_2PIPt{\cdot}2H_2O$: C 49.83, H 3.69, N 3.42; found: C 47.78, H 3.67, N 2.96.

[Pt(L''-H)(Me)$_2$(I)(PCy$_3$)], 3 f(ax): (1 h, 35 °C, ppt with *n*-pentane). Yield 63%; m.p. 185–190 °C; ^{1}H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 10.06$ (d sat, J(H,H) = 5.4 Hz, ^3J(H,Pt) = 17 Hz, 1H; H_6), 8.73 (d, J(H,H) = 7.1 Hz, 1H; H_3), 8.16–8.00 (m, 3H; $H_4 + H_{4'} + H_{5'}$ or $H_{8'}$), 7.79 (d, J(H,H) = 7.8 Hz, 1H; $H_{8'}$ or $H_{5'}$), 7.67 (dd, J(H,H) = 7.4, 6.7 Hz, 1H, $H_{6'}$ or $H_{7'}$), 7.61–7.46 (m, 2H; $H_{7'}$ or $H_{6'} + H_5$), 2.00–0.82 (m, 33H; PCy_3), 1.85 (d sat (overlapping), ^3J(H,P) = 6 Hz, ^2J(H,Pt) = 72 Hz, 3H; Pt-Me); 1.01 (d sat, ^3J(H,P) = 7 Hz, ^2J(H,Pt) = 57 Hz, 3H; Pt-Me); ^{31}P NMR ($CDCl_3$, 25 °C, 85% H_3PO_4): $\delta = -17.60$ (s sat, ^1J(P,Pt) = 945 Hz, PCy_3); elemental analysis calcd (%) for $C_{35}H_{51}N_2PIPt$: C 49.30, H 6.03, N 3.29; found: C 49.36, H 6.40, N 2.97.

Synthesis of complexes 4-BF$_4$

A 10% excess of $AgBF_4$ (0.22 mmol) was added to a solution of **3** (0.20 mmol) in acetone (15 mL) under stirring. 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_2O. The precipitate formed was filtered, washed with Et_2O, and vacuum-dried to give the analytical sample as a pale yellow solid.

[Pt(κ^2-*N*,*N*-3-Me-2,2′-bipyridine)(Me)(PPh$_3$)][BF$_4$] (4 a-BF$_4$): Yield 70%. Selected ^{1}H NMR data ($CDCl_3$, 25 °C, TMS), **4 a′**: $\delta = 9.07$ (m, 1H; H_6), 8.59 (d, 1H; $H_{3'}$), 8.43 (d, 1H; H_4), 7.93 (dd, 1H; H_3), 7.88 (m, 6H; H_{ortho} PPh_3), 2.98 (s, 3H; Me-bipy), 0.78 (d sat, ^3J(H,P) = 3.5 Hz, ^2J(H,Pt) = 71 Hz, 3H; Pt-Me). **4 a″**: $\delta = 9.19$ (m, 1H; $H_{6'}$), 8.69 (dd, 1H; H_3), 8.58 (dd, 1H; $H_{4'}$), 8.17 (dd, 1H; H_4), 8.03 (m, 1H; $H_{5'}$), 7.88 (m, 6H; H_{ortho} PPh_3), 2.94 (s, 3H; Me-bipy), 0.81 (d sat, ^3J(H,P) = 3.5 Hz, ^2J(H,Pt) = 72 Hz, 3H; Pt-Me); ^{31}P NMR ($CDCl_3$, 25 °C, 85% H_3PO_4): $\delta = 19.2$ ppm (s sat, ^1J(P,Pt) = 4294), 18.9 ppm (s sat, ^1J(P,Pt) = 4318 Hz).

[Pt(κ^2-*N*,*N*-3-Me-2,2′-bipyridine)(Me)(PCy$_3$)][BF$_4$] (4 c-BF$_4$): Yield: 98%; m.p. 160–165 °C; ^{1}H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 8.95$ (d, J(H,H) = 6.2 Hz, 1H; H_6), 8.80 (d, J(H,H) = 5.0 Hz, 1H; $H_{6'}$), 8.49–8.36 (m, 2H; $H_3 + H_4$), 8.16 (t, J(H,H) = 8.6, 8.5 Hz, 1H; $H_{4'}$), 7.85–7.68 (m, 2H; $H_5 + H_{5'}$), 2.90 (d, 3H; Me-bipy), 2.45–1.19 (m, 33H; PCy_3), 1.01 (d sat, ^3J(H,P) = 2 Hz, ^2J(H,Pt) = 72 Hz, 3H; Pt-Me), 0.94 (d sat, ^3J(H,P) = 2 Hz, ^2J(H,Pt) = 53 Hz, 3H; Pt-Me); ^{31}P NMR ($CDCl_3$, 25 °C, 85% H_3PO_4): $\delta = 16.8$ (s sat, ^1J(P,Pt) = 4074 Hz, PCy_3); 16.1 (s sat, ^1J(P,Pt) = 4034 Hz, PCy_3); IR (Nujol): $\nu = 1080$ cm^{-1} (BF_4^-); Λ_M (acetone, 5 10^{-4} M) = 120 cm^2 ohm^{-1} mol^{-1}; elemental analysis calcd (%) for $C_{30}H_{46}BF_4N_2PPt$: C 48.20, H 6.20, N 3.75; found: C 43.70, H 5.61, N 3.43.

[Pt(κ^2-*N*,*N*-3,6-Me$_2$-2,2′-bipyridine)(Me)(PPh$_3$)][BF$_4$] (4 d-BF$_4$): (3 h, RT) Yield 98%; m.p. 160–165 °C; ^{1}H NMR ($CDCl_3$, 25 °C, TMS): $\delta =$ 8.85 (m, ^3J(H,Pt) = 38 Hz, 1H; H_6 cis-Pt-Me), 8.50–7.20 (m, aromatics), 6.90 (m, 2H), 2.95 (s, 3H; Me-bipy), 2.92 (s, 3H; Me-bipy), 2.84 (s, 3H; Me-bipy), 1.94 (s, 3H; Me-bipy (cis-Pt-PPh_3)), 0.81 (d sat, ^3J(H,P) = 3.5 Hz, ^2J(H,Pt) = 70 Hz, 3H; Pt-Me); 0.46 (d sat, ^3J(H,P) = 4.5 Hz, ^2J(H,Pt) = 70 Hz, 3H; Pt-Me); ^{31}P NMR ($CDCl_3$, 25 °C, 85% H_3PO_4): $\delta = 18.22$ (s sat, ^1J(P,Pt) = 4463 Hz, PPh_3); 15.27 (s sat, ^1J(P,Pt) = 4463 Hz, PPh_3). IR (Nujol): $\nu = 1060$ cm^{-1} BF_4^- (broad); 696 cm^{-1} Ph (PPh_3); elemental analysis calcd (%) for $C_{31}H_{30}BF_4N_2PPt$: C 50.08, H 4.07, N 3.77; found: C 49.57, H 4.32, N 3.36.

[Pt(κ^2-*N*,*N*-3-Me-2-(2′-pyridyl)quinoline)(Me)(PPh$_3$)][BF$_4$] (4 e-BF$_4$): Yield 70%. NMR selected signals: ^{1}H NMR ($CDCl_3$, 25 °C, TMS): $\delta =$ 9.05 (d, 1H), 8.97 (m sat, ^3J(H,Pt) = n.r., 1H; H_6), 8.85–6.75 (m, aromatics), 3.17 (s, 3H; Me-pyquinoline, species B), 3.16 (s, 3H; Me-pyquinoline, species A), 0.95 (d sat, ^2J(H,Pt) = 73 Hz, 3H; Pt-Me species B), 0.47 (d sat, ^2J(H,Pt) = 72 Hz, 3H; Pt-Me species A); ^{31}P NMR ($CDCl_3$, 25 °C, 85% H_3PO_4): $\delta = 18.52$ (s sat, ^1J(P,Pt) = 4470 Hz, species A, PPh_3); 16.69 (s sat, ^1J(P,Pt) = 4325 Hz, species B, PPh_3). ^{31}P NMR spectrum shows the presence of an unidentified third species (40% ca.) which has a chemical shift of 31.9 ppm with ^1J(P,Pt) = 3144 Hz. NOE-1d: irradiating at 0.47 ppm (Pt-Me, species A) there is enhancement of the doublet at 8.28 ppm attributable to the H_8 of the species A.

[Pt(κ^2-*N*,*N*-3-Me-2-(2′-pyridyl)quinoline)(Me)(PCy$_3$)][BF$_4$] (4 f-BF$_4$): (3 h, 35 °C) Yield 68%; ^{1}H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 9.00$–7.76 (m, 9H; broad overlapping signals); 3.11 (s, 3H; Me-bipy); 2.45–0.75 (m, 33H; PCy_3), 0.54 (s br sat, ^2J(H,Pt) = 74 Hz, 3H; Pt-Me); ^{31}P NMR ($CDCl_3$, 25 °C, 85% H_3PO_4): 15.34 (s br sat, ^1J(P,Pt) = 4157 Hz, PCy_3).

3-Methyl-2,2′-bipyridine (5): To a solution of [Pt(κ^2-*N*,*N*-3-Me-2,2′-bipyridine)(Me)(PCy_3)][BF_4] (71.1 mg; 0.0948 mmol) in CH_2Cl_2 (15 mL) dppe was added under stirring (38.1 mg, 0.0956 mmol). The solution was stirred for 15 min at room temperature. The solution immediately became colorless. The solution was concentrated to small volume, treated with Et_2O and filtered. The desired product was obtained by flash chromatography using Et_2O as eluent.

^{1}H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 8.69$ (ddd, J(H,H) = 4.8, 1.6, 0.9 Hz, 1H; H_6), 8.54 (d, J(H,H) = 4.8 Hz, 1H; $H_{6'}$), 7.83 (td, 1H; H_4), 7.78 (dd, 1H; H_3), 7.62 (d, J(H,H) = 7.8 Hz, 1H; $H_{4'}$), 7.30 (ddd, J(H,H) = 7.6, 4.8, 1.8 Hz, 1H; H_5); 7.25 (dd, J(H,H) = 7.7, 4.8 Hz, 1H; $H_{5'}$); 2.51 (d, 3H; Me-bipy); ^{13}C NMR ($CDCl_3$): 158.91, 156.31, 148.47, 146.69, 139.19, 136.54, 132.26, 124.16, 123.01, 122.64, 19.89 (Me-bipy); MS: *m/z* found 171.0915, calculated for $C_{11}H_{11}N_2$ $[M+H]^+$, 171.0917.

3,6-Dimethyl-2,2′-bipyridine (6): To a solution of [Pt(κ^2-*N*,*N*-3,6-Me_2-2,2′-bipyridine)(Me)(PPh_3)][BF_4] (51 mg; 0.0659 mmol) in CH_2Cl_2 (15 mL) dppe was added under stirring (25.8 mg, 0.0647 mmol). The solution was stirred for 15 min at room temperature. The solution immediately became colorless. The solution was concentrated to small volume, treated with Et_2O and filtered. The desired product was obtained by flash chromatography using Et_2O as eluent.

^{1}H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 8.69$ (d, J(H,H) = 4.8 Hz, 1H; H_6), 7.81 (ddd, J(H,H) = 7.8, 7.5 Hz, 1H; H_4), 7.73 (d, J(H,H) = 7.8 Hz, 1H; H_3), 7.51 (d, J(H,H) = 7.9 Hz, 1H; $H_{4'}$), 7.10 (d, J(H,H) = 7.9 Hz, 1H; $H_{5'}$), 2.58 (s, 3H; Me-bipy), 2.41 (s, 3H; Me-bipy); MS: *m/z* found 185.1075, calculated for $C_{12}H_{13}N_2$ $[M+H]^+$, 185.1073.

3-Methyl-2-(2′-pyridyl)quinoline (7): To a solution of [Pt(κ^2-*N*,*N*-3-Me-2-(2′-pyridyl)quinoline)(Me)(PPh_3)][BF_4] (35 mg; 0.0440 mmol) in CH_2Cl_2 (15 mL) dppe was added under stirring (20 mg, 0.0502 mmol). The solution was stirred for 15 min at room temperature. The solution immediately became colorless. The solution was concentrated to small volume, treated with Et_2O and filtered. The desired product was obtained by flash chromatography using Et_2O as eluent.

^{1}H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 8.72$ (ddd, J(H,H) = 4.8 Hz, 1H; H_6), 8.13 (d, J(H,H) = 8.5 Hz, 1H; H_8), 8.05 (s, 1H; $H_{4'}$), 7.89–7.84 (m, 2H; $H_3 + H_4$), 7.80 (d, J(H,H) = 8.2 Hz, 1H; $H_{5'}$); 7.67 (m, 1H; $H_{6'}$ or $H_{7'}$); 7.54 (m, 1H; $H_{6'}$ or $H_{7'}$); 7.30 (m, 1H; H_5); 2.62 (s, 3H; Me); MS: *m/z* found 221.1073, calculated for $C_{15}H_{13}N_2$ $[M+H]^+$, 221.1073.

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