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Mesoionic Complexes of Platinum(II) Derived from "Rollover" Cyclometalation: A Delicate Balance between Pt−C(sp^3) and Pt−C(sp^2) Bond Cleavage as a Result of Different Reaction Conditions

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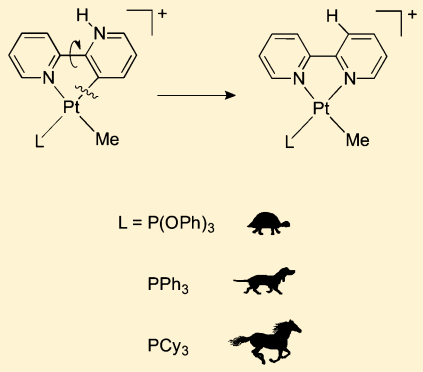
Supporting Information

ABSTRACT: "Rollover" cyclometalation is a particular case of metal-mediated C−H bond activation, and the resulting complexes constitute an emerging class of cyclometalated compounds. In the case of 2,2′-bipyridine "rollover cyclometalation" has been used to synthesize the complexes [Pt(bipy-H)(Me)(L)] (L = PPh_3, PCy_3, $P(OPh)_3$, $P(p\text{-tolyl})_3$), whose protonation produces a series of stable corresponding pyridylenes $[Pt(bipy^*)(Me)(L)]^+$. The unusual bipy* ligand may be described as an abnormal-remote heterocyclic chelated carbene or simply as a mesoionic cyclometalated ligand. These cationic species spontaneously convert in solution, through a retro-rollover reaction, to the corresponding isomers $[Pt(bipy)(Me)(L)]^+$, where the 2,2′-bipyridine is coordinated in the classical N,N bidentate mode. Isomerization is achieved at different rates (ranging over three orders of magnitude), depending on the nature of the phosphane ligand, the most basic (PCy_3) providing the fastest reaction. The mesoionic species $[Pt(bipy^*)(Me)(L)]^+$ contain two Pt−C bonds: the balance between the Pt−C(sp^2) and Pt−C(sp^3) bond rupture is subtle, and competition is observed according to the reaction conditions. In the presence of an external neutral ligand L′ methane is released to give the cationic derivatives $[Pt(bipy\text{-}H)(L)(L')]^+$, whereas reaction of the neutral [Pt(bipy-H)(Me)(L)] with HCl may follow different routes depending on the nature of the neutral ligand L. Assuming all reactions take place through the formation of a hydride intermediate, quantum chemical calculations show that computed energy barriers are qualitatively consistent with observed reaction rates.



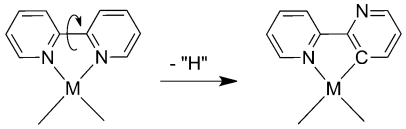
INTRODUCTION

Classical spectator ligands such as 2,2′-bipyridine 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 center in response to alterations in the solution environment, such as changes in pH. Nitrogen donors capable of forming N−H bonds, recently defined "ligands with multiple personalities",[1] seem particularly suitable for this purpose, showing interesting perspectives in different fields, such as the design of molecular devices (e.g., molecular machines[2] and organometallic sensors[3]) or C−H bond activation.[4]

Among classical ligands 2,2′-bipyridine plays an important role, being arguably the most studied ligand in inorganic chemistry;[5] in its common coordinative behavior it acts as a chelated ligand even if monodentate[6] and bridging coordinations are also known.[7]

In addition to the classical coordination as a neutral N,N ligand, 2,2′-bipyidine may behave in a different way (see Scheme 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_3−H bond to give a five-membered cyclometalated complex.[8]

Scheme 1. "Rollover" Cyclometalation



This unusual reaction, called "rollover" cyclometalation, is raising a growing interest, as demonstrated by the publication of a very recent review.[9] It is worth noting that the reaction is not restricted to 2,2′-bipyridines: other chelated heteroaromatic ligands, such as pyrazolylmethanes,[10] 2-phenylpyridines,[11] and *N*-(2′-pyridyl)-7-azaindole,[12] may react in a similar way. Moreover, cyclometalated complexes of 2,2′-bipyridine closely resemble those of cyclometalated 2-phenylpyridine, whose platinum(II) complexes showed interesting properties in catalysis, reactivity, and medicinal chemistry,[13] with the additional function of the second nitrogen atom.

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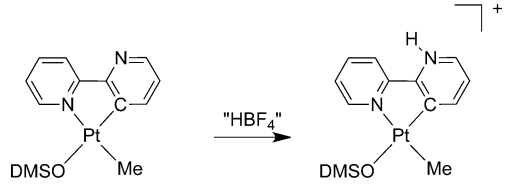
In fact, compounds derived from "rollover" cyclometalation represent a new emerging class of cyclometalated complexes, due to the presence of the uncoordinated nitrogen atom, able to strongly influence the reactivity of the complex. In the case of platinum(II) these species have shown noteworthy potentialities, e.g. in platinum-[14] and palladium-mediated[15] C−C bond forming and in dehydrosulfurization and oxidative C−C bond coupling of thioethers in the gas phase.[16] Very recently, two independent research groups reported catalytic applications involving rhodium-mediated "rollover" cyclometalation.[17]

The first complex of this family appeared in the literature, an iridium species with three coordinated 2,2′-bipyridines, was completely characterized, through a single-crystal X-ray determination, only at the end of a long and controversial debate as $[Ir(bipy)_2(bipy^*)]^{3+}$.[18] The zwitterionic bipy* ligand is an N,C-bonded isomer of 2,2′-bipyridine, and this iridium complex has been described only recently as the first *abnormal* pyridylene complex.[19] In recent years were called "abnormal"[19] 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.

The class of pyridylenes is receiving growing interest due to their intriguing properties;[20] 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;[21] however, the term "carbene" is often used to highlight the relationship of these species with normal heterocyclic and Fischer carbenes.

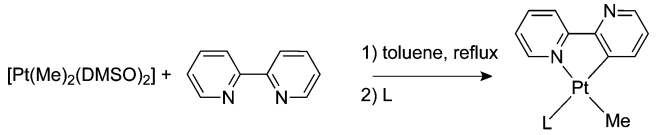
The unusual bipy* ligand may be obtained also by treatment of the platinum(II) species [Pt(bipy-H)(Me)(DMSO)] (**1a**) with acids having poorly coordinating anions, such as [18-crown-6-H_3O][BF_4]. The reaction results in the synthesis of the corresponding *mesoionic* complex $[Pt(bipy^*)(Me)(DMSO)]^+$ (**2a**) without involving the rupture of the Pt−C bonds present in the molecule.



As a part of our continuous efforts in the study of cyclometalated 2,2′-bipyridines[22] we report here some aspects of the chemical behavior of a series of mesoionic complexes derived from "rollover" cyclometalation.

RESULTS AND DISCUSSION

Starting from the parent complex **1a**, a series of complexes of general formula [Pt(bipy-H)(X)(L)] (X = anionic ligand, L = neutral ligand) can be isolated in the solid state and characterized. The clean synthesis of the methyl species [Pt(bipy-H)(Me)(L)] (**1**) has been reported only recently.[23] 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 **1a**, 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. This procedure permits us to prepare in good yields even complexes that cannot be obtained with the classical substitution reaction: i.e., with L = PCy_3, $P(OPh)_3$.

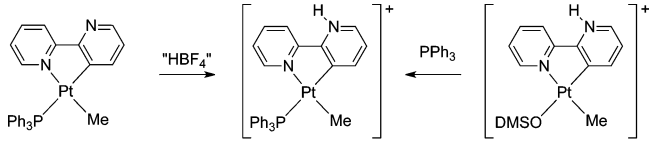


L = PPh_3 **1b**
PCy_3 **1c**
$P(OPh)_3$ **1d**
$P(p\text{-tolyl})_3$ **1e**

The new series of complexes [Pt(bipy-H)(Me)(L)] (L = PPh_3 (**1b**), PCy_3 (**1c**), $P(OPh)_3$ (**1d**), $P(p\text{-tolyl})_3$ (**1e**)) was chosen in order to furnish different steric and electronic properties to the complexes, PPh_3 and $P(p\text{-tolyl})_3$ lying in the middle for both electronic and steric parameters.[24] All synthesized complexes were characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analysis.

Only one of the two possible geometric isomers for **1b−e** 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 $C_{3'}$ carbon (e.g., $^2J_{P-C3'}$ = 119.6 Hz, $^2J_{P\text{-}CH3}$ = 4.7 Hz, and $^1J_{Pt-P}$ = 2229 Hz for **1b**). Furthermore, in the ^1H NMR spectrum the methyl resonances appear as doublets, due to the phosphorus atom in a cis position, with satellites.

Protonation of **1b** with [18-crown-6-H_3O][BF_4] proceeds smoothly to the corresponding cationic complex $[Pt(bipy^*)(Me)(PPh_3)][BF_4]$ (**2b**-BF_4), which was isolated and characterized. The same complex may also be obtained by a substitution reaction, from $[Pt(bipy^*)(Me)(DMSO)][BF_4]$ (**2a**-BF_4) and PPh_3.



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

First, the ^{13}C NMR spectra allowed us to identify the cyclometalated $C_{3'}$ resonance with its satellites. Due to the protonation the $C_{3'}$ signal shifts downfield from δ 158.35 (**1b**) to δ 163.41 (**2b**) while $^1J_{Pt-C}$ increases from 970 (**1b**) to 997 Hz (**2b**). These data may be compared to those recently reported

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for the analogous complex $[Pt(L_1*)(Me)(PPh_3)]^+$ (δ 160.27 ppm, $^1J_{Pt-C}$ = 990 Hz, L_1 = (5*S*,7*S*)-5,7-methane-6,6-dimethyl-2-(pyridin-2-yl)-5,6,7,8-tetrahydroquinoline).[25]

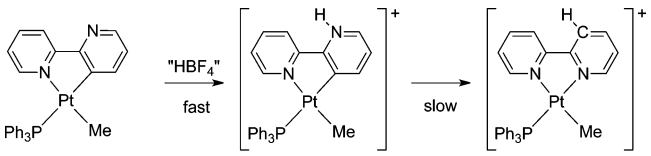
The $C_{3'}$ signal is not particularly shifted to high frequencies for a carbon which may be defined as "carbenic", but it can be compared to the signals for platinum(II) C_2-pyridylene complexes reported by Bercaw and co-workers[26] (δ ca. 160–170 ppm). Furthermore, in contrast to C_2 and C_4 "normal" pyridylenes, which often show chemical shift values above 190 ppm, "abnormal" C_3-pyridylenes usually have values of chemical shifts (δ ca. 160–170 ppm) 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,[19] and overall cannot be simply described in terms of valence bond theory.[20]

The enhancement of the Pt–C_3 coupling constant from **1b** to **2b** 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.

Complexes **1** and **2** have a good thermal stability; for example, **1b** and **2b**-BF_4 are stable up to 215 and 183 °C, respectively, after which decomposition occurs.

A new reaction was observed when complex **2b** was left in solution for several days: complex **2b** slowly converts into a new species with a completion time of ca. 30 days. The compound formed was isolated in the solid state and characterized as the adduct $[Pt(bipy)(Me)(PPh_3)][BF_4]$ (**3b**-BF_4) (Scheme 2).

Scheme 2



In the ^{31}P NMR spectrum a strong $^1J_{Pt-P}$ coupling constant (4351 Hz) is in agreement with a phosphorus trans to a pyridine nitrogen. The $^3J_{P-H}$ and $^2J_{Pt-H}$ values in the adduct **3b** are particularly small: ca. 3 and 69 Hz, respectively (vs 7.1 and 82 Hz in **2b**).

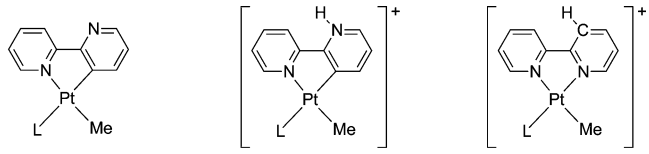
Complexes **2b** and **3b** are isomers; therefore, this reaction corresponds to an isomerization process. The rate of the reaction may be influenced by addition of DMSO to the solution: the reaction evolves completely in 2 days either in CD_2Cl_2 with 10 drops of DMSO or in DMSO-d_6 solution. It is also worth noting that excess $[18\text{-crown-6-}H_3O][BF_4]$ does not influence the rate of the process.

The reaction is unprecedented for 2,2′-bipyridine, being the very first example of a "retro-rollover" reaction in solution of a bipy 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 bipy fragment and dimethyl sulfide.[27] A related reversible reaction, driven by a change of solvent, has also been recently reported by Rourke and co-workers for a cyclometalated phenylpyridine.[11]

The reversibility of the rollover process opens up the possibility to design catalytic cycles based on rollover and retro-rollover reactions, with the bipy ligand playing an active role, behaving as a hydrogen reservoir/acceptor.

At variance with **2b**, the protonated complex $[Pt(bipy*)(Me)(PCy_3)]^+$ (**2c**) shows an enhanced reactivity and rapidly converts into the corresponding adduct $[Pt(bipy)(Me)(PCy_3)]^+$ (**3c**) (Chart 1). Even with short reaction times at room temperature a

Chart 1



mixture of **2c** and **3c** is formed (e.g., 9:1 molar ratio after 10 min) so that complex **2c** 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 $[Pt(bipy*)(Me)(P(OPh)_3)]^+$ (**2d**) is kinetically much more stable and can be easily characterized. The subsequent isomerization to the adduct **3d** is extremely slow with a completion time of about 3 months at room temperature.

The last series of complexes, **1e**–**3e**, was studied in order to evaluate only the electronic factors by direct comparison with the PPh_3 series (**1b**–**3b**). The $P(p\text{-tolyl})_3$ ligand, according to the Tolman cone angle θ, is equivalent to PPh_3 but is more basic due to the presence of the methyl groups.[28]

Despite the close similarity between these two phosphines the observed difference is striking when 10^{-2} M solutions in CD_2Cl_2 of **2b**,**e** are followed by means of ^1H and ^{31}P NMR spectroscopy at room temperature: after 6 days a 90% conversion was observed for **2e**, in contrast to the 33% conversion observed for **2b**.

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 $P(OPh)_3$, with PPh_3 and $P(p\text{-tolyl})_3$ in the middle, a trend compatible with a hypothetical mechanism where the proton migrates to the Pt(II) center to give a Pt(IV) hydride, from which, after reductive elimination of C_3–H, the final product is formed. On the basis of our experimental data we cannot rule out the possibility of a concerted electrophilic attack at the metal–carbon bond; moreover, a different mechanism may be operating for different phosphane donors.

The most electron-rich Pt(II) center in complex **2c** is likely to undergo the oxidative addition pathway more easily than **2b**,**d**; however, it is important to note that steric factors may also play a role in the process and should not be completely ruled out.

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Table 1. Selected Distances, in Å, for the Complexes Optimized at the PBE0/def2-SVP Level

	Pt−P	Pt−CH_3	Pt−$C_{3'}$	Pt−N_1	N_1−C_2	C_2−$C_{2'}$	$C_{2'}$−$C_{3'}$	$N_{1'}$−H	Pt−H
1b	2.34920	2.04446	2.03727	2.19397	1.35079	1.47052	1.41345		
2b	2.36436	2.03797	2.02873	2.20444	1.35299	1.46847	1.40741	1.01689	
Hb	2.46720	2.04693	2.04123	2.21437	1.34998	1.47216	1.41048		1.50983
3b[a]	2.27258	2.03849	2.12163	2.18233	1.35094	1.47742	1.35180		
1c	2.40027	2.04067	2.03832	2.21738	1.35093	1.46757	1.41271		
2c	2.40918	2.03327	2.02920	2.23252	1.35285	1.46587	1.40664	1.01677	
Hc	2.51660	2.04334	2.04468	2.23873	1.34975	1.47012	1.40850		1.50872
3c[a]	2.29789	2.03400	2.13049	2.20572	1.35081	1.47454	1.34985		
1d	2.25061	2.06163	2.04933	2.17416	1.35008	1.47131	1.41211		
2d	2.27117	2.05302	2.04268	2.18241	1.35286	1.46877	1.40528	1.01712	
Hd	2.38265	2.06188	2.03600	2.18655	1.35048	1.47228	1.41045		1.51744
3d[a]	2.19685	2.05451	2.12177	2.16400	1.35100	1.47653	1.35130		
1e	2.35137	2.04418	2.03725	2.19300	1.35083	1.47055	1.41361		
2e	2.36572	2.03767	2.02858	2.20293	1.35298	1.46842	1.40770	1.01686	
He	2.46324	2.04638	2.04338	2.21426	1.34998	1.47236	1.41052		1.50942
3e[a]	2.27449	2.03797	2.12314	2.18154	1.35088	1.47758	1.35162		

[a]Distances involve the $N_{1'}$ instead of the $C_{3'}$ atom.

Table 2. Selected Angles, in deg, for the Complexes Optimized at the PBE0/def2-SVP Level

	P−Pt−CH_3	CH_3−Pt−$C_{3'}$	$C_{3'}$−Pt−N_1	N_1−Pt−P	N_1−Pt−CH_3	P−Pt−$C_{3'}$
1b	92.77	90.12	79.47	97.68	169.39	176.84
2b	91.90	90.64	79.03	98.47	169.49	177.30
Hb	90.59	92.38	79.67	97.27	171.93	175.78
3b[a]	90.44	92.85	76.91	99.99	168.91	175.83
1c	91.77	88.19	78.84	101.26	166.63	178.74
2c	90.47	88.95	78.27	102.52	166.29	177.43
Hc	90.51	89.87	79.03	100.54	168.85	178.24
3c[a]	87.31	92.24	76.06	106.39	161.80	171.18
1d	88.29	89.89	79.41	102.42	169.29	177.39
2d	86.25	91.10	78.96	103.68	170.03	177.21
Hd	85.85	92.05	79.98	102.22	170.83	177.46
3d[a]	84.10	93.24	76.92	105.74	170.09	177.33
1e	92.74	90.20	79.47	97.64	169.47	176.80
2e	91.88	90.74	79.04	98.37	169.62	177.22
He	90.55	92.44	79.62	97.31	171.93	175.79
3e[a]	90.59	92.79	76.89	99.85	169.14	176.08

[a]Angles involve the $N_{1'}$ instead of the $C_{3'}$ atom.

Under these experimental conditions, therefore, selective Pt−C(sp^2) vs Pt−C(sp^3) bond breaking is observed in compounds **2**. 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. 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 center is favored.[29] 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.[30]

Ab Initio 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., **1**−**3**. On the basis of the results of previous studies on similar reactions,[31] 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 three reactions discussed above. All calculations were performed with the hybrid functional PBE0,[32] using the Firefly QC package.[33] The def2-SVP[34] basis set was used for all atoms; for Pt an effective core potential was used to take into account 60 core electrons. Convergence criteria for energy minimization and geometry optimization were set to 10^{-6}. All optimized geometries were validated as minima by inspecting the eigenvalues of the normal-mode analysis. Harmonic frequencies were then used to compute the reported energies of all species. Calculations with a larger basis set (def2-TZVP) performed on the **1b**−**3b** series of complexes agree with a maximum discrepancy of 2% in bond distances, thus confirming the validity of the results obtained with a smaller basis set (see the Supporting Information).

Selected data for the optimized geometries can be found in Tables 1 and 2.

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Protonation of the neutral species **1b–e** has very little influence on the bond distances and angles; it is worth noting that there are no differences above 0.02 Å, the largest ones involving the elongation of Pt–P and Pt–N_1 bonds. As expected, all the bonds connected to the protonation site, e.g. the $N_{1'}$ 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 2), with the heteroaromatic ligand lying on the plane; the lowest values for the $C_{3'}$–Pt–CH_3 and $C_{3'}$ –Pt–N_1 angles are found for the PCy_3 ligand.

A comparison of the proposed hydride intermediates **Hb–e** permits us to note that all the bonds involving platinum are elongated with respect to both the protonated (**2b–e**) and neutral (**1b–e**) 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 center but also with the steric requirements of each phosphane.

Finally, for species **3b–e**, we notice that, by comparison with the corresponding species **1**, **2**, and **H**, (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–CH_3 and Pt–N_1 increase and decrease respectively, (c) the C_2–$C_{2'}$ distances remain substantially unchanged from **Hb–e** but increase in comparison to those in **3b–e**, and (d) P–Pt–CH_3 and $C_{3'}$ –Pt–N1 angles tighten while $C_{3'}$–Pt–CH_3 and N_1–Pt–P widen. Figure 1 reports the geometry-optimized minimum structures of complexes **1b**, **2b**, **Hb**, and **3b**.

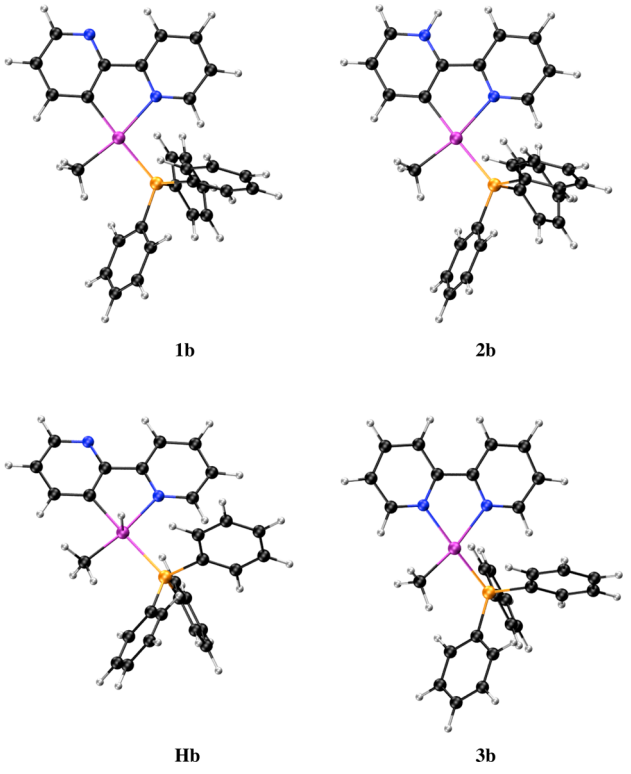

Figure 1. Geometry-optimized minimum structures of complexes **1b**, **2b**, **Hb**, and **3b**.

In Table 3 we report the (zero point energy corrected) enthalpies for all the species involved in the experimental study.

Table 3. Calculated Enthalpies, in kJ/mol at 298.15 K and 101325 Pa, for the Complexes Optimized at the PBE0/def2-SVP Level

	2	H	3
PPh_3	0.00	78.75	−92.78
PCy_3	0.00	72.71	−96.57
$P(OPh)_3$	0.00	93.01	−91.66
$P(p\text{-tolyl})_3$	0.00	73.75	−95.01

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:[35] 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 (PCy_3), 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 $P(p\text{-tolyl})_3$ is faster than PPh_3, 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 **3** is considerably higher, in absolute value, than that of the protonated complexes **2**, 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.

The energy profile for the retro-rollover reaction is reported in Figure 2.

The synthesis of adduct species **3b–e** is not trivial. To the best of our knowledge, only the adduct [Pt(bipy)(Me)(PPh_3)]

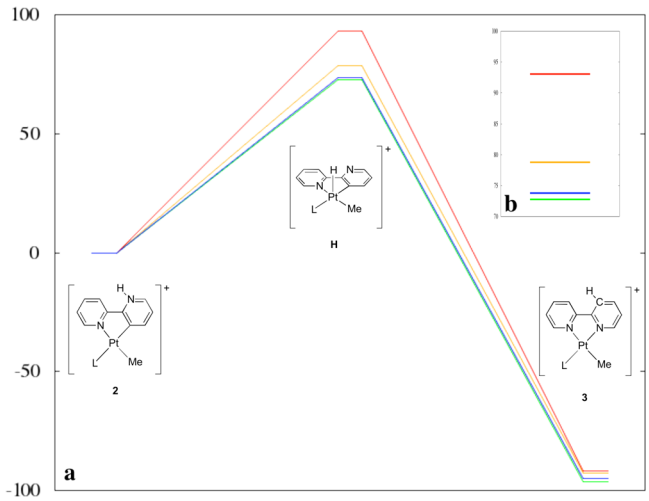

Figure 2. (a) Energy profile for the retro-rollover reaction: (green) PCy_3; (blue) $P(p\text{-tolyl})_3$; (orange) PPh_3; (red) $P(OPh)_3$. (b) Expansion of the hydride intermediate region.

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Cl has been reported in the literature,[36] being detected only in solution but not isolated as a pure species in the solid state. The diimino cationic complexes $[Pt(N,N)(R)(L)]^+$ are of interest for their activity in C−H bond activation,[37] and their synthesis is not so straightforward. Complex **3b** has been previously obtained and fully characterized in our laboratory[38] following a different synthetic procedure.

NMR Data of Neutral and Protonated Species 1 and 2. The analysis of ^1H, ^{31}P, and ^{13}C NMR spectra of species **1** and **2** shows, after protonation, an enhancement of the coupling constants related to the mutually trans Pt−P and Pt−C(sp^2) bonds (e.g., $^1J_{Pt-C3}$ in **1b** and **2b**, $^3J_{Pt-H4}$ = 46.4 Hz in **1d** and 49 Hz in **2d**; $^1J_{Pt-P}$ = 2229 Hz in **1b** and 2500 Hz in **2b**).

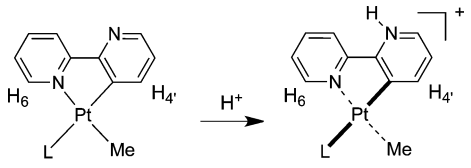
In contrast, coupling constants related to Pt−L bonds cis to C3 show a small decrease after protonation (e.g., the Pt−CH_3 bond: $^1J_{Pt-C}$ = 725 Hz in **1b** and 716 Hz, **2b**). Pt−N bonds may be evaluated by comparison of the $^3J_{Pt-H6}$ values (e.g., 16.0 Hz in **1d** and 15 Hz in **2d**).

On the whole, the rationale of the observed NMR trends for species **1** and **2** 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,[39] provided such bonds involve hybrid orbitals with some s character;[40] as an example, a correlation of Pt−P bond lengths with Pt−P coupling constants has been recently reported by Wollins and co-workers.[41]

In those cases in which greater values of $^1J_{Pt-P}$ 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.[42]

In addition, charge effects may operate and the presence of a protonated nitrogen in species **2** should influence the coupling constant values; however, back-donation in Pt(II) complexes may be considered of little relevance[43] and it has also been reported that Pt^{II}−P bonds are weaker when the metal atom is less positively charged[41] with a negligible Pt−P π donation in cationic complexes.

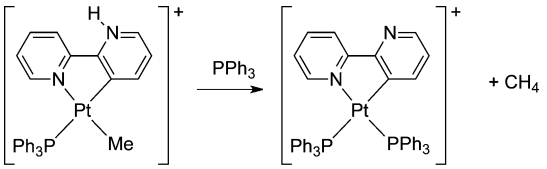


After protonation:

increase of J(Pt-P, Pt-C(sp^2))
decrease of J(Pt-C(sp^3))

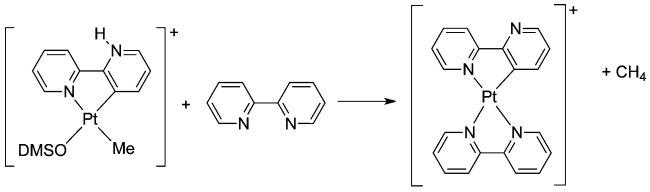
As for chemical shift value, protonation of species **1a−e** produces a shift to high frequency of most of the metalated bipyridine hydrogens, as may be expected from the presence of a positive charge. This effect is more evident in the metalated-protonated pyridine ring, and it is clearly associated with the electron deficiency of the complex.

Competition between Pt−C(sp^2) and Pt−C(sp^3) Bond Breaking. The isomerization process from species **2** to **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 **2b** 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 $[Pt(L\text{-}H)(PPh_3)_2]^+$ (**4**).



The same result was obtained by starting from **2a** and 2 equiv of PPh_3. Complex **4** 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_{Pt-P} = 2105 Hz) and P−Pt−N (J_{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 is also confirmed by the value of the P−P coupling constant ($^2J_{P-P}$ = 19 Hz). Furthermore, when the reaction is followed by means of ^1H NMR spectroscopy a signal at 0.22 ppm, due to free methane, is observed.[44] The same behavior is observed with bidentate donors, such as 1,2-bis(diphenylphosphino)ethane (dppe) and 2,2′-bipyridine (bipy). Addition of dppe or bipy to a solution of **2a** results in Pt−C(sp^3) bond cleavage, and [Pt(bipy-H)(dppe)]-[BF_4] (**5**-BF_4) and [Pt(bipy-H)(bipy)][BF_4] (**6**-BF_4) may be isolated in the solid state and characterized.

Complex **6** has some points of interest, having two coordinated 2,2′-bipyridines, one in the classical κ^2N,N and the other in the κ^2N,C mode.



Complex **5** was easily characterized by means of NMR spectroscopy. 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 51.81 ppm, $^1J_{Pt-P}$ = 1949 Hz) and a P trans to N (δ 42.64 ppm, $^1J_{Pt-P}$ = 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). 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 center.

Both of 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.

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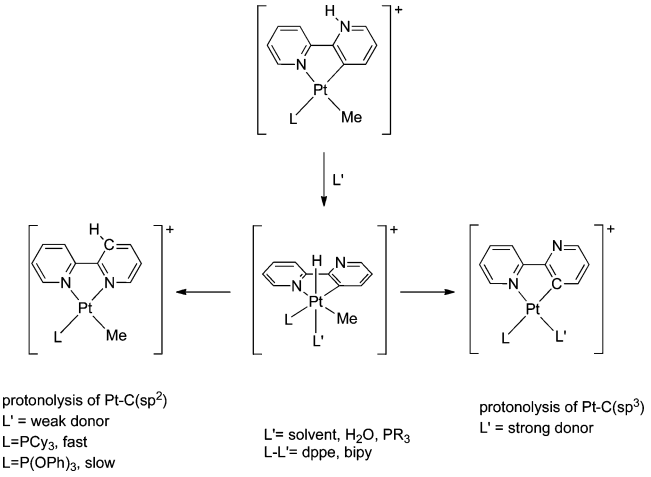
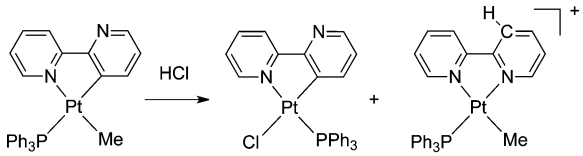
Scheme 3



Reaction with HCl. As previously reported, the reaction of **1a** with an acid having a coordinating anion, such as HCl, gives the corresponding chloride [Pt(bipy-H)Cl(DMSO)] (**7a**) and free methane.[8b]

The same product, **7a**, can be obtained with good yields by reaction of **1a** with [18-crown-6-H_3O][BF_4] in acetone in the presence of LiCl. The reaction likely proceeds through protonation of the uncoordinated nitrogen atom, followed by a mechanism similar to that operating in the presence of 2 equiv of PPh_3, with the anionic ligand Cl^- in place of neutral PPh_3.

The reaction of the species [Pt(bipy-H)(Me)(L)] with HCl, however, is not as straightforward: the corresponding reaction of **1b**, having PPh_3 in place of DMSO, shows a competition between the two protonolysis processes, and a mixture of [Pt(bipy-H)(Cl)(PPh_3)] (**7b**) and [Pt(bipy)(Me)(PPh_3)]Cl (**3b-Cl**) in a 1:4 molar ratio is formed. Their identification in solution was ascertained through NMR spectroscopy by comparison with literature data.[23,26]



In contrast, the reaction of **1c** with HCl gives the cationic adduct [Pt(bipy)(Me)(PCy_3)]Cl (**3c-Cl**) as the main species, in addition to a minor species (in a 1:3 molar ratio) not corresponding to the expected rollover complex [Pt(bipy-H)Cl(PCy_3)]. Despite several efforts, we were not able to separate and characterize the second species.

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.

CONCLUSIONS

Great efforts have been devoted to the comprehension of the mechanisms operating in alkane C−H activation by platinum complexes.[45] 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 protonation.[46]

In the protonation reaction of the so-called "rollover complexes" a competition between two Brønsted−Lowry bases, i.e. the uncoordinated nitrogen and the platinum lone pairs, may occur, in addition to electrophilic attack at the Pt−C(sp^2) and Pt−C(sp^3) bonds. The nitrogen is likely to be the kinetic protonation site to give the uncommon cationic species **2**, $[Pt(bipy^*)(Me)(L)]^+$, which contains the unusual bipy* ligand described as an abnormal-remote pyridylene or as a mesoionic cyclometalated ligand.

The protonated species converts 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 unique retro-rollover reaction occurs to give the cationic adducts $[Pt(bipy)(Me)(L)]^+$. The rate of this isomerization process is dramatically dependent on the nature of the neutral ligand L, the more basic PCy_3 ligand providing the fastest reaction among the phosphanes used in this study. 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 center.

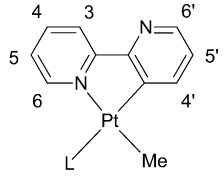
Several factors are active in the course of the protonolysis reaction, and a subtle balance between them may drive the reaction toward different routes.

The comprehension of the factors leading the rollover and retro-rollover processes would give the possibility of designing catalytic cycles where the bipy and bipy* 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.

EXPERIMENTAL SECTION

cis-[$Pt(Me)_2(DMSO)_2$] was synthesized according to ref 47. All of the solvents were purified and dried according to standard procedures.[48] Elemental analyses were performed with a Perkin-Elmer 240B elemental analyzer by Mr. Antonello Canu (Dipartimento di Chimica, Università degli Studi di Sassari, Italy).

Infrared spectra were recorded with a FT-IR Jasco 480P using Nujol mulls. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded with Varian VXR 300 and Bruker Avance III 400 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. NOE difference, 2D-COSY and ^{13}C apt (attached proton test) experiments were performed by means of standard pulse sequences. The numerical scheme for NMR data is as follows:



numerical scheme for NMR data

Preparations. *[Pt(bipy-H)(Me)(PPh_3)] (**1b**). Method A.* For the reaction of [Pt(bipy-H)(Me)(DMSO)] with PPh_3, see ref 8b (yield 67%).

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Method B. To a solution of *cis*-[Pt(Me)$_2$(DMSO)$_2$] (50.1 mg, 0.131 mmol) in anhydrous toluene an excess of 2,2′-bipyridine (63.5 mg, 0.406 mmol) 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 PPh_3 (37.8 mg, 0.144 mmol) 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%. Mp: 215 °C. Anal. Calcd for $C_{29}H_{25}N_2PPt\cdot{}^1/_2H_2O$: C, 54.72; H, 4.12; N, 4.40. Found: C, 54.67; H, 3.79; N, 4.51. ^{1}H NMR ($CDCl_3$): 8.40 (m, 1H, $H_{6'}$); 8.31 (dd, 1H, J_{H-H} = 8.0 Hz, J_{H-H} = 1.5 Hz, H_3); 8.24 (ddd with sat, 1H, $^3J_{Pt-H}$ = 48.0 Hz, J_{H-H} = 7.5 Hz, J_{H-H} = 5.4 Hz, J_{H-H} = 1.8 Hz, $H_{4'}$); 7.79−7.72 (m, 7H, H_4 + H_o PPh_3); 7.46−7.35 (m, 10H, H_6 + H_m + H_p PPh_3) 7.22 (ddd, 1H, J_{H-H} = 7.8 Hz, J_{H-H} = 7.5, J_{H-H} = 1.7, $H_{5'}$); 6.67 (td, 1H, J_{H-H} = 5.4 Hz, J_{H-H} = 1.5 Hz, H_5); 0.74 (s with sat, 3H, $^2J_{Pt-H}$ = 83 Hz, $^3J_{P-H}$ = 7.7 Hz, Pt-CH_3). ^{13}C NMR ($CDCl_3$): 165.71 (s with sat, $^2J_{Pt-C}$ = 19.6 Hz, C_2 or $C_{2'}$); 164.69 (d with sat, $^2J_{Pt-C}$ = 48.3 Hz, $^3J_{P-C}$ = 3.5 Hz, C_2 or $C_{2'}$); 155.35 (d with sat, J_{Pt-C} = 970.3 Hz, $^2J_{P-C}$ = 119.6 Hz, $C_{3'}$); 150.49 (d with sat, $^3J_{Pt-C}$ = 13.7 Hz, $^4J_{P-C}$ = 3.8 Hz, C_6); 144.98 (s, C_4); 140.08 (s with sat, $^2J_{Pt-C}$ = 82.4 Hz, $C_{4'}$); 137.51 (s, $C_{6'}$); 134.99 (d with sat, $^3J_{Pt-C}$ = 17.1 Hz, $^2J_{P-C}$ = 11.9 Hz, C_o PPh_3); 132.14 (d with sat, $^2J_{Pt-C}$ = 17.0 Hz, J_{P-C} = 44.0 Hz, C_{ipso} PPh_3); 130.26 (d, $^4J_{P-C}$ = 1.7 Hz, C_p PPh_3); 126.30 (d, $^3J_{P-C}$ = 9.8 Hz, C_m PPh_3); 124.48 (d with sat, $^2J_{Pt-C}$ = 53.4 Hz, $^3J_{P-C}$ = 5.6 Hz, $C_{5'}$); 123.73 (s with sat, $^3J_{Pt-C}$ = 11.1 Hz, C_5); 121.38 (s with sat, $^3J_{Pt-C}$ = 20.1 Hz, C_3); −12.37 (d with sat, $^1J_{Pt-C}$ = 725.3 Hz, $^2J_{P-C}$ = 4.7 Hz, CH_3). ^{31}P NMR ($CDCl_3$): 33.59 (s with sat, $^1J_{Pt-P}$ = 2229 Hz, PPh_3).

*[Pt(bipy-H)(Me)(PCy$_3$)] (**1c**).* To a solution of *cis*-[Pt(Me)$_2$(DMSO)$_2$] (209.1 mg, 0.548 mmol) in anhydrous toluene was added an excess of 2,2′-bipyridine (267.4 mg, 1.71 mmol) 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) of PCy_3 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%. Mp: 229 °C. Anal. Calcd for $C_{29}H_{43}N_2PPt$: C, 53.94; H, 6.71; N 4.34. Found: C, 54.28; H, 6.32; N, 4.70. ^{1}H NMR ($CDCl_3$): 8.75 (d with sat, 1H, $^3J_{Pt-H}$ = 12.4 Hz, J_{H-H} = 5.6 Hz, H_6); 8.33−8.40 (m, 2H, H_3 + $H_{6'}$); 8.20 (ddd with sat, 1H, $^3J_{Pt-H}$ = 45.2 Hz, $^4J_{P-H}$ = 5.1 Hz, J_{H-H} = 7.6 Hz, J_{H-H} = 1.7 Hz, $H_{4'}$); 7.91 (ddd, 1H, J_{H-H} = 8.4 Hz, J_{H-H} = 5.6 Hz, J_{H-H} = 1.3 Hz, H_4); 7.13−7.26 (m, 2H, H_5 + $H_{5'}$); 1.20−2.40 (m, 33H, Cy); 1.00 (d with sat, 3H, $^2J_{Pt-H}$ = 84.3 Hz, $^3J_{P-H}$ = 5.5 Hz, Pt-CH_3). ^{31}P NMR ($CDCl_3$): 19.30 (s with sat, $^1J_{Pt-P}$ = 2083 Hz, PCy_3).

*[Pt(bipy-H)(Me)(P(OPh)$_3$)] (**1d**).* To a solution of *cis*-[Pt(Me)$_2$(DMSO)$_2$] (103.0 mg, 0.270 mmol) in anhydrous toluene was added an excess of 2,2′-bipyridine (123.5 mg, 0.791 mmol) 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) 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 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%. Mp: 90−95 °C. Anal. Calcd for $C_{29}H_{25}N_2O_3PPt$: C, 51.56; H, 3.73; N, 4.15. Found: C, 52.02; H, 3.49; N, 3.62. ^{1}H NMR ($CDCl_3$): 9.25 (d with sat, 1H, $^3J_{Pt-H} \approx$ 16 Hz, H_6); 8.34 (dt broad, 1H, J_{H-H} = 4.6 Hz, $H_{6'}$); 8.30 (d broad, 1H, J_{H-H} = 7.6 Hz, H_3); 8.02 (ddd with sat, 1H, $^3J_{Pt-H}$ = 23.2 Hz, J_{P-H} = 9.3 Hz, J_{H-H} = 7.6 Hz, J_{H-H} = 1.7 Hz, $H_{4'}$); 7.91 (td, 1H, J_{H-H} = 7.6 Hz, J_{H-H} = 1.6 Hz, H_4); 7.37−7.08 (m, 17H, H_5 + $H_{5'}$ + H_o + H_m + H_p $P(OPh)_3$); 0.83 (d with sat, 3H, $^2J_{Pt-H}$ = 83.6 Hz, $^3J_{P-H}$ = 7.1 Hz, Pt-CH_3). ^{31}P NMR ($CDCl_3$): 117.96 (s with sat, $^1J_{Pt-P}$ = 3848 Hz, $P(OPh)_3$).

*Synthesis of [Pt(bipy-H)(Me)(P(p-tolyl)$_3$)] (**1e**).* To a solution of *cis*-[Pt(Me)$_2$(DMSO)$_2$] (66.2 mg, 0.174 mmol) in anhydrous toluene was added an excess of 2,2′-bipyridine (57.3 mg, 0.367 mmol) under a nitrogen atmosphere. The solution became suddenly red and was heated to reflux for 3 h; then 69.0 mg (0.227 mmol) of P(*p*-tolyl)$_3$ was added to the hot solution and left to react for about 1 h. Complex **1e** was extracted with water (3 × 10 mL), and the aqueous phase was back-extracted with CH_2Cl_2 (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%. Anal. Calcd for $C_{32}H_{31}N_2PPt$: C, 57.39; H, 4.66; N, 4.18. Found: C, 57.22; H, 4.85; N, 4.03. ^{1}H NMR (CD_2Cl_2, 400 MHz): 8.38 (d br, 1H, J_{H-H} = 4.9 Hz, $H_{6'}$); 8.33 (dd, 1H, J_{H-H} = 8.2, 1.3 Hz, H_3); 8.18 (ddd sat, 1H, $^3J_{Pt-H}$ = 48 Hz, $^4J_{P-H}$ = 5.4 Hz, J_{H-H} = 7.6, 1.6 Hz, $H_{4'}$); 7.86−7.79 (m, 2H, H_4 + $H_{5'}$); 7.64 (dd, 6H, $^3J_{P-H}$ = 10.2 Hz, J_{H-H} = 8.1 Hz, H_o P(*p*-tol)$_3$); 7.24 (d br, 7H, J_{H-H} = 8.3 Hz, H_6 + H_m P(*p*-tol)$_3$); 6.73 (ddd, 1H, J_{H-H} = 7.2, 5.8, 1.5 Hz, H_5); 2.41 (s, 9H, CH_3 P(*p*-tol)$_3$); 0.66 (d sat, 3H, $^2J_{Pt-H}$ = 84 Hz, $^3J_{P-H}$ = 7.7 Hz, Pt-CH_3). ^{31}P NMR (ppm, CD_2Cl_2, 161.9 MHz): 30.0 (s sat, 1P, J_{Pt-P} = 2245 Hz, P(*p*-tol)$_3$).

[Pt(bipy)(Me)(PPh$_3$)][BF$_4$] (**2b-BF$_4$**). Method A.* To a stirred pale yellow solution of [Pt(bipy-H)(Me)(PPh_3)] (50.3 mg, 0.080 mmol) in 10 mL of CH_2Cl_2 was added at room temperature, under a nitrogen atmosphere, 29.5 mg (0.081 mmol) of [18-crown-6-H_3O][BF_4]. The solution was stirred for 30 min; then it was concentrated to 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(bipy*)(Me)(DMSO)][BF_4] (65.1 mg, 0.1226 mmol) in CH_2Cl_2 (30 mL) was added under a nitrogen atmosphere 32.3 mg of PPh_3 (0.1233 mmol). The solution was stirred for 1 h 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: 85%. Anal. Calcd for $C_{29}H_{28}BF_4N_2OPPt\cdot H_2O$: C, 47.49; H, 3.85; N, 3.82. Found: C, 47.88; H, 3.98; N, 3.87. Mp: 183 °C. ^{1}H NMR ($CDCl_3$): 13.5 (s broad, 1H, N−H); 8.97 (m with sat, 1H, $^3J_{Pt-H}$ = 50 Hz, $^4J_{P-H}$ = 6.3 Hz, J_{H-H} = 7.5 Hz, J_{H-H} = 1.2 Hz, $H_{4'}$); 8.69 (dd, 1H, J_{H-H} = 5.4 Hz, J_{H-H} = 1.2 Hz, $H_{6'}$); 8.48 (d, 1H, J_{H-H} = 8.2 Hz, H_3); 8.16 (td, 1H, J_{H-H} = 7.9 Hz, H_4); 7.88 (dd with sat, 1H, $^3J_{Pt-H}$ = 10 Hz, J_{H-H} = 5.3 Hz, H_6); 7.78 (m, 1H, J_{H-H} = 7.2 Hz, J_{H-H} = 5.4 Hz, $H_{5'}$); 7.64−7.71 (m, 6H, H_m (PPh_3)); 7.42−7.50 (m, 9H, H_o + H_p (PPh_3)); 6.96 (ddd, 1H, J_{H-H} = 7.6 Hz, H_5); 0.83 (d with sat, 3H, $^2J_{Pt-H}$ = 82 Hz, $^3J_{P-H}$ = 7.1 Hz, Pt-CH_3). ^{13}C NMR ($CDCl_3$): 163.41 (d with sat, J_{Pt-C} = 997 Hz, J_{P-C} = 122.6 Hz, $C_{3'}$); 156.75 (s with sat, J_{Pt-C} = 24 Hz, C_2 or $C_{2'}$); 155.44 (d with sat, J_{Pt-C} = 49 Hz, J_{P-C} = 4.0 Hz, $C_{2'}$ or C_2); 151.83 (d with sat, J_{Pt-C} = 12 Hz, J_{P-C} = 3.5 Hz, C_6); 149.83 (s with sat, J_{Pt-C} = 75.8 Hz, $C_{4'}$); 139.77 (s, C_4); 136.80 (s, $C_{6'}$); 134.75 (d with sat, J_{Pt-C} = 17.4 Hz, J_{P-C} = 11.9 Hz, C_o PPh_3); 130.89 (d, J_{P-C} = 2.4 Hz, C_p PPh_3); 130.66 (d with sat, J_{Pt-C} = 19 Hz, J_{P-C} = 48.0 Hz, C_{ipso} PPh_3); 128.63 (d, J_{P-C} = 9.9 Hz, C_m PPh_3); 127.39 (s with sat, J_{Pt-C} = 5.1 Hz, C_5); 125.63 (d with sat, J_{Pt-C} = 54.7 Hz, J_{P-C} = 5.6 Hz, $C_{5'}$); 121.79 (s with sat, J_{Pt-C} = 15.5 Hz, C_3); −11.59 (d with sat, J_{Pt-C} = 716 Hz, J_{P-C} = 5.5 Hz, Pt-CH_3). ^{31}P NMR ($CDCl_3$): 32.13 (s with sat, J_{Pt-P} = 2500 Hz, PPh_3). IR (Nujol, ν_{max}/cm^{-1}): 3563 N−H; 1060 (broad) BF_4^-.

[Pt(bipy)(Me)(PCy$_3$)][BF$_4$] (**2c-BF$_4$**).* To a stirred solution of [Pt(bipy-H)(Me)(PCy_3)] (0.116 mmol) in 10 mL of distilled CH_2Cl_2 was added at room temperature, under a nitrogen atmosphere, 43.5 mg (0.118 mmol) of [18-crown-6-H_3O][BF_4]. After 15 min of reaction at room temperature the dark solution was concentrated to give an oil: treatment with diethyl ether gave, after stirring, a pale yellow solid, which was filtered off and washed with diethyl ether. ^{1}H and ^{31}P NMR spectra show a mixture of two species, **2c** and **3c**, in a 2:1 molar ratio. Selected NMR data for **2c** are as follows. ^{1}H NMR ($CDCl_3$): 13.6 (br, 1H, N−H); 9.06−8.90 (m, 2H, H_6 + $H_{6'}$); 8.62 (m, 1H, $H_{4'}$); 8.49 (d, J_{H-H} = 8.1 Hz, H_3); 8.25 (t br, J_{H-H} = 7.14 Hz, H_4); 7.71 (ov, $H_{5'}$ or H_5); 7.57 (t br, J_{H-H} = 6.22 Hz, H_5 or $H_{5'}$); 2.45−1.20 (m, 33H, Cy); 1.09 (d with sat, 3H, $^2J_{Pt-H}$ = 83.1 Hz, $^3J_{P-H}$ = 4.9 Hz, Pt-CH_3). ^{31}P NMR ($CDCl_3$): 19.32 (s with sat, J_{Pt-P} = 2337 Hz, PCy_3).

[Pt(bipy)(P(OPh)$_3$)(Me)][BF$_4$] (**2d-BF$_4$**) and [Pt(bipy)(P(OPh)$_3$)-(Me)][BF$_4$] (**3d-BF$_4$**).* In an NMR tube 13.3 mg (0.020 mmol) of

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[Pt(bipy-H)(Me)(P(OPh)$_3$)][BF$_4$] was dissolved in ca. 1 mL of CD_2Cl_2, giving a light yellow solution. A 7.4 mg portion (0.020 mmol) of [18-crown-6-H$_3$O][BF$_4$] 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 **2d** was formed in an almost quantitative yield (^{1}H and ^{31}P NMR criteria). After 3 months complete conversion of **2d** to **3d** occurred. Selected NMR data for **2d** are as follows. ^{1}H NMR (CD_2Cl_2): 9.58 (d with sat, 1H, $^3J_{Pt-H}$ = ca. 15 Hz, J_{H-H} = 5.4 Hz, H$_6$); 8.73 (dd, 1H, $^3J_{Pt-H}$ = 49 Hz, J_{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$_{5'}$); 7.09−7.36 (m, 15H, H$_o$ + H$_m$ + H$_p$ P(OPh)$_3$); 0.90 (d with sat, 3H, $^2J_{Pt-H}$ = 82.0 Hz, $^3J_{P-H}$ = 6.3 Hz, Pt-CH$_3$). ^{31}P NMR (CD_2Cl_2): 111.6 (s with sat, J_{Pt-P} = 4254.8 Hz, P(OPh)$_3$). Selected NMR data for **3d** are as follows. ^{1}H NMR ($CDCl_3$): 9.47 (d with sat, 1H, H$_6$ J_{H-H} = 5.2 Hz, J_{Pt-H} not resolved); 8.68 (m with sat, 1H, J_{Pt-H} not resolved); 8.52 (m, 2H); 8.35 (m, 2H); 7.74 (m, 2H); 7.10−7.41 (m, 14H); 6.83 (m, 1H); 0.84 (s with sat, 3H, J_{Pt-H} = 66.3 Hz, J_{P-H} not resolved). ^{31}P NMR ($CDCl_3$): 69.72 (s with sat, J_{Pt-P} = 7164.9 Hz, P(OPh)$_3$).

Synthesis of [Pt(bipy)(Me)(P(p-tolyl)$_3$)][BF$_4$] (**2e-BF$_4$**).* At room temperature, in an NMR tube, 6.7 mg (0.01 mmol) of **1e** was dissolved in 1.0 mL of CD_2Cl_2 and 5.3 mg of [18-crown-6-H$_3$O][BF$_4$] (0.014 mmol) was added. The solution instantly changed color, becoming bright yellow and remaining clear. The reaction was then followed by NMR spectroscopy.

Complex **2e-BF$_4$** slowly converts to the adduct **3e-BF$_4$** (ca. 90% of conversion after 6 days, almost complete conversion after two weeks).

2e-BF$_4$. ^{1}H NMR (ppm, CD_2Cl_2, 400 MHz): 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 (d br 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(*p*-tolyl)$_3$); 7.27 (dd, 4H, $^4J_{P-H}$ = 1.5 Hz, J_{H-H} = 7.9 Hz, H$_m$ P(*p*-tolyl)$_3$); 7.02 (ddd, 1H, J_{H-H} = 7.6,5.6,1.0 Hz, H$_5$); 2.42 (s, 9H, CH$_3$ P(*p*-tolyl)$_3$); 0.82 (d sat, 3H, $^2J_{Pt-H}$= 83 Hz, $^3J_{P-H}$ = 7.0 Hz, Pt-CH$_3$). ^{31}P NMR (ppm, CD_2Cl_2, 161.9 MHz): 28.7 (s sat, 1P, J_{Pt-P} = 2502 Hz, P(*p*-tolyl)$_3$).

3e-BF$_4$. ^{1}H NMR (CD_2Cl_2): 9.02 (dm with 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, H$_{ortho}$, *p*-tolyl, 6H, J_{H-H} = 7.8 Hz, J_{P-H} = 11.2 Hz); 7.31 (d, H$_{meta}$, *p*-tolyl, 6H, J_{H-H} = 7.8 Hz); 7.26 (d, 1H, J_{H-H} = 7.8 Hz); 7.08 (m, 1H, J_{H-H} = 6.8 Hz); 2.44 (s, CH$_3$ *p*-tolyl, 9H); 0.80 (d with sat, 3H, $^2J_{Pt-H}$ = 72 Hz, $^3J_{P-H}$ = 3.3 Hz, Pt-CH$_3$). ^{31}P NMR ($CDCl_3$): 16.76 (s with sat, $^1J_{Pt-P}$ = 4343 Hz, P(*p*-tolyl)$_3$).

*[Pt(bipy)(Me)(PPh$_3$)][BF$_4$] (**3b-BF$_4$**). Method A.* To a solution of [Pt(bipy-H)(Me)(PPh$_3$)] (57.9 mg, 0.090 mmol) in 10 mL of CH_2Cl_2 was added, under a nitrogen atmosphere, 47.0 mg (0.127 mmol) of [18-crown-6-H$_3$O][BF$_4$]. 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(bipy*)(Me)(DMSO)][BF$_4$] (48.0 mg, 0.0904 mmol) in CH_2Cl_2 was added with stirring 24.0 mg of PPh$_3$ (0.0916 mmol) 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%. Mp: 187 °C. Anal. Calcd: C, 48.77; H, 3.50; N, 3.92. Found: C, 49.05; H, 3.58; N, 3.59. ^{1}H NMR ($CDCl_3$): 8.95 (m, 1H, $^2J_{Pt-H}$ = ca. 32 Hz, H$_{6'}$); 8.75 (d, 1H, J_{H-H} = 8.0 Hz, H$_3$ or H$_{3'}$); 8.66 (d, 1H, J_{H-H} = 8.0 Hz, H$_{3'}$ or H$_3$); 8.42 (m, 1H, J_{H-H} = 8.0 Hz, J_{H-H} = 7.6 Hz, H$_4$ or H$_{4'}$); 8.20 (m, 1H, J_{H-H} = 8.0 Hz, J_{H-H} = 7.6 Hz, H$_{4'}$ or H$_4$); 7.83 (m, 1H, H$_{5'}$); 7.71−7.89 (m, 6H, H$_o$ (PPh$_3$)); 7.58−7.40 (m, 10H, H$_6$ + H$_m$ + H$_p$ (PPh$_3$)); 7.03 (m, 1H, H$_5$); 0.78 (d with sat, 3H, $^2J_{Pt-H}$ = 69.0 Hz, $^3J_{P-H}$ = 3.4 Hz, Pt-CH$_3$). ^{31}P NMR ($CDCl_3$): 20.36 (s with sat, J_{Pt-P} = 4351 Hz, PPh$_3$). IR (Nujol, ν_{max}/cm^{-1}): 1058 s br, BF$_4^-$.

*[Pt(bipy)(Me)(PCy$_3$)][BF$_4$] (**3c-BF$_4$**).* Under an N$_2$ atmosphere 71.0 mg (0.11 mmol) of [Pt(bipy-H)(Me)(PCy$_3$)] was dissolved in 10 mL of CH_2Cl_2, and 44.4 mg (0.12 mmol) of [18-crown-6-H$_3$O][BF$_4$] 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%. Mp: 254−256 °C. Anal. Calcd for $C_{29}H_{44}N_2PPtBF_4\cdot H_2O$: C, 46.35; H 6.17; N, 3.73. Found: C, 46.32; H 5.73; N, 3.85. ^{1}H NMR ($CDCl_3$): 8.84 (m, 2H, H$_6$ + H$_{6'}$); 8.73 (d br, 2H, H$_3$ + H$_{3'}$); 8.38 (t br, 2H, H$_4$ + H$_{4'}$); 8.74 (t br, 2H, H$_5$ + H$_{5'}$); 1.18−2.42 (m, 33H, Cy); 1.00 (d with sat, 3H, $^2J_{Pt-H}$ = 71.6 Hz, $^3J_{P-H}$ = 1.5 Hz, Pt-CH$_3$). ^{31}P NMR ($CDCl_3$): 16.41 (s with sat, J_{Pt-P} = 4068 Hz, PCy$_3$).

*[Pt(bipy-H)(PPh$_3$)$_2$][BF$_4$] (**4-BF$_4$**).* To a solution of [Pt(bipy-H)(Me)(DMSO)][BF$_4$] (36.2 mg; 0.0683 mmol) in CH_2Cl_2 was added at room temperature 36.0 mg of PPh$_3$ (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. Mp: 183 °C. Anal. Calcd for $C_{46}H_{37}BF_4N_2P_2Pt$: C, 57.45; H, 3.88; N, 2.91. Found: C, 57.22; H, 3.96; N, 3.29. ^{1}H NMR ($CDCl_3$): 6.67 (dd, 1H), 6.84 (t, 1H), 7.26−7.62 (m, 18H), 7.94 (m, 1H), 8.35 (m, 1H). ^{31}P NMR ($CDCl_3$) 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(bipy-H)(bipy)][BF$_4$] (**5-BF$_4$**). Method A.* To a solution of [Pt(bipy*)(Me)(DMSO)][BF$_4$] (54.1 mg; 0.102 mmol) in CH_2Cl_2 was added 16.1 mg of 2,2′-bipyridine (0.103 mmol). 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 pentane; the precipitate that formed was filtered off, washed with pentane, and vacuum-pumped to give the analytical sample as an orange solid. Yield: 65%.

Method B. To a solution of [Pt(bipy-H)(Me)(DMSO)][BF$_4$] (81.3 mg; 0.183 mmol) in CH_2Cl_2 was added 44.4 mg of 2,2′-bipyridine (0.284 mmol) and 68.3 mg of [18-crown-6-H$_3$O][BF$_4$] (0.184 mmol). The solution was stirred for 2 h 30 min at room temperature; then it was concentrated to a small volume and treated with pentane. The precipitate that formed was filtered off, washed with pentane, and vacuum-pumped to give the analytical sample as an orange solid. Yield: 55%. Anal. Calcd: C, 40.49; H, 2.55; N, 9.44. Found: C, 39.63; H, 2.39; N, 9.46. Mp: 232 °C. ^{1}H NMR (CD_2Cl_2): 9.35 (d, 1H); 9.10−9.20 (m, 1H); 8.96−9.08 (d, 1H); 8.71−8.77 (m, 2H); 8.39−8.51 (m, 3H); 8.26−8.38 (m, 1H); 8.17−8.25 (m, 1H); 7.95−8.17 (m, 1H); 7.86−7.88 (m, 1H); 7.78- 7.84 (d, 1H); 7.62−7.66 (m, 1H); 7.21−7.25 (q, 1H).

*[Pt(bipy-H)(dppe)][BF$_4$] (**6-BF$_4$**).* To a solution of [Pt(bipy*)(Me)-(DMSO)][BF$_4$] (39.4 mg, 0.074 mmol) in CH_2Cl_2 was added 29.4 mg of 1,2-bis(diphenylphosphino)ethane (dppe; 0.074 mmol). The solution was stirred at room temperature under a nitrogen atmosphere for 1 h and then 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 whitish solid. Yield: 55%. Mp: 162 °C. Anal. Calcd for $C_{36}H_{31}BF_4N_2P_2Pt$: C, 51.75; H, 3.74; N, 3.35. Found: C, 51.45; H, 3.49; N, 3.07. ^{1}H NMR (CD_2Cl_2): 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, 2H). ^{31}P NMR ($CDCl_3$): 51.81 (s, P trans C, J_{Pt-P} = 1949 Hz); 42.64 (s, P *trans* N, J_{Pt-P} = 3691 Hz).

Reaction of [Pt(bipy-H)(Me)(L)] Complexes with HCl (L = DMSO, PPh$_3$, PCy$_3$). *L = DMSO.* The reaction of [Pt(bipy-H)(Me)-(DMSO)] (**1a**) with HCl has been reported in ref 18.

L = PPh$_3$, PCy$_3$. To a solution of [Pt(bipy-H)(Me)(L)] (0.10 mol) in acetone (20 mL) was added an equimolar amount of aqueous 0.1 M HCl. The mixture was stirred at room temperature for 24 h and then evaporated to dryness, extracted with CH_2Cl_2, and analyzed by means of NMR spectroscopy.

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L = *PPh*$_3$. ^{1}H NMR ($CDCl_3$): the spectrum shows a series of overlapping signals attributable to two species in a 4:1 molar ratio, identified as the cationic adduct [Pt(bipy)(Me)(PPh_3)]Cl (main species) and [Pt(bipy-H)(Cl)(PPh_3)] (minor species) on the basis of literature data (ref 38 for [Pt(bipy)(Me)(PPh_3)]Cl and ref 18 for [Pt(bipy-H)(Cl)(PPh_3)]). ^{31}P NMR ($CDCl_3$): 23.43, J_{Pt-P} = 4285 Hz ([Pt(bipy-H)(Cl)(PPh_3)]); 20.40, J_{Pt-P} = 4347 Hz ([Pt(bipy)(Me)-(PPh_3)]Cl).

L = *PCy*$_3$. ^{1}H NMR ($CDCl_3$): the spectrum shows a series of overlapping signals attributable to two species in a 3.5:1 molar ratio, identified as the cationic adduct [Pt(bipy)(Me)(PCy_3)]Cl (main species) and a minor species that was not characterized; 9.60 (m, 1H, minor species, H4′); 9.50 (d, 1H, minor species, J_{H-H} = 7.8 Hz); 9.40 (d, 1H, minor species, J_{H-H} = 7.9 Hz); 9.31 (d, 1H, main species, J_{H-H} = 8.0 Hz); 8.35−8.91 (m, overlapping signals); 7.69−7.95 (m, overlapping signals); 7.30−7.55 (m, overlapping signals); 1.14−2.65 (m, overlapping signals); 0.99 (broad s with satellites, 3H, main species, $^2J_{Pt-H}$ = 67.0 Hz, CH_3). ^{31}P NMR ($CDCl_3$): 16.30 (s with satellites, main species, J_{Pt-P} = 4064 Hz); 14.40 (s with satellites, minor species, J_{Pt-P} = 3431 Hz).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables and figures giving details of the calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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