Activation of a C−H Bond in a Pyridine Ring. Reaction of 6-Substituted 2,2′-Bipyridines with Methyl and Phenyl Platinum(II) Derivatives: N′,C(3)-"Rollover" Cyclometalation

Giovanni Minghetti, Sergio Stoccoro, Maria Agostina Cinellu, Barbara Soro, and Antonio Zucca*

Dipartimento di Chimica, Università di Sassari, Via Vienna 2, I-07100 Sassari, Italy

Received March 5, 2003

The reaction of the electron-rich derivatives *cis*-[Pt(R)$_2$(DMSO)$_2$] (R = Me, Ph) with a series of 6-substituted-2,2′-bipyridines, HL, occurs with loss of methane or benzene, respectively, to yield cyclometalated platinum(II) species [Pt(R)(L)(DMSO)] where L is an anionic ligand N′,C(3) coordinated. The unusual C−H activation entails a consecutive reaction process through a detectable intermediate. The reaction is peculiar of 6-substituted ligands: for comparison no reaction occurs with 6,6′-Me$_2$-2,2′-bipy and an adduct, [Pt(R)$_2$(HL)], is obtained with 5-Me-2,2′-bipy.

Introduction

Cyclometalated complexes arising from direct C−H activation of 6-substituted 2,2′-bipyridines are well known: they include both N,N,C(sp^2)-M as well as N,N,C(sp^3)-M species, the former ones being more common.[1]

In contrast, although reported first several years ago, still very rare is the direct metal-mediated activation of a C−H bond of a pyridyl ring. As far as we know, N′,C(3) five-membered rings have been observed in an Ir(III) 2,2′-bipyridine (bipy) complex,[2] in some platinum derivatives with N-substituted-2,2′-bipyridines,[3] and quite recently in a palladium and a platinum species, [PdCl(L)]$_2$ and [PtCl(L)(SMe$_2$)], respectively[4] (HL = 6-alkyl-2,2′-bipy). Furthermore the formation of Ar−H in a process of thermal rearrangement of [Pt(Ar)$_2$(bipy)] derivatives was explained assuming activation of a C−H bond of the bipy ligand.[5]

In platinum(II) chemistry examples of activation of a C−H bond of the heterocyclic ring promoted by platinum(II) chlorides such as [PtCl$_4$]$^{2-}$ or [PtCl$_2$(L)$_2$] adducts have not been reported. In the case of the intermediates *trans*-[Pt(R)Cl(SMe$_2$)$_2$] (R = Me, Ph) the reaction with 6-substituted-2,2′-bipyridines, HL, mostly gives adducts [Pt(R)Cl(HL)] or cyclometalated species [PtCl(L)] where L is the anionic N,N,C ligand arising from activation of a C−H bond of the substituent.[6] Only with HL = 6-C(Me)$_3$-2,2′-bipy does the methyl-chloro intermediate *trans*-[Pt(Me)Cl(SMe$_2$)$_2$] give the aforementioned rollover N′,C(3) cyclometalated species [PtCl(L)(SMe$_2$)] with loss of methane.[4] Here we report on the reaction of the electron-rich [Pt(Me)$_2$(DMSO)$_2$] and [Pt(Ph)$_2$(DMSO)$_2$] derivatives with 6-alkyl-, benzyl-, and aryl-substituted 2,2′-bipyridines, HL, to give new "rollover" cyclometalated species [Pt(Me)(L)(DMSO)] and [Pt(Ph)(L)(DMSO)] through methane or benzene elimination.

A preliminary communication relevant to 6-Ph-2,2′-bipy has been recently reported.[7]

Aspects of the reactivity of the new species will also be discussed.

Results and Discussion

The ligands HL^n, shown in Scheme 1, include alkyl-, benzyl-, and phenyl-6-substituted-2,2′-bipyridines.

* Corresponding author. E-mail: zucca@uniss.it. Fax: +39 079 229559.

(1) N,N,C(sp^2)-M derivatives: (a) Minghetti, G.; Cinellu, M. A.; Chelucci, G.; Gladiali, S.; Demartin, F.; Manassero, M. *J. Organomet. Chem.* **1986**, *307*, 107. (b) Constable, E. C.; Henney, R. P. G.; Leese, T. A.; Tocher, T. A. *J. Chem. Soc., Chem. Commun.* **1990**, 513. (c) Constable, E. C.; Henney, R. P. G.; Leese, T. A.; Tocher, T. A. *J. Chem. Soc., Dalton Trans.* **1990**, 443. (d) Cheung, T. C.; Cheung, K. K.; Peng, S. M.; Che, C. M. *J. Chem. Soc., Dalton Trans* **1996**, 1645−1651. (e) Sanna, G.; Minghetti, G.; Zucca, A.; Pilo, M. I.; Seeber, R.; Laschi, F. *Inorg. Chim. Acta* **2000**, *305/2*, 189−205. N,N,C(sp^3)-M derivatives: (f) Newkome, G. R.; Evans, D. W.; Kiefer, G. E.; Theriot, K. J. *Organometallics* **1988**, *7*, 2537−2542. (g) Stoccoro, S.; Chelucci, G.; Cinellu, M. A.; Zucca, A.; Minghetti, G. *J. Organomet. Chem.* **1993**, *450*, C15. (h) Minghetti, G.; Cinellu, M. A.; Stoccoro, S.; Zucca A.; Manassero, M. *J. Chem. Soc., Dalton Trans.* **1995**, 777−781. (i) Zucca, A.; Stoccoro, S.; Cinellu, M. A.; Minghetti, G.; Manassero, M.; Sansoni, M. *Eur. J. Inorg. Chem.* **2002**, 3336−3346. N,N,C(sp^2)-M and N,N,C-(sp^3)-M derivatives: (j) Cinellu, M. A.; Zucca, A.; Stoccoro, S.; Minghetti, G.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1996**, 4217. (k) Zucca, A.; Stoccoro, S.; Cinellu, M. A.; Minghetti, G.; Manassero, M. *J. Chem. Soc., Dalton Trans.* **1999**, 3431. (l) Zucca, A.; Cinellu, M. A.; Pinna, M. V.; Stoccoro, S.; Minghetti, G.; Manassero, M.; Sansoni, M.; *Organometallics* **2000**, *199*, 4295−4304.

(2) (a) Nord, G.; Hazell, A. C.; Hazell R. G.; Farver, O. *Inorg. Chem.* **1983**, *22*, 3429. (b) Spellane, P. J.; Watts, R. J.; Curtis, C. J. *Inorg. Chem.* **1983**, *22*, 4060. (c) Braterman, P. S.; Heat, G. H.; Mackenzie, A J.; Noble, B. C.; Peacock, R. D.; Yellowlees, L. J. *Inorg. Chem.* **1984**, *23*, 3425.

(3) (a) Dholakia, S.; Gillard, R. D.; Wimmer, F. L. *Inorg. Chim. Acta* **1983**, *69*, 179. (b) Castan, P.; Dahan, F.; Wimmer, F. L.; Wimmer, S. *J. Chem. Soc., Dalton Trans*, **1990**, 2971. (c) Castan, P.; Labiad, B.; Villemin, D.; Wimmer, F. L.; Wimmer, S. *J. Organomet. Chem.* **1994**, *479*, 153−157.

(4) Minghetti, G.; Doppiu, A.; Zucca, A.; Stoccoro, S.; Cinellu, M. A.; Manassero, M.; Sansoni, M. *Chem. Heterocycl. Compd.* (N.Y.) **1999**, *35* (8), 992.

(5) Skapski, A. C.; Sutcliffe, V. F.; Young, G. B. *Chem. Commun.* **1985**, 609.

(6) Doppiu, A.; Cinellu, M. A.; Minghetti, G.; Stoccoro, S.; Zucca, A.; Manassero, M.; Sansoni, M. *Eur. J. Inorg. Chem.* **2000**, 2555−2563.

(7) Zucca, A.; Doppiu, A.; Cinellu, M. A.; Minghetti, G.; Stoccoro, S.; Manassero, M. *Organometallics* **2002**, *21*, 783−785.

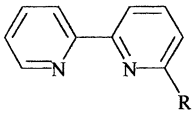
10.1021/om0301583 CCC: $25.00
Publication on Web 10/16/2003

Table 1. Selected ^{1}H NMR Data[a]

		Me	DMSO	H(4)	H(5)	H(6)
[Pt(Me)(L^1)(DMSO)]	**1a**	0.69 [82.0]	3.24 [19.3]	7.88 (8.0) [53.0]	7.04 (8.0) [18.6]	9.67 (5.9) [14.0]
[Pt(Me)(L^2)(DMSO)]	**2a**	0.70 [82.0]	3.24 [18.3]	7.88 (7.7) [52.6]	6.98 (7.6) [18.9]	9.66 (6.1) [14.1]
[Pt(Me)(L^3)(DMSO)]	**3a**	0.69 [82.3]	3.23 [18.1]	7.89 [51.9]	7.21 [18]	9.65 [13.8]
[Pt(Me)(L^4)(DMSO)]	**4a**	0.66 [82.0]	3.21 [18.1]	7.85 (7.8) [52.9]	7.01 (7.8) [18.1]	9.66 (6.6) [13.8]
[Pt(Me)(L^5)(DMSO)]	**5a**	0.66 [82.0]	3.23 [18.1]	7.75 (8.1) [51.8]	6.84 (8.1) [17.6]	9.58 (6.3) [13.7]
[Pt(Me)(L^6)(DMSO)]	**6a**	0.75 [81.8]	3.26 [18.3]	8.07 (8.1) [52.0]	7.65 (8.1) [17.8]	9.71 (5.6) [13.7]
[Pt(Ph)(L^3)(DMSO)]	**3b**		2.95 [17.6]	6.77 (8.1) [61.0]	6.94 (8.1) [16.6]	9.56 (5.6) [12.6]
[Pt(Ph)(L^6)(DMSO)]	**6b**		2.98 [17.6]	6.94 (7.8) [62.8]	*b*	9.63 (5.4) [12.7]
[Pt(Cl)(L^3)(DMSO)]	**3c**		3.63 [24.7]	8.53 (8.3) [41.0]	7.19 (8.3) [13.2]	9.57 (5.8) [35.4]
[Pt(Cl)(L^6)(DMSO)]	**6c**		3.67 [24.2]	8.64 (8.3) [42.0]	7.55 (8.3) [13.0]	9.59 (5.8) [31.1]
[Pt(Me)(L^3)(CO)]	**13**	1.19 [86.2]		7.96 (7.8) [45.9]	7.29 (7.8) [*b*]	8.61 (5.4) [19]
[Pt(Me)(L^3)(3,5-(Me)$_2$py)]	**14**	0.93 [84.0]		7.96 (8.0) [54.6]	7.13 (8.0) [11.4]	7.72 (5.4)
[Pt(Me)(L^6)(PPh$_3$)]	**15**	0.79 [83.0]		8.31 (8.1) [46.5]	*b*	*b*

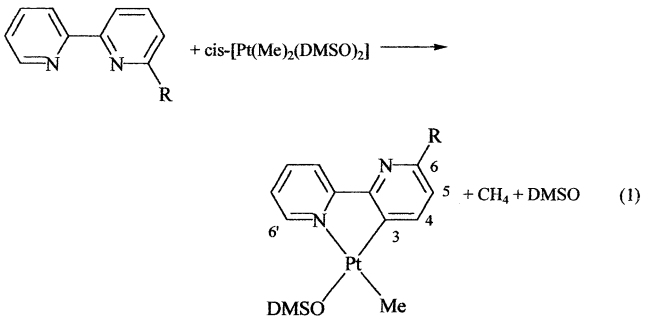
[a] Room temperature, solvent $CDCl_3$, chemical shifts in ppm from internal $SiMe_4$, coupling constants in Hz, J(H−H) in parentheses, J(Pt−H) in square brackets. [b] Signals partially overlapping.

Scheme 1



R = Me	**HL^1**	R = CH(CH$_2$Me)Ph	**HL^4**
R = CH$_2$C(Me)$_3$	**HL^2**	R = C(Me)$_2$Ph	**HL^5**
R = C(Me)$_3$	**HL^3**	R = Ph	**HL^6**

The reaction of *cis*-[Pt(Me)$_2$(DMSO)$_2$] with the ligands has been carried out both in acetone at room or reflux temperature and in toluene at 70−90 °C with a Pt/L 1:1 molar ratio.



1a-6a

With the ligands HL$^{1-6}$ the reaction is straightforward and yields, at least in acetone solution, are fairly good.[8] In toluene at 70−90 °C, partial decomposition to metal occurs. The isolated species, **1a**−**6a**, are stable in the solid state, soluble in several organic solvents, and not electrolytes in acetone. They have been fully characterized by elemental analyses and by ^{1}H NMR and FAB-MS spectroscopy. In the FAB-MS spectra, besides the molecular ions, $[M]^+$, both the $[M - Me]^+$ and $[M - DMSO]^+$ ions are observed (compounds **2a**, **3a**, **5a**, and **6a**). The ^{1}H NMR spectra provide evidence for only one out of the two possible isomers. The resonance of the methyl bonded to the platinum atom, at high field (δ 0.66−0.75, $CDCl_3$ solution), is a singlet with satellites: the ^{195}Pt−H coupling constants, ca. 82 Hz, fit a methyl *trans* to a nitrogen atom.[9] On the other hand, the rather small ^3J(Pt−H) values, ca. 18 Hz, relative to the protons of DMSO, are consistent with a ligand *trans* to a C(sp^2).[7,10] The aromatic region shows six resonances: an AB system due to H(4) and H(5) with satellites (e.g., compound **3a**: δ (H$_4$) 7.89, ^3J(Pt−H) = 51.9 Hz; δ (H$_5$) 7.21, ^4J(Pt−H) = 18.0 Hz) confirms coordination of platinum to the C(3) atom. The H(6′) proton is remarkably deshielded, ca. 9.6−9.7 ppm (see Table 1), and coupled to ^{195}Pt: the ^3J(Pt−H) values, ca. 14 Hz, reflect the high *trans* influence of the methyl group. The resonances of the aliphatic protons in the substituent, which are far away from the platinum atom, are very slightly affected by coordination. Compound **3a** has been fully characterized by means of ^{1}H, ^{1}H NOE difference, ^{13}C{^{1}H}, ^{13}C APT, and ^{1}H single frequency decoupled ^{13}C NMR experiments, allowing a full assignment of ^{1}H and ^{13}C resonances. Finally, ^{1}H NOE difference experiments agree with the proposed geometry of the complex (e.g., irradiation of the Pt-Me at 0.69 ppm gives enhancement at 3.23 (coordinated DMSO) and 7.89 ppm (H(4)).

In agreement with the ^{1}H NMR data, the ^{13}C{^{1}H} NMR spectrum of **3a** shows an aromatic carbon atom bonded to platinum at 141.31 ppm, with $^1J_{Pt-C}$ = 1086 Hz, to be compared with previously reported data for N,C(sp^2) cyclometalated Pt(II) derivatives.[11] In addition the ^{13}C APT spectrum shows in the aromatic region only six tertiary and four quaternary carbon atoms, the metalated one included. In the aliphatic region two resonances, at −13.91 ppm (^1J(^{13}C−^{195}Pt) = 763.8 Hz)) and 43.69 ppm (^2J(^{13}C−^{195}Pt) = 42.5 Hz), give clear evidence for coordinated Me and DMSO groups, respectively.

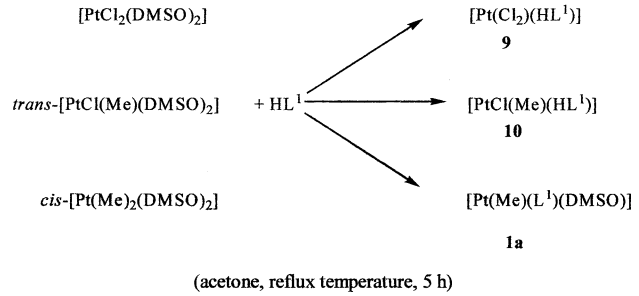
A series of ^{1}H single frequency decoupled ^{13}C NMR spectra allowed us to assign the C resonances, showing that the ^{195}Pt−^{13}C coupling constants of the carbon atoms of the metalated pyridine are much larger than those of the N-bonded pyridinic ring (e.g., C5, J(Pt−C) = 59.7 Hz; C5′, J(Pt−C) = 9.9 Hz).

The N′,C(3) metalation seems to be peculiar of electron-rich derivatives. To point out the role of the substitution of a methyl for a chloride, the behavior of the strictly homologous species [Pt(Me)$_2$(DMSO)$_2$], [PtCl(Me)(DM-

(8) An additional ligand was investigated, namely, 6-(1-methylbenzyl)2,2′-bipyridine: although ^{1}H NMR spectra give evidence for N′,C(3) metalation, a number of other species are formed, hampering isolation of a pure compound

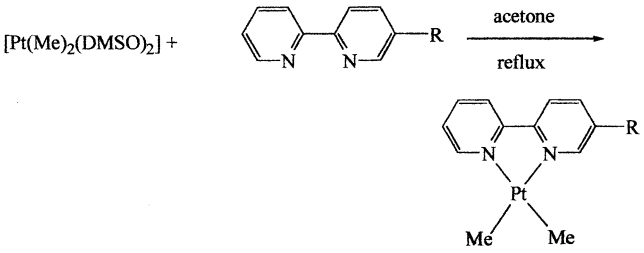
(9) Monaghan, P. K.; Puddephatt, R. J. *Inorg. Chim. Acta* **1982**, *65*, L59−L61.
(10) Doppiu, A.; Minghetti, G.; Cinellu, M. A.; Stoccoro, S.; Zucca, A.; Manassero, M. *Organometallics* **2001**, *20*, 1148−1152.
(11) Chassot, L.; von Zelewsky, A. *Inorg. Chem.* **1987**, *26*, 2814−18.

Scheme 2



$SO)_2$], and $[PtCl_2(DMSO)_2]$ toward ligand HL^1 has been compared under the same conditions, Scheme 2. As can be seen C(3)−H activation is achieved only with the dimethyl derivative, at least under these experimental conditions.

A substituent in 6 position is of paramount importance to achieve N′,C(3) metalation. By comparison, the reaction of $[Pt(Me)_2(DMSO)_2]$ with 5-Me-2,2′-bipyridine (HL^7) or the unsubstituted 2,2′-bipy (HL^8), carried out under the same experimental conditions (acetone, reflux), affords the adducts $[Pt(Me)_2(HL^n)]$ (n = 7, 8) (**7**, **8**); with the disubstitued 6,6′-Me_2-2,2′-bipyridine no reaction occurs at room temperature, whereas heavy decomposition is observed in refluxing acetone.



R = Me, **7**

R = H, **8**

The nature of the electronic and steric properties of the 6-substituent of HL^n does not remarkably affect the reaction, which in most cases, e.g., n = 1, 2, 3, and 6, occurs even at room temperature.

The progress of the N′,C(3) metalation was investigated following by ^{1}H NMR spectroscopy the reaction of $[Pt(Me)_2(DMSO)_2]$ with the ligands HL^1 and HL^2 in acetone at room temperature (see Experimental Section).

The ^{1}H NMR spectrum ($(CD_3)_2CO$) of the starting complex $[Pt(Me)_2(DMSO)_2]$ shows a sharp peak at δ 3.12 (12H) with ^{195}Pt satellites (^3J(Pt−H) = 13.3 Hz), due to the S-bonded Me_2SO, and a singlet at δ 0.56 due to Pt-Me (^2J(Pt−H) = 80.2 Hz). After addition of the ligand HL^1 a rapid decrease of these signals is observed; in the aliphatic region of the spectra the signal of coordinated DMSO, δ 3.12, partially converts into a singlet characteristic of free DMSO, δ 2.52. At the same time a new species, **i**, is formed, characterized by a H(6′) resonance at low field (δ 9.11), with no coordinated DMSO. After a few minutes after the mixing of the reactants, the spectra show, in low concentration, the final reaction products, $[Pt(L^1)(Me)(DMSO)]$ and methane (δ = 0.16).

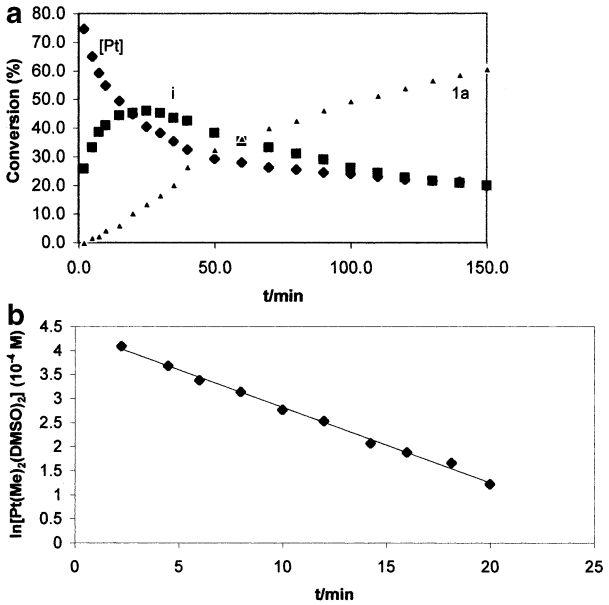


Figure 1. (a) ^{1}H NMR progress of the reaction of $[Pt(Me)_2DMSO_2]$ with HL^1 (1:1 molar ratio) in $(CD_3)_2CO$, [Pt] = $[Pt(Me)_2(DMSO)_2]$; (b) plot of ln$[Pt(Me)_2(DMSO)_2]$ vs time with a large excess of HL^1.

The reaction is almost complete after 24 h. Conversion of species **i** to complex **1a** or **3a** is relatively slow, but not enough to allow isolation of the intermediates.

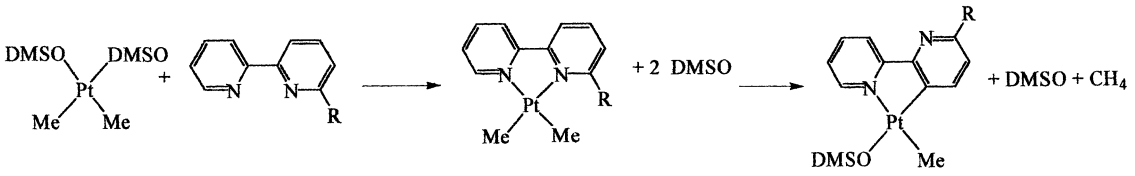
On the whole in the progress of the reaction only three platinum(II) species are detected in solution: the reactant ($[Pt(Me)_2(DMSO)_2]$), the final product ($[Pt(L)(Me)(DMSO)]$), and the new complex **i**. No other DMSO-containing Pt(II) complex is observed.

The ^{1}H NMR spectrum of the intermediate species **i** shows only the signals of two Pt-Me groups and of a coordinated HL unit. The resonances of the Pt-methyl protons are very close, e.g., for HL^1, δ 1.02, s, ^2J(Pt−H) = 89 Hz; 1.03, s, ^2J(Pt−H) = 87 Hz. Both the nitrogen donors of the bipyridine seem to be coordinated: the H(6′) proton is shifted to low field and coupled to platinum (e.g., for HL^1 δ 9.11 d, $H_{6'}$, ^3J(Pt−H) = 23 Hz) and the 6-Me protons resonate at δ 2.83, a value very similar to that previously observed for the isomer of $[Pt(HL^1)(Me)I]$, having the coordinated Me group close to the 6-Me (δ 2.87). It is worth noting that in the rollover species the chemical shift of the latter protons is usually very similar to that of the free ligand (e.g., δ(Me): **1a**, 2.46; HL^1, 2.57). On the whole, the spectrum of complex **i** strictly reminds us of those of the isolated adducts **7** and **8** (see Experimental Section), so that we feel confident to identify compound **i** as the adduct $[Pt(Me)_2(HL^1)]$. Attempts to isolate the adduct by reaction of $[Pt(Me)_2(COD)]$ with HL^1 were unsuccessful: no reaction occurs even at reflux temperature.

A plot of the concentrations of $[Pt(Me)_2(DMSO)_2]$, **i**, and **1a** versus time (see Figure 1a) shows a pattern consistent with a two-step consecutive reaction (Scheme 3). ^{1}H NMR follow-up of the reaction with a large excess of the ligand HL^1 indicates that overall the reaction is first order in $[Pt(Me)_2(DMSO)_2]$ with k_{obs} = 0.16 s^{-1} at 18.5 °C. A plot of ln$[Pt(Me)_2(DMSO)_2]$ versus time is shown in Figure 1b.

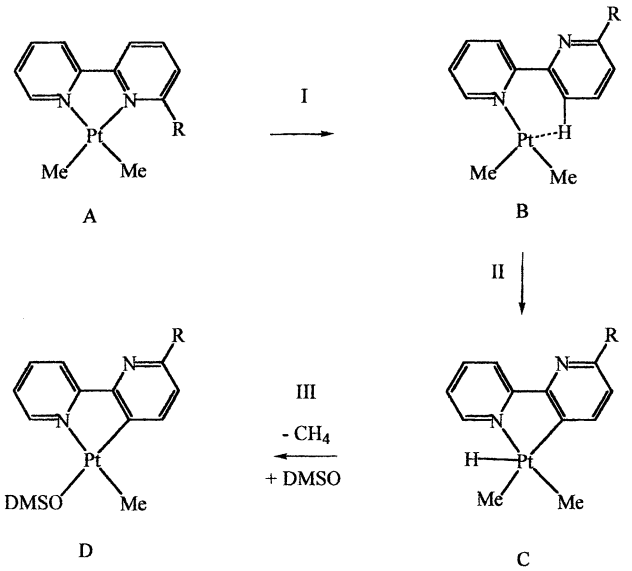
A plausible pathway for the conversion of the adduct to the N′,C(3) cyclometalated species is shown in

Scheme 3

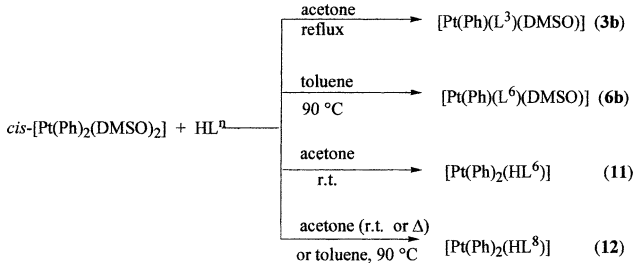


i

Scheme 4



Scheme 5

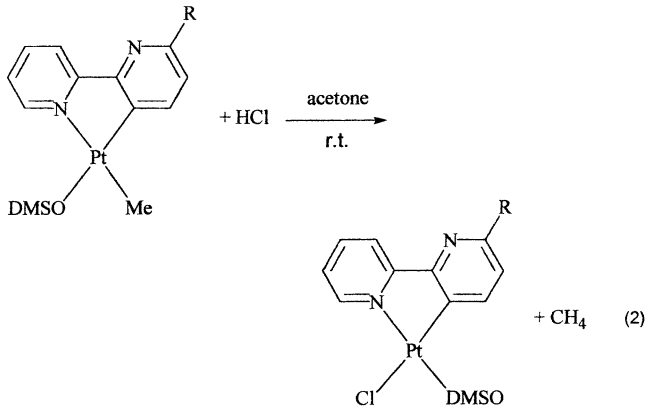


Scheme 4. The steric hindrance due to the substitution in **6** makes the adduct A unstable and allows the cleavage of a Pt−N bond weakened by the strong *trans* influence of the methyl group. Rotation of a pyridine ring around the C(2)−C(2′) bond brings a C−H bond close to the metal, B. The pseudo coordinatevely unsaturated intermediate B[12] promotes the C(sp^2)-H oxidative addition to yield the pentacoordinated hydridoplatinum(IV), C.[13,14] From C, loss of methane eventually leads to the platinum(II) N′-C(3) cyclometalated species as the thermodynamically stable isomer D. An oxidative addition from B to C is supported by the observation that the formation of Ar−H in the thermal rearrangement of [Pt(Ar)$_2$(bipy)] is strongly favored in the case of Ar = 4-CMe_3−C_6H_4 versus Ar = 4-CF_3−C_6H_4 (the former reacts 62 times faster than the latter).[5,15]

Accordingly, the *cis*-[Pt(Ph)$_2$(DMSO)$_2$] complex seems to be somewhat less prone than the corresponding dimethyl derivative to give N′-C(3) cyclometalation: indeed this can be achieved under more severe conditions such as refluxing acetone for HL[3] or toluene at 90 °C for HL.[6] Under mild conditions adducts, e.g., [Pt(Ph)$_2$(HL[6])] and [Pt(Ph)$_2$(HL[8])], are obtained.

On the whole, the ^{1}H NMR spectra of **3b** and **6b** are similar to those of the corresponding methyl derivatives. Evidence for the isomer having the phenyl *trans* to the nitrogen atom is provided by the upfield shift with respect to **3a** and **6a** ($\Delta\delta$ 1.12−1.13 ppm) of the resonances of the H(4) protons, due to the shielding effect of the adjacent phenyl ring.

In complexes **3a** and **6a** the platinum−C(sp^3) bond was cleaved by reaction with HCl in acetone at room temperature (reaction *2*):



R = $C(Me)_3$, **3c**

R = Ph, **6c**

The metal−carbon bond inside the five-membered N,C cycle is unaffected. One isomer is selectively formed; the correct assignment of the isomer can be attained through the IR and NMR spectra. In the IR spectrum (complex **3c**) a strong absorption at 276 cm^{-1} is consistent with the stretching vibration of a Pt−Cl bond *trans* to a ligand with a high *trans* influence.[16] In the ^{1}H NMR spectra the ^3J(Pt−H) relevant to the methylic protons of DMSO, 24.7 Hz, agrees with a DMSO *trans* to a nitrogen atom.

The mononuclear chloride species are accompanied by a minor product, [PtCl(L)]$_2$, formed by elimination of DMSO and poorly soluble, as often observed for this type of chloro-bridged dimers. In its turn the bridge can be opened by DMSO to restore the mononuclear complexes.

(12) The X-ray structure of a 14-electron platinum(II) complex stabilized by an agostic interaction has been quite recently reported: Baratta, W.; Stoccoro, S.; Doppiu, A.; Herdtweck, E.; Zucca, A.; Rigo, P. *Angew. Chem.* **2003**, *42* (1), 105−109.

(13) Puddephatt, R. J. *Coord. Chem. Rev.* **2001**, *219*−*221*, 157−185.

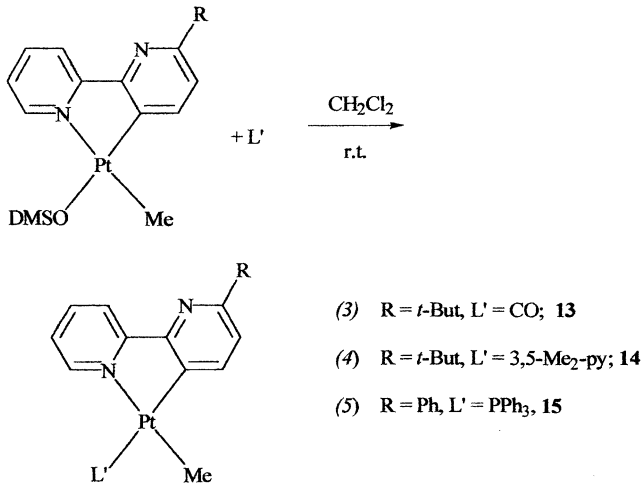
(14) Sixteen-electron platinum(IV) species have been recently characterized by X-ray structure: (a) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 6423. (b) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 6425.

(15) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403−424.

(16) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335−422.

Reaction 2 is likely to occur through oxidative addition of HCl followed by fast reductive elimination of CH_4: no hydrido-alkyl species is detected.[13] The different *trans* influence of the donors accounts for the isomer having a *trans* Cl−Pt−C arrangement.

As shown, inter alia, by the reaction with HCl, the N′,C(3) five-membered ring is rather robust, and a variety of species can be obtained by substitution of DMSO with neutral ligands, e.g., CO, 3,5-Me_2pyridine, and PPh_3, reactions 3−5.



Reactions 3−5 occur in dichloromethane solution at room temperature, i.e., in very mild conditions. Compounds containing a single molecule of DMSO have been reported to be rather inert[17] to substitution; in complexes such as **3a** and **6a**, the easy displacement of DMSO by neutral ligands is promoted by the metal−carbon σ-bond in *trans* position. Compounds **13**−**15** contain four different groups coordinated to the metal center. Complex **13** in particular is not trivial, having three different metal−carbon bonds, M−C(sp^3), M−C(sp^2), and M−C(sp), respectively. ^{1}H NMR data are consistent with the isomer having an N−Pt−Me arrangement. A NOE difference experiment supports this assignment: irradiation of the resonance of the methyl bound to the platinum atom, δ 1.19, gives enhancement of the signal of H(4), δ 7.96.

The present results point out that an interesting intramolecular activation of a C−H bond of 6-substituted pyridine rings can be attained by reaction of electron-rich platinum(II) derivatives. Although the presence of a substituent in 6-position is crucial in driving the reaction toward the N′,C(3) metalation, we have evidence (^{1}H NMR spectroscopy) that in the case of [Pt($Me)_2$(DMSO)$_2$] activation of a C−H bond of a pyridine ring occurs even with the unsubstituted 2,2′-bipyridine. However, the process requires harsh conditions, e.g., refluxing toluene,[5] and is accompanied by heavy decomposition to metal. A dynamic behavior implying dissociation−association of a nitrogen donor has been previously observed in some palladium(II) 2,2′-bipy complexes.[18]

Finally it is worth mentioning that with the 6-alkyl- and benzyl-substituted ligands, HL^1−HL^5, we were unable to attain multiple C−H bond activation, as recently reported in the case of 6-phenyl-2,2′-bipyridine, HL.[6,7] Nevertheless, the FAB mass spectra of compounds **2a**, **3a**, and **5a** provide evidence for dinuclear species (e.g., **2a**, *m/z* 613 [Pt_2(L-2H)$^+$]) in the vapor phase.

Experimental Section

The ligands were prepared according to literature methods.[19]

All the reactions were carried out under argon. The solvents have been purified and dried according to standard methods.[20] Compounds *cis*-[Pt($Me)_2$(DMSO)$_2$], *cis*-[Pt($Ph)_2$(DMSO)$_2$], and *trans*-[Pt(Me)Cl(DMSO)$_2$] were prepared according to literature procedures.[21] Elemental analyses were performed with a Perkin-Elmer 240B elemental analyzer by Mr. A. Canu (Dipartimento di Chimica, Università di Sassari). Infrared spectra were recorded with a Perkin-Elmer 983 using Nujol mulls. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded with a Varian VXR 300 spectrometer operating at 300.0, 75.4, and 121.4 MHz, respectively.

Chemical shifts are given in ppm relative to internal TMS (^{1}H, ^{13}C) and external 85% H_3PO_4 (^{31}P). NOE difference spectra were performed by means of standard pulse sequences. The mass spectrometric measurements were performed on a VG 7070EQ instrument, equipped with a PDP 11-250J data system and operating under positive ion fast atom bombardment (FAB) conditions with 3-nitrobenzyl alcohol as supporting matrix.

Preparations. General Procedures for Preparation of Compounds 1a−6a. Method A. To a suspension of *cis*-[Pt($Me)_2$(DMSO)$_2$] (88 mg, 0.231 mmol) in toluene (7 mL) were added under stirring 0.236 mmol of HL^n (n = 1−6). The yellow solution was heated to 70−80 °C, then evaporated to dryness. The crude product was dissolved in CH_2Cl_2, filtered over Celite, and treated with pentane. The precipitate obtained was filtered, washed with pentane, and vacuum-dried to give the analytical sample as a pale yellow solid.

Method B. To a solution of the ligand HL^n (n = 1−6, 0.30 mmol) in acetone (15 mL) was added under stirring 114 mg of *cis*-[Pt($Me)_2$(DMSO)$_2$] (0.30 mmol). The yellow solution was refluxed, then concentrated to small volume and treated with pentane. The precipitate obtained was filtered, washed with pentane, and vacuum-dried to give the analytical sample as a pale yellow solid.

[Pt(Me)(L^1)(DMSO)], 1a. Compound **1a** was obtained according to method B (5 h), yield 68%, mp 140−3 °C. Anal. Calcd for $C_{14}H_{18}N_2OPtS$: C 36.76, H 3.97, N 6.12. Found: C 37.13, H, 3.65, N, 6.06. ^{1}H NMR ($CDCl_3$): δ 0.69 (s, 3H, Me-Pt, $^2J_{Pt-H}$ = 82.0 Hz), 2.52 (s, 3H, Me-bipy), 3.24 (s, 6H, Me(DMSO), $^3J_{Pt-H}$ =

(17) (a) Monsù Scolaro, L.; Mazzaglia, L.; Romeo, A.; Plutino, M. R.; Castriciano, M.; Romeo, R. *Inorg. Chim. Acta* **2002**, *330*, 189−196. (b) Romeo, R.; Cusumano, M. *Inorg. Chim. Acta* **1981**, *49*, 167.

(18) Markies, B. A.; Kruis, D.; Rietveld, M. H. P.; Verkerk, K. A. N.; Boersma, J.; Kooijman, H.; Lakin, M. T.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1995**, *117*, 5263−5274.

(19) (a) Kauffmann, T.; Konig, J.; Woltermann, A. *Chem. Ber.* **1976**, *109*, 3864. (b) Azzena, U.; Chelucci, G.; Delogu, G.; Gladiali, S.; Marchetti, M.; Soccolini F.; Botteghi, C. *Gazz. Chim. Ital.* **1986**, *116*, 307. (c) Botteghi, C.; Chelucci, G.; Chessa, G.; Delogu, G.; Gladiali S.; Soccolini, F. *J. Organomet. Chem.* **1986**, *304*, 217. (d) Polin, J.; Schmohel, E.; Balzani, V. *Synthesis* **1998**, 321−324.

(20) *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman Scientific and Technical: Harlow, 1989.

(21) (a) Eaborn, C.; Kundu, K.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1981**, 933. (b) Romeo, R.; Monsù Scolaro, L. *Inorg. Synth.* **1998**, *32*, 153.

19.3 Hz), 7.04 (d, 1H, H_5, $^3J_{H-H}$ = 8.0 Hz, $^4J_{Pt-H}$ = 18.6 Hz), 7.31 (m, 1H, $H_{5'}$), 7.88 (d, 1H, H_4, $^3J_{H-H}$ = 8.0 Hz, $^3J_{Pt-H}$ = 53.0 Hz), 7.91 (td, 1H, $H_{4'}$ (partially overlapping)), 8.31 (d, 1H, $H_{3'}$, $^3J_{H-H}$ = 7.6 Hz), 9.67 (d, 1H, $H_{6'}$, $^3J_{H-H}$ = 5.9 Hz, $^3J_{Pt-H}$ = ca. 14 Hz).

[Pt(Me)(L²)(DMSO)], 2a. Method A (80 °C, 16 h), yield 60%; method B, yield 81%; mp 145 °C (dec). Anal. Calcd for $C_{18}H_{26}N_2OPtS\cdot 0.5DMSO$: C 41.29, H 5.29, N 5.07. Found: C 40.98, H 5.12, N 5.11. ^{1}H NMR ($CDCl_3$): δ 0.70 (s, 3H, Me-Pt, $^2J_{Pt-H}$ = 82.0 Hz), 0.96 (s, 9H, $(Me)_3C$); 2.65 (s, 2H, CH_2), 3.24 (s, 6H, Me-(DMSO) $^3J_{Pt-H}$ = 18.3 Hz), 6.98 (d, 1H, H_5, $^3J_{H-H}$ = 7.6 Hz, $^4J_{Pt-H}$ = 18.9 Hz) 7.32 (td, 1H, $H_{5'}$) 7.88 (d, 1H, H_4, $^3J_{H-H}$ = 7.6 Hz, $^3J_{Pt-H}$ = 52.6 Hz), 7.91 (1H, $H_{4'}$ (overlapping)); 8.34 (d, 1H, $H_{3'}$; $^3J_{H-H}$ = 7.9 Hz), 9.66 (d, 1H, $H_{6'}$, $^3J_{H-H}$ = 6.1 Hz, $^3J_{Pt-H}$ =14.1 Hz). MS-FAB$^+$ (*m*/*z*): 513 $[M]^+$, 498 $[M - Me]^+$, 435 $[M - DMSO]^+$, 419 $[M - DMSO - CH_4]^+$, 403 $[M - DMSO - 2\,CH_4]^+$, 363 $[M - DMSO - C(Me)_3 - Me]^+$.

[Pt(Me)(L³)(DMSO)], 3a. Method A (70 °C, 14 h), yield. 61%; method B, yield 88%; mp 187 °C. Anal. Calcd for $C_{17}H_{24}N_2OPtS$: C 40.87, H 4.84, N 5.61. Found: C 40.51, H 4.54, N 5.42. ^{1}H NMR ($CDCl_3$): δ 0.69 (s, 3H, Me-Pt, $^2J_{Pt-H}$ = 82.3 Hz), 1.38 (s, 9H, $(Me)_3C$); 3.23 (s, 6H, Me(DMSO) $^3J_{Pt-H}$ = 18.1 Hz); 7.21 (d, 1H, H_5, $^3J_{H-H}$ = 8.1 Hz, $^4J_{Pt-H}$ = 18.0 Hz), 7.31 (ddd, 1H, $H_{5'}$, $^3J_{H-H}$ = 7.3 Hz, $^3J_{H-H}$ = 5.6 Hz, $^4J_{H-H}$ = 1.5 H), 7.89 (d, 1H, H_4, $^3J_{Pt-H}$ = 51.9 Hz, $^3J_{H-H}$ = 8.1 Hz), 7.91 (m, 1H, $H_{4'}$ (overlapping)), 8.36 (d, 1H, $H_{3'}$, $^3J_{H-H}$ = 8.1 Hz), 9.65 (d, 1H, $H_{6'}$, $^3J_{Pt-H}$ = 19.8 Hz, $^3J_{H-H}$ = 5.6 Hz). ^{13}C-{^{1}H} NMR: δ −13.91 (*C*H_3-Pt, $^1J_{Pt-C}$ = 763.8 Hz), 30.21 (*C*-(CH_3)), 43.69 (CH_3 (DMSO), $^2J_{Pt-C}$ = 42.5 Hz), 119.37 ((C5), J_{Pt-C} = 59.7 Hz), 121.35 (C3′, J_{Pt-C} = 24.2 Hz), 124.07 (C5′, J_{Pt-C} = 9.9 Hz), 138.25 (C4′, J_{Pt-C} = n.r.), 140.21 (C4, J_{Pt-C} = 90.8 Hz), 141.31 (C3, $^1J_{Pt-C}$ = 1086 Hz), 150.11 (C6′, J_{Pt-C} = 7.7 Hz). MS-FAB$^+$ (*m*/*z*): 499 $[M]^+$, 484 $[M - Me]^+$, 421 $[M - DMSO]^+$, 405 $[M - DMSO - CH_4]^+$, 390 $[M - DMSO - CH_4 - Me]^+$, 375 $[M - DMSO - 2Me - CH_4]^+$, 349 $[M - DMSO - C(Me)_3 - Me]^+$.

[Pt(Me)(L⁴)(DMSO)], 4a. Method B (1.5 h), yield 99%; mp 172−174 °C. Anal. Calcd for $C_{22}H_{26}N_2OPtS$: C 47.05, H 4.67, N 4.99. Found: C 46.72, H 4.39, N 5.38. ^{1}H NMR ($CDCl_3$): δ 0.66 (s, 3H, Me-Pt, $^2J_{Pt-H}$ = 82.0 Hz), 0.90 (t, 3H, *Me*CH_2, $^3J_{H-H}$ = 7.3 Hz), 2.08 (m, 1H, CH_2), 2.37 (m, 1H, CH_2), 3.21 (s, 6H, Me(DMSO), $^3J_{Pt-H}$ = 18.1 Hz), 3.90 (t, 1H, CH, $^3J_{H-H}$ = 7.7 Hz), 7.01 (d, 1H, H_5, $^3J_{H-H}$ = 7.8 Hz, $^4J_{Pt-H}$ = 18.1 Hz), 7.12−7.37 (m, 6H, aromatics), 7.85 (d, 1H, H_4, $^3J_{H-H}$ = 7.8 Hz, $^3J_{Pt-H}$ = 52.9 Hz), 7.92 (td, 1H), $H_{4'}$, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.5 Hz), 8.39 (d, 1H, $H_{3'}$, $^3J_{H-H}$ = 7.6 Hz), 9.66 (dd, 1H, $H_{6'}$, $^3J_{H-H}$ = 6.6 Hz, $^3J_{Pt-H}$ = 13.8 Hz).

[Pt(Me)(L⁵)(DMSO)], 5a. Method B (2.5 h): yield 73%; mp dec 155 °C. Anal. Calcd for $C_{22}H_{26}N_2OPtS$: C 47.05, H 4.67, N 4.99. Found: C 46.55, H, 4.24, N, 5.10. ^{1}H NMR ($CDCl_3$): δ 0.66 (s, 3H, Me-Pt, $^2J_{Pt-H}$ = 82.0 Hz), 1.77 (s, 6H, $(Me)_2C$), 3.23 (s, 6H, Me(DMSO), $^3J_{Pt-H}$ = 18.1 Hz), 6.84 (d, 1H, H_5, $^3J_{H-H}$ = 8.1 Hz, $^4J_{Pt-H}$ = 17.6 Hz), 7.04−7.26 (m, 6H), 7.75 (d, 1H, H_4, $^3J_{H-H}$ = 8.1 Hz, $^3J_{Pt-H}$ = 51.8 Hz), 7.83 (td, 1H, $H_{4'}$, $^3J_{H-H}$ = 7.8 Hz, $^4J_{H-H}$ = 1.3 Hz), 8.27 (d, 1H, $H_{3'}$, $^3J_{H-H}$ = 7.8 Hz), 9.58 (d, 1H, $H_{6'}$, $^3J_{H-H}$ = 6.3 Hz, $^3J_{Pt-H}$ = 13.7 Hz). MS-FAB$^+$ (*m*/*z*): 561 $[M]^+$, 546 $[M - Me]^+$, 483 $[M - DMSO]^+$, 467 $[M - DMSO - CH_4]^+$, 453 $[M - DMSO - 2Me]^+$.

[Pt(Me)(L⁶)(DMSO)], 6a. Method A (2 h), yield 93%; method B (1 h, reflux temp), yield 89%; mp 174−176 °C. Anal. Calcd for $C_{19}H_{20}N_2OPtS$: C 43.93, H 3.88, N 5.39. Found: C 43.73, H 3.63, N 5.20. ^{1}H NMR ($CDCl_3$): δ 0.75 (s, 3H, Me-Pt, $^2J_{Pt-H}$ = 81.8 Hz), 3.26 (s, 6H, $(Me)_2SO$, $^3J_{Pt-H}$ = 18.3 Hz), 7.32−7.54 (m, 4H, aromatics), 7.65 (d, 1H, H_5, $^3J_{H-H}$ = 8.1 Hz, $^4J_{Pt-H}$ = 17.8 Hz), 7.97 (dt, 1H, $H_{4'}$, $^4J_{H-H} \approx 1$ Hz $^3J_{H-H}$ = 7.8 Hz), 8.07 (d, 1H, H_4, $^3J_{H-H}$ = 8.1 Hz, $^3J_{Pt-H}$ = 52.0 Hz), 8.14 (d, 2H, H*o* (Ph), $^3J_{H-H}$ = 7.8 Hz), 8.50 (ddd, 1H, $H_{3'}$, $^3J_{H-H}$ = 7.3 Hz), 9.71 (ddd, 1H, $H_{6'}$, $^3J_{H-H}$ = 5.6 Hz, $^3J_{Pt-H}$ = 13.7 Hz). ^{13}C NMR (DMSO-d_6): δ −13.83 (s, J_{C-Pt} = 772.5 Hz), 120.06 (s, J_{C-Pt} = 60.0 Hz), 121.12 (s, J_{C-Pt} = 20.0 Hz), 125.09 (s), 125.93 (s), 128.46 (s), 128.67 (s), 138.87 (s, J_{C-Pt} = 90.6 Hz), 139.28 (s), 140.78 (s, J_{C-Pt} = 90.2 Hz), 145.52 (s), 149.86 (s), 151.35 (s, J_{C-Pt} = 214.7 Hz), 161.65 (s, J_{C-Pt} = 56.4 Hz), 164.01 (s, J_{C-Pt} = 25.0 Hz). MS-FAB$^+$ (*m*/*z*): 519 $[M]^+$, 504 $[M - Me]^+$, 441 $[M - DMSO]^+$, 426 $[M - DMSO - Me]^+$.

[Pt(Ph)(L³)(DMSO)], 3b. Complex **3b** was obtained according to method B (5 h) using $[Pt(Ph)_2(DMSO)_2]$ instead of $[Pt(Me)_2(DMSO)_2]$, pale yellow, yield 44%; mp 225 °C. Anal. Calcd for $C_{22}H_{26}N_2OPtS$: C 47.05, H 4.67, N 4.99. Found: C 47.36, H 4.57, N 4.99. ^{1}H NMR ($CDCl_3$): δ 1.32 (s, 9H, $(Me)_3C$), 2.95 (s, 3H, Me(DMSO), $^3J_{Pt-H}$ = 17.6 Hz), 6.77 (d, 1H, H_4, $^3J_{H-H}$ = 8.1 Hz, $^3J_{Pt-H}$ = 61.0 Hz), 6.94 (d, 1H, H_5, $^3J_{H-H}$ = 8.1 Hz, $^4J_{Pt-H}$ = 16.6 Hz), 6.98−7.11 (m, 3H), 7.34 (m, 1H), 7.48 (dd, 2H, H*o* (Ph), $^3J_{H-H}$ = 8.1 Hz, $^4J_{H-H}$ = 1.5 Hz, $^3J_{Pt-H}$ = 66.9 Hz), 7.93 (td, 1H, $H_{4'}$, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.4 Hz), 8.37 (dd, 1H, $H_{3'}$, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 0.7 Hz), 9.56 (ddd, 1H, $H_{6'}$, $^3J_{Pt-H}$ = 12.6 Hz, $^3J_{H-H}$ = 5.6 Hz,$^4J_{H-H}$ = 1.4 Hz, $^5J_{H-H}$ = 0.7 Hz). MS-FAB$^+$ (*m*/*z*): 562 $[MH]^+$, 483 $[M - DMSO]^+$, 406 $[M - DMSO - Ph]^+$, 391 $[M - DMSO - Ph - Me]^+$.

Synthesis of [Pt(Ph)(L⁶)(DMSO)], 6b. Complex **6b** was obtained according to method A (90 °C, 8.5 h), using $[Pt(Ph)_2(DMSO)_2]$ instead of $[Pt(Me)_2(DMSO)_2]$; pale yellow, yield 51%; mp 240 °C. Anal. Calcd for $C_{24}H_{22}N_2OPtS$: C 49.56, H 3.81, N 4.82. Found: C 49.43, H 3.85, N 4.72. ^{1}H NMR ($CDCl_3$): δ 2.98 (s, 6H, Me(DMSO), $^3J_{Pt-H}$ = 17.6 Hz), 6.94 (d, 1H, H_4, $^3J_{H-H}$ = 7.8 Hz, $^3J_{Pt-H}$ = 62.8 Hz), 7.03−7.47 (m, 8H, aromatics), 7.51 (d, 2H, H*o* (Ph-Pt), $^3J_{H-H}$ = 6.8 Hz, $^3J_{Pt-H}$ 65.0 Hz), 7.98 (t, 1H, $H_{4'}$, $^3J_{H-H}$ = 7.7 Hz), 8.02 (d, 2H, H*o* Ph bipy, $^3J_{H-H}$ = 7.8 Hz), 9.63 (d, 1H, $H_{6'}$, $^3J_{H-H}$ = 5.4 Hz, $^3J_{Pt-H}$ = 12.7 Hz). MS-FAB$^+$ (*m*/*z*): 503 $[M - DMSO]^+$, 426 $[M - DMSO - Ph]^+$.

[Pt(Cl)(L³)(DMSO)] (3c) and [Pt₂(μ-Cl)₂(L³)₂] (3d). To a solution of **3a** (157.0 mg, 0.315 mmol) in acetone (20 mL) was added under stirring 3.2 mL of 0.1 M HCl (0.320 mmol). The color of the solution changed immediately to orange-yellow and a precipitate was formed. The suspension was stirred for 4 h; after that the precipitate was filtered and washed with acetone, to give compound **3d** as a yellow solid. The filtered solution was concentrated to small volume. The precipitate formed was filtered and washed with H_2O, EtOH, and Et_2O to give compound **3c**.

3d, [Pt₂(μ-Cl)₂(L³)₂]: yield 15%; mp > 260 °C. Anal. Calcd for $C_{28}H_{30}Cl_2N_4Pt_2\cdot H_2O$: C 37.32, H 3.55, N 6.22. Found: C 36.73, H 3.20, N 5.93. IR (Nujol, ν_{max}/cm^{-1}):

330 (s), 347 (s), 371 (s), 393 (s). ^{1}H NMR ($CDCl_3$): δ 1.38 (s, 18H, $(Me)_3C$), 7.06 (d, 2H), ca. 7.3 (2H, partially hidden by the solvent), 7.58 (d, 2H), 7.91 (t, 2H, $H_{4'}$), 8.08 (d, 2H), 8.80 (d + d, 2H, $H_{6'}$). MS-FAB$^+$ (*m*/*z*): 884 $[M + 2H]^+$, 848 $[MH - Cl]^+$, 441 $[M/2]^+$, 405 $[M/2 - HCl]^+$, 390 $[M/2 - HCl - Me]^+$.

3c, [Pt(Cl)(L^3)(DMSO)] yield 60%; mp 210 °C. Anal. Calcd for $C_{16}H_{21}ClN_2OPtS\cdot H_2O$: C 35.72, H 4.31, N 5.21. Found: C 35.47, H 3.99, N 4.95. IR (Nujol,ν_{max}/cm^{-1}): 276 (s), 316 (m). ^{1}H NMR (acetone-d_6): δ 1.38 (s, 9H, $(Me)_3C$), 3.63 (s, 6H, Me(DMSO), $^3J_{Pt-H}$ = 24.7 Hz), 7.19 (d, 1H, H_5, $^4J_{Pt-H}$ = 13.2 Hz, $^3J_{H-H}$ = 8.3 Hz), 7.62 (m, 1H, $H_{5'}$), 8.22 (td, 1H, $H_{4'}$), 8.29 (dd, 1H, $H_{3'}$), 8.53 (d, 1H, H_4, $^3J_{Pt-H}$ = 41.0 Hz, $^3J_{H-H}$ = 8.3 Hz), 9.57 (d, 1H, $H_{6'}$, $^3J_{Pt-H}$ = 35.4 Hz, $^3J_{H-H}$ = 5.8 Hz).

[Pt(Cl)(L^6)(DMSO)], 6c. To a solution of **6a** (46.1 mg; 0.089 mmol) in acetone (15 mL) was added, under vigorous stirring, 0.9 mL of 0.1 M HCl (0.09 mmol). The color of the solution became immediately orange-yellow and a precipitate formed. The suspension was stirred for 6 h and concentrated to small volume. The precipitate was filtered, washed with acetone, and vacuum-dried to give the analytical sample. Yield 58%; mp 215 °C. Anal. Calcd for $C_{18}H_{17}ClN_2OPtS$: C 40.04, H 3.17, N 5.19. Found: C 39.86, H 3.12, N 5.27. ^{1}H NMR ($CDCl_3$): δ 3.67 (s, 6H, Me(DMSO), $^3J_{Pt-H}$ = 24.2 Hz), 7.38−7.51 (m, 4H, aromatics), 7.55 (d, 1H, H_5, $^3J_{H-H}$ = 8.3 Hz, $^4J_{Pt-H}$ = 13.0 Hz), 8.01 (dt, 1H, $H_{4'}$, $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-H}$ = 1.5 Hz), 8.10 (d, 2H, H*o* Ph), 8.39 (d, 1H, $H_{3'}$, $^3J_{H-H}$ = 7.2 Hz), 8.64 (d, 1H, H_4, $^3J_{H-H}$ = 8.3 Hz, $^3J_{Pt-H}$ = 42.0 Hz), 9.59 (ddd, 1H, $H_{6'}$, $^3J_{H-H}$ = 5.8 Hz,$^3J_{Pt-H}$ = 31.1 Hz).

[Pt(Me)$_2$(HL^7)], 7. Method B: yield 90%; mp 152−154 °C. Anal. Calcd for $C_{13}H_{16}N_2Pt$: C 39.49, H 4.08, N 7.09. Found: C 39.13, H 4.34, N 6.77. ^{1}H NMR ($CDCl_3$): δ 2.89 (s, 3H, bipy-Me), 0.94 (s, 3H, Pt-Me, $^2J_{Pt-H}$ = ca. 85 Hz), 0.95 (s, 3H, Pt-CH_3, $^2J_{Pt-H}$ = ca. 85 Hz), 7.63 (m, 1H), 8.09 (d, 1H), 8.22−8.36 (m, 3H), 8.98 (s (br), 1H, H_6, $^3J_{Pt-H}$ = 21 Hz), 9.20 (dd, 1H, $H_{6'}$, $^3J_{Pt-H}$ = 22 Hz).

[Pt(Me)$_2$(HL^8)], 8. Method B: 30 min, room temperature, yield 92%. Spectroscopic data in agreement with those reported in ref 22.[22]

[Pt Cl$_2$ (HL^1)], 9. Complex **9** was obtained according to method B (30 h) using $[PtCl_2(DMSO)_2]$ instead of $[Pt(Me)_2(DMSO)_2]$. Yield: 89%, mp: on heating a change of color from yellow to brick red occurs at 230−232 °C; no further decomposition up to 270 °C. Anal. Calcd for $C_{11}H_{10}Cl_2N_2Pt$: C 30.29, H 2.31, N 6.42. Found: C 30.15, H 2.39, N 6.20. ^{1}H NMR ($CDCl_3$): δ 3.18 (s, 3H, Me), 7.40 (dd, 1H), 7.48 (m, 1H), 7.91−7.99 (m, 3H), 8.13 (td, 1H), 9.69 (d, 1H, $^3J_{Pt-H}$ = ca. 33 Hz).

[PtCl(Me)(HL^1)], 10. Complex **10** was obtained according to method B (30 h) using *trans*-$[PtCl(Me)(DMSO)_2]$ instead of $[Pt(Me)_2(DMSO)_2]$. Spectroscopic and analytical data in agreement with those reported in ref 6.

[Pt(Ph)$_2$(HL^6)], 11. Complex **11** was obtained according to method B (2.5 h, at room temperature) using $[Pt(Ph)_2(DMSO)_2]$ instead of $[Pt(Me)_2(DMSO)_2]$. Yield: 90%; mp 180 °C (dec). Anal. Calcd for $C_{28}H_{22}N_2Pt\cdot 0.5DMSO$: C 56.12, H 4.06, N 4.51. Found: C 56.10, H 3.93, N 4.64. ^{1}H NMR (CD_2Cl_2): δ 6.34−8.17 (m, 21H, aromatics), 8.38 (d, 1H, $H_{6'}$).

[Pt(Ph)$_2$(HL^8)], 12. Complex **12** was obtained according to method B, 30 min, room temperature, yield 95%. Spectroscopic data in agreement with those reported in ref 23.[23]

[Pt(Me)(L^3)(CO)], 13. CO (1 atm) was bubbled for 3 h into a solution of **3a** (81.9 mg, 0.164 mmol) in CH_2Cl_2 (15 mL). The solution was concentrated to small volume, then Et_2O was added. The precipitate formed was filtered, washed with Et_2O, and vacuum-dried to give the analytical sample as a yellow solid. Yield: 75%; mp 160 °C. Anal. Calcd for $C_{16}H_{18}N_2OPt$: C 42.76, H 4.04, N 6.23. Found: C 42.69, H 3.70, N 6.04. IR (Nujol,ν_{max}/cm^{-1}): 1159 (w), 1259 (w), 1569 (m), 1608 (m), 2049 (s). ^{1}H NMR ($CDCl_3$): δ 1.19 (s, 3H, Me-Pt, $^2J_{Pt-H}$ = 86.2 Hz), 1.38 (s, 9H, $(Me)_3C$), 7.29 (d, 1H, H_5, $^3J_{H-H}$ = 7.8 Hz (partially overlapping)), 7.31 (m, 1H, $H_{5'}$, (partially overlapping)), 7.96 (d, 1H, H_4, $^3J_{Pt-H}$ = 45.9 Hz, $^3J_{H-H}$ = 7.8 Hz), 8.00 (td, 1H, $H_{4'}$, $^3J_{H-H}$ = 7.8 Hz, $^4J_{H-H}$ = 1.6 Hz), 8.39 (ddd, 1H, $H_{3'}$, $^3J_{H-H}$ = 8.0 Hz), 8.61 (ddd, 1H, $H_{6'}$, $^3J_{H-H}$ = 5.4 Hz, $^3J_{Pt-H}$ = 19 Hz). MS-FAB$^+$ (*m*/*z*): 450 $[MH]^+$, 434 $[M - Me]^+$, 421 $[M - CO]$, 405 $[M - H - Me - CO]^+$, 391 $[M - 2Me - CO]^+$.

[Pt(Me)(L^3)(3,5-(Me)$_2$py)], 14. To a solution of **3a** (70.6 mg; 0.141 mmol) in CH_2Cl_2 (15 mL) was added, under vigorous stirring, 93.9 mg (0.876 mmol) of 3,5-$(Me)_2$py. The solution was stirred for 3.5 h, then concentrated to small volume and treated with hexane. The precipitate formed was filtered, washed with hexane, and vacuum-dried to give the analytical sample as a yellow solid. Yield: 50%. Anal. Calcd for $C_{22}H_{27}N_3Pt$: C 49.99, H 5.15, N 7.95. Found: C 49.60, H 4.82, N 7.66. ^{1}H NMR ($CDCl_3$): δ 0.93 (s, 3H, Me-Pt, $^2J_{Pt-H}$ = 84.0 Hz), 1.37 (s, 9H, $(Me)_3C$), 2.38 (s, 6H, Me (lutidine)), 7.08 (m, 1H, $H_{5'}$), 7.13 (d, 1H, H_5, $^3J_{Pt-H}$ = 11.4 Hz, $^3J_{H-H}$ = 8.0 Hz), 7.48 (s, 1H, H_4 (lutidine)), 7.72 (d, 1H, $H_{6'}$), 7.84 (td, 1H, $H_{4'}$), 7.96 (d, 1H, H_4, $^3J_{Pt-H}$ = 54.6 Hz, $^3J_{H-H}$ = 8.0 Hz), 8.32 (d, 1H, $H_{3'}$), 8.51 (s, 2H, H_2(lutidine) $^3J_{Pt-H}$ = 21 Hz).

[Pt(Me)(L^6)(PPh$_3$)], 15. To a solution of **6a** (55.2 mg, 0.106 mmol) in CH_2Cl_2 (15 mL) was added, under vigorous stirring, 28.6 mg of PPh_3 (0.109 mmol). The solution was stirred for 4 h, then concentrated to small volume and treated with hexane. The precipitate formed was filtered, washed with hexane, and vacuum-dried to give the analytical sample as a pale yellow solid. Yield: 76%; mp 245 °C. Anal. Calcd for $C_{35}H_{29}N_2PPt\cdot 0.5$ CH_2Cl_2: C 57.15, H 4.05, N 3.75. Found: C 56.85, H 3.84, N 3.96. IR (Nujol,ν_{max}/cm^{-1}): 654 (s),774 (s), 1097 (s), 1569 (m), 1604 (m). ^{1}H NMR ($CDCl_3$): δ 0.79 (d, 3H, Me-Pt, $^2J_{Pt-H}$ = 83.0 Hz, $^3J_{P-H}$ = 7.7 Hz), 6.68 (m, 1H), 7.35−7.80 (m, 21H, aromatics), 8.15 (d, 2H, $^3J_{H-H}$ = 7.6 Hz), 8.31 (dd, 1H, H_4, $^3J_{H-H}$ = 8.1 Hz, $^4J_{P-H}$ = 5.1 Hz, $^3J_{Pt-H}$ = 46.5 Hz), 8.53 (dd, 1H, $H_{3'}$, $^3J_{H-H}$ = 7.8 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 33.01 (s, $^1J_{P-Pt}$ = 2233 Hz).

NMR Follow-Up Experiments. The rollover metalation was monitored by ^{1}H NMR spectroscopy. In a typical experiment 10.0 mg of $[Pt(Me)_2(DMSO)_2]$ and an equimolar amount of HL^n (n = 1, 3) were dissolved in 1.0 mL of acetone-d_6. The solution was rapidly mixed,

(22) Monaghan, P. K.; Puddephatt, R. J. *Organometallics* **1984**, *3*, 444−449.

(23) Rashidi, M.; Fakhroeian, Z.; Puddephatt, R. J. *J. Organomet. Chem.* **1990**, *406*, 261−267.

and ^{1}H NMR spectra were recorded at regular intervals until completion of the reaction at room temperature (18.5 °C, HL^1 and HL^2) and at −60 °C (HL^2). Selected peaks (e.g., H(6′) or Pt-Me) were integrated, and the values obtained were reported versus time.

The study was repeated with a large excess of ligand in the case of HL^1 (>10:1), and ln[$Pt(Me)_2(DMSO)_2$] was plotted versus time, showing a pseudo-first-order rate.

In solution the presence of the starting reactants ([$Pt(Me)_2(DMSO)_2$] and HL^n), the reaction products (the rollover species [$Pt(Me)(L^n)(DMSO)$], free DMSO, and methane ($\delta = 0.16$ ppm)), and a reaction intermediate, formulated as the adduct species [$Pt(Me)_2(HL^n)$], was observed.

[$Pt(Me)_2(HL^1)$]: ^{1}H NMR δ 1.02 (s, Pt-Me, $^2J_{Pt-H}$ = 89 Hz), 1.03 (s, Pt-Me, $^2J(Pt-H) = 87$ Hz), 2.83 (s, Me), 8.06−8.29 (m, 4H, H_3, $H_{3'}$, H_4, $H_{4'}$), 7.56−7.63 (m, 2H, H_5, $H_{5'}$), 9.11 (d, $H_{6'}$, $^3J(Pt-H) = 23$ Hz).

[$Pt(Me)_2(HL^2)$]: ^{1}H NMR δ ca. 1.0 (m (signals overlapping), Pt-Me, $C(Me)_3$), 3.41 (s, CH_2), 8.10−8.35 (m, 4H, H_3, $H_{3'}$, H_4, $H_{4'}$), 7.56−7.63 (m, 2H, H_5, $H_{5'}$), 9.07 (d, $H_{6'}$, $^3J_{Pt-H}$ = 23 Hz).

Acknowledgment. Financial support from Università di Sassari is gratefully acknowledged. We thank one of the reviewers for helpful suggestions.

OM0301583