Cyclometalation of 2,2'-Bipyridine. Mono- and Dinuclear C,N Platinum(II) Derivatives

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Received October 27, 2008

Reaction of the electron-rich derivative cis-[Pt(Me)₂(DMSO)₂] with 2,2'-bipyridine (L) affords the mononuclear "rollover" N',C(3) cyclometalate [Pt(L-H)(Me)(DMSO)] (1a) or the unusual dinuclear species $[Pt_2(\mu-L-2H)(Me)_2(DMSO)_2]$ (2a), depending on the Pt/L molar ratio. The latter complex, 2a, can be obtained either directly from cis-[Pt(Me)₂(DMSO)₂] or by a two-step process through complex 1a. The synthesis of 2a implies a double C-H bond activation, with loss of two molecules of methane: the 2-fold deprotonated 2,2'-bipyridine links two [Pt(Me)(DMSO)] fragments, acting as a π -delocalized $C,N \land N,C$ eight-electron donor. From 1a and 2a displacement of DMSO with two-electron-donor ligands such as PPh₃, (b), CO (c), and 3,5-Me₂py (d) gives two series of complexes, 1b-d and 2b-d, respectively. Reaction of 1a and 2a with HCl affords the corresponding chlorides [Pt(L-H)(Cl)(DMSO)] (3a) and $[Pt_2(\mu-L-2H)(Cl)_2(DMSO)_2]$ (4a), from which complexes 3b-d and 4b,d can be obtained by substitution of DMSO. The crystal structures of the mono- and dinuclear complexes [Pt(L-H)(Cl)(PPh₃)] (3b) and $[Pt_2(\mu-L-2H)(Cl)_2(PPh_3)_2]$ (4b) have been solved by X-ray diffraction. Protonation of the uncoordinated nitrogen atom in **1a** can be achieved by reaction with 18-crown-6•HBF₄: [Pt(L*)(Me)(DMSO)][BF₄] (5), where the zwitterionic ligand L* is still N'-C(3) bonded to platinum(II), can be isolated in the solid state. Taking advantage of the two-step approach used for the synthesis of complex 2a, unsymmetric species where the platinum atoms are in different environments, e.g. [(DMSO)(Cl)Pt(µ-L-2H)Pt-(Me)(DMSO)] (6), [(PPh₃)(Me)Pt(μ -L-2H)Pt(Me)(DMSO)] (7), and [(CO)(Cl)Pt(μ -L-2H)Pt(Me)(DMSO)] (8), can be prepared in good yields. Attempts to build up a platinum(II)-gold(III) species by reaction of **3a** with Na[AuCl₄] failed: no platinum–gold derivative was obtained but a platinum(IV) complex, [Pt(L-H)(Cl)₃(DMSO)] (9), likely due to the strong oxidative capability of gold(III).

Introduction

In the chemistry of transition metals with heterocyclic nitrogen ligands, 2,2'-bipyridines have been very popular since the early days of coordination chemistry.¹ The title of a recent review, "bipyridine: the most widely used ligand...",² gives an idea of their importance.

Mostly they were, and still are, found as neutral N,N' ligands bonded to early and late transition metals, in a variety of oxidation states, low states included.³ As the years went by and interest in heterocyclic nitrogen molecules grew, the potential role of the 2,2'-bipyridines was thoroughly investigated: in the case of the late transition metals they now appear to be involved



in a number of species with applications spanning from medicinal chemistry⁴ to novel materials.⁵

Of the two possible coplanar conformations, cis and trans (Chart 1, **a** and **b**), which differ in several aspects such as dipole moment and charge distribution, it is well-known that the most

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Reedijk, J. In *Comprehensive Coordination Chemistry*; Wilkinson,
 G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K.,
 1987; Vol. 2, p 73.

^{1987;} Vol. 2, p 73.
(2) Kaes, C.; Katz, A.; Hosseini, M. W. *Chem. Rev.* 2000, 100, 3553.
(3) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed., Wiley: New York, 1988; pp 348-350.

⁽⁴⁾ For example: (a) Elwell, K. E.; Hall, C.; Tharkar, S.; Giraud, Y.; Bennett, B.; Bae, C.; Carper, S. W. *Bioorg. Med. Chem.* **2006**, *14*, 8692–8700. (b) Chan, H.-L.; Ma, D.-; Yang, M.; Che, C.-M. J. Biol. Inorg. Chem. **2003**, *8*, 761–769.

^{(5) (}a) Marder, S. R. In *Inorganic Materials*; Bruce, D. W., O'Hare, D., Eds.; Wiley: New York, 1997; p 115. (b) Sun, W.; Zhu, H.; Barron, P. M. *Chem. Mater.* **2006**, *18*, 2602–2610.

stable form, both in the solid state and in solution, is the trans species, $\mathbf{b}^{.6}$ The cis coplanar form may be disfavored by H---H steric interactions and Coulombic repulsions of the nitrogen lone pairs.

In spite of this, the common graphic representation of 2,2'bipy is that corresponding to the cis conformation, **a**, because as a neutral ligand 2,2'-bipy almost invariably acts as an N,N' chelating ligand (**c**), whereas derivatives such as **d** (monodentate), **e** (bridging), and **f** (N'-C bonded tautomeric form) are rare or extremely rare. The type **b** conformation, however, may play a role favoring, with an appropriate metal intermediate, activation of a C-H bond of a pyridine ring, forming an N'-C(3) five-membered cyclometalated ring, **g**.

This peculiar metalation was first observed in a reaction with platinum derivatives by Young and co-workers many years ago and reported in a preliminary communication:⁷ few experimental details were given, and no mononuclear derivative was isolated. In recent years we have found that in the case of 6-substituted 2,2'-bipyridines electron-rich platinum intermediates containing a "Pt(R)₂" fragment readily promote N',C(3) cyclometalation. Platinum(II) complexes, [Pt(L-H)(X)(L')] (L = 6-substituted 2,2'-bipyridine; X = Me, Ph, Cl; L' = neutral two-electron ligand), were isolated in the solid state and fully characterized,⁸ in some cases also by X-ray diffraction. In contrast, in the course of our studies, we were unable to isolate analogous derivatives from the reaction of the unsubstituted 2,2'-bipyridine, though some faint NMR evidence suggested their presence in solution.^{8b}

Herein we report that under definite conditions even metalation of 2,2'-bipyridine is promoted by the platinum(II) intermediates [Pt(Me)₂(L')₂]: the first cyclometalated derivatives of 2,2'-bipyridine, [Pt(L-H)X(L')] (L = 2,2'-bipy; X = Me, Cl), have been isolated and fully characterized. The 2-(pyridyl)pyridine forms a five-membered cyclometalated ring reminiscent of that of the most common 2-(phenyl)pyridine, a ligand widespread in the chemistry of late transition metals.⁹ In addition to a likely different charge distribution inside the ligand, a remarkable difference between the two systems is the presence in the (pyridyl)pyridine species of an uncoordinated nitrogen atom potentially available for protonation, further coordination, or other chemical reactions or weak interactions. Taking advantage of the uncoordinated nitrogen atom, a two-step approach allowed us to build up dinuclear platinum species, both symmetric and nonsymmetric: $[Pt_2(\mu-L-2H)(X)_2(L')_2]$ (X = Me, Cl).

Protonation of one of the mononuclear species with 18-crown- $6 \cdot HBF_4$ gives a cationic complex, isolated in the solid state, where a neutral bipyridine acts as a zwitterionic N,C endobidentate ligand.



To the best of our knowledge, this behavior of 2,2'-bipyridine is unprecedented in platinum chemistry and, on the whole, extremely rare, an example being an iridium(III) derivative that was a matter of long debate and was reported many years ago¹⁰

Results and Discussion

With the exception of the preliminary communication by Young and co-workers on the reaction of *cis*- $[Pt(Ph)_2(DMSO)_2]$,⁷ platinum(II) C-3 metalation of the unsubstituted 2,2'-bipyridine was never reported. As mentioned above, in the course of our previous investigations we were unable to isolate cyclometalated derivatives of the unsubstituted 2,2'-bipyridine: to force metalation, we decided to operate under conditions more severe than those previously used. In toluene at 110 °C, the reaction of *cis*- $[Pt(Me)_2(DMSO)_2]$ with 2,2'-bipy (L) results in C(3)–H bond activation and metalation in high yields. To avoid decomposition, the reaction requires strictly controlled conditions: e.g., anhydrous solvents and nitrogen atmosphere.

The outcome of the reaction depends on the Pt/L molar ratio. When a bipyridine excess is employed, a mononuclear complex, [Pt(L-H)(Me)(DMSO)] (1a), is formed. The reaction, which occurs with loss of methane, proceeds in almost quantitative yield. At variance, with Pt/L = 2/1, a dinuclear species, [Pt₂(μ -L-2H)(Me)₂(DMSO)₂] (2a), can be isolated and characterized. With a 1/1 Pt/L molar ratio a mixture of 1a and 2a is obtained: the mono- and dinuclear species can be separated by taking advantage of their different solubilities.

Mononuclear Complexes. Complex 1a, the first mononuclear platinum N'-C(3) derivative of 2,2'-bipy, is a yellow air- and moisture stable compound, which was characterized by elemental analyses and NMR spectroscopy.



In particular, in the ¹H NMR spectrum the absence of the C(3)–H resonance and the strong coupling to platinum of the H(4) proton (dd, δ 8.01, ³*J*_{Pt-H} = 56.0 Hz) confirm the metalation. A singlet at δ 3.25, flanked by satellites (³*J*_{Pt-H} = 18.3 Hz), is consistent with an S-bonded DMSO trans to an sp² carbon atom;¹¹ the chemical shift and coupling constant (δ 0.70, ³*J*_{Pt-H} = 82 Hz) of the coordinated methyl are in line with a Me trans to a nitrogen atom.¹¹ The geometry of the complex has been confirmed by a NOE difference spectrum (see the Experimental Section). In the ¹³C NMR spectrum direct evidence

⁽⁶⁾ Goller, A. H.; Grummt, U. W. Chem. Phys. Lett. 2002, 354, 233-242.

⁽⁷⁾ Skapski, A. C.; Sutcliffe, V. F.; Young, G. B. J. Chem. Soc., Chem. Commun. 1985, 609–611.

^{(8) (}a) Minghetti, G.; Doppiu, A.; Zucca, A.; Stoccoro, S.; Cinellu, M. A.; Manassero, M.; Sansoni, M. *Chem. Heterocycl. Compd.* **1999**, *35*, 992–1000. (b) Minghetti, G.; Stoccoro, S.; Cinellu, M. A.; Soro, B.; Zucca, A. *Organometallics* **2003**, 4770–4777.

⁽⁹⁾ For example: (a) Omae, I. *Coord. Chem. Rev.* 2004, 248, 995–1023.
(b) Craig, C. A.; Garces, F. O.; Watts, R. J.; Palmans, R.; Frank, A. J. *Coord. Chem. Rev.* 1990, 97, 193–208. (c) Mdeleni, M. M.; Bridgewater, J. S.; Watts, R. J.; Ford, P. C. *Inorg. Chem.* 1995, 34, 2334–2342. (d) Okada, T.; El-Mehasseb, I. M.; Kodaka, M.; Tomohiro, T.; Okamoto, K. I.; Okuno, H. J. Med. Chem. 2001, 44, 4661–4667. (e) Niedermair, F.; Waich, K.; Kappaun, S.; Mayr, T.; Trimmer, G.; Mereiter, K.; Slugovc, C. *Inorg. Chim. Acta* 2007, 360, 2767–2777. (f) Mamtora, J.; Crosby, S. H.; Newman, C. P.; Clarkson, G. J.; Rourke, J. P. *Organometallics* 2008, 27, 5559–5565. (g) Yagyu, T.; Ohashi, J.; Maeda, M. *Organometallics* 2007, 26, 2383–2391, and references therein.

^{(10) (}a) Spellane, P. J.; Watts, R. J.; Curtis, C. J. *lnorg. Chem.* 1983, 22, 4060–4062. (b) Braterman, P. S.; Heat, G. H.; Mackenzie, A. J.; Noble, B. C.; Peacock, R. D.; Yellowlees, K. J. *lnorg. Chem.* 1984, 23, 3425.

^{(11) (}a) Owen, J. S.; Labinger, J. A.; Bercaw, J. E. J. Am. Chem. Soc.
2004, 126, 8247–8255. (b) Zucca, A.; Doppiu, A.; Cinellu, M. A.; Minghetti,
G.; Stoccoro, S.; Manassero, M. Organometallics 2002, 21, 783–785. (c)
Doppiu, A.; Minghetti, G.; Cinellu, M. A.; Stoccoro, S.; Zucca, A.;
Manassero, M. Organometallics 2001, 20, 1148–1152.

 Table 1. Selected NMR and IR Data for Mononuclear Species^a

compd	H6	H5	H4	H6′	H5′	H4′	H3′	CH ₃	other data
\mathbf{L}^{b}	8.65	7.21	7.73						8.42 (H3)
1a	8.36	7.17	8.01 (56.0)	9.71 (14)	7.36	7.95	8.29	0.70 (82)	$3.25 (18.3)^c$
1b	8.40	7.22	8.24 (48)	d	6.67	d	8.31	0.74 (83)	33.6 (2229) ^e
1c	8.40	7.24 (17.4)	8.06 (46.0)	8.65 (19.8)	7.35	8.03 (17.4)	8.33	1.19 (85.7)	2044 IR ($\nu_{\rm CO}$)
1d	ca. 8.25 ^d	7.07	8.10 (60.4)	7.76 (20)	7.14	7.88	ca. 8.25 ^d	0.94 (84.2)	8.51 (23.1) ^f
3a	8.37	7.08 (16.5)	8.60 (42)	9.59 (36)	7.40	7.98	8.22		$3.65 (24.2)^c$
3b	8.17	6.42	6.85 (49)	9.85 (31)	d	8.00	8.26		$23.6 (4285)^e$
3c	8.45	7.06 (18)	7.78 (62.7)	9.50 (34)	7.53	8.07	8.26		2107 IR ($\nu_{\rm CO}$)
3d	8.30	6.88	6.70 (48.3)	9.67 (39.5)	7.30	7.92	8.10		8.61 (23.4) ^f

^{*a*} Conditions for ¹H NMR: 300 MHz, room temperature, solvent CDCl₃. J_{Pt-H} and J_{Pt-P} , in parentheses, are given in Hz. ^{*b*} See ref 26. ^{*c*} In DMSO. ^{*d*} Signals overlapping. ^{*e*} Conditions for ³¹P NMR: 121.4 MHz, PPh₃. ^{*f*} H_o py.

Table 2. Selected NMR and IR Data for Dinuclear Species^a

				•	
compd	H6	H5	H4	Pt-CH ₃	other data
2a	9.14	7.14	8.05 (51.3)	0.67 (80.8)	3.23 (18.7) DMSO
2b	ca. 7.4^{b}	6.57	8.13 (42.0)	0.62 (81.4)	$33.29(2347)^c$
2c	8.27 (22)	7.20	8.16 (45)	1.17 (83.8)	2048 IR ($\nu_{\rm CO}$)
2d	7.25^{b}	6.88	8.05 (54.6)	0.91 (82.8)	8.52 (23.4) H _o py
4a	8.95	7.07	6.64		3.27 (23.0) DMSO
4b	9.06	6.51	6.81 (44.8)		$19.55 (4135)^c$
4d	8.90 (39)	6.78^{d}	6.78^{d}		8.86 (41.7) H _o py

^{*a*} Conditions for ¹H NMR: 300 MHz, solvent CDCl₃, room temperature. J_{Pt-H} and J_{Pt-P} , in parentheses, are given in Hz. ^{*b*} Partially overlapping. ^{*c*} Conditions for ³¹P NMR: 121.4 MHz, PPh₃. ^{*d*} Signals overlapping.

for the metalation is given by a quaternary carbon at δ 145.10, with ${}^{1}J_{\text{Pt-C}} = 1090$ Hz, a value that fits previously reported data 11a for sp² carbons bonded to platinum. Two signals in the aliphatic region, $\delta - 13.38$ ($J_{\text{Pt-C}} = 763$ Hz) and δ 43.73 ($J_{\text{Pt-C}} = 42.1$ Hz), are assignable to the Pt-CH₃ and the Pt-DMSO carbons, respectively.

The adduct $[Pt(L)(Me)_2]$ is the first and only product formed when $[Pt(DMSO)_2(Me)_2]$ is reacted with 2,2'-bipyridine at room temperature.^{8b} Heating the adduct in toluene in the absence of DMSO results in partial decomposition to metal and a mixture of unidentified products. In toluene at 90 °C, in the presence of a small amount of DMSO, the rollover species [Pt(L-H)(Me)(DMSO)] is formed, providing evidence for the role of $[Pt(L)(Me)_2]$ as an intermediate in the formation of the rollover species.

From complex **1a** a series of mononuclear compounds can be synthesized by substitution of neutral ligands for DMSO (eq 2). The reaction occurs under mild conditions, likely favored by the lability of DMSO coordinated trans to a carbon atom.¹²



Complexes **1b-d**, [Pt(L-H)(Me)(L')], are air-stable compounds and have been characterized by analytical and spectroscopic methods (see Table 1 and the Experimental Section). In particular in the ¹H NMR spectra the values of ${}^{2}J_{\text{Pt-H}}$, relevant to the methyl protons, are all in the range 82–86 Hz, typical for a methyl trans to a nitrogen atom,¹¹ while the chemical shifts depend on the nature of the cis ligand L'. The effect of L' is also observed on the H6' and H4 protons. As expected (see Table 1), the H6' resonances have similar ${}^{3}J_{\text{Pt-H}}$ values but chemical shifts dependent on L'. In contrast, the chemical shifts of the H4 protons are almost invariant, whereas ${}^{3}J_{\text{Pt-H}}$ is dependent on L' and reflects its trans influence.

In addition to the ¹H NMR, the ³¹P NMR of **1b** (δ 33.6, ¹J_{Pt-P} = 2229 Hz) and the IR spectrum of **1c** (ν_{CO} 2044 cm⁻¹)^{11c} also support the proposed geometry.

The cyclometalated ring in complex **1a** is rather robust and, at least under mild conditions, e.g. at room temperature, it is not attacked by HCl or neutral two-electron ligands. The reaction of **1a** with HCl (1/1 Pt/HCl molar ratio) gives the chloride complex [Pt(L-H)(Cl)(DMSO)] (**3a**) with loss of methane (eq 3).



Under our reaction conditions, neither protonation of the free nitrogen atom nor cleavage of the Pt–C(sp²) bond is observed. Reaction 3 occurs with isomerization to a trans Cl–Pt–C arrangement, as previously observed with related species.^{8b} Assignment of the geometry mainly rests on the ¹H NMR spectra. The H6' resonance is strongly deshielded (δ 9.59), as expected, due to the close proximity of the chloride.¹³ Further evidence is provided by the ³*J*_{Pt–H} value of the DMSO methyl protons, 24.2 Hz, typical of a DMSO coordinated trans to a pyridine nitrogen atom.^{8b}

At variance with reaction 3, which leads to the corresponding chloride **3a** as the main product (yield ca. 70%), reaction of **1a** with excess HCl gives a mixture of products that was not further pursued. To shed some light on the behavior of the nitrogen atom toward protonation, the reaction of **1a** was carried out with HBF₄ • 18-crown-6, having a noncoordinating anion. Surprisingly, no attack at the platinum-methyl bond occurs, only selective protonation of the uncoordinated nitrogen to give $[Pt(L^*)(Me)(DMSO)][BF_4]$ (**5**), where the zwitterionic ligand L* is still N,C bonded to platinum.

Complex 5 is an interesting compound due to the nature of the ligand L^* which can be envisaged as a tautomeric form of the neutral 2,2'-bipyridine. Its characterization mainly rests on NMR, IR, and analytical data. In particular, the ¹H NMR

⁽¹²⁾ In this series, obtained by direct substitution of DMSO, we isolated also the carbonyl complex 1c, in contrast with the behavior of the analogous phenylpyridine cyclometalated complex.^{11a}



spectrum clearly shows a broad signal at δ ca. 13, due to the N–H proton. Complex **5** is rather stable in solution. After 24 h at room temperature or 1 h at 50 °C in CDCl₃ no decomposition is observed by ¹H NMR. Heating in acetone results in methane loss (from NH⁺ and Pt-CH₃) and unidentified species are formed.

From **3a** other complexes can be obtained by substitution of DMSO with PPh₃ (**b**), CO (**c**), and 3,5-(Me)₂-py (**d**): [Pt(L-H)(Cl)(PPh₃)] (**3b**), [Pt(L-H)(Cl)(CO)] (**3c**), and [Pt(L-H)(Cl)(3,5-(Me)₂-py)] (**3d**).



In the ¹H NMR spectra the H6' resonance is observed in all cases at very low field, due to the proximity of the coordinated chloride. The H₄ proton is shielded in **3b,d**, owing to the effect of the aromatic rings in PPh₃ and 3,5-(Me)₂-py, respectively. In the IR spectrum of **3c**, ν_{CO} is observed at 2107 cm⁻¹, as expected at higher wavenumber, in comparison to 2044 cm⁻¹ in **1c**.

The crystal structure of complex 3b has been determined by X-ray diffraction. It consists of the packing of **3b** molecules with no unusual van der Waals contacts. In the asymmetric unit there are two crystallographically independent **3b** molecules, hereinafter called molecule 1 and molecule 2. Molecules 1 and 2 are very similar to each other (see Table 3). An $ORTEP^{14}$ view of molecule 1 is shown in Figure 1. Selected bond lengths and angles for both molecules are reported in Table 3. In both molecules the platinum atom displays a square-planar coordination with a slight tetrahedral distortion. Maximum distances from the best planes are +0.043(2) and -0.050(3) Å for atoms N1 and C7, respectively, in molecule 1 and +0.071(1) and -0.105(2) Å for atoms Cl and N1, respectively, in molecule 2. Bond parameters reported in Table 3 can be compared with corresponding parameters found in $[PtCl(L^1)(SMe_2)]$ (HL¹ = 6-tert-butyl-2,2'-bipyridine),^{8a} the only "rollover" mononuclear bipyridine complex so far characterized by X-ray analysis. In the latter species, having a sulfur atom in place of a phosphorus, Pt-Cl = 2.395(2) Å, Pt-N = 2.042(4) Å, and Pt-C7 =1.990(5) Å. The agreement with the values reported in Table 3 is good, with the exception of the present average Pt-N, 2.094(2) Å, which can be considered elongated by the higher trans influence of phosphorus with respect to that of sulfur. The present average Pt-P distance, 2.230(1) Å, is statistically



Figure 1. ORTEP view of molecule 1 in 3b. Ellipsoids are drawn at the 30% probability level.

Table 3. Selected Bond Distances (Å) and Angles (deg) in the Two
Independent Molecules of 3b, with Estimated Standard Deviations
(Esd's) on the Last Figure Given in Parentheses

	molecule 1	molecule 2
Pt-Cl	2.380(1)	2.379(1)
Pt-P	2.233(1)	2.228(1)
Pt-N1	2.097(2)	2.091(2)
Pt-C7	2.008(3)	2.002(3)
N1-C1	1.349(3)	1.348(3)
C1-C6	1.463(4)	1.467(4)
C6-C7	1.416(4)	1.413(4)
Cl-Pt-P	92.75(2)	93.35(2)
Cl-Pt-N1	90.77(6)	91.51(6)
Cl-Pt-C7	170.97(7)	171.59(7)
P-Pt-N1	176.24(6)	171.86(5)
P-Pt-C7	95.80(7)	94.68(8)
N1-Pt-C7	80.77(10)	80.82(9)

coincident with the average value of 2.228(1) Å found in $[Pt_2(L^2)Cl(PPh_3)_2]$ (H₃L² = 6-phenyl-2,2'-bipyridine¹⁵).

Dinuclear Complexes. When the reaction of $[Pt(Me)_2(DMSO)_2]$ with 2,2'-bipy is carried out with a 2/1 Pt/L molar ratio, a double C–H bond activation occurs and the dinuclear species $[Pt_2(\mu-L-2H)(Me)_2(DMSO)_2]$ (**2a**) is obtained. The second metalation appears to be slightly favored with respect to the first one, as complex **2a** is also produced with a 1/1 Pt/L molar ratio.



Alternatively, 2a can be obtained by a two-step approach:

⁽¹³⁾ For example: (a) Byers, P. K.; Canty, A. J. *Organometallics* **1990**, *9*, 210. (b) Sanna, G.; Minghetti, G.; Zucca, A.; Pilo, M. A.; Seeber, R.; Laschi, F. *Inorg. Chim. Acta* **2000**, *305*, 189–205.

⁽¹⁴⁾ Johnson, C. K.; ORTEP, Report No. ORNL-5138; Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

 $[Pt(Me)_2(DMSO)_2] + 2, 2'-bipy \rightarrow$

$$\frac{[Pt(L-H)(Me)(DMSO)]}{1a}$$
(1)

$$[Pt(L-H)(Me)(DMSO)] + [Pt(Me)_2(DMSO)_2] \rightarrow [Pt_2(\mu-L-2H)(Me)_2(DMSO)_2]$$

$$2a \qquad (5)$$

The second step of the synthesis underlines the potential ability of the mononuclear derivate to act as a Lewis base, at least toward $[Pt(Me)_2(DMSO)_2]$.

In the ¹H NMR spectrum the presence of one set only of signals and the absence of the C(3)-H protons support a symmetric 2-fold metalated structure for **2a**. Also in this case the geometry has been definitively confirmed by NOE difference experiments (see the Experimental Section).

Substitution of DMSO in $[Pt_2(\mu-L-2H)(Me)_2(DMSO)_2]$ (2a) with PPh₃, CO, and 3,5-(Me)₂-py is straightforward, giving complexes 2b-d, respectively:

$$[Pt_{2}(\mu-L-2H)(Me)_{2}(DMSO)_{2}] + L' \rightarrow 2a$$

$$[Pt_{2}(\mu-L-2H)(Me)_{2}(L')_{2}]$$

2b,
$$L' = PPh_3$$

2c, $L' = CO$
2d, $L' = 3,5-(Me)_2$ -py (6)

The reaction of 2a with HCl is also comparable to that of the corresponding mononuclear derivative 1a: also in this case only the Pt-CH₃ bond is attacked.

$$[Pt_{2}(\mu-L-2H)(Me)_{2}(DMSO)_{2}] + 2HCI \rightarrow 2a$$

$$[Pt_{2}(\mu-L-2H)(Cl)_{2}(DMSO)_{2}] + 2CH_{4}$$

$$4a \qquad (7)$$

Exchange of L' for DMSO allows us to obtain other dinuclear derivatives: $[Pt_2(\mu-L-2H)(Cl)_2(PPh_3)_2]$ (**4b**) and $[Pt_2(\mu-L-2H)(Cl)_2(3,5-(Me)_2-py)_2]$ (**4d**).

Complexes 2 and 4 are not trivial species: the 2-fold deprotonated 2,2'-bipyridine acts on the whole as an eightelectron, tetradentate dianionic ligand. The bridging organic moiety comprises two fused five-membered cyclometalated rings in addition to the pyridine rings.¹⁶



Figure 2. ORTEP view of **4b**. The molecule lies on a crystallographic inversion center. Ellipsoids are as in Figure 1.

Table 4. Selected Bond Lengths (Å) and	Angles (deg) in 4b, with				
Estimated Standard Deviations (Esd's) on	the Last Figure Given in				
Parentheses					

Pt-Cl1 Pt-N N-C(1) C1'-C2'	2.351(1) 2.107(2) 1.349(3) 1.401(3)	Pt-P Pt-C2' C1-C1'	2.236(1) 2.016(2) 1.439(3)
Cl1-Pt-P Cl1-Pt-C2' P-Pt-C2'	93.41(2) 170.56(6) 94.89(6)	Cl1-Pt-N P-Pt-N N-Pt-C2'	90.41(5) 176.03(5) 81.40(7)

The crystal structure of the complex 4b • 2CHCl₃ consists of the packing of **4b** and CHCl₃ molecules in the molar ratio 1/2 with no unusual van der Waals contacts. An ORTEP¹⁴ view of 4b is shown in Figure 2. Selected bond distances and angles are reported in Table 4. Molecule 4b lies on a crystallographic inversion center. The platinum atom displays a square-planar coordination with a tetrahedral distortion. Maximum distances from the best plane are +0.068(2) and -0.055(2) Å for atoms C(2') and N(2), respectively. The two fused pentaatomic rings Pt-N-C2'-C1'-C1-N'-Pt'-C2 are quasi-planar, maximum distances from the best plane being +0.019(2) and -0.019(2)Å for atoms C2 and C2', respectively. Bond parameters reported in Table 5 can be compared with corresponding parameters found in $[Pt_2(L^2)Cl(PPh_3)_2]$ (H₃L² = 6-phenyl-2,2'-bipyridine),¹⁵ where the atom Pt(1) is in the same environment found here: Pt1-Cl1 = 2.347(1) Å, Pt1-P1 = 2.225(1) Å, Pt1-N2 =2.119(3) Å, and Pt1-C3 = 2.010(4) Å. An inspection of Table 4 shows that in all cases the agreement is very good.

Reaction 5, i.e. the second step in the synthesis of these dinuclear derivatives, calls attention to the capability of the mononuclear species to act as a Lewis base, at least toward the $[Pt(Me)_2(DMSO)_2]$ precursor. It is worthy of note that in the case of 6-substitued 2,2'-bipyridines this chemical behavior is not common. With most of the substituents studied (Me, C(Me)_3, CH_2Ph, etc.) the second rollover metalation was not observed. Only in the case of a phenyl substituent did the reaction proceed to give C,N,C pincer complexes.^{11b,17} The peculiar reactivity of the uncoordinated nitrogen atom in the 2,2'-bipyridine mononuclear derivatives makes the two-step

⁽¹⁵⁾ Zucca, A.; Cinellu, M. A.; Minghetti, G.; Stoccoro, S.; Manassero, M. Eur. J. Inorg. Chem. 2004, 4484–4490.

⁽¹⁶⁾ Comparison of the ¹H NMR spectra of **1a** and **2a** deserve comments with regard to the resonances of the H6/H6' protons. In the mononuclear species 1a, coordination to the metal leads to an opposite effect in the two rings: in comparison with the free ligand, H6' is strongly deshielded, with $\Delta \delta (\delta_{\text{complex}} - \delta_{\text{ligand}}) = \text{ca. 1.1 ppm, and H6 slightly shielded, with } \Delta \delta =$ ca. -0.25 ppm. The deshielding of H6' has been previously observed in analogous cyclometalates involving 6-substituted 2,2'-bipyridines: $\Delta\delta$ is known to be mainly dependent on the nature of the ligand close to H6'. The upfield shift of H6 is obviously observed here for the first time. In 2a the protons close to the nitrogen atoms, H6, are equivalent and less deshielded, $\Delta \delta = ca. 0.55$ ppm, than H6' in **1a**, even though the chemical environment around the platinum atoms in 2a is the same as in 1a. The opposite effects on the charge distribution inside the bridging ligand, observed in the mononuclear 1a, are roughly averaged in the dinuclear 2a. The same is also observed comparing the corresponding chlorides 3a and 4a. A recent work⁶ has pointed out that in 2,2'-bipyridine rotation around the C2-C2' bond on going from the anti to the cis conformation inherently entails a change in the charge distribution inside the rings.

Cyclometalation of 2,2'-Bipyridine

approach a synthetic strategy of great potential. Indeed, in addition to the symmetric species $2\mathbf{a}-\mathbf{d}$ and $4\mathbf{a}-\mathbf{d}$, taking advantage of the two-step approach, it is also possible to build up dinuclear unsymmetric systems where the platinum atoms are in different environments, e.g. the complexes [(DMSO)-(Cl)Pt(μ -L-2H)Pt(Me)(DMSO)] (**6**; different anions, Me and Cl), [(PPh₃)(Me)Pt(μ -L-2H)Pt(Me)(DMSO)] (**7**; different ligands, PPh₃ and DMSO), and [(CO)(Cl)Pt(μ -L-2H)Pt(Me)(DMSO)] (**8**; different anions and ligands), obtained according to reactions 8-10.

$$[Pt(L-H)(Cl)(DMSO)] + [Pt(Me)_2(DMSO)_2] \rightarrow [(DMSO)(Cl)Pt(\mu-L-2H)Pt(Me)(DMSO)]$$

$$6 \qquad (8)$$

$$[Pt(L-H)(Me)(PPh_3)] + [Pt(Me)_2(DMSO)_2] \rightarrow [(PPh_3)(Me)Pt(\mu-L-2H)Pt(Me)(DMSO)] 7$$
(9)

$$[Pt(L-H)(Cl)(CO)] + [Pt(Me)_2(DMSO)_2] \rightarrow [(CO)(Cl)Pt(\mu-L-2H)Pt(Me)(DMSO)]$$
8 (10)

Compounds **6–8** can be isolated in reasonable yields and are stable in air: they have been characterized by elemental analyses and, for **6** and **7**, by NMR spectra. The ¹H NMR spectra of **6** and **7** give clear evidence of the lack of symmetry, exhibiting six well-separated resonances for the aromatic protons. Characterization in solution of compound **8** is hampered by its solubility: in the IR spectra v_{CO} is observed at 2090 cm⁻¹, a value consistent for a carbonyl in a platinum—chloride system.

In a first attempt to study the coordinating behavior of the second nitrogen atom toward a different metal, we studied the reaction of **3a** with Na[AuCl₄]. The reaction did not afford platinum–gold derivatives but, likely due to the strong oxidative capability of gold(III), gave a platinum(IV) complex, [Pt(L-H)Cl₃(DMSO)] (**9**), which was isolated and characterized.

Conclusions

In the present study we have described aspects of the reactivity of 2,2'-bipyridine, one of the most common ligands in the coordination chemistry of transition metal ions; we have shown the following.

(i) Under specific conditions, direct C(3) metalation of 2,2'bipy can be achieved by reaction with adducts of the "Pt(Me)₂" fragment. Series of mononuclear, [Pt(bipy-H)(X)(L)], and dinuclear, [Pt₂(bipy-2H)(X)₂(L)₂], cyclometalates (X = Me, Cl; L = neutral ligands) have been synthesized and characterized in solution and, in two cases, in the solid state (X-ray analysis).

(ii) In the mononuclear derivatives protonation of the uncoordinated nitrogen atom can be accomplished. Reaction with an acid having a noncoordinating anion allowed, at least in one case, isolation and characterization of a cationic species where the N'-C(3) coordinated zwitterionic ligand can be envisaged as a tautomeric form of 2,2'-bipyridine.

(iii) Dinuclear derivatives can be built up by a two-step approach to get species with different anions and different ligands on each platinum center. This strategy allows us to tune the electronic and steric properties of the environment around each platinum atom, making the dinuclear species good substrates for studies relevant, for example, to oxidative addition reactions.¹⁸ Furthermore, preliminary results indicate that the



same strategy can successfully be applied to the synthesis of noteworthy heterodinuclear derivatives.¹⁸

Experimental Section

[Pt(Me)₂(DMSO)₂] was synthesized according to ref 19.

All the solvents were purified and dried according to standard procedures.²⁰ Elemental analyses were performed with a Perkin-Elmer 240B elemental analyzer by Mr. Antonello Canu (Dipartimento di Chimica, Università degli studi di Sassari, Sassari, Italy). Infrared spectra were recorded with a FT-IR Jasco 480P instrument using Nujol mulls. ¹H, ¹³C{¹H}, and ³¹P{¹H} 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 for ¹H and ¹³C{¹H} and external 85% H₃PO₄ for ³¹P{¹H}. J values are given in Hz. NOE difference, 2D-COSY, and 2D-HETCOR experiments were performed by means of standard pulse sequences. Conductivities were measured with a Philips PW 9505 conductimeter. The ESI mass spectrometric measurements were performed on a quadrupole time-of-flight nano ESI-Q-TOF instrument (Q-Tof Ultima, Waters, Manchester, U.K.) equipped with a nanoelectrospray ion source, calibrated in positive mode. Compounds 1a-d, 2a-d, 3a-d, and 4a-c are shown in Chart 2, and the numbering scheme used is given in Chart 3.

Synthesis of [Pt(L-H)(Me)(DMSO)] (1a). To a solution of 2,2'bipyridine (430 mg, 2.75 mmol) in anhydrous toluene (50 mL) was added 350 mg of *cis*-[Pt(Me)₂(DMSO)₂] (0.918 mmol): the color of the solution rapidly changed to red. The stirred solution, kept under a nitrogen atmosphere, was heated to 110 °C. During the heating, the solution color changed from red to yellow. After 3 h the mixture was cooled to room temperature, concentrated to a small volume, and treated with *n*-hexane to form a yellow precipitate. The solid was filtered off, washed with *n*-hexane, and vacuum-

⁽¹⁷⁾ Zucca, A.; Petretto, G. L.; Stoccoro, S.; Cinellu, M. A.; Minghetti, G.; Manassero, M.; Manassero, C.; Male, L.; Albinati, A. *Organometallics* **2006**, *25*, 2253–2265.

⁽¹⁸⁾ Work in progress.

^{(19) (}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.

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



pumped to give an analytical sample as a yellow solid in almost quantitative yield. Mp: 95 °C. Anal. Calcd for C13H16N2OPtS: C. 35.21; H, 3.64; N, 6.32. Found: C, 35.49; H, 3.20; N, 6.42. ¹H NMR (CDCl₃): δ 9.71 (dd, 1H, $J_{H-H} = 5.2$ Hz, $J_{Pt-H} = 14$ Hz, $H_{6'}$), 8.36 (dd, 1H, $J_{H-H} = 5.4$ Hz, $J_{H-H} = 1.2$ Hz, H_{6}), 8.29 (d, 1H, $J_{H-H} = 7.5$ Hz, $H_{3'}$), 8.01 (dd, 1H, $J_{Pt-H} = 56.0$ Hz, $J_{H-H} =$ 1.5 Hz, $J_{H-H} = 7.8$ Hz, H₄), 7.95 (td, 1H, $J_{H-H} = 7.5$ Hz, H₄'), 7.36 (m, 1H, $J_{H-H} = 5.2$ Hz, $J_{H-H} = 7.5$ Hz, $J_{H-H} = 1.5$ Hz, $H_{5'}$), 7.17 (dd, 1H, $J_{H-H} = 4.5$ Hz, $J_{H-H} = 7.8$ Hz, H₅), 3.25 (s, 6H, $J_{\text{Pt-H}} = 18.3 \text{ Hz}, \text{ Me(DMSO)}, 0.70 \text{ (s, 3H, } J_{\text{Pt-H}} = 82 \text{ Hz}, \text{ Me-}$ Pt). NOE difference spectrum (CDCl₃): irradiation at δ 0.70 (CH₃-Pt) gives enhancement of the signals at δ 8.01 (dd, H₄) and 3.25 (coordinated DMSO). ¹³C NMR (75.4 MHz; CDCl₃): δ –13.4 $(CH_3-Pt, J_{Pt-C} = 763 \text{ Hz}), 43.73 \text{ (DMSO, } J_{Pt-C} = 42.1 \text{ Hz}), 121.17$ (CH), 123.87 (CH), 124.50 (CH), 138.51 (CH), 140.26 (CH), 145.10 $(C-Pt, {}^{1}J_{Pt-C} = 1090 \text{ Hz}), 145.76 (CH), 150.33 (CH), 162.50 (Cq,$ $J_{\text{Pt-C}} = 55 \text{ Hz}$), 164.80 (Cq, $J_{\text{Pt-C}} = 24 \text{ Hz}$).

Synthesis of [Pt(L-H)(Me)(PPh₃)] (1b). To a solution of 1a (50.6 mg, 0.12 mmol) in CH₂Cl₂ (15 mL) was added 31.6 mg of PPh₃ (0.12 mol): the solution was stirred and kept under a nitrogen atmosphere. After 2 h the solution was concentrated to a small volume under reduced pressure 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: 67%. Mp: 215 °C. Anal. Calcd for C₂₉H₂₅N₂PPt · ¹/₂H₂O: C, 54.72; H, 4.12; N, 4.40. Found: C, 54.67; H, 3.79; N, 4.51. ¹H NMR (CDCl₃): δ 8.40 (m, 1H, H₆), 8.31 (dd, 1H, $J_{H-H} = 8.0$ Hz, $J_{\text{H-H}} = 1.5 \text{ Hz}, \text{H}_{3'}$, 8.24 (ddd, 1H, $J_{\text{H-H}} = 1.8 \text{ Hz}, J_{\text{H-H}} = 5.4$ Hz, $J_{H-H} = 7.5$ Hz, $J_{Pt-H} = 48$ Hz, H₄), 7.79–7.72 (m, 7H, H_{4'} + H_o PPh₃), 7.46-7.35 (m, 10H, H₆' + H_{m+p} PPh₃), 7.22 (ddd, 1H, $J_{\text{H-H}} = 1.7 \text{ Hz}, J_{\text{H-H}} = 7.8 \text{ Hz}, J_{\text{H-H}} = 7.5 \text{ Hz}, H_5$, 6.67 (td, 1H, $J_{\text{H-H}} = 1.5 \text{ Hz}, J_{\text{H-H}} = 5.4 \text{ Hz}, \text{H}_{5'}$, 0.74 (d, 3H, $J_{\text{P-H}} = 7.7 \text{ Hz}$, $J_{\text{Pt-H}} = 83 \text{ Hz}, \text{ Me-Pt}$). ³¹P NMR (121.4 MHz; CDCl₃; H₃PO₄): δ 33.59 (s, $J_{Pt-P} = 2229$ Hz, PPh₃).

Synthesis of [Pt(L-H)(Me)(CO)] (1c). In a solution of 1a (50.0 mg, 0.113 mmol) in 15 mL of CH₂Cl₂, CO was bubbled at room temperature. After 3 h the solution was concentrated to a small volume under reduced pressure and treated with *n*-hexane. The precipitate that formed was filtered, washed with *n*-hexane, and vacuum-pumped to give the analytical sample as a dark solid. Yield: 41%, Mp: 137 °C dec. Anal. Calcd for C₁₂H₁₀N₂OPt: C, 36.65; H, 2.56; N, 7.12. Found: C, 36.42; H, 2.31; N, 6.98. ¹H NMR (CDCl₃): δ 8.65 (dd, 1H, $J_{\text{H-H}} = 5.1$ Hz, $J_{\text{Pt-H}} = 19.8$ Hz, $H_{6'}$), 8.40 (dd, 1H, $J_{H-H} = 1.5$ Hz, $J_{H-H} = 4.8$ Hz, H₆), 8.33 (d, 1H, $J_{H-H} = 8.0$ Hz, H_{3'}), 8.06 (dd, 1H, $J_{Pt-H} = 46$ Hz, $J_{H-H} = 1.6$ Hz, $J_{H-H} = 7.8$ Hz, H₄), 8.03 (ddd, 1H, $J_{H-H} = 7.6$ Hz, $J_{H-H} = 8.0$ Hz, $J_{H-H} =$ 1.6 Hz, $J_{Pt-H} = 17.4$ Hz, $H_{4'}$), 7.35 (ddd, 1H, $J_{H-H} = 1.5$ Hz, J_{H-H} = 5.1 Hz, J_{H-H} = 7.6 Hz, $H_{5'}$), 7.24 (dd, 1H, J_{Pt-H} = 17.4 Hz, $J_{\text{H}-\text{H}} = 4.8 \text{ Hz}, J_{\text{H}-\text{H}} = 7.8 \text{ Hz}, \text{H}_5$, 1.19 (s, 3H, $J_{\text{Pt}-\text{H}} = 85.7 \text{ Hz}$ CH₃-Pt). FT-IR (Nujol; cm⁻¹): 2044, s.

Synthesis of [Pt(L-H)(Me)(3,5-Me₂-pyridine)] (1d). To a solution of 1a (50 mg, 0.113 mol) in acetone (15 mL) was added 0.06 mL of 3,5-Me₂-pyridine (0.56 mmol, d = 0.939 g/mL, ca. 5-fold excess): the solution was stirred and heated to reflux under a nitrogen atmosphere. After 2 h the solvent was concentrated to a small volume under reduced pressure and treated with *n*-hexane to form a precipitate. The solid obtained was filtered off, washed with *n*-hexane, and vacuum-pumped to give the analytical sample as a

yellow solid. Yield: 66%. Mp: 215 °C dec. Anal. Calcd for $C_{18}H_{19}N_3Pt$: C, 45.76; H, 4.05; N, 8.89. Found: C, 45.51; H, 3.86; N, 8.92. ¹H NMR (CDCl₃): δ 8.51 (s, 1H, $J_{Pt-H} = 23.1$ Hz, H_o lutidine), 8.29–8.24 (m, 2H, H₆ + H₃'), 8.10 (dd, 1H, $J_{H-H} = 1.5$ Hz, $J_{H-H} = 7.8$ Hz, $J_{Pt-H} = 60.4$ Hz, H₄), 7.88 (broad td, 1H, $J_{H-H} = 7.8$ Hz, $H_{4'}$), 7.76 (d, 1H, $J_{H-H} = 5.4$ Hz, $J_{Pt-H} = ca. 20$ Hz, H₆'), 7.50 (s, 1H, H_p lutidine), 7.14 (t, 1H, $J_{H-H} = 5.4$ Hz, H₅'), 7.07 (dd, 1H, $J_{H-H} = 4.8$ Hz, $J_{H-H} = 7.6$ Hz, H₅), 2.39 (s, 6H, CH₃ 3,5-lutidine), 0.94 (s, 3H, $J_{Pt-H} = 84.2$ Hz, CH₃–Pt).

Synthesis of [Pt₂(L-2H)(Me)₂(DMSO)₂] (2a). To a solution of 2,2'-bipyridine (61.5 mg, 0.394 mmol) in anhydrous toluene (25 mL) was added 300 mg of cis-[Pt(Me)₂(DMSO)₂] (0.787 mmol): the color of the solution rapidly changed to red. The stirred solution, kept under a nitrogen atmosphere, was heated to 110 °C. During the heating, the color of the solution changed from red to yellow. After 8 h the mixture was cooled to room temperature, concentrated to a small volume, and treated with diethyl ether to form a yellow precipitate. The solid was filtered off, washed with diethyl ether, and vacuum-pumped to give the analytical sample as a yellow solid in almost quantitative yield. Mp: >260 °C. Anal. Calcd for C₁₆H₂₄N₂O₂Pt₂S₂: C, 26.30; H, 3.31; N, 3.83. Found: C, 26.56; H, 3.19; N, 3.78. ¹H NMR (CDCl₃): δ 9.14 (dd, 2H, $J_{H-H} = 5.2$ Hz, $J_{\text{H-H}} = 1.3 \text{ Hz}, \text{H}_{6}/\text{H}_{6'}$, 8.05 (dd, 2H, ${}^{3}J_{\text{H-H}} = 7.8 \text{ Hz}, {}^{4}J_{\text{H-H}} = 1.3$ Hz, ${}^{3}J_{Pt-H} = 51.3$ Hz, H₄/H₄'), 7.14 (dd, 2H, ${}^{3}J_{H-H} = 5.2$, 7.8 Hz, $H_5/H_{5'}$), 3.23 (s, 6H, ${}^{3}J_{Pt-H} = 18.7$ Hz, CH₃ (DMSO)), 0.67 (s, 3H, ${}^{2}J_{\text{Pt}-\text{H}} = 80.8 \text{ Hz}, \text{CH}_{3}-\text{Pt}$). NOE difference spectrum (CDCl₃): irradiation at δ 0.67 (s, CH₃-Pt) gives enhancement of the signals at δ 8.05 (dd, H₄) and 3.23 (s, coordinated DMSO). ¹³C NMR (75.4 MHz; CDCl₃): δ 15.2 ($J_{Pt-C} = 740.2$ Hz, CH₃-Pt), 43.83 ($J_{Pt-C} =$ 45.7 Hz, DMSO), 123.75 ($J_{Pt-C} = 61.9$ Hz, CH), 141.9 (J = 87.5Hz, CH), 141.6 (Cq), 145.9 (CH), 173.2 (Cq).

Synthesis of $[Pt_2(L-2H)(Me)_2(PPh_3)_2]$ (2b). To a solution of 2a (30.0 mg, 0.041 mmol) in CH₂Cl₂ (10 mL) was added 21.5 mg of PPh₃ (0.082 mmol): the solution was stirred under a nitrogen atmosphere for 2 h. During the reaction a yellow precipitate was formed. The solid was filtered off, washed with diethyl ether, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 71%. Mp: >260 °C. Anal. Calcd for C₄₈H₄₂N₂P₂Pt₂·H₂O: C, 51.61; H, 3.97%; N, 2.51. Found: C, 51.56; H, 3.12; N, 2.48. ¹H NMR (CDCl₃): δ 8.13 (m, 2H, J_{Pt-H} = 42 Hz, J_{H-H} = J_{P-H} = ca. 6.5 Hz, H_{4/4}'), 7.76 (m, 12H, H_o PPh₃), 7.40 (m, 20H, H_p + H_m (PPh₃) + H_{6/6}'), 6.57 (m, 2H, J_{H-H} = 5.4 Hz, J_{H-H} = 7.5 Hz, J_{P-H} = 2.1 Hz, H_{5/5}'), 0.62 (d, 6H, J_{P-H} = 7.4 Hz, J_{Pt-H} = 81.4 Hz, CH₃-Pt). ³¹P NMR (121.4 MHz; CDCl₃): δ 33.29 (¹J_{Pt-P} = 2347 Hz).

Synthesis of $[Pt_2(L-2H)(Me)_2(CO)_2]$ (2c). In a solution of 2a (25.0 mg, 0.034 mmol) in 15 mL of CH₂Cl₂, CO was bubbled at room temperature. After 3 h the solution was concentrated to a small volume in vacuo and treated with diethyl ether. The precipitate that formed was filtered, washed with *n*-pentane, and vacuum-pumped to give the analytical sample as a red solid. Yield: 90%. Mp: 255 °C dec. Anal. Calcd for C₁₄H₁₂N₂O₂Pt₂: C, 26.67; H, 1.92; N, 4.44. Found: C, 26.62; H, 1.64; N, 4.23. ¹H NMR (CDCl₃): δ 8.27 (dd, 2H, $J_{H-H} = 5.2$ Hz, $J_{H-H} = 1.4$ Hz, $J_{Pt-H} = 22$ Hz, $H_{6/6'}$, 8.16 (dd, 2H, $J_{H-H} = 7.4$ Hz, $J_{H-H} = 1.3$ Hz, $J_{Pt-H} = 45$ Hz, $H_{4/4'}$), 7.20 (m, 2H, overlapping with the solvent, $H_{5/5'}$), 1.17 (s, 6H, $J_{Pt-H} = 83.8$ Hz, CH₃-Pt). FT-IR (Nujol; cm⁻¹): 2048, s.

Synthesis of [Pt₂(L-2H)(Me)₂(3,5-Me₂Py)₂] (2d). To a solution of 2a (50.0 mg, 0.068 mmol) in 15 mL of acetone was added 1.37 mmol of 3,5-Me₂Py. The solution was stirred and heated to reflux. After 8 h the solvent was concentrated to a small volume under reduced pressure and treated with *n*-pentane. The precipitate that formed was filtered, washed with *n*-pentane, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 76%. Mp: >260 °C. Anal. Calcd for C₂₆H₃₀N₄Pt₂: C, 39.59; H, 3.83; N, 7.10. Found: C, 39.17; H, 3.54; N, 6.80. ¹H NMR (CDCl₃): δ 8.52 (s, 4H, J_{Pt-H} = 23.4 Hz, H_o lutidine), 8.05 (dd, 2H, J_{H-H} = 1.2 Hz, $J_{\text{H}-\text{H}} = 7.7 \text{ Hz}, J_{\text{Pt}-\text{H}} = 54.6 \text{ Hz}, H_{4/4'}$), 7.47 (s, 2H, H_p lutidine), 7.25 (m, partially overlapping with the solvent, H_{6/6'}), 6.86 (dd, 2H, $J_{\text{H}-\text{H}} = 5.1 \text{ Hz}, J_{\text{H}-\text{H}} = 7.7 \text{ Hz}, H_{5/5'}$), 2.38 (s, 12H, CH₃ 3,5-lutidine), 0.91 (s, $J_{\text{Pt}-\text{H}} = 82.8 \text{ Hz}, 6\text{H}, \text{CH}_3-\text{Pt}$).

Synthesis of [Pt(L-H)(Cl)(DMSO)] (3a). To a solution of 1a (200 mg, 0.451 mmol) in 50 mL of acetone were added with vigorous stirring 2 mL of DMSO and 4.5 mL of aqueous 0.1 M HCl (0.451 mmol). After 8 h the solution was concentrated to a small volume: complex 3a was extracted with CH2Cl2, dried with Na₂SO₄, and concentrated to a small volume. The residue was then treated with *n*-hexane to form a precipitate which was filtered, washed with *n*-hexane, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 70%. Mp: 142 °C. Anal. Calcd for C₁₂H₁₃N₂ClOPtS: C, 31.07; H, 2.82; N, 6.04. Found: C, 31.41; H, 2.89; N, 5.86. ¹H NMR (CDCl₃): δ 9.59 (dd, 1H, $J_{H-H} = 0.8$, 1.6, 5.2 Hz, $J_{Pt-H} = 36$ Hz, $H_{6'}$), 8.60 (dd, 1H, $J_{H-H} = 1.5$, 8.0 Hz, $J_{\text{Pt-H}}$ = 42 Hz, H₄), 8.37 (dd, 1H, $J_{\text{H-H}}$ = 1.5, 4.8 Hz, H₆), 8.22 (d br, 1H, $J_{H-H} = 7.7$ Hz, $H_{3'}$), 7.98 (td, 1H, $J_{H-H} = 1.6$, 7.7 Hz, $H_{4'}$), 7.40 (m, 1H, $J_{H-H} = 1.6$, 5.2, 7.7 Hz, $H_{5'}$), 7.08 (dd, 1H, $J_{H-H} =$ 4.8, 8.0 Hz, $J_{Pt-H} = 16.5$ Hz, H₅), 3.65 (s, 6H, $J_{Pt-H} = 24.2$ Hz, CH₃(DMSO)). ¹³C NMR (75.4 MHz; CDCl₃): δ 47.02 (J_{Pt-C} = 59.8 Hz, CH₃ DMSO); 121.4 ($J_{Pt-C} = 41.2$ Hz, C₃'), 123.8 (J_{Pt-C} = 31.8 Hz, $C_{5'}$), 124.6 (J_{Pt-C} = 45.8 Hz, C_{5}), 136.5 (J_{Pt-C} = 1102.9 Hz, C_3 -Pt), 140.8 (n.o., $C_{4'}$), 141.2 ($J_{Pt-C} = 48.9$ Hz, C_4), 145.6 (n.o., C₆), 149.3 ($J_{Pt-C} = 21.0 \text{ Hz}$, C₆'), 162.1 ($J_{Pt-C} = 59.5 \text{ Hz}$), 163.4 ($J_{Pt-C} = 74.1 \text{ Hz}$) (C₂ and C_{2'}). ¹H and ¹³C assignments were made on the basis of ¹H-¹H COSY and ¹H-¹³C HETCOR spectra.

Synthesis of [Pt(L-H)(Cl)(PPh₃)] (3b). To a solution of 3a (140 mg, 0.304 mmol) in CH₂Cl₂ (25 mL) was added 79.6 mg of PPh₃ (0.304 mol): the solution was stirred and kept under a nitrogen atmosphere for 2 h. The solvent was concentrated to a small volume under reduced pressure and treated with n-hexane to form a precipitate which was filtered off, washed with n-hexane, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 88%. Mp >260 °C. Anal. Calcd for $C_{29}H_{25}N_2PPt$: C, 55.50; H, 4.02; N, 4.46. Found: C, 55.18; H, 3.87; N, 4.71. ¹H NMR (CDCl₃): δ 9.85 (m, 1H, broad, $J_{Pt-H} = 31$ Hz, H₆'), 8.26 (d, 1H, $J_{\text{H-H}} = 8.2 \text{ Hz}, \text{H}_{3'}$), 8.17 (dd, 1H, $J_{\text{H-H}} = 4.8 \text{ Hz}, \text{H}_{6}$), 8.0 (t, 1H, $J_{\text{H-H}} = 6.6 \text{ Hz}, J_{\text{H-H}} = 7.6 \text{ Hz}, H_{4'}), 7.82 - 7.62 \text{ (m, 6H, H}_o \text{ PPh}_3),$ 7.46–7.36 (m, 10H, $H_{5'} + H_{m+p}$ PPh₃), 6.85 (dd, 1H, $J_{H-H} = 8.0$ Hz, $J_{Pt-H} = 49$ Hz, H₄), 6.42 (dd, 1H, $J_{H-H} = 4.8$ Hz, $J_{H-H} = 8.0$ Hz, H₅). ³¹P NMR (124.8 MHz; CDCl₃; H₃PO₄): δ 23.6 (s, $J_{Pt-P} =$ 4285 Hz, PPh₃).

Synthesis of [Pt(L-H)(Cl)(CO)] (3c). In a solution of **3a** (80 mg, 0.17 mmol) in 25 mL of CH₂Cl₂, CO was bubbled at room temperature. After 3 h the solution was concentrated to a small volume under reduced pressure and treated with *n*-hexane. The precipitate that formed was filtered, washed with *n*-hexane, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 74%. Mp: 248 °C dec. Anal. Calcd for C₁₁H₇ClN₂OPt: C, 31.93; H, 1.71; N, 6.77. Found: C, 32.25; H, 1.04; N, 6.75. ¹H NMR (CDCl₃): δ 9.50 (dd, 1H, $J_{H-H} = 5.2$ Hz, $J_{Pt-H} = 34$ Hz, H₆'), 8.45 (dd, 1H, $J_{H-H} = 1.5$ Hz, $J_{H-H} = 5.2$ Hz, $J_{H-H} = 7.9$ Hz, H₄'), 7.78 (dd, 1H, $J_{Pt-H} = 62.7$ Hz, $J_{H-H} = 1.8$ Hz, $J_{H-H} = 7.9$ Hz, H₄), 7.53 (m, 1H, $J_{H-H} = 1.5$ Hz, $J_{H-H} = 5.2$ Hz, $J_{H-H} = 7.9$ Hz, H₅'), 7.06 (dd, 1H, $J_{Pt-H} = 18$ Hz, $J_{H-H} = 5.2$ Hz, $J_{H-H} = 7.8$ Hz, H₅). FT-IR (CH₂Cl₂, cm⁻¹): 2107, s.

Synthesis of [Pt(L-H)(Cl)(3,5-Me₂-pyridine)] (3d). To a solution of 3a (130 mg, 0.28 mmol) in acetone (25 mL) was added 0.12 mL of 3,5-Me₂-pyridine (1.23 mmol, d = 0.939 g/mL, ca. 4-fold excess): the solution was stirred and heated to reflux under a nitrogen atmosphere. After 4 h the solvent was concentrated to a small volume under reduced pressure and treated with *n*-hexane. The precipitate that formed was filtered off, washed with *n*-hexane, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 92%. Mp: 210 °C Anal. Calcd for C₁₇H₁₆ClN₃Pt: C, 41.43;

H, 3.27; N, 8.53. Found: C, 41.33; H, 3.03; N, 8.64. ¹H NMR (CDCl₃): δ 9.67 (s, 1H, $J_{Pt-H} = 39.5$ Hz, $J_{H-H} = 5.2$ Hz, $H_{6'}$), 8.61 (s, 2H, $J_{Pt-H} = 23.4$ Hz, H_o lutidine), 8.31 (dd, 1H, $J_{H-H} = 4.9$ Hz, H_6), 8.09 (d, 1H, $J_{H-H} = 8.0$ Hz, $H_{3'}$), 7.92 (t, 1H, $J_{H-H} = 7.6$ Hz, $J_{H-H} = 8.0$ Hz, $H_{4'}$), 7.49 (s, 1H, H_p lutidine), 7.30 (m, 1H, overlapping with CDCl₃, $H_{5'}$), 6.88 (dd, 1H, $J_{H-H} = 4.9$ Hz, $J_{H-H} = 7.8$ Hz, H_5), 6.68 (dd, 1H, $J_{Pt-H} = 7.8$ Hz, H_4), 2.38 (s, 6H, CH₃ 3,5-lutidine).

Synthesis of $[Pt_2(L-2H)(Cl)_2(DMSO)_2]$ (4a). To a suspension of 2a (84.0 mg, 0.115 mmol) in 40 mL of acetone were added 2 mL of DMSO and 2.3 mL of 0.1 M aqueous HCl (0.23 mmol). The suspension was stirred for 8 h, and then the solvent was concentrated to a small volume. Complex 4a was extracted with CH₂Cl₂, dried with Na₂SO₄, and concentrated to a small volume. The residue was then treated with diethyl ether to form a precipitate which was filtered and washed with diethyl ether to give the analytical sample as a yellow solid. Yield: 70%. Mp: >260 °C. Anal. Calcd for C₁₄H₁₈Cl₂N₂O₂Pt₂S₂: C, 21.80; H, 2.35; N, 3.63%. Found: C, 21.94; H, 1.72; N, 3.53. ¹H NMR (CDCl₃): δ 8.95 (d, 2H, J_{H-H} = 5.2 Hz, H_{6/6}), 6.64 (d, 2H, J_{H-H} = 7.6 Hz, H_{4/4}), 7.07 (dd, 2H, J_{H-H} = 5.2 Hz, J_{H-H} = 7.6 Hz, H_{5/5}), 3.27 (s, 12H, J_{Pt-H} = 23.0 Hz, CH₃ (DMSO)).

Synthesis of [Pt₂(L-2H)(Cl)₂(PPh₃)₂] (4b). To a suspension of 4a (56.1 mg, 0.073 mmol) in CH₂Cl₂ (20 mL) was added 38.2 mg of PPh₃ (0.146 mmol). The suspension was stirred under a nitrogen atmosphere for 2 h. The solution that was obtained was concentrated to a small volume under reduced pressure 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: 75%. Mp: >260 °C. Anal. Calcd for C₄₈H₃₆N₂Cl₂P₂Pt₂: C, 48.47; H, 3.18; N, 2.46. Found: C, 48.61; H, 2.79; N, 2.37. ¹H NMR (CDCl₃): δ 9.06 (m, 2H, H_{6/6}), 7.81–7.75 (m, 12H, H_o PPh₃), 7.47–7.37 (m, 18H, H_{p+m} PPh₃), 6.81 (d, 2H, J_{H-H} = 7.9 Hz, J_{Pt-H} = 44.8 Hz, H_{4/4}), 6.51 (m, 2H, J_{H-H} = 7.9 Hz, H_{5/5}). ³¹P NMR (121.4 MHz; CDCl₃; H₃PO₄): δ 19.55 (s, J_{Pt-P} = 4135 Hz, PPh₃).

Synthesis of [Pt₂(L-2H)(Cl)₂(3,5-Me₂-pyridine)₂] (4d). To a suspension of 4a (35 mg, 0.045 mmol) in 20 mL of acetone was added 0.45 mmol of 3,5-Me₂Pyridine (10-fold excess). The suspension was stirred and heated to reflux for 8 h and then concentrated to a small volume under reduced pressure and treated with *n*-pentane. The precipitate that formed was filtered, washed with diethyl ether, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 82%. Mp: >260 °C. Anal. Calcd for C₂₄H₂₄Cl₂N₄Pt₂: C, 34.75; H, 2.92; N, 6.75. Found: C, 34.06; H, 2.75; N, 6.34. ¹H NMR (CDCl₃): δ 8.90 (d, 2H, J_{H-H} = 4.8 Hz, J_{Pt-H} = 39 Hz, H₆($_{6}$), 8.86 (s, 4H, J_{Pt-H} = 41.7 Hz, H_o), 7.50 (s, 2H, H_p lutidine), 6.78 (d, overlapping 4H, H_{4/4}', H_{5/5}'), 2.38 (s, 12H, CH₃ 3,5-lutidine).

Synthesis of [Pt(L*)(DMSO)(Me)][BF₄] (5). To a solution of 1a (55.5 mg, 0.125 mmol) in acetone was added with stirring 18crown-6 · HBF₄ · H₂O in a 1/1 molar ratio. The solution was stirred for 3 h and then concentrated to a small volume and treated with diethyl ether. The precipitate that formed was filtered and washed with diethyl ether to give the analytical sample in almost quantitative yield. Mp: 110 °C dec. Anal. Calcd for C₁₃H₁₇BF₄N₂OPtS: C, 29.39; H, 3.23; N, 5.27. Found: C, 29.28; H, 3.09; N, 4.98. ¹H NMR (CDCl₃): δ 13.8 (broad, 1H, NH), 9.95 (dd, 1H, $J_{H-H} = 4.8$ Hz, $J_{Pt-H} = ca. 15$ Hz, H₆'), 8.75 (dd, 1H, $J_{H-H} = 8.1$ Hz), 8.68 (dd, 1H, $J_{H-H} = 5.4$ Hz), 8.51 (d, 1H, $J_{H-H} = 8.1$ Hz), 8.24 (td, 1H, 7.4 Hz), 7.72–7.60 (m, 2H), 3.30 (s, 6H, $J_{Pt-H} = 20.5$ Hz, CH₃ DMSO), 0.78 (s, 3H, $J_{Pt-H} = 81$ Hz, CH₃–Pt). IR (Nujol; cm⁻¹): 3295 m, 3190 m, 1087 s br.

Synthesis of $[Pt_2(L-2H)(Cl)(Me)(DMSO)_2]$ (6). To a solution of **3a** (90.0 mg, 0.194 mmol) in 35 mL of toluene was added 73.9 mg of $[Pt(Me)_2(DMSO)_2]$ (0.194 mmol). The solution was heated to 80 °C and stirred for 24 h and then evaporated to dryness. The

formula $C_{28}H_{22}ClN_2PPt$ $C_{48}H_{38}Cl_8N_2P_2Pt_2$ M_r 648.021378.60coloryellowyellowcryst systtriclinicmonoclinicspace group $P\bar{1}$ $P2_1/n$ a/Λ 10.8349(6)9.7794(5) b/Λ 13.6678(7)23.9415(12)	
$M_{\rm r}$ 648.02 1378.60 color yellow yellow cryst syst triclinic monoclinic space group $P\bar{1}$ $P2_1/n$ $a/Å$ 10.8349(6) 9.7794(5) $b/Å$ 13.6678(7) 23.9415(12)	
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a/Å 10.8349(6) 9.7794(5) b/Å 13.6678(7) 23.9415(12)	
b/Å 13.6678(7) 23.9415(12)	
c/A 17.7696(9) 10.3588(5)	
α/deg 101.229(1) 90	
β/deg 100.839(1) 90.000(1)	
y/deg 106.739(1) 90	
U/Å ³ 2386.8(2) 2425.3(2)	
Z 4 2	
F(000) 1256 1324	
$D_{\rm c}/{\rm g~cm^{-3}}$ 1.803 1.888	
<i>T/</i> K 150 295	
cryst dimens (mm) $0.12 \times 0.21 \times 0.23$ $0.12 \times 0.14 \times 0.23$	
μ (Mo K α)/cm ⁻¹ 61.4 63.7	
min-max transmissn factors 0.768-1.000 0.720-1.000	
scan mode ω ω	
frame width/deg 0.30 0.30	
time per frame/s 10 20	
no. of frames 3660 3360	
detector-sample dist/cm 6.00 6.00	
θ range/deg 3–27 3–28	
reciprocal space explored full sphere full sphere	
no. of rflns (total; indep) 44 199; 12 219 42 242; 6439	
R _{int} 0.0285 0.0217	
final R2 and R2w indices ^{<i>a</i>} (F^2 , all rflns) 0.030, 0.040 0.025, 0.040	
conventional R1 index $(I > 2\sigma(I))$ 0.020 0.018	
no. of rflns with $I > 2\sigma(I)$ 9719 5423	
no. of variables 595 280	
goodness of fit ^b 0.96 0.98	

 ${}^{a} \operatorname{R2} = [\Sigma(|F_{o}^{2} - kF_{c}^{2}|)/\Sigma F_{o}^{2}]. \operatorname{R2w} = [\Sigma w/(F_{o}^{2} - kF_{c}^{2})^{2}/\Sigma w(F_{o}^{2})^{2}]^{1/2}. {}^{b} [\Sigma w(F_{o}^{2} - kF_{c}^{2})^{2}/(N_{o} - N_{v})]^{1/2}, \text{ where } w = 4F_{o}^{2}/\sigma(F_{o}^{2})^{2}, \sigma(F_{o}^{2}) = [\sigma^{2}(F_{o}^{2}) + (pF_{o}^{2})^{2}]^{1/2}. N_{o} \text{ is the number of observations, } N_{v} \text{ is the number of variables, and } p = 0.02.$

residue was recrystallized from CH₂Cl₂/*n*-pentane to give the analytical sample as a green solid. Yield: 63%. Mp: >260 °C. Anal. Calcd for C₁₅H₂₁ClN₂O₂Pt₂S₂: C, 23.99; H, 2.82; N, 3.73. Found: C, 24.14; H, 2.42; N, 3.66. ¹H NMR (CDCl₃): δ 9.13 (d, 1H, *J*_{H-H} = 5.0 Hz, *J*_{Pt-H} = ca. 10 Hz, H₆' trans Me), 8.98 (d, 1H, *J*_{H-H} = 7.8 Hz, *J*_{Pt-H} = 42 Hz, H₄ trans DMSO), 8.61 (dd, 1H, *J*_{H-H} = 5.0 Hz, *J*_{Pt-H} = 41 Hz, H₆ trans DMSO), 8.06 (d, 1H, *J*_{H-H} = 7.8 Hz, H₅ or H_{5'}), 7.06 (dd, 1H, *J*_{H-H} = 5.0 Hz, *J*_{H-H} = 7.8 Hz, H₅ or H_{5'}), 7.06 (dd, 1H, *J*_{H-H} = 5.0 Hz, *J*_{H-H} = 7.8 Hz, H₅ or H_{5'}), 3.62 (s, 6H, *J*_{Pt-H} = 22.8 Hz, DMSO trans N), 3.23 (s, 6H, *J*_{Pt-H} = 19.5 Hz, DMSO trans C), 0.71 (s, 3H, *J*_{Pt-H} = 81.3 Hz, Pt-Me).

Synthesis of [Pt₂(L-2H)(Me)₂(DMSO)(PPh₃)] (7). To a solution of 1b (65.8 mg, 0.105 mmol) in 20 mL of toluene was added 40.0 mg of [Pt(Me)₂(DMSO)₂] (0.105 mmol). The solution was heated to reflux and stirred for 4 h and then evaporated to dryness. The residue was recrystallized from CH₂Cl₂/Et₂O to give the analytical sample as a yellow solid. Yield: 60%. Mp: >250 °C. Anal. Calcd for C₃₂H₃₃N₂OPPt₂S · H₂O: C, 41.20; H, 3.78; N, 3.00. Found: C, 41.33; H, 3.58; N, 2.97. ¹H NMR (CDCl₃): δ 9.14 (d, 1H, J_{H-H} = 5.2 Hz, H₆' *cis* DMSO), 8.13 (m, J_{Pt-H} broad, H₄' *trans* PPh₃), 8.05 (dd, J_{H-H} = 7.8 Hz, J_{Pt-H} = 42 Hz, H₄ *trans* DMSO), 7.78–7.73 (m, 6H, H_o PPh₃), 7.42–7.33 (m, 10H, H_{m+p} PPh₃ + H₆ *cis* PPh₃), 7.15 (dd, 1H, $J_{H-H} = 5.2$ Hz, $J_{H-H} = 7.8$ Hz, $H_5 \ cis$ PPh₃), 6.57 (m, 1H, $H_{5'} \ cis$ DMSO), 3.23 (s, 6H, $J_{Pt-H} = 19.2$ Hz, DMSO), 0.67 (s, 3H, $J_{Pt-H} = 80$ Hz, Pt-Me), 0.62 (d, 3H, $J_{Pt-H} = 81$ Hz, $J_{P-H} = 7.5$ Hz, Pt-Me cis PPh₃).

Synthesis of [Pt₂(L-2H)(Me)(Cl)(DMSO)(CO)] (8). To a solution of 3c in toluene (82.8 mg, 0.20 mmol, 30 mL) was added with vigorous stirring 76.3 mg of [Pt(DMSO)₂Me₂] (0.20 mmol). The solution was refluxed for 4 h. The precipitate that formed was filtered and washed with toluene and diethyl ether to give the analytical sample as a dark yellow solid. Yield: 90%. Mp: >260 °C. Anal. Calcd for $C_{14}H_{15}ClN_2O_2Pt_2S$: C, 23.99; H, 2.16; N, 4.00. Found: C, 23.65; H, 2.08; N, 3.76. IR (Nujol; cm⁻¹): 2090, s. NMR: insoluble in common organic solvents.

Synthesis of [Pt(L-H)(Cl)₃(DMSO)] (9). To a solution of 3a (79.9 mg, 0.236 mmol) in MeCN (10 mL) was added with stirring an aqueous solution of NaAuCl₄ (0.236 mmol in 10 mL, obtained from HAuCl₄ and NaHCO₃ in a 1/1 molar ratio). The mixture was heated to 100 °C for 8 h. The suspension that formed was filtered off, washed with water, dried, and recrystallized from CH2Cl2/Et2O to give the analytical sample as a cream-colored solid. Yield: 65%. Anal. Calcd for $C_{12}H_{13}Cl_3N_2OPtS \cdot H_2O: C, 26.07; H, 2.74; N, 5.07.$ Found: C, 25.74; H, 2.30; N, 4.79. ¹H NMR (CD₂Cl₂): δ 9.71 (dd, 1H, $J_{H-H} = 4.9$ Hz, $J_{Pt-H} = 25$ Hz, $H_{6'}$), 5.86 (dd, 1H, $J_{H-H} = 8.1$ Hz, $J_{H-H} = 1.2$ Hz, $J_{Pt-H} = 18$ Hz, H₄), 8.46 (dd, 1H, $J_{H-H} = 4.8$ Hz, $J_{H-H} = 1.2$ Hz, H₆), 8.40 (dd, 1H, $J_{H-H} = 8.0$ Hz, $J_{H-H} =$ 1.4 Hz), 8.13 (td, $J_{H-H} = 7.8$ Hz, $J_{H-H} = 1.4$ Hz, $H_{4'}$), 7.60 (m, 1H, H_{5'}), 7.30 (ddd, $J_{H-H} = 8.4$ Hz, $J_{H-H} = 4.8$ Hz, $J_{Pt-H} = 7$ Hz, H₅), 3.93 (s, $J_{Pt-H} = 14.3$ Hz, CH₃ DMSO). ESI-MS (CH₂Cl₂): m/z 498 [M - Cl]⁺.

X-ray Data Collection and Structure Determination. Crystal data are summarized in Table 5. The diffraction experiments were carried out on a Bruker SMART CCD area-detector diffractometer at 150 K for **3b** and at 295 K for **4b** • 2CHCl₃, using Mo Kα

⁽²¹⁾ SAINT Reference Manual; Siemens Energy and Automation, Madison, WI, 1994–1996.

⁽²²⁾ Sheldrick, G. M. SADABS, Empirical Absorption Correction Program,; University of Gottingen, Gottingen, Germany, 1997.

⁽²³⁾ Frenz, B. A. Comput. Phys. 1988, 2, 42

⁽²⁴⁾ Crystallographic Computing 5; Oxford University Press: Oxford, U.K., 1991; Chapter 11, p 126.

⁽²⁵⁾ Sheldrick, G. M. SHELXS 86: Program for the Solution of Crystal Structures; University of Gottingen, Gottingen, Germany, 1985.

⁽²⁶⁾ Castellano, S.; Günther, H.; Eberaole, S. J. Phys. Chem. 1965, 69, 4166.

Cyclometalation of 2,2'-Bipyridine

radiation ($\lambda = 0.71073$ Å) with a graphite crystal monochromator in the incident beam. No crystal decay was observed, so that no time-decay correction was needed. The collected frames were processed with the software SAINT,²¹ and an empirical absorption correction was applied (SADABS)²² to the collected reflections. The calculations were performed using the Personal Structure Determination Package²³ and the physical constants tabulated therein.²⁴ The structures were solved by direct methods (SHELXS)²⁵ and refined by full-matrix least squares using all reflections and minimizing the function $\Sigma w (F_o^2 - kF_c^2)^2$ (refinement on F^2). All the non-hydrogen atoms were refined with anisotropic thermal factors. The hydrogen atoms were placed in their ideal positions (C–H = 0.97 Å), with the thermal parameter *U* being 1.10 times that of the carbon atom to which they are attached, and not refined. In the final Fourier maps the maximum residuals were as follows: for **3b**, 0.91(35) e Å⁻³ at 0.95 Å from Pt'; for **4b** • 2CHCl₃, 0.85(16) e Å⁻³ at 0.12 Å from Cl(4). CCDC Nos. 696077 (**3b**) and 696078 (**4b**) contain the supplementary crystal-lographic data for this paper.

Acknowledgment. Financial support from the Università di Sassari (FAR) and Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR, PRIN 2007) is gratefully acknowledged. We thank Johnson Matthey for a generous loan of platinum salts.

Supporting Information Available: CIF files giving crystal data for **3b** and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM801033G