Dinuclear, Tricyclometallated Platinum(II) Derivatives − Substitution Reactions and Reactivity of the Platinum−Carbon Bonds

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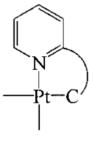
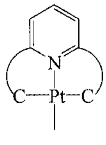
In the recently reported dinuclear cyclometallated species $[Pt_2(R)(L)(DMSO)_2]$ [H_3L = 6-phenyl-2,2′-bipyridine; R = Me (**1a**), Ph (**1b**)] the threefold deprotonated ligand L links the two platinum atoms acting as an N′,C(3) and a C,N,C donor. Aspects of their reactivity have been studied first with regards to the substitution of the two DMSO ligands, which are coordinated to the platinum atom *trans* to a nitrogen and a carbon atom, respectively. Substitution of DMSO with neutral two-electron donors affords several new species, all having the same bridging ligand L: $[Pt_2(R)(L)(L')_2]$ [L′ = PPh_3 (**2a**, **2b**), CO (**3a**, **3b**)] and $[Pt_2(R)(L)(L')(DMSO)]$ [L′ = 3,5-Me_2-py (**4a**)]. The potentially bidentate diphosphane $Ph_2P(CH_2)_3PPh_2$ (dppp) gives a more complex species having both chelating and bridging dppp ligands $[\{Pt(Me)(L)(dppp)\}_2(\mu\text{-}dppp)]$ (**5a**). The reactivity of the platinum–carbon bonds with HCl has been studied in complexes **1a**, **1b** and **2a**, **2b** and found to be strongly dependent on the nature of the ancillary ligands. To discern the most labile of the four metal–carbon bonds, the reaction has been carried out with 1 equiv. of HCl under mild conditions. Although the reaction is not selective and minor species are formed, cleavage of the Pt–Me (**1a**) and Pt–Ph (**1b**) bonds is favoured — $[Pt_2(L)Cl(DMSO)_2]$ (**6**) can be isolated and spectroscopically characterised from the reaction with either **1a** or **1b**. Substitution of PPh_3 for DMSO in **6** gives $[Pt_2(L)Cl(PPh_3)_2]$ (**7**) as the thermodynamically stable isomer having a *trans* Cl–Pt–C arrangement. The structure of complex **7** has been solved by X-ray crystallography. In contrast, reaction of **2a** or **2b** with HCl proceeds by another route: even with excess HCl the Pt–Me and Pt–Ph bonds are unaffected whereas one of the Pt–C bonds of the pincer-like C,N,C system is cleaved to selectively give $[Pt_2(R)(HL)Cl(PPh_3)_2]$ [R = Me (**8a**), Ph (**8b**)]. The same bond is cleaved also in **1a** and **1b** by excess HCl to give $[Pt_2(HL)(Cl)_2(DMSO)_2]$ (**9**).

Introduction

Cyclometallated platinum(II) complexes containing substituted pyridines and 2,2′-bipyridines are well documented.[1] They comprise mono- and dimetallated species (**I−IV**) with various donor sequences.[2−5]



I



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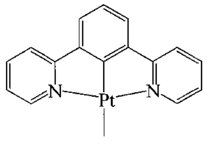
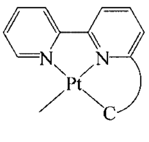


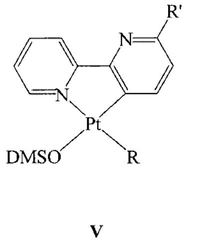
III



IV

Both five- and six-membered rings are known, and both Pt−C(sp^2) and Pt−C(sp^3) bonds have been reported, the former being more common. The variety of possible coordination modes allows one to obtain species with different properties and an array of potential applications. In particular, it is worth noting that species of type **II**,[3] with a *trans* C−Pt−C arrangement, are still rare and often cannot be obtained by direct activation of a C−H bond.

Recently, a new type of cyclometallation, which entails activation of a C−H bond of a pyridine ring, has been described: reaction of 6-substituted 2,2′-bipyridines with *cis*-$[Pt(R)_2(DMSO)_2]$ (R = Me, Ph) gave a series of "rollover" cyclometallated species (**V**).[6]



R = Me. Ph

V

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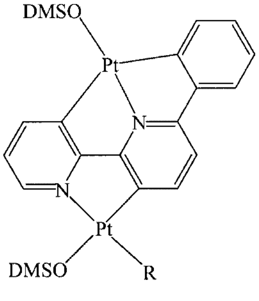
In the case of 6-phenyl-2,2′-bipyridine (6-Ph-2,2′-bipy), further reaction of complexes of type **V** with *cis*-$[Pt(R)_2(DMSO)_2]$ allowed us to isolate the dinuclear complexes **1a** (R = Me) and **1b** (R = Ph).[7]



1a, R = Me
1b, R = Ph

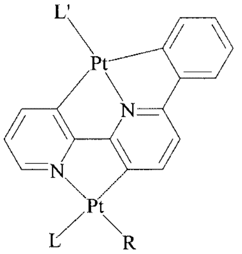
Compounds **1a** and **1b** were fully characterised by means of NMR spectroscopy and FAB mass spectrometry, and, in the case of **1b**, by X-ray crystallography. They are rare examples of multiple C−H bond activation: indeed 6-Ph-2,2′-bipy displays an unprecedented behaviour, acting as a threefold deprotonated ligand. Compounds **1a** and **1b** are unique in several aspects, having (i) three five-membered rings assembled in the same molecule, (ii) a ten-electron bridging ligand, and (iii) a rare C,N,C sequence of donor atoms. Furthermore, in each of the two molecules a pincer-like system with a *trans* C−Pt−C arrangement coexists with an N′−C(3) cycle having two *cis* platinum−carbon bonds. Due to these interesting features, we deemed it worthwhile to synthesise analogous species by substitution of neutral ligands for DMSO and to study some aspects of the reactivity of the four different platinum−carbon bonds assembled in each of these unusual molecules.

Results and Discussion

Reaction with Neutral Ligands

We have recently reported that the reaction of *cis*-$[Pt(Me)_2(DMSO)_2]$ and *cis*-$[Pt(Ph)_2(DMSO)_2]$ with 6-Ph-2,2′-bipy gives compounds **1a** and **1b**, respectively, in fairly good yields (ca. 60−65%).[7]

The neutral ligands PPh_3 and CO easily displace both the DMSO molecules, whereas only one DMSO is substituted by a nitrogen donor such as 3,5-dimethylpyridine (3,5-Me_2-py; Scheme 1). With PPh_3 the reaction proceeds under mild conditions to give the disubstituted complexes $[Pt_2(R)(L)(PPh_3)_2]$ [R = Me (**2a**), Ph (**2b**)] in high yields (ca. 90%).



compd.	R	L	L'
1a	Me	DMSO	DMSO
1b	Ph	DMSO	DMSO
2a	Me	PPh_3	PPh_3
2b	Ph	PPh_3	PPh_3
3a	Me	CO	CO
3b	Ph	CO	CO
4a	Me	3,5-Me_2-py	DMSO

Scheme 1

$$[Pt_2(R)(L)(DMSO)_2] + 2\,PPh_3 \longrightarrow [Pt_2(R)(L)(PPh_3)_2] + 2\,DMSO$$

With 1 equiv. of PPh_3 a mixture of starting material and mono- and disubstituted products is obtained, indicating nonselective DMSO substitution.

Compounds **2a**,**b** were characterised by analytical and spectroscopic methods: in particular the $^{31}P\{^1H\}$ NMR spectra show two resonances [e.g. δ = 26.52 and 32.44 ppm (**2a**)] with very different ^{195}Pt-^{31}P coupling constants (3931 and 2412 Hz) in agreement with phosphorus atoms *trans* to donors with a low (N) and high (C) *trans* influence, respectively.[8] In the ^1H NMR spectrum of **2a** the Me group, which is slightly shielded with respect to **1a**, appears as a doublet due to coupling with a ^{31}P nucleus ($^3J_{P,H}$ = 7.6 Hz), suggesting a PPh_3 ligand in a *cis* position.

The coordinated DMSO can also be easily displaced from **1a** and **1b** by CO at atmospheric pressure. In this case, however, the reaction products, compounds **3a** and **3b**, are almost insoluble in common organic solvents, hampering their characterisation by NMR spectroscopy. Analytical and spectroscopic data fit the formulation $[Pt_2(R)(L)(CO)_2]$: in particular the IR spectra show two bands in the region of terminal carbonyl ligands (2050, 2063 cm^{-1} for **3a** and 2066, 2073 cm^{-1} for **3b**) supporting substitution of both the DMSO ligands. To completely rule out the possibility of the coordination of only one CO ligand, compound **3a** was treated with PPh_3 in a 1:1 Pt/P molar ratio. The almost insoluble complex **3a** reacts immediately with loss of gas (CO): the ^1H NMR spectrum of the solution shows the formation of complex **2a**, and no free or coordinated DMSO is detected.

With a nitrogen donor such as 3,5-Me_2-py, only one of the DMSO ligands is substituted, yielding $[Pt_2(Me)(L)(DMSO)(3,5\text{-}Me_2\text{-}py)]$ (**4**). The ^1H NMR spectra give evidence for a DMSO coordinated *trans* to a nitrogen atom (δ = 3.63, $J_{Pt,H}$ = 25.6 Hz);[9] only the more labile DMSO *trans* to the carbon atom is displaced. Even with excess 3,5-Me_2-py or at higher temperature the disubstituted product is not obtained. The low affinity of the nitrogen donor for platinum(II) likely accounts for this behaviour.

Displacement of the DMSO ligands from **1a** was also attained by reaction with a bidentate phosphane such as 1,3-bis(diphenylphosphanyl)propane (dppp). The outcome of the reaction, however, was unexpected: the analytical values point to a species, **5a**, with a Pt/dppp molar ratio of 4:3. The ^1H NMR spectrum shows, in the aliphatic region, a methyl resonance at δ = 0.30 ppm, at high field with respect to **1a**, coupled to ^{195}Pt ($^2J_{Pt,H}$ = 67 Hz) and to two phosphorus nuclei ($^3J_{P,H}$ = 8.0 Hz and 6.7 Hz). The $^{31}P\{^1H\}$ spectrum exhibits a singlet at δ = 17.71 ppm ($^1J_{Pt,P}$ = 3913 Hz) and two doublets at δ = −0.31 ppm

($^1J_{Pt,P}$ = 1918, $^2J_{P,P}$ = 22.9 Hz) and δ = 1.35 ppm ($^1J_{Pt,P}$ = 2106, $^2J_{P,P}$ = 22.9 Hz). Coupling of the methyl group to two ^{31}P nuclei indicates an endobidentate diphosphane whereas the chemical shift of the singlet, δ = 17.71 ppm, and the absence of a P-P coupling, suggests a bridging dppp ligand. The high value of $^1J_{Pt,P}$ (3913 Hz) observed for the latter resonance is consistent with a phosphorus atom *trans* to a nitrogen atom. In the absence of X-ray data, a plausible description of **5a** which accounts for the experimental, analytical and spectroscopic data is shown in Figure 1.

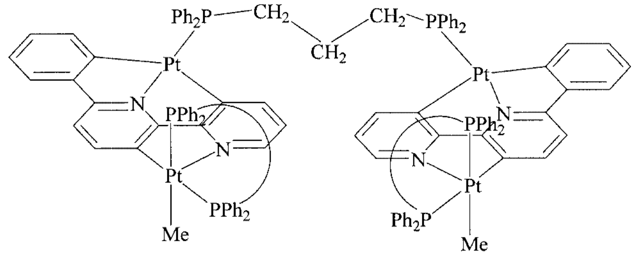


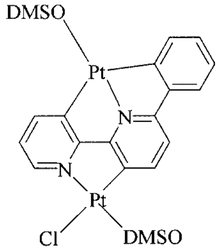
Figure 1. A plausible description of complex **5a**

The small differences between the two $^3J_{P,H}$ coupling constants (8.0, 6.7 Hz), makes a pentacoordinate arrangement more likely than a square-planar one. In the latter geometry, which entails the cleavage of the Pt−N bond of the chelated N′,C(3) ring, the phosphorus atoms of the chelated dppp should be *cis* and *trans*, respectively, to the methyl group.

It seems, therefore, that a variety of molecules with ancillary ligands having different electronic and steric properties can be synthesised from compounds **1** by substitution reactions without disruption of the dinuclear cyclometallated core of the system. All the new species **2**−**5** exhibit high thermal stability.

Reaction with Acids

Compounds **1a** and **1b** have four Pt−C bonds: in **1a** one of them is a C(sp^3)−Pt bond, whereas in **1b** all of them are C(sp^2)−Pt bonds. Regardless of the presence of two Pt−C(sp^2) bonds in mutual *trans* positions, the trimetallated compounds are stable in air both in solution and in the solid state. With the aim of investigating the reactivity of these platinum−carbon bonds, we have studied the behaviour of **1a** and **1b** toward HCl, an acid having a coordinating anion. To detect the most labile of the Pt−C bonds, the reaction was first carried out under mild conditions with a 1:1 L/HCl molar ratio. Under these conditions the platinum−methyl and the platinum−phenyl bond in **1a** and **1b**, respectively, were preferentially cleaved. The reaction is not selective and other species are also formed; however, according to their ^{1}H NMR spectra none of them contains an Me or a Ph group bound to the metal atom. One product could be isolated in pure form by chromatography, albeit in low yield. It was fully characterised and the analytical and spectroscopic data agree with the formulation [$Pt_2Cl(L)(DMSO)_2$] (**6**). In particular, a band at 292 cm^{-1} in the IR spectrum supports the thermodynamically favoured isomer having the chlorine atom *trans* to a carbon atom.[10]



6

Reaction of complex **6** with PPh_3 under mild conditions leads to substitution of the DMSO ligands to give [$Pt_2Cl(L)(PPh_3)_2$] (**7**) for which crystals suitable for an X-ray structure determination were obtained.

The structure consists of the packing of **7** and $CHCl_3$ molecules in the molar ratio 2:3. An ORTEP view of **7** is shown in Figure 2 and principal bond parameters are listed in Table 1. The two platinum atoms are essentially square-planar coordinated with slight square-pyramidal distortions. For Pt(1) the maximum distances from the best plane are +0.041(1) and −0.055(4) Å for Pt(1) and N(2), respectively. For Pt(2) the maximum distances from the best plane are +0.017(1) and −0.021(3) Å for Pt(2) and N(1), respectively. The dihedral angle between these two least-squares planes is 7.5(2)°, a value which shows that the overall planarity of the $Pt_2ClP_2N_2C_{16}$ moiety is less rigorous than that of the analogous $Pt_2S_2N_2C_{17}$ fragment of [$Pt_2Ph(L)(DMSO)_2$],[7] where the analogous dihedral angle

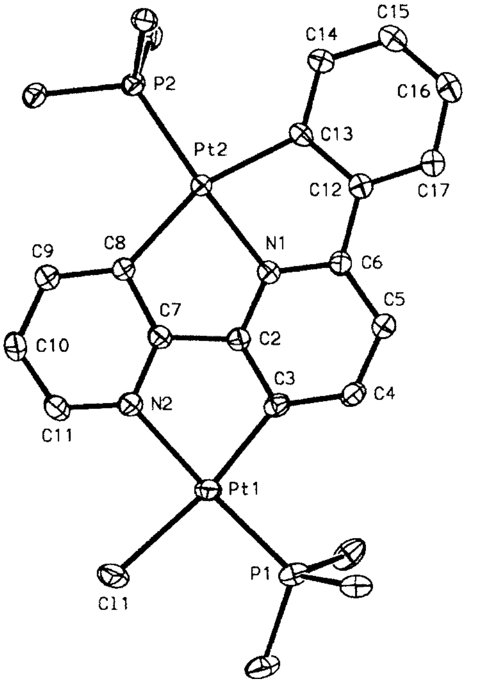


Figure 2. ORTEP view of **7**; ellipsoids are drawn at the 30% probability level; only the first carbon atoms of the phosphane phenyl rings are shown for clarity

Table 1. Selected distances [Å] and angles [°] in **7**·1.5CHCl$_3$ with estimated standard deviations in parentheses

Pt(1)−Cl(1)	2.347(1)	Pt(1)−P(1)	2.225(1)
Pt(1)−N(2)	2.119(3)	Pt(1)−C(3)	2.010(4)
Pt(2)−P(2)	2.231(1)	Pt(2)−N(1)	2.024(3)
Pt(2)−C(8)	2.103(4)	Pt(2)−C(13)	2.071(4)
Cl(1)−Pt(1)−P(1)	94.1(1)	Cl(1)−Pt(1)−N(2)	89.6(1)
Cl(1)−Pt(1)−C(3)	171.3(1)	P(1)−Pt(1)−N(2)	173.9(1)
P(1)−Pt(1)−C(3)	94.5(1)	N(2)−Pt(1)−C(3)	81.8(1)
P(2)−Pt(2)−N(1)	175.7(1)	P(2)−Pt(2)−C(8)	103.3(1)
P(2)−Pt(2)−C(13)	97.3(1)	N(1)−Pt(2)−C(8)	80.6(1)
N(1)−Pt(2)−C(13)	78.8(1)	C(8)−Pt(2)−C(13)	159.4(1)

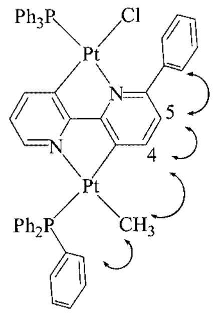


Figure 3. Complex **8a** with selected NOE contacts

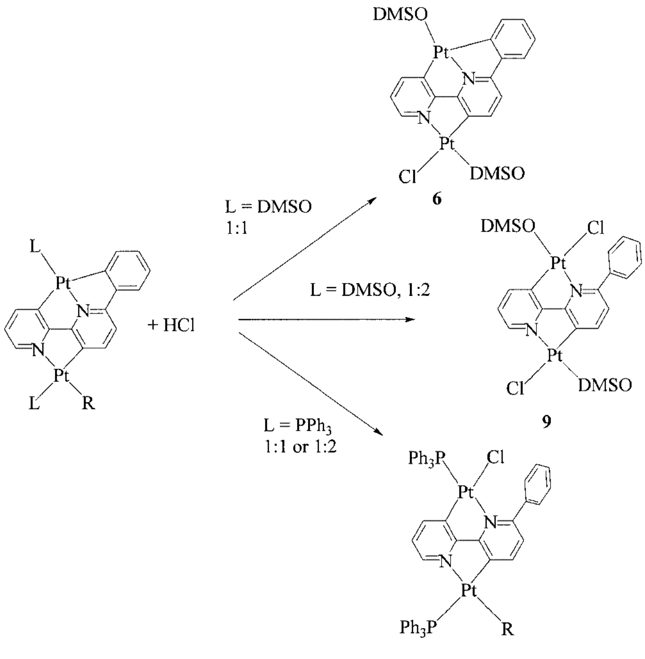
is 1.7(6)°. The Pt(1)−N(2) bond length [2.119(3) Å] is normal for a Pt−N bond *trans* to phosphorus.[11] The Pt(2)−N(1) distance [2.024(3) Å], however, is much shorter. This shortness is a common feature of the central bonds of bicyclic systems: see, for instance, the Pt−N bond length [1.937(7) Å] in [PtCl(L′)] (HL′ = 6-*tert*-butyl-2,2′-bipyridine).[5c] Similarly, the C(8)−Pt(2)−C(13) angle [159.4(1)°] is very far from 180° because of the relative rigidity of the tricyclic ligand. All the other bond lengths and angles are as expected if the *trans* influence of the carbon atoms is taken into account.

The reaction with HCl was also studied in the case of complexes **2a** and **2b**. In contrast with the behaviour of **1a**, in the case of **2a** the platinum−methyl bond is not cleaved, even with an excess of HCl. The ^{1}H NMR spectrum of the reaction product **8a** [δ = 0.68 (d, $^2J_{\mathrm{Pt,H}}$ = 80.8, $^3J_{\mathrm{P,H}}$ = 7.3 Hz, Me) ppm] indicates that the N′,C(3) chelated part of the complex does not undergo substantial changes. In agreement, in the ^{31}P{^{1}H} spectrum one of the resonances, assignable to a phosphorus atom *trans* to a carbon atom (δ = 33.07 ppm, $^1J_{\mathrm{Pt,P}}$ = 2405 Hz) is observed at a value very close to that of complex **2a** (δ = 32.44 ppm, $^1J_{\mathrm{Pt,P}}$ = 2412 Hz) as well as to that of the analogous mononuclear species [Pt(Me)(H$_2$L)(PPh$_3$)] (δ = 33.01 ppm, $^1J_{\mathrm{Pt,P}}$ = 2233 Hz).[6] However, the environment of the platinum atom coordinated by the C,N,C pincer part of the bridging ligand is significantly modified. (e.g. ^{31}P NMR: δ = 13.14 vs. δ = 26.53 ppm in **2a**), suggesting that one of the Pt−C bonds of the strained [5+5] fused-ring system has been cleaved. A ^{1}H 2D-COSY spectrum allowed us to ascribe three spin systems, with three, two and five protons, respectively, to the bridging ligand, the latter being assignable to a monosubstituted phenyl ring [δ = 8.56 (d, 2 H, H$_{ortho}$), 7.86 (m, 2 H, H$_{meta}$), 7.71 (t, 1 H, H$_{para}$) ppm]. A ^{1}H NOE difference spectrum shows contacts between the Pt−Me group, the *ortho* protons of the coordinated PPh$_3$ ligand, and the 4-H proton, as well as between the 4-H and the 5-H protons and between 5-H and the doublet at δ = 8.56 ppm ascribed to the *ortho* protons of the phenyl ring. On the whole the ^{1}H NMR spectra taken together with the ^{31}P{^{1}H}NMR spectra provide evidence for complex **8a** being [Pt$_2$Cl(Me)(HL)(PPh$_3$)$_2$] (Figure 3).

Complex **2b** reacts with HCl in a similar manner to **2a**, to give **8b**, as shown, in particular, by the ^{31}P NMR spectrum, which is similar to that of **8a**. In this case the two platinum−carbon bonds — Pt−Ph and Pt−C(sp^2) — in the five-membered N′,C(3) cycle are unaffected.

Finally, it is worth noting that the same platinum−carbon bond of the pincer C,N,C ligand can also be broken in complexes **1a** and **1b** upon addition of excess HCl to give [Pt$_2$Cl$_2$(HL)(DMSO)$_2$] (**9**). The ^{1}H NMR spectrum is consistent with a species having two DMSO ligands *trans* to nitrogen atoms [δ = 3.47 ($^3J_{\mathrm{Pt,C}} \approx$ 24.5 Hz), 3.64 ($^3J_{\mathrm{Pt,C}} \approx$ 22 Hz) ppm] and ten aromatic protons with a pattern similar to that of compound **8**.

The reactions of compound **1** (a and b) and **2** (a and b) with HCl are summarised in Scheme 2. The reactivity of the Pt−C bonds appears to be strongly dependent on the nature of the spectator ligands. Substitution of PPh$_3$ for



Scheme 2

DMSO makes the Pt−Me (or Pt−Ph) bond less prone to cleavage by HCl. Indeed, even in the related mononuclear "rollover" derivatives [Pt(R)(H_2L)(DMSO)] the reaction with HCl gives selective and fast attack at the Pt−Me and Pt−Ph centres, respectively, whereas [Pt(Me)(H_2L)(PPh_3)] reacts slowly. After 4 h, about half of the starting compound is recovered unchanged, and prolonged reaction times are required to achieve quantitative attack at the Pt−Me bond. A more marked effect is observed in the case of the dinuclear species: the methyl group of compound **2a** is not cleaved even with excess HCl, suggesting a non-negligible degree of electronic communication between the two platinum atoms through the unsaturated bridging ligand.

Experimental Section

General: All the reactions were carried out under argon. The solvents were purified and dried according to standard methods.[12] Elemental analyses were performed with a Perkin−Elmer Elemental Analyser 240B by Mr. A. Canu (Dipartimento di Chimica, Università di Sassari). Infrared spectra were recorded with a Perkin−Elmer 983 spectrometer as Nujol mulls. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ 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 (^1H, ^{13}C) or external 85% H_3PO_4 (^{31}P). 2D-COSY and NOE difference spectra were performed by means of standard pulse sequences. The mass spectrometric measurements were performed with 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. *cis*-[Pt(Me)$_2$(DMSO)$_2$] and *cis*-[Pt(Ph)$_2$(DMSO)$_2$] were prepared according to literature procedures,[13] as were the ligand HL[14] and complexes **1a** and **1b**.[7]

[Pt$_2$(Me)(L)(PPh$_3$)$_2$] (2a): PPh_3 (84.9 mg, 0.324 mmol) was added, under vigorous stirring, to a solution of **1a** (125.0 mg, 0.158 mmol) in CH_2Cl_2 (15 mL). The solution was stirred for 2 h, then concentrated to a small volume and treated with hexane (15 mL). The precipitate formed was filtered and washed with hexane to give the analytical sample as a yellow solid. Yield: 90% (169.0 mg), m.p. 210 °C. $C_{53}H_{42}N_2P_2Pt_2\cdot 1/3C_6H_{14}$ (1187.7) calcd. C 55.62, H 3.96, N 2.36; found C 55.48, H 3.95, N 2.37. IR (Nujol): $\tilde{\nu}$ = 1097 (s), 1557 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 0.62 (d, $^2J_{Pt,H}$ = 76.2, $^3J_{P,H}$ = 7.6 Hz, 3 H, CH_3Pt, 5.95 (m, 2 H), 6.28 (d, $J_{H,H}$ = 7.3 Hz, 1 H), 6.59 (m, 1 H), 6.88 (m, 1 H), 6.98 (m, 1 H), 7.26−7.50 (m, 20 H), 7.68−7.77 (m, 6 H), 7.80−7.89 (m, 6 H), 8.07 (dd, $^4J_{P,H}$ = 4.8, $^3J_{H,H}$ = 7.7, $^3J_{Pt,H}$ = 38 Hz, 1 H, 4-H) ppm. ^{31}P NMR (CD_2Cl_2): δ = 26.52 (s, $^1J_{P,Pt}$ = 3931 Hz, P *trans* N), 32.44 (s, $^1J_{P,Pt}$ = 2412 Hz, P *trans* C) ppm. MS (FAB$^+$): *m*/*z* = 1143 [M − CH_3]$^+$, 895 [M − PPh_3 − H]$^+$, 801 [M −PPh_3 − C_6H_6 − CH_3 − 2 H]$^+$, 725 [M − PPh_3 − 2 C_6H_6 − CH_3]$^+$. Compound **2a** can be obtained in almost quantitative yield also by reaction of [Pt$_2$(CO)$_2$(CH$_3$)(L)] with PPh_3 in a 1:2 molar ratio.

[Pt$_2$(Ph)(L)(PPh$_3$)$_2$] (2b): Complex **2b** was obtained as for complex **2a**, using **1b** instead of **1a**. Yield: 88%; m.p. > 260 °C. $C_{58}H_{44}N_2P_2Pt_2\cdot 2H_2O$ (1257.1): calcd. C 55.41, H 3.85, N 2.23; found C 55.69, H 3.91, N 2.25. IR (Nujol): $\tilde{\nu}$ = 1096 (s), 1560 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 5.94 (m, 2 H), 6.19 (d, J_{H-H} = 7.1 Hz, 1 H), 6.59 (m, 4 H), 6.84 (t, J_{H-H} = 7.4 Hz, 1 H), 6.93−7.44 (m, 24 H), 7.48−7.55 (m, 6 H), 7.82−7.89 (m, 6 H) ppm. ^{31}P NMR ($CDCl_3$): δ = 26.86 (s, $^1J_{P,Pt}$ = 3937 Hz, P *trans* N), 30.58 (s, $^1J_{P,Pt}$ = 2363 Hz, P *trans* C) ppm.

[Pt$_2$(Me)(L)(CO)$_2$] (3a): CO (1 atm) was bubbled for 1 h through a solution containing **1a** (63.5 mg, 0.080 mmol) in 20 mL of CH_2Cl_2. The precipitate formed was filtered and washed with Et_2O (3 × 5 mL), to give the analytical sample as an orange-yellow solid. Yield: 82% (45.4 mg); m.p. 245 °C (dec.). $C_{19}H_{12}N_2O_2Pt_2$ (690.5): calcd. C 33.05, H 1.74, N 4.06; found C 33.07, H 1.34, N 3.93. IR (Nujol): $\tilde{\nu}$ = 1037 (w), 1127 (m), 1558 (m), 1580 (m), 2050 (s), 2063 (s) cm^{-1}.

[Pt$_2$(Ph)(L)(CO)$_2$] (3b): Complex **3b** was obtained as for **3a** using **1b** instead of **1a**. Yield: 64%; m.p. 235 °C (dec.). $C_{24}H_{14}N_2O_2Pt_2$ (752.5): calcd. C 38.30, H 1.88, N 3.72; found C 37.94, H 1.80, N 4.02. IR (Nujol): $\tilde{\nu}$ = 1024 (w),1065 (w), 1560 (m), 1575 (m), 2066 (s), 2073 (s) cm^{-1}.

[Pt$_2$(Me)(L)(3,5-Me$_2$-py)DMSO] (4a): 3,5-Dimethylpyridine (3,5-Me$_2$-py; 42 mg, 0.39 mmol) was added, under vigorous stirring, to a solution of **1a** (58 mg, 0.073 mmol) in CH_2Cl_2 (20 mL) The solution, whose colour changed immediately to orange yellow, was stirred for 30 min, then concentrated to a small volume and treated with Et_2O (10 mL). The precipitate formed was filtered and washed with Et_2O (3 × 5 mL) to give an analytical sample as a yellow solid. Yield: 45% (26.9 mg); m.p. > 250 °C. $C_{26}H_{27}N_3OPt_2S$ (819.7): calcd. C 38.10, H 3.32, N 5.13; found C 38.26, H 3.46, N 5.17. ^1H NMR ($CDCl_3$): δ = 1.00 (s, $^2J_{Pt,H}$ = 85.7 Hz, 3 H, CH_3Pt), 2.38 (s, 6 H, CH_3 of 3,5-Me$_2$-py), 3.63 (s, $^3J_{Pt,H}$ = 25.6 Hz, 6 H, CH_3 of DMSO), 6.88−7.49 (m, 8 H), 7.93 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 4-H), 8.17 (dd, $^3J_{H,H}$ = 7.6 Hz, 1 H), 8.48 (s, $^3J_{Pt,H}$ = 22.7 Hz, 2 H, 2-H of 3,5-Me$_2$-py) ppm.

[{Pt$_2$(Me)(L)(dppp)$_2$}$_2$(μ-dppp)] (5a): dppp (97.2 mg, 0.236 mmol) was added, under vigorous stirring, to a solution of **1a** (88.3 mg; 0.112 mmol) in CH_2Cl_2 (20 mL). The solution, whose colour changed immediately from yellow to orange-yellow, was stirred for 90 min, then concentrated to a small volume and treated with hexane (15 mL). The precipitate formed was filtered off and washed with hexane (3 × 5 mL) to give the analytical sample as a yellow solid. Yield 43% (60.6 mg); m.p. 211−214 (dec.). $C_{115}H_{102}N_4P_6Pt_4$ (2506.2): calcd. C 55.11, H 4.10, N 2.24; found C 54.80, H 4.14, N 2.28. IR (Nujol): $\tilde{\nu}$ = 1100 (m), 1549 (w), 1569 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.30 (dd, $^2J_{Pt,H}$ = 67, $^3J_{P,H}$ = 6.7, 8.0 Hz, 6 H, CH_3Pt), 2.06−2.94 [br. m, 18 H, CH_2 (dppp)], 6.32−8.21 (m, 78 H, aromatic H) ppm. ^{31}P NMR ($CDCl_3$): δ = −0.31 (d, $^1J_{P,Pt}$ = 1918, $^2J_{P,P}$ = 22.9 Hz, 2 P), 1.35 (d, $^1J_{P,Pt}$ = 2106, $^2J_{P,P}$ = 22.9 Hz, 2 P), 17.71 (s, $^1J_{P,Pt}$ = 3913 Hz, 2 P) ppm.

[Pt$_2$(Cl)(L)(DMSO)$_2$] (6): Aqueous 0.1 M HCl (2.0 mL) was added, under vigorous stirring, to a solution of **1a** (152.3 mg, 0.193 mmol) in acetone (25 mL). The mixture was stirred for 2 h, then concentrated to a small volume. The brick-red precipitate formed was filtered and washed with EtOH (3 × 5 mL) and Et_2O (3 × 5 mL). The crude product thus obtained was purified by chromatography on silica gel (Merck, 230−400 mesh; eluent: benzene/acetone, 2:1) to give an analytical sample as a yellow solid. Yield: 25% (39.0 mg); m.p. 206 (dec.). $C_{20}H_{21}ClN_2O_2Pt_2S_2$ (811.1): calcd. C 29.61, H 2.61, N 3.45; found C 30.52, H 2.33, N 3.82. IR (Nujol): $\tilde{\nu}$ = 292 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 3.61 (s, $J_{Pt,H}$ not resolved, 6 H, CH_3 of DMSO), 3.63 (s, $J_{Pt,H}$ not resolved, 6 H, CH_3 of DMSO), 7.03−7.44 (m, 6 H), 8.23 (dd, $^3J_{H,H}$ = 7.3, $^4J_{H,H}$ = 1.2 Hz, 1 H, 4′-H), 8.32 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, 4-H), 8.77 (d, $^3J_{H,H}$ = 5.7, $^4J_{H,H}$ = 1.2 Hz, 1 H, 6′-H) ppm. MS (FAB$^+$): *m*/*z* = 811 [MH]$^+$, 810 [M]$^+$, 775 [M − Cl]$^+$, 732 [M − DMSO]$^+$, 697 [M − DMSO − Cl]$^+$, 654 [M − 2 DMSO]$^+$, 619 [M − 2 DMSO − Cl]$^+$.

[Pt_2(Cl)(L)(PPh_3)$_2$] (7): PPh_3 (0.020 mmol) was added to an NMR tube containing a solution of **6** (8.1 mg, 0.010 mmol) in $CDCl_3$. The reaction was monitored by ^1H and ^{31}P NMR spectroscopy, showing a fast reaction that produced complex **7** almost quantitatively. A slow evaporation of the solvent gave crystals suitable for an X-ray analysis. ^1H NMR ($CDCl_3$): $\delta = 6.12$ (d, $J_{H-H} = 7.5$ Hz, 1 H), 6.24 (d, $J_{H-H} = 8.1$ Hz, 1 H), 6.58 (m, 2 H), 6.80 (t, broad, 1 H), 7.13 (d, $J_{H-H} = 7.1$ Hz, 1 H), 7.30−7.49 (m, 22 H), 7.74−7.90 (m, 10 H), 8.88 (m, 1 H, 6′-H) ppm. ^{31}P NMR ($CDCl_3$): $\delta = 25.93$ (s, $^1J_{Pt,P} = 4146$ Hz, P *trans* N), 18.32 (s, $^1J_{Pt,P} = 3952$ Hz, P *trans* N) ppm.

[Pt_2(Me)(HL)(Cl)(PPh_3)$_2$] (8a): Aqueous 0.1 M HCl (1.7 mL, 0.17 mmol, molar ratio 1:2), was added, under vigorous stirring, to a solution of **2a** (67.4 mg, 0.085 mmol) in acetone (20 mL). The solution became pale yellow and was stirred for 16 h. The precipitate formed was filtered and washed with $(CH_3)_2CO$ (3 × 5 mL). From the filtered solution a second pale-yellow sample was obtained by concentration and filtration. The filtered precipitate was washed with $(CH_3)_2CO$ and Et_2O and added to the first sample. Yield: 89% (94.6 mg); m.p. 215 (dec.). $C_{53}H_{43}N_2ClP_2Pt_2\cdot 3H_2O$ (1249.5): calcd. C 50.94, H 3.95, N 2.24; found C 50.27, H 3.51, N 2.28. IR (Nujol): $\tilde{\nu} = 1097$ (s),1292 (s), 1585 (m), 1595 (m), 1715 (s), 296 m, 305 (m) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 0.68$ (d, $^2J_{Pt,H} = 80.8$ Hz $^3J_{P,H} = 7.3$ Hz, 3 H, CH_3Pt), 5.98 (dd, $^3J_{H,H} = 7.9$, $^3J_{H,H} = 5.2$ Hz, 1 H, 5′-H), 6.94−7.00 (m, 6 H), 7.16−7.26 (m, 10 H), 7.38−7.46 (m, 9 H), 7.47 (d, 1 H, 4′-H or 6′-H), 7.54−7.69 (m, 5 H), 7.71 (t, $J_{H-H} = 7.8$ Hz, 1 H, H_{para}, Ph bipy), 7.78 (d, $^3J_{H,H} = 8.0$ Hz, 1 H, 5-H), 7.86 (t, $^3J_{H,H} = 7.8$ Hz, 2 H, H_{meta}, Ph bipy), 8.01 (d, $^3J_{H,H} = 7.9$ Hz, 1 H, 6′-H or 4′-H), 8.56 (d, $^3J_{H,H} = 7.8$ Hz, 2 H, H_{ortho}, Ph bipy), 8.74 (dd, $^3J_{H,H} = 8.0$, $^4J_{P,H} = 5.7$, $^3J_{Pt,H} = 52$ Hz, 1 H, 4-H) ppm. ^{31}P NMR ($CDCl_3$): $\delta = 33.07$ (s, $^1J_{P,Pt} = 2405$ Hz, P *trans* C), 13.14 (s, $^1J_{P,Pt} = 4580$ Hz, P *trans* N) ppm.

[Pt_2(Ph)(HL)(Cl)(PPh_3)$_2$] (8b): Aqueous 0.1 M HCl (0.7 mL, 0.07 mmol) was added, under vigorous stirring, to a solution of **2b** (81.7 mg, 0.067 mmol) in acetone (20 mL). The solution became yellow and was stirred for 13 h. The precipitate formed was filtered and washed with acetone (3 × 5 mL) to give the analytical sample as a yellow solid. Yield: 55% (47.3 mg); m.p. 205 °C. $C_{58}H_{45}N_2ClP_2Pt_2\cdot H_2O$ (1275.6): calcd. C 54.61, H 3.71, N 2.20; found C 54.75, H 3.53, N 2.28. IR (Nujol): $\tilde{\nu} = 700$ (s), 750 (s), 1100 (s), 1550 (m) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 5.99$ (m, 1 H, 5′-H), 6.62−7.75 (m, 39 H), 7.83 (t, $J_{H-H} = 7.5$ Hz, 2 H, H_{meta}, Ph bipy), 8.01 (d, $J_{H-H} = 8.3$ Hz, 1 H, 6′-H or 4′-H), 8.47 (d, $J_{H-H} = 7.5$ Hz, 2 H, H_{ortho}, Ph bipy) ppm. ^{31}P NMR ($CDCl_3$) = 30.68 (s, $^1J_{P,Pt} = 2352$ Hz, P *trans* C), 13.10 (s, $^1J_{P,Pt} = 3725$ Hz, P *trans* N) ppm.

[Pt_2(HL)(Cl)$_2$(DMSO)$_2$] (9): Aqueous 0.1 M HCl (0.65 mL, 0.065 mmol) was added, under vigorous stirring, to a solution of **1b** (52.3 mg, 0.061 mmol) in acetone (20 mL). After 4 h, a second quantity of HCl was added (1.35 mL). The mixture was stirred for 15 h, then concentrated to dryness and crystallised from CH_2Cl_2/Et_2O to give an analytical sample as a yellow solid. Yield: 46% (24.0 mg); m.p. 215−218 °C (dec.). $C_{20}H_{22}Cl_2N_2O_2Pt_2S_2$ (847.6):calcd. C 28.34, H 2.62, N 3.31; found C 28.09, H 2.33, N 3.24. ^1H NMR ($CDCl_3$): $\delta = 3.47$ (s, $J_{Pt,H} \approx 24.5$ Hz, 6 H, CH_3 of DMSO), 3.64 (s, $^3J_{Pt,H} \approx 22$ Hz, 6 H, CH_3 of DMSO), 7.07 (dd, $J_{H-H} = 5.6$ Hz, $J_{H-H} = 7.8$ Hz, 1 H, 5′-H), 7.18 (d, $J_{H-H} = 8.1$ Hz, 1 H, 5-H), 7.42−7.48 (m, 3 H, H_{meta} and H_{para}), 7.73 (d, $J_{H-H} = 8.1$ Hz, 2 H, H_{ortho}), 8.63−8.69 (m, 2 H, 4′-H and 4-H), 8.98 (dd, $J_{H-H} = 5.6$ Hz, $J_{H-H} = 1.2$ Hz, 1 H, 6′-H) ppm.

X-ray Data Collection and Structure Determination: Crystal data are summarised in Table 2. The diffraction experiment was carried out with a Bruker SMART CCD area-detector diffractometer at 223 K. No crystal decay was observed, therefore no time-decay correction was needed. The collected frames were processed with the software SAINT,[15] and an empirical absorption correction was applied (SADABS)[16] to the collected reflections. The calculations were performed using the Personal Structure Determination Package[17] and the physical constants tabulated therein.[18] The structure was solved by direct methods (SHELXS)[19] and refined by full-matrix least squares using all reflections and minimising the function $\Sigma w(F_o^2 - kF_c^2)^2$ (refinement on F^2). One of the two chloroform solvent molecules is disordered around a twofold axis and its atoms have been given occupancy factors of 0.50. 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 B set to 1.10-times that of the carbon atom to which they are attached, and not refined. In the final Fourier map the maximum residual was 3.86(20) e·Å^{-3} at 0.62 Å from Pt(1). CCDC-236975 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystallographic data of **7**·1.5$CHCl_3$

Empirical formula	$C_{53.5}H_{40.5}Cl_{5.5}N_2P_2Pt_2$
Formula mass	1358.55
Colour	yellow
Crystal system	monoclinic
Space group	$C2/c$
a [Å]	31.238(3)
b [Å]	17.779(2)
c [Å]	18.688(2)
β [°]	110.48(1)
V [Å^3]	9723(2)
Z	8
$F(000)$	1284
$D_{calcd.}$ [g cm^{-3}]	1.856
T [K]	223
Crystal dimensions [mm]	0.338 × 0.450 × 0.507
μ(Mo-K_α) [cm^{-1}]	62.2
Min./max. transmission factors	0.759/1.000
Scan mode	ω
Frame width [°]	0.30
Time per frame [s]	15
No. of frames	2750
Detector−sample distance [cm]	4.00
θ range [°]	3−28
Reciprocal space explored	full sphere
No. of reflections (total/independent)	89654/14815
R_{int}	0.0326
Final R_2 and R_{2w} indices[a] (F^2/all reflections)	0.053/0.110
Conventional R_1 index[b][$I > 2\sigma(I)$]	0.036
Reflections with $I > 2\sigma(I)$	11770
No. of variables	604
Goodness of fit[c]	1.29

[a] $R_2 = [\Sigma(|F_o^2 - kF_c^2|/\Sigma F_o^2]$, $R_{2w} = [\Sigma w/(F_o^2 - kF_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [b] $R_1 = [\Sigma(|F_o - k|F_c||/\Sigma F_o)$. [c] $[\Sigma w(F_o^2 - kF_c^2)^2/(N_o - N_v)]^{1/2}$, where $w = 4F_o^2/\sigma(F_o^2)^2$, $\sigma(F_o^2) = [\sigma^2(F_o^2) + (pF_o^2)^2]^{1/2}$, where N_o is the number of observations, N_v the number of variables, and p, the ignorance factor (0.06).

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