

Intramolecular Redox and Methyl for Chloride Exchange Processes at Platinum(II) Metal Centers Bridged by the Short Bite Ligand 2-(Diphenylphosphino)pyridine

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The reaction of *cis*-[Pt(DMSO)₂Cl₂] (DMSO = dimethyl sulfoxide) with 2-(diphenylphosphino)pyridine (Ph₂PPy) leads, as major product, to the square planar platinum(II) species *cis*-[Pt(DMSO)(Ph₂PPy)Cl₂] (**1**), in which the Ph₂PPy is η¹-bonded through the phosphorus atom to metal center. The NMR spectra, in chloroform solution, indicates that **1** is in equilibrium with a species containing the Ph₂PPy as a chelating ligand, namely [Pt(Ph₂PPy)Cl₂]. The binuclear compounds [(CH₃)ClPt(μ-Cl)(μ-Ph₂PPy)Pt(CH₃)(DMSO)]DMSO (**2**) and [Pt₂(μ-Ph₂PPy)₂Cl₂]DMSO (**3**) have been isolated from the reaction of **1** with an equimolar amount of *cis*-[Pt(DMSO)₂(CH₃)₂]. Compounds **2** and **3** have been structurally characterized by an X-ray diffraction study. A plausible reaction scheme which accounts for the formation of both **2** and the platinum(I)–platinum(I) complex **3**, by intramolecular processes, is discussed; the first step of the reaction involves the formation of the binuclear species [(DMSO)Cl₂Pt(μ-Ph₂PPy)Pt(CH₃)₂(DMSO)] (**4**) by nucleophilic attack of the pyridine nitrogen atom of **1** on the platinum(II) center of the coordinately unsaturated species [Pt(DMSO)(CH₃)₂]. Compound **2** crystallizes in the monoclinic space group C2/c with *a* = 35.105(4) Å, *b* = 11.578(2) Å, *c* = 14.572(2) Å, β = 111.81(2)°, *V* = 5499(1) Å³, *Z* = 8. On the basis of 4131 independent observations and 309 parameters, the structure was refined to *R* = 0.035 and *R*_w = 0.041. Each platinum atom is in a nearly square planar environment and is surrounded by the Ph₂PPy and the chloride atom of the bridging ligands. The coordination around Pt(1) is completed by the nitrogen atom from the Ph₂PPy bridging ligand, the sulfur atom of DMSO, and one methyl group; the coordination around the Pt(2) involves, beyond the chloride bridged atom and the phosphorus of Ph₂PPy, one methyl group and the terminal chloride. The P(1)Pt(2)Pt(1)N(1) torsion angle of 35.2(2)° is indicative of a rather strong steric hindrance in the complex. Compound **3** crystallizes in the monoclinic space group C2/c with *a* = 30.296(4) Å, *b* = 17.805(3) Å, *c* = 12.992(2) Å, β = 98.14(1)°, *V* = 6937(2) Å³, and *Z* = 8. On the basis of 5022 independent observations and 422 parameters, the structure was refined to *R* = 0.032 and *R*_w = 0.035. The platinum atoms are in a nearly square planar environment, the angles at platinum centers between mutually *cis* ligands being in the range 79.42(5)–99.11(7)°. The platinum centers are joined by a short metal–metal bond (2.5853(6) Å). The metal coordination planes are twisted about the Pt–Pt vector giving a dihedral angle of 35.6(1)°. The Pt(1)–Cl(1) and Pt(2)–Cl(2) bond distances of 2.397(2) and 2.420(2) Å reflect the high *trans* influence of the platinum–platinum bond.

Homo- and heterobinuclear complexes in which d⁸ metal atoms are surrounded by two binucleating ligand molecules have been extensively studied.^{2–4} In such complexes the space between the metal atoms can be used to trap small molecules or moieties, such as CO, SO₂, halide, or CH₂.^{2–4} For these processes reaction pathways have been proposed in which both metal centers take part to the substrate activation; however initial activation of the substrate in a site far apart from the space between the metal centers has been also suggested.⁵

Recently we have been interested⁶ in the synthesis, reactivity, structural studies and catalysis of d⁸–d⁸ homo- and heterobinuclear complexes in which the metal centers are surrounded by only one short bite bridging ligand. The presence of only one bridging

binucleating ligand increases the space between the metal centers available to trap the substrate molecule; thus the occurrence of reactions in which both metal atoms are involved in the substrate activation process can give a very favorable result.

We observed that rhodium–palladium binuclear complexes^{6,7} in which the metal centers are held in close proximity by the geometric requirements of one Ph₂PPy(Ph₂PPy = 2-(diphenylphosphino)pyridine) bridging ligand, give transfer of coordinated ligands from a metal center to the other; these reaction steps in some cases formally implied an intramolecular oxidative addition process.

In this paper we report the synthesis of *cis*-[Pt(DMSO)(Ph₂PPy)Cl₂] (DMSO = dimethyl sulfoxide) (**1**) and its reaction with *cis*-[Pt(DMSO)₂(CH₃)₂]. We were able to isolate only two products from the latter reaction, the binuclear platinum(II)–platinum(II) [(CH₃)ClPt(μ-Cl)(μ-Ph₂PPy)Pt(CH₃)(DMSO)]DMSO (**2**) and the binuclear platinum(I)–platinum(I) [Pt₂(μ-Ph₂PPy)₂Cl₂]DMSO (**3**) complexes. The formation of **2** appears to be the result of a methyl for chloride exchange process while complex **3** indicates the occurrence of a redox process in solution.

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The X-ray crystal structures of **2** and **3** are also reported. Compound **1** has been previously obtained by us^{6a} from the reaction of [Rh(COD)(Ph₂PPy)Cl] (COD = cyclooctadiene) with *cis*-[Pt(DMSO)₂Cl₂] while the compound [Pt₂(μ-Ph₂PPy)₂Cl₂] was obtained by Balch et al.⁸ by the redox reaction occurring between [Pt(Ph₂PPy)₂Cl₂] and [Pt(dba)₂] (dba = dibenzylideneacetone); the X-ray crystal structure of [Pt₂(μ-Ph₂PPy)₂Cl₂] is here reported for the first time.

Experimental Section

Established methods were used to prepare the compounds *cis*-[Pt(DMSO)₂Cl₂],⁹ *cis*-[Pt(DMSO)₂(CH₃)₂],¹⁰ and Ph₂PPy.¹¹ All other reagents were purchased and used as supplied. Solvents were dried by standard procedures. All experiments were performed under an atmosphere of purified nitrogen. IR spectra were obtained as Nujol mulls on KBr or CsI plates using a Perkin-Elmer FTIR 1720 spectrophotometer. ¹H, and ³¹P NMR spectra were recorded on a Bruker WP80-SY or on a Varian Model Gemini-300 spectrometer.

¹H NMR spectra were referenced to internal tetramethylsilane and ³¹P spectra to external 85% H₃PO₄; positive chemical shifts are for all nuclei to higher frequency. Conductivity measurements were made with a Radiometer CDM 3 conductivity meter. Molecular weights were determined with a Knauer vapor pressure osmometer. Elemental analyses were performed by Malissa-Reuter Mikroanalytisches Laboratorium, Elbach, Germany, and by the Microanalytical Laboratory of the Organic Chemistry Institute of Milan.

Preparation of *cis*-[Pt(DMSO)(Ph₂PPy)Cl₂] (1**).** A dichloromethane solution of Ph₂PPy (0.062 g, 0.237 mmol) was added dropwise to a suspension of *cis*-[Pt(DMSO)₂Cl₂] (0.1 g, 0.237 mmol) in the same solvent (15 mL). Over 30 min, the suspension disappeared while the solution turned to pale-yellow. The solution was reduced in volume to ca. 10 mL, and diethyl ether (20 mL) was added to give a pale-yellow solid. This was filtered and washed with diethyl ether. The cold crystallization from dichloromethane and diethyl ether gave the pure product **1** as a pale-yellow crystalline solid (0.057 g, 0.095 mmol) in 40% yield. Anal. Calcd for C₁₉H₂₀Cl₂NSOPPt: C, 37.57; H, 3.32; N, 2.31. Found: C, 37.59; H, 3.30; N, 2.32. IR (CsI, Nujol): ν(SO) 1144, ν(Pt-Cl) 340, 308 cm⁻¹. ³¹P{¹H} NMR (CDCl₃): δ 17.6 (¹J_{PtP} = 3672 Hz); δ -52.2 (¹J_{PtP} = 3439 Hz) (see Results and Discussion).

Reaction of **1 with [Pt(CH₃)₂(DMSO)₂].** A dichloromethane solution (10 mL) of *cis*-[Pt(DMSO)₂(CH₃)₂] (0.099 g, 0.260 mmol) was added dropwise to a solution of *cis*-[Pt(DMSO)(Ph₂PPy)Cl₂] (0.158 g, 0.260 mmol) in the same solvent (25 mL) and the resulting mixture stirred for about 2 h. During this time, the color of the solution turned from pale-yellow to orange. Then, the volume of the solution was reduced to ca. 10 mL, and by addition of petroleum ether (20 mL) a yellow-orange precipitate was formed. This was filtered and washed with diethyl ether. The cold-fractionated crystallization from dichloromethane and diethyl ether gave the pure product **2** as a pale-yellow crystalline solid (0.083 g, 0.091 mmol). Anal. Calcd for C₂₃H₃₂Cl₂NPS₂O₂Pt₂: C, 30.33; H, 3.54; N, 1.54; Cl, 7.79. Found: C, 30.48; H, 3.50; N, 1.56; Cl, 7.65. IR (CsI, Nujol): ν(SO) 1132, ν(Pt-Cl) 295, 275 cm⁻¹. ¹H NMR (CDCl₃): δ 8.81 (6-H), 3.64 (²J_{PtH} = 31.6), 3.84 (²J_{PtH} = 32.6), 0.79 (d, PtCH₃, ³J_{PH} = 3.9 Hz), 0.09 (s, PtCH₃, ²J_{PtH} = 86.7 Hz). ³¹P{¹H} NMR (CDCl₃): δ 20.9 (¹J_{PtP} = 4876 Hz).

The complex [Pt₂(μ-Ph₂PPy)₂Cl₂]-DMSO (**3**) was obtained, as orange crystals, by crystallization from the mother liquor, in 38% yield (0.055 g, 0.052 mmol). IR (CsI, Nujol): ν(Pt-Cl) 254 cm⁻¹. The NMR data, in CDCl₃, are as in given ref 8.

X-ray Data Collection and Structure Refinement. Suitable red-orange crystals of **2** and **3**, of prismatic habit, were obtained by slow evaporation of the solvent from dichloromethane solutions.

Diffraction measurements were made on a Siemens-R3m/ν four-circle diffractometer using graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. Accurate unit-cell dimensions and crystal orientation matrices were obtained from least-squares refinement of 2θ, ω, χ, and ψ values of 25 strong reflections in the range 15° < 2θ < 30° for both (**2** and **3**) compounds. Lorentz and polarization corrections were applied to the intensity data, absorption correction was made using an empirical method

Table I. Crystallographic Data for Complexes **2** and **3**

	2	3
formula	C ₂₃ H ₂₇ S ₂ Cl ₂ NO ₂ PPt ₂	C ₃₆ H ₃₄ Cl ₂ N ₂ OSP ₂ Pt ₂
fw	905.66	1065.78
a, Å	35.105(4)	30.296(4)
b, Å	11.578(2)	17.805(3)
c, Å	14.572(2)	12.992(2)
β, deg	111.81(1)	98.14(1)
V, Å ³	5498.8(16)	6937.5(18)
Z	8	8
space group	C2/c	C2/c
T, °C	23	21
λ	0.710 73	0.710 73
ρ _{calcd}	2.11	1.97
μ, cm ⁻¹	106.2	84.4
R ^a	0.035	0.032
R _w ^b	0.041	0.035

$$^a R = [\sum |F_o| - |F_c|] / \sum |F_o|, \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}; \quad w = n / (\sigma^2(F_o))$$

based on ψ scans (ψ = 0–360° every 10°) for χ values near 90°. During the course of the intensity data collection the crystals showed no loss in intensity. Crystallographic data and other pertinent information are summarized in Table I and Table SVII.

Both of the structures were solved by using standard Patterson methods, successive least-squares refinements, and difference Fourier maps. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Hydrogen atoms were added at calculated positions and included in the structure factor calculations with a common thermal parameter (U = 0.06 Å²).

Disorder of the atoms of the DMSO molecule of crystallization in both the compounds was evident in the bond distances and in the shape and size of the thermal ellipsoids. The distances are shorter or longer than the expected values for the corresponding single C—S and S=O bonds, and the vibration amplitudes for S and C were unreasonably large. Attempts were made to resolve the disorder by creating two half-weighted atoms. The least-squares refinement was unsuccessful, and this approach was abandoned.

The weighting scheme used in the last refinement cycles was as follows: w = 1.00/(s²(F_o) + 0.00053F_o²) for **2** and w = 1.00/(s²(F_o) + 0.001505F_o²) for **3**, which showed reasonable consistency in a test of ωΔ² for data sectioned with respect to both F_o and (sin θ)/λ.

Scattering factors for non-hydrogen atoms were taken from ref 12 and for hydrogen atoms from ref 13. Anomalous dispersion corrections for Pt and P atoms were taken from ref 14.

All calculations were performed with the SHELX76¹⁵ and PARST¹⁶ sets of programs on the VAX3400 computer at the Centro Interdipartimentale di servizi per la Diffrazione a raggi-X dell'Università di Messina. Hydrogen coordinates and anisotropic temperature factors are available as supplementary material. Non-hydrogen coordinates are shown in Table II and III.

Results

Reaction of *cis*-[Pt(DMSO)₂Cl₂] with Ph₂PPy. When Ph₂PPy is added to a suspension of *cis*-[Pt(DMSO)₂Cl₂] in dichloromethane the colour turns yellow while the precipitate slowly dissolves. From the solution, by crystallization, the *cis*-[Pt(DMSO)(Ph₂PPy)Cl₂] (**1**) was isolated as a pale yellow crystalline solid, soluble in chlorinated solvents and moderately soluble in benzene.

Complex **1** is a *cis* square planar platinum(II) species; the Ph₂PPy is η¹-bonded through the phosphorus atom to the metal center. The IR spectrum (Nujol mull) shows two ν(PtCl) at 340 and 308 cm⁻¹; the DMSO is S-bonded to platinum center as evidenced¹⁷ by the presence of the ν(SO) at 1144 cm⁻¹. The NMR spectra, in CDCl₃, suggests that **1** is in slow equilibrium,

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Table II. Fractional Atomic Coordinates with Their Equivalent Isotropic Thermal Parameters (\AA^2)^a for Complex 2

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{equiv}
Pt(1)	0.06894(1)	-0.19200(3)	0.31696(2)	3.72(0.01)
Pt(2)	0.15208(1)	-0.04036(3)	0.34215(3)	3.69(0.01)
P(1)	0.15879(6)	-0.2150(2)	0.2937(2)	3.65(0.05)
Cl(1)	0.07850(7)	-0.0149(2)	0.2389(2)	4.53(0.06)
Cl(2)	0.14969(9)	0.1441(2)	0.4080(2)	5.58(0.08)
S(1)	0.05790(7)	-0.1081(2)	0.4398(2)	4.71(0.06)
N(1)	0.0779(2)	-0.2706(7)	0.1994(6)	3.92(0.19)
O(1)	0.0327(3)	-0.1656(8)	0.4859(6)	6.10(0.24)
C(1)	0.2015(3)	-0.2331(8)	0.2532(7)	3.95(0.24)
C(2)	0.2063(3)	-0.158(1)	0.184(1)	5.95(0.37)
C(3)	0.2380(4)	-0.171(1)	0.152(1)	6.82(0.38)
C(4)	0.2661(3)	-0.256(1)	0.1875(9)	5.81(0.35)
C(5)	0.2622(4)	-0.331(1)	0.256(1)	6.54(0.39)
C(6)	0.2304(3)	-0.321(1)	0.2876(9)	5.24(0.29)
C(7)	0.0488(3)	-0.310(1)	0.1262(9)	5.27(0.30)
C(8)	0.0462(3)	-0.345(1)	0.0369(8)	5.38(0.30)
C(9)	0.0831(4)	-0.340(1)	0.0236(9)	6.08(0.36)
C(10)	0.1171(3)	-0.300(1)	0.0988(8)	5.32(0.30)
C(11)	0.1144(3)	-0.2657(8)	0.1882(7)	4.22(0.23)
C(12)	0.1654(3)	-0.3282(8)	0.3836(7)	4.15(0.24)
C(13)	0.1603(3)	-0.4459(9)	0.3538(9)	5.29(0.28)
C(14)	0.1679(4)	-0.531(1)	0.422(1)	6.54(0.45)
C(15)	0.1809(4)	-0.508(1)	0.519(1)	7.21(0.48)
C(16)	0.1857(4)	-0.395(1)	0.5517(9)	6.36(0.40)
C(17)	0.1777(3)	-0.3052(9)	0.4829(8)	4.81(0.26)
C(18)	0.0623(4)	-0.3506(9)	0.3702(9)	5.64(0.34)
C(19)	0.2132(3)	-0.047(1)	0.430(1)	5.59(0.33)
C(20)	0.0378(6)	0.034(1)	0.408(1)	8.06(0.52)
C(21)	0.1058(4)	-0.078(2)	0.5333(9)	7.39(0.44)
O(2)	0.3795(5)	-0.158(2)	0.341(1)	5.51(0.50)
S(2)	0.4470(5)	-0.104(1)	0.278(1)	11.86(0.50)
S(2')	0.410(1)	-0.114(1)	0.3486(9)	18.29(1.23)
O(2')	0.4724(7)	-0.188(2)	0.258(1)	6.86(0.63)
C(22)	0.423(1)	-0.217(2)	0.304(1)	11.48(0.90)

^a Equivalent *B* is defined as one-third of the trace of the orthogonalized β_{ij} .

on the NMR time scale, with a species in which the Ph₂PPy acts as a chelating ligand. In fact the ³¹P{¹H} NMR of the pale yellow crystals dissolved in chloroform shows two resonances both flanked by ¹⁹⁵Pt satellites; the former at δ 17.6 ppm (¹*J*(PtP) = 3672 Hz) is consistent with a Ph₂PPy η^1 -bonded through the phosphorus atom. To a square planar platinum(II) center, the latter at δ -52.2 ppm (¹*J*(PtP) = 3439 Hz) strongly suggests the presence of a species involving the phosphorus donor atom in a four-membered chelate ring, as expected for a pyridine nitrogen atom chelation process. Conductivity measurements, in chlorinated solvents, exclude the presence in solution of ionic species formed by displacement of the coordinated chloride in the chelation process. The formation of a pentacoordinated platinum(II) species seems unlikely considering the nature of the coordinated ligands.¹⁸ Thus the chelation process occurs by displacement of coordinated DMSO; accordingly, the ¹H NMR spectrum, in CDCl₃, shows the presence in solution of free DMSO. The reaction of *cis*-[Pt(DMSO)₂Cl₂] with bidentate ligands containing nitrogen donor atoms leads either to cationic [Pt(N-N)(DMSO)-Cl]Cl^{19a} (N-N = aliphatic diamines) or neutral [Pt(N-N)Cl₂] (N-N = 2,2'-bithiazoline) species.^{19b}

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Table III. Fractional Atomic Coordinates with Their Equivalent Isotropic Thermal Parameters (\AA^2)^a for Complex 3

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{equiv}
Pt(1)	0.37720(1)	0.29342(2)	0.37126(2)	3.01(0.01)
Pt(2)	0.40157(1)	0.16872(2)	0.29430(2)	2.70(0.01)
P(1)	0.34423(6)	0.1975(1)	0.1804(1)	2.78(0.04)
P(2)	0.39415(6)	0.2314(1)	0.5161(1)	3.03(0.05)
Cl(1)	0.34649(8)	0.4028(1)	0.4421(2)	4.95(0.07)
Cl(2)	0.41950(7)	0.0479(1)	0.2257(2)	3.87(0.05)
N(1)	0.3614(2)	0.3421(3)	0.2247(5)	3.20(0.15)
C(1)	0.3657(3)	0.4159(5)	0.2069(7)	4.63(0.22)
C(2)	0.3454(4)	0.4455(5)	0.1105(8)	5.39(0.23)
C(3)	0.3373(3)	0.4022(5)	0.0293(7)	4.84(0.22)
C(4)	0.3325(3)	0.3254(5)	0.0449(6)	3.91(0.19)
C(5)	0.3450(3)	0.2975(4)	0.1449(6)	3.24(0.17)
C(6)	0.2917(3)	0.1811(4)	0.2268(6)	3.18(0.16)
C(7)	0.2864(3)	0.1143(5)	0.2772(8)	5.45(0.23)
C(8)	0.2452(3)	0.0954(6)	0.3016(9)	6.08(0.25)
C(9)	0.2090(3)	0.1447(6)	0.2807(8)	5.43(0.21)
C(10)	0.2151(3)	0.2118(6)	0.2345(8)	5.51(0.24)
C(11)	0.2560(3)	0.2310(5)	0.2084(8)	4.88(0.21)
C(12)	0.3359(3)	0.1528(4)	0.0529(6)	3.09(0.17)
C(13)	0.3727(3)	0.1366(5)	0.0040(6)	4.12(0.19)
C(14)	0.3677(3)	0.1027(6)	-0.0917(7)	5.31(0.24)
C(15)	0.3252(4)	0.0842(5)	-0.1408(7)	5.06(0.23)
C(16)	0.2893(3)	0.1017(5)	-0.0949(7)	4.60(0.21)
C(17)	0.2936(3)	0.1337(5)	0.0018(6)	3.69(0.18)
N(2)	0.4514(2)	0.1501(3)	0.4218(5)	2.99(0.14)
C(18)	0.4437(3)	0.1726(5)	0.5153(6)	3.34(0.18)
C(19)	0.4720(3)	0.1517(6)	0.6026(7)	4.88(0.23)
C(20)	0.5082(3)	0.1067(6)	0.5966(7)	4.81(0.24)
C(21)	0.5163(3)	0.0867(5)	0.5002(6)	3.79(0.18)
C(22)	0.4872(2)	0.1093(4)	0.4133(6)	3.22(0.17)
C(23)	0.4078(3)	0.2846(5)	0.6357(6)	3.64(0.19)
C(24)	0.4002(3)	0.2557(6)	0.7307(6)	4.36(0.21)
C(25)	0.4124(4)	0.2983(8)	0.8205(8)	6.28(0.26)
C(26)	0.4298(4)	0.3651(8)	0.8160(9)	7.04(0.27)
C(27)	0.4393(4)	0.3943(6)	0.7226(9)	6.33(0.26)
C(28)	0.4283(3)	0.3538(6)	0.6329(8)	5.01(0.24)
C(29)	0.3233(3)	0.0464(5)	0.5832(7)	4.88(0.21)
C(30)	0.3575(3)	0.0921(5)	0.5644(7)	4.24(0.21)
C(31)	0.3510(3)	0.1665(4)	0.5436(6)	3.24(0.17)
C(32)	0.3084(3)	0.1972(6)	0.540(1)	6.53(0.26)
C(33)	0.2742(3)	0.1509(7)	0.5626(9)	6.19(0.27)
C(34)	0.2812(3)	0.0748(6)	0.5807(7)	5.17(0.22)
S(1)	0.490(1)	0.341(2)	0.116(2)	28.09(0.41)
S(1')	0.0036(5)	0.9339(7)	0.088(1)	15.72(0.33)
C(40)	-0.004(2)	0.894(3)	0.202(3)	14.89(0.39)
C(40')	0.0000	0.798(3)	0.2500	21.04(0.40)
O(40)	-0.0395(3)	0.7956(7)	0.123(1)	10.83(0.29)

^a Equivalent *B* is defined as one-third of the trace of the orthogonalized β_{ij} .

Compound 1 has been already obtained by us^{6a} from the reaction of [Rh(COD)(Ph₂PPy)Cl] (COD = cyclooctadiene) with *cis*-[Pt(DMSO)₂Cl₂], but its characterization was not reported.

Reaction of *cis*-[Pt(DMSO)(Ph₂PPy)Cl₂] with *cis*-[Pt(DMSO)₂(CH₃)₂]. Treatment of a solution of *cis*-[Pt(DMSO)(Ph₂PPy)-Cl₂] (1) in dichloromethane, at room temperature, with an equimolar amount of *cis*-[Pt(DMSO)₂(CH₃)₂] in the same solvent gives a yellow-orange solution from which the binuclear complexes [(CH₃)ClPt(μ -Cl)(μ -Ph₂PPy)Pt(CH₃)(DMSO)]·DMSO (2) and [Pt₂(μ -Ph₂PPy)₂Cl₂]·DMSO (3) have been isolated and fully characterized by spectroscopic methods and X-ray diffraction. Complex 3 (without DMSO of crystallization) has been previously obtained by Balch et al.⁸ from the reaction of [Pt(Ph₂PPy)₂Cl₂] with [Pt(dba)₂] (dba = dibenzylideneacetone); the X-ray crystal structure of [Pt₂(μ -Ph₂PPy)₂Cl₂] is here reported the first time.

The binuclear complex 2 was isolated as pale-yellow crystals that have good solubility in chlorinated solvents but negligible solubility in alcohol and benzene. On the basis of the molecular diamagnetism and the lack of a metal-metal bond, the compound can be considered a platinum(II)-platinum(II) species. In the IR spectrum (Nujol mull), the bands at 298 and 275 cm⁻¹ indicate the presence of both terminal and bridging chloride ligands; the

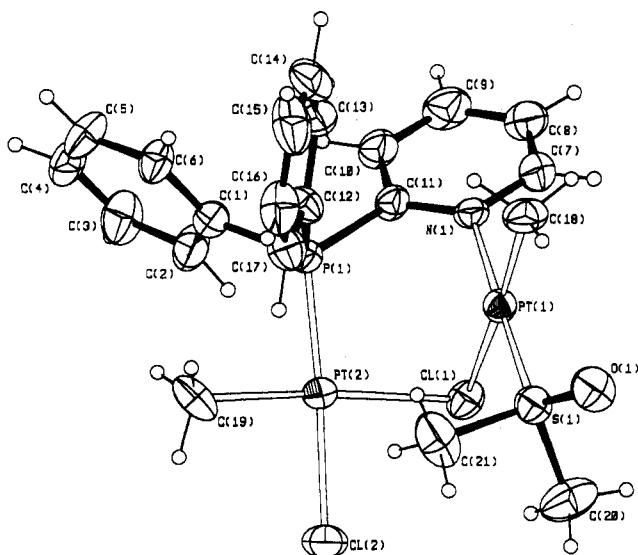


Figure 1. View of the structure of the complex $[(\text{CH}_3)\text{ClPt}(\mu\text{-Cl})(\mu\text{-Ph}_2\text{PPy})\text{Pt}(\text{CH}_3)(\text{DMSO})]\text{DMSO}$ (**2**) with the atomic numbering scheme.

shift at lower wavenumber of the bridging $\nu(\text{PtCl})$ is due to the presence of the strong labilizing methyl groups trans to this ligand. The band at 1132 cm^{-1} is in agreement with the S-coordination of the DMSO to the platinum center.¹⁷ In the $^1\text{H NMR}$ spectrum of **2**, in CDCl_3 at room temperature, the 6-hydrogen of the pyridine ring results shifted to higher frequency (δ 8.81 ppm) as usually observed when the pyridine nitrogen atom is coordinated. The protons of the coordinated DMSO are split into two resonances at δ 3.84 and 3.64 ppm, each presenting ^{195}Pt satellites ($^2J(\text{PtH}) = 32.6$ and 31.6 Hz respectively); the magnetic inequivalence of the two DMSO methyl groups is a consequence of the asymmetry introduced by the five-membered Pt,P,N,Pt,Cl ring. The methyl bonded to the platinum(II) coordinated to the phosphorus donor atom of the Ph₂PPy is split in a doublet (δ 0.79 ppm, $^3J(\text{PH}) = 3.9$ Hz) with ^{195}Pt satellites ($^2J(\text{PtH}) = 79.5$ Hz). The methyl bonded to the platinum(II) coordinated to the nitrogen is a singlet with ^{195}Pt satellites (δ 0.09 ppm, $^2J(\text{PtH}) = 86.7$ Hz). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in CDCl_3 shows a single resonance at δ 20.9 ppm, with ^{195}Pt satellites ($^1J(\text{PtP}) = 4876$ Hz); the exceptionally high $^1J(\text{PtP})$ values compare with those reported²⁰ for planar platinum(II) complexes, such as $[\text{Pt}(\text{CH}_3\text{CN})(\text{CH}_3)(\text{dppe})]\text{BF}_4$ [$\text{dppe} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$; $^1J(\text{PtP})_{\text{trans to CH}_3\text{CN}} = 4370$ Hz], $[\text{PtClX}(\text{dppe})]$ [$\text{X} = 1\text{-cyclohexenyl}$, $^1J(\text{PtP})_{\text{trans to Cl}} = 4418$ Hz; $\text{X} = \text{C}_2\text{H}_5$, $^1J(\text{PtP})_{\text{trans to Cl}} = 4386$ Hz; $\text{X} = \text{CH}_2\text{C}_6\text{H}_5$, $^1J(\text{PtP})_{\text{trans to Cl}} = 4332$ Hz] and *cis*- $[\text{Pt}(\text{PEt}_3)_2(\text{neopentyl})\text{Cl}]$ [$^1J(\text{PtP})_{\text{trans to Cl}} = 4427$ Hz].

Compound **3** was isolated as orange crystals that are stable as a solid. The IR spectrum (Nujol mull) shows one $\nu(\text{PtCl})$ terminal band at 254 cm^{-1} along with bands associated with the Ph₂PPy ligand; the low value of the $\nu(\text{PtCl})$ can be attributed to the high trans influence of the metal-metal bond. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectral data, in CDCl_3 , are in accordance with those reported by Balch et al.⁸

Crystal Structure of $[\text{Pt}_2(\text{CH}_3)_2(\text{DMSO})\text{Cl}(\mu\text{-Cl})(\mu\text{-Ph}_2\text{PPy})]\text{DMSO}$ (2**).** The structure of **2** is depicted in Figure 1 together with the atomic numbering scheme; selected bond distances and angles are given in Table IV. The crystal structure of **2** consists of dimeric molecules, with no unusual intermolecular contacts, that contain two platinum atoms and one dimethyl sulfoxide crystallization molecule. The disordered DMSO of solvation has been omitted in the figures for clarity.

Table IV. Selected Bond Distances (Å) and Angles (deg) for Complex **2**

Distances			
Pt(1)–Pt(2)	3.3075(6)	S(1)–C(21)	1.76(1)
Pt(1)–Cl(1)	2.428(3)	N(1)–C(7)	1.33(1)
Pt(1)–S(1)	2.194(3)	N(1)–C(11)	1.35(1)
Pt(1)–N(1)	2.063(9)	Pt(2)–C(19)	2.05(1)
Pt(1)–C(18)	2.04(1)	P(1)–C(1)	1.81(1)
Pt(2)–P(1)	2.183(2)	P(1)–C(11)	1.832(8)
Pt(2)–Cl(1)	2.477(2)	P(1)–C(12)	1.81(1)
Pt(2)–Cl(2)	2.356(3)	S(1)–O(1)	1.46(1)
S(1)–C(20)	1.78(1)		
Angles			
Pt(1)–Cl(1)–Pt(2)	84.81(8)	Pt(2)–P(1)–C(12)	116.0(3)
N(1)–Pt(1)–C(18)	89.6(4)	Pt(2)–P(1)–C(11)	114.0(3)
S(1)–Pt(1)–C(18)	90.5(4)	Pt(2)–P(1)–C(1)	114.4(3)
S(1)–Pt(1)–N(1)	178.6(2)	C(11)–P(1)–Cl(2)	102.5(4)
Cl(1)–Pt(1)–C(18)	173.5(3)	C(1)–P(1)–C(12)	104.7(4)
Cl(1)–Pt(1)–N(1)	83.9(2)	C(1)–P(1)–C(11)	103.8(4)
Cl(1)–Pt(1)–S(1)	96.03(9)	Pt(1)–S(1)–C(21)	108.2(5)
Cl(2)–Pt(2)–C(19)	88.1(4)	Pt(1)–S(1)–C(20)	111.6(5)
Cl(1)–Pt(2)–C(19)	175.1(3)	Pt(1)–S(1)–O(1)	119.7(4)
Cl(1)–Pt(2)–Cl(2)	87.28(9)	C(20)–S(1)–C(21)	101.1(8)
P(1)–Pt(2)–C(19)	87.4(4)	O(1)–S(1)–C(21)	107.6(6)
P(1)–Pt(2)–Cl(2)	174.8(1)	O(1)–S(1)–C(20)	107.0(7)
P(1)–Pt(2)–Cl(1)	97.32(9)	Pt(1)–N(1)–C(11)	121.6(6)
Pt(1)–N(1)–C(7)	117.4(7)		

Each platinum atom is in a nearly square planar environment surrounded by the Ph₂PPy and the chloride Cl(1) atoms of the bridging ligands. The coordination around the Pt(1) is completed by the nitrogen atom from the Ph₂PPy bridging ligand, the sulfur atom of DMSO and one methyl group; the coordination around the Pt(2) involves, beyond the chloride bridged atom and the phosphorus of Ph₂PPy, the C(19) carbon atom from a methyl group and the terminal chloride Cl(2). The methyl groups are in trans-position to the Cl(1) bridging atom. The Pt(1)⋯Pt(2) separation of 3.3075(6) Å is too long to be considered indicative of a metal-metal bond; in accordance the P(1)⋯N(1) separation of 2.734(3) Å is shorter than the Pt⋯Pt one. In the unsymmetrical chloro bridge, the Pt(1)–Cl(1) and Pt(2)–Cl(1) distances of 2.428(3) and 2.477(2) Å, respectively, are somewhat long as a consequence of the high trans influence of the σ -bonded carbon of the methyl group. The difference in the Pt(1)–Cl(1) and Pt(2)–Cl(1) bond distances (0.049 Å) is a consequence of distortions in the Pt(1) and Pt(2) coordination planes due to the rigidity and short bite angle of the bridging ligand Ph₂PPy.

The P(1)Pt(2)Pt(1)N(1) torsion angle of $35.2(2)^\circ$ is indicative of a rather strong steric hindrance in the complex. The Ph₂PPy twisting about the Pt–Pt vector avoids the unfavorable contacts of the phenyl groups with the methyl group coordinated to Pt(2) and of DMSO with Cl(1) bridging ligand; in agreement, the separations C(19)⋯C(1), C(19)⋯C(17) and C(1)⋯C(19) are 3.26(2), 3.44(2) and 3.26(2) Å respectively.

The bond distances and angles are consistent with a nearly square planar geometry at platinum atoms. The maximum deviation from the square planar coordination involves the chloro bridge; in fact the Cl(1)–Pt(1)–N(1) and Cl(1)–Pt(1)–S(1) angles are respectively $83.9(2)^\circ$ and $96.03(9)^\circ$, and the Cl(1)–Pt(2)–P(1) angle is $97.32(9)^\circ$. Maximum deviations from the mean Pt(2)Cl(1)Cl(2)P(1)C(19) coordination plane are 0.052 Å for C(19), of -0.055 Å for Cl(2) and -0.034 Å for P(1); the deviations from the mean Pt(1)N(1)S(1)Cl(1)C(18) square planar coordination plane are of minor extent.

The Pt(2)–P(1) (2.183(2) Å), Pt(1)–N(1) (2.063(9) Å), and Pt(1)–S(1) (2.194(3) Å) bond distances lie within the expected range as observed for other related complexes.

Crystal Structure of $[\text{Pt}_2\text{Cl}_2(\mu\text{-Ph}_2\text{PPy})_2]\text{DMSO}$ (3**).** A view of the molecule of **3** with the atomic numbering scheme is depicted in Figure 2; selected bond distances and angles are given in Table V. The crystal structure consists of discrete binuclear $[\text{Pt}_2\text{Cl}_2(\mu\text{-Ph}_2\text{PPy})_2]$ and a disordered DMSO molecule of solvation in a 1:1

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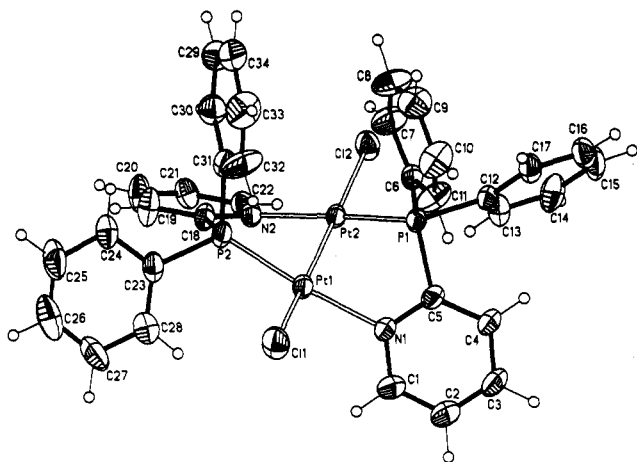


Figure 2. View of the structure of the complex $[\text{Pt}_2(\mu\text{-Ph}_2\text{PPy})_2\text{Cl}_2]\text{DMSO}$ (3) with the atomic numbering scheme.

Table V. Selected Bond Distances (Å) and Angles (deg) for Complex 3

Distance			
Pt(1)–Pt(2)	2.5853(6)	P(1)–C(12)	1.823(7)
Pt(1)–P(2)	2.180(2)	P(2)–C(18)	1.832(8)
Pt(1)–Cl(1)	2.397(2)	P(2)–C(23)	1.817(8)
Pt(1)–N(1)	2.085(6)	P(2)–C(31)	1.817(8)
Pt(2)–P(1)	2.178(2)	N(1)–C(1)	1.34(1)
Pt(2)–Cl(2)	2.420(2)	N(1)–C(5)	1.345(9)
Pt(2)–N(2)	2.104(6)	N(2)–C(18)	1.33(1)
P(1)–C(5)	1.839(8)	N(2)–C(22)	1.322(9)
P(1)–C(6)	1.805(8)		
Angles			
Cl(1)–Pt(1)–N(1)	87.8(2)	C(23)–P(2)–C(31)	104.3(4)
P(2)–Pt(1)–N(1)	174.0(2)	C(18)–P(2)–C(31)	104.5(4)
P(2)–Pt(1)–Cl(1)	97.87(8)	C(18)–P(2)–C(23)	102.4(4)
Pt(2)–Pt(1)–N(1)	92.6(2)	Pt(1)–N(1)–C(5)	118.1(5)
Pt(2)–Pt(1)–Cl(1)	173.57(7)	Pt(1)–N(1)–C(1)	123.3(5)
Pt(2)–Pt(1)–P(2)	81.59(6)	C(1)–N(1)–C(5)	118.6(7)
Pt(1)–Pt(2)–N(2)	92.5(2)	N(1)–C(1)–C(2)	121.4(8)
Pt(1)–Pt(2)–Cl(2)	175.82(6)	N(1)–C(5)–C(4)	122.0(7)
Pt(1)–Pt(2)–P(1)	79.42(5)	P(1)–C(5)–C(4)	124.6(6)
Cl(2)–Pt(2)–N(2)	88.6(2)	P(1)–C(5)–N(1)	113.2(5)
P(1)–Pt(2)–N(2)	170.7(2)	P(1)–C(6)–C(11)	122.6(6)
P(1)–Pt(2)–Cl(2)	99.11(7)	P(1)–C(6)–C(7)	117.8(6)
Pt(2)–P(1)–C(12)	120.6(3)	P(1)–C(12)–C(17)	122.5(6)
Pt(2)–P(1)–C(6)	113.0(3)	P(1)–C(12)–C(13)	119.2(6)
Pt(2)–P(1)–C(5)	111.2(3)	Pt(2)–N(2)–C(22)	121.8(5)
Pt(1)–P(1)–C(12)	165.4(3)	Pt(2)–N(2)–C(18)	118.1(5)
Pt(1)–P(1)–C(6)	91.2(2)	P(2)–C(18)–N(2)	115.3(6)
Pt(1)–P(1)–C(5)	69.5(2)	P(2)–C(23)–C(28)	119.4(6)
C(6)–P(1)–C(12)	102.5(3)	P(2)–C(23)–C(24)	121.4(7)
C(5)–P(1)–C(12)	101.6(3)	P(2)–C(31)–C(30)	124.9(6)
C(5)–P(1)–C(6)	106.5(4)	P(2)–C(31)–C(32)	115.5(6)
Pt(1)–P(2)–C(31)	113.8(3)	Pt(1)–P(2)–C(18)	112.2(3)
Pt(1)–P(2)–C(23)	118.1(3)		

ratio. The molecules of solvation have been omitted from Figure 2 for clarity; there is no interaction of the solvation molecules with $[\text{Pt}_2\text{Cl}_2(\mu\text{-Ph}_2\text{PPy})_2]$.

The coordination geometry around the platinum atoms is nearly square planar; the deviation from the square planar coordination plane is largest for Pt(1), with least-squares plane deviations for atoms ranging from -0.174 [N(1)] to 0.026 Å [Cl(1)]. In both metal centers the largest deviations are observed with the phosphorus and chloro atoms; in fact the P(1)–Pt(2)–Cl(2) and P(2)–Pt(1)–Cl(1) angles are $99.11(7)$ and $97.87(8)^\circ$ while the P(1)–Pt(2)–Pt(1) and P(2)–Pt(1)–Pt(2) angles are $79.42(5)$ and $81.59(6)^\circ$, respectively. This could be to minimize nonbonded contacts between the chloride atoms and the phenyl ring [Cl(1)⋯C(28) = $3.36(1)$ Å and Cl(2)⋯C(13) = $3.414(8)$ Å].

The metal coordination planes are twisted about the Pt–Pt vector giving a dihedral angle of $35.6(1)^\circ$; the torsion angles

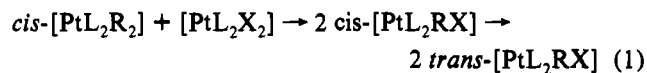
N(2)–Pt(2)–Pt(1)–P(2) and N(1)–Pt(1)–Pt(2)–P(1) are $-35.1(2)$ and $-38.6(2)^\circ$, respectively.

The Pt–Pt bond length of $2.5853(6)$ Å is somewhat shorter than that found in the $[\text{Pt}_2\text{Cl}_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2]^{21}$ and is at lower limit of the Pt–Pt distances (2.581 – $2.628(1)$ Å) reported for platinum(I) complexes.²² The Pt(1)–Pt(2)–Cl(2) and Pt(2)–Pt(1)–Cl(1) angles are respectively $175.82(6)$ and $173.57(7)^\circ$; the Pt(1)–Cl(1) and Pt(2)–Cl(2) bond distances of $2.397(2)$ and $2.420(2)$ Å are in substance the same as those found in the $[\text{Pt}_2\text{Cl}_2(\text{dppm})_2]$ and reflect the high trans influence of the metal–metal bond. The Pt(1)–N(1) and Pt(2)–N(2) bond lengths of $2.085(6)$ and $2.104(6)$ Å are consistent with the relative trans influence of the phosphine groups, while the Pt–P bond lengths are in the range normally found. The overall structural features of 3 are similar to that of the analogous palladium complex $[\text{Pd}_2\text{Cl}_2(\mu\text{-Ph}_2\text{PPy})_2]$.²³

Discussion

The reaction of 1 with *cis*- $[\text{Pt}(\text{DMSO})_2(\text{CH}_3)_2]$ is a very complex one as evidenced by monitoring the reaction course by NMR spectroscopy and as indicated by the nature of the isolated products. The formation of the platinum(I)–platinum(I) binuclear complex 3 suggests that a redox process occurs in solution; we did not succeed in identifying the oxidation product whose characterization has been probably prevented by a decomposition process. Formation of 2 appears to be the result of a methyl for chloride exchange process at the platinum(II) centers bridged by the Ph_2PPy ligand and the reaction can be considered a symmetrization one.

A systematic study of the symmetrization reactions (eq 1) (R = alkyl or aryl; X = halide; L = neutral ligand) has been previously



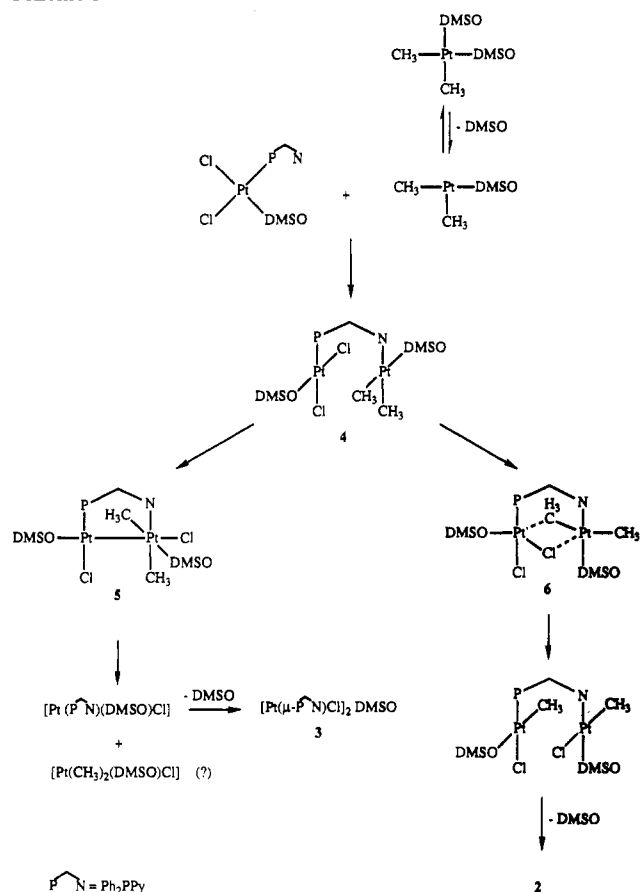
undertaken by Puddephatt et al.^{24–26} A mechanism involving either a cyclic binuclear intermediate containing bridged methyl and chloride ($\text{X} = \text{Cl}$) groups or an oxidative addition of the Pt–Cl bond into the platinum center of $[\text{PtR}_2\text{L}_2]$ has been considered to be operative when L is a tertiary phosphine or arsine. Kinetic evidences indicated that these reactions occur without prior dissociation of a ligand L from the starting platinum(II) species.

When L is a labile neutral ligand which can also act as bridging ligand, such as $\text{S}(\text{CH}_3)_2$, kinetic studies showed that the methyl for chloride exchange reaction between *cis*- $\{\text{Pt}(\text{CH}_3)_2[\text{S}(\text{CH}_3)_2]_2\}$ and *cis*- or *trans*- $\{\text{PtCl}_2[\text{S}(\text{CH}_3)_2]_2\}$ to give *trans*- $\{\text{Pt}(\text{CH}_3)\text{Cl}[\text{S}(\text{CH}_3)_2]_2\}$ occurs with preliminary dissociation of $\text{S}(\text{CH}_3)_2$ from *cis*- $\{\text{Pt}(\text{CH}_3)_2[\text{S}(\text{CH}_3)_2]_2\}$ by steps involving donation of a lone pair from either the chloride or $\text{S}(\text{CH}_3)_2$ to the T-shaped unsaturated species $\{\text{Pt}(\text{CH}_3)_2[\text{S}(\text{CH}_3)_2]\}$ and formation of binuclear intermediates. The formation of the final products has been explained by steps involving either an intramolecular oxidative addition–reductive elimination or a S_E^2 mechanism.

The reaction between *cis*- $[\text{Pt}(\text{DMSO})(\text{Ph}_2\text{PPy})\text{Cl}_2]$ (1) and *cis*- $[\text{Pt}(\text{DMSO})_2(\text{CH}_3)_2]$ offers further insight into the pathway

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Scheme I.



proposed by Puddephatt for the symmetrization reactions (eq 1). Although a kinetic study was not undertaken, the pathway showed in Scheme I seems to be very likely in the light of the proposal of Puddephatt et al.²⁶ for the reactions of platinum(II) substrates containing $\text{S}(\text{CH}_3)_2$ as neutral ligand L. The first step implies nucleophilic attack of the Ph_2PPy nitrogen atom of **1** on the platinum(II) center of $[\text{Pt}(\text{DMSO})(\text{CH}_3)_2]$ to give the binuclear intermediate **4**; the formation of the unsaturated T-shape species $[\text{Pt}(\text{DMSO})(\text{CH}_3)_2]$, in dichloromethane solutions containing

$\text{cis-}[\text{Pt}(\text{DMSO})_2(\text{CH}_3)_2]$ by a dissociative path, has been well documented by kinetic studies.²⁷ Very likely the reaction intermediate **4** can undergo two different processes: (a) oxidative addition of a Pt–Cl bond across the other platinum(II) center, which is made sufficiently basic by the presence of the strong σ -donor methyl groups and the Ph_2PPy pyridine nitrogen atom (intermediate **5**) or (b) a simultaneous bridging coordination of chloride and methyl ligands (intermediate **6**). The ability of the short bite angle Ph_2PPy bridging ligand to hold the metal centers in close proximity seems to be a very important factor in promoting both these reaction paths. Recently we observed⁶ intramolecular oxidative addition processes in heterobinuclear complexes containing the Ph_2PPy as bridging ligand and a sufficiently basic metal center. The product of the oxidative addition should be a very unstable $\text{Pt}^{\text{I}}\text{--Pt}^{\text{III}}$ intermediate, whose binuclear structure can be disrupted, breaking the Pt–N bond. Although recently we have demonstrated⁶ the importance of the steric requirements of the Ph_2PPy when coordinated as bridging ligand in determining the breaking of a metal–ligand bond, we consider the instability of the $\text{Pt}^{\text{I}}\text{--Pt}^{\text{III}}$ intermediate to be due essentially to electronic factors; to our knowledge binuclear $\text{Pt}^{\text{I}}\text{--Pt}^{\text{III}}$ complexes have never been isolated. The most likely moiety derived from the $\text{Pt}^{\text{I}}\text{--Pt}^{\text{III}}$ intermediate that gives complex **3** should be the platinum(I) species $[\text{Pt}(\text{DMSO})(\text{Ph}_2\text{PPy})\text{Cl}]$; an intermolecular nucleophilic attack of the pyridine nitrogen atom on the Pt^{I} center, with concomitant displacement of DMSO, could lead to the binuclear complex **3**.

The expected unstability of the $\text{Pt}^{\text{I}}\text{--Pt}^{\text{III}}$ species could explain the lack of meaningful spectroscopic evidence concerning this intermediate.

The methyl for chloride exchange process affording **2** occurs through the intermediate **6** containing both these ligands bridging to metal centers and subsequent release of DMSO. The presence of the short bite Ph_2PPy bridging ligand favors this process.

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Supplementary Material Available: Tables SI–SVIII, giving hydrogen atom coordinates, complete bond lengths and angles, anisotropic thermal parameters, and crystal data and details of the structure determination (8 pages). Ordering information is given on any current masthead page.

(27) Romeo, R., *Comments Inorg. Chem.* **1990**, *11*, 21 and references therein.