Journal of Organometallic Chemistry, 406 (1990) 261–267
Elsevier Sequoia S.A., Lausanne
JOM 21392

Studies of binuclear methyl and phenyl derivatives of platinum(II)

Mehdi Rashidi *, Zahra Fakhroeian
Chemistry Department, College of Sciences, Shiraz University, Shiraz (Iran)

and Richard J. Puddephatt
Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7 (Canada)

(Received August 28th, 1990)

Abstract

Some reactions of the binuclear organoplatinum complexes $[Pt_2R_4(\mu\text{-}SMe_2)_2]$, where R = Me or Ph are described, and a new synthetic method for the complex with R = Ph is reported. The dimethylsulphide ligands are easily displaced by other ligands, L, to give *cis*-$[PtR_2L_2]$. When R = Me, reaction with MeI and $Ph_2PCH_2PPh_2$, dppm, gives $[\{PtMe_3(\mu\text{-}I)\}_2(\mu\text{-dppm})]$, whereas when R = Ph, reaction with MeI gives $[(PtPh_2MeI)_4]$, which has been characterized as its adduct with 2,2′-bipyridine $[PtIMePh_2(bipy)]$. The latter complex exists as a mixture of two isomers, though the reaction between $[PtPh_2(bipy)]$ and MeI initially gives only one isomer of $[PtIMePh_2(bipy)]$, formed by *trans*-oxidative addition. The reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with hydrochloric acid yields a 1:1 mixture of $[PtCl_2(SMe_2)_2]$ and $[(PtMe_3Cl)_4]$, and it is suggested that this reaction involves an intramolecular methyl group transfer between the platinum atoms of the dimer.

Introduction

The complexes $[Pt_2Me_4(\mu\text{-}SR_2)_2]$ were first prepared and studied by Vrieze and coworkers [1,2]. They have become standard precursors to other organoplatinum complexes since the dialkylsulphide ligands are easily displaced by other ligands L to give *cis*-$[PtMe_2L_2]$ and since oxidation with silver(I) or mercury(II) carboxylates gives interesting diplatinum(III) complexes $[Pt_2Me_4(\mu\text{-}O_2CR)_2(SR_2)_2]$ while oxidation with alkyl halides gives diplatinum(IV) complexes [1–10]. This article reports some new reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and of the phenylplatinum analogue $[Pt_2Ph_4(\mu\text{-}SMe_2)_2]$.

Results and discussion

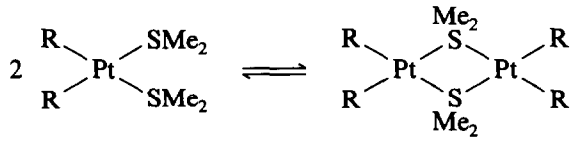
The most useful property of the dialkylsulphide complexes of platinum is the ease of displacement of the dialkylsulphide ligand by many other ligands (eq. 1).

(1)

(**1**, R = Me; **2**, R = Ph)

0022-328X/91/$03.50

The dimethylsulphide ligand dissociates easily and gives the sulphur-bridged dimers (eq. 2).



$$2\ cis\text{-}[PtR_2(SMe_2)_2] \rightleftharpoons [Pt_2R_4(\mu\text{-}SMe_2)_2] + 2SMe_2 \qquad (2)$$

(**3**, R = Me; **4**, R = Ph)

Again, treatment of **3** or **4** with ligands L leads to formation of *cis*-$[PtR_2L_2]$ in almost quantitative yield. Examples are reported with L = PMe_2Ph, PPh_3, SMe_2 or SEt_2 and L_2 = 2,2′-bipyridine (see Experimental Section).

The equilibrium constant for eq. 2 is large when R = Me and it is not possible to synthesize *cis*-$[PtMe_2(SMe_2)_2]$ in pure form since partial dissociation of SMe_2 always occurs to give some dimer [6]. However, when R = Ph, the equilibrium constant is small and *cis*-$[PtPh_2(SMe_2)_2]$, **2**, is readily prepared [10]. We find that the complex $[Pt_2Ph_4(\mu\text{-}SMe_2)_2]$, **4**, is easily prepared in pure form by slow evapora-

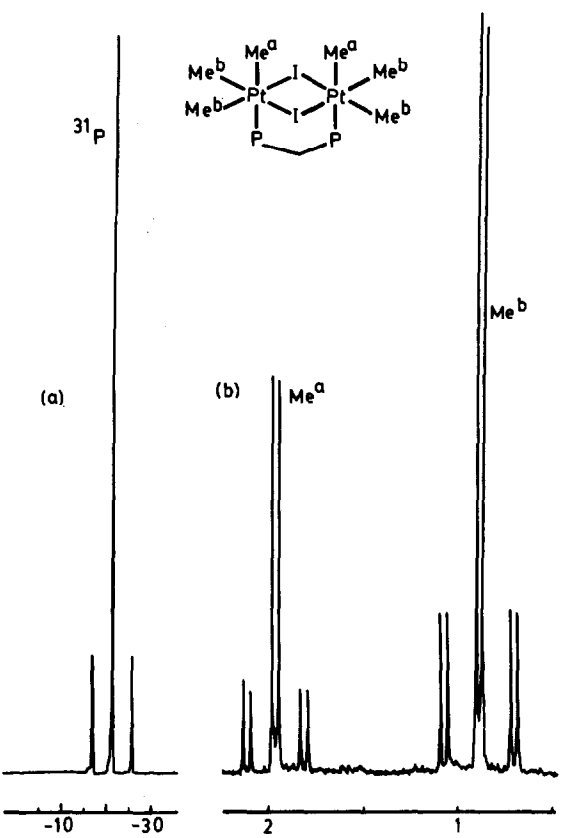
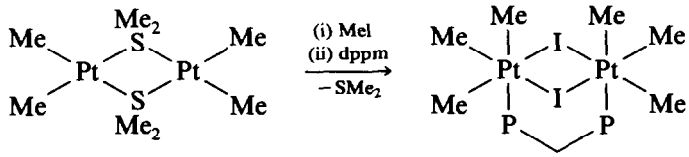


Fig. 1. NMR spectra of $[Pt_2(\mu\text{-}I)_2Me_6(\mu\text{-dppm})]$; (**a**) ^{31}P NMR spectrum (121.5 MHz, $\delta = -21.9$, $^1J(PtP) = 1056$ Hz, long range PtP coupling not resolved); (*b*) ^1H NMR spectrum in the MePt region.

tion of a solution of monomer **2** in chloroform, during which period dimethylsulphide dissociates and evaporates, followed by recrystallization of **4**. It reacts very rapidly with dimethylsulphide to regenerate **2** and with many other ligands L to give *cis*-$[PtPh_2L_2]$.

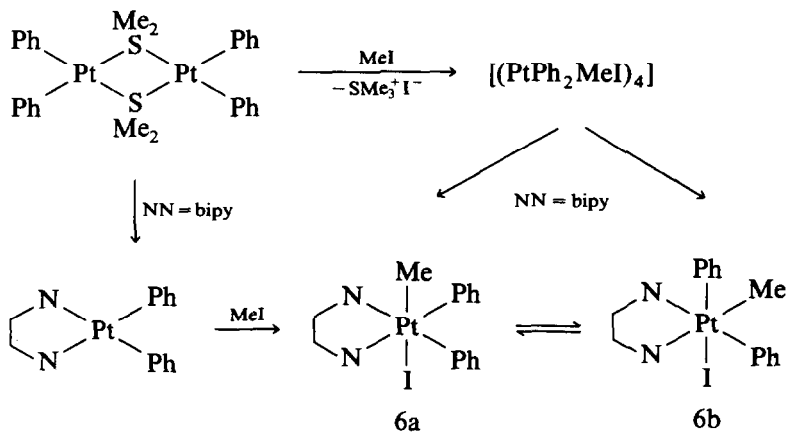
Reaction of **3** with MeI is known to give a mixture of $[\{PtMe_3I(\mu\text{-}SMe_2)\}_2]$, *fac*-$[PtIMe_3(SMe_2)_2]$ and $[(PtMe_3I)_4]$ [1,2,7]. We now find that reaction of this mixture with $Ph_2PCH_2PPh_2$, dppm, gives $[\{PtMe_3(\mu\text{-}I)\}_2(\mu\text{-dppm})]$, **5**, in very high yield according to eq. 3, $\widehat{P\ P}$ = dppm.



(3)

Complex **5** was readily characterized by elemental analysis and by ^1H and ^{31}P NMR spectroscopy (Fig. 1). In particular, the ^1H NMR spectrum contained two methylplatinum resonances in a 2:1 ratio and with coupling constants $^2J(PtCH_3)$ expected for methyl groups *trans* to iodide and phosphorus respectively, while the ^{31}P chemical shift in the ^{31}P NMR was characteristic of bridging dppm [11]. Related complexes $[\{PtMe_3(\mu\text{-}X)\}_2(\mu\text{-}Me_2AsSAsMe_2)]$, X = I, Br, Cl have been characterized by Abel and co-workers [12].

Complex **4** also reacted with MeI, though more slowly, and gave a mixture of insoluble white and yellow solids, thought to be $SMe_3^+I^-$ and $[(PtPh_2MeI)_4]$ (eq. 4).



(4)

6a 6b

The latter was characterized by its reaction with 2,2′-bipyridine to give $[PtIMePh_2(bipy)]$ as a mixture of isomers **6a** and **6b**, eq. 4, formed in a 1:2 molar ratio. Reaction of $[PtPh_2(2,2'\text{-bipyridine})]$ with MeI gave the isomer **6a** only, by *trans* oxidative addition, but this gave the same 1:2 mixture of **6a** and **6b** after isolation and redissolution. This rearrangement to the equilibrium mixture probably occurs by dissociation of I^- followed by rearrangement within a 5-coordinate intermediate and then recoordination of I^-.

The most unusual reaction which has been discovered during this research occurs between $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, **3**, and hydrochloric acid. This reaction reproducibly

gave $[PtCl_2(SMe_2)_2]$, $[(PtMe_3Cl)_4]$, in equimolar amounts, and methane. The simplest equation which accounts for these products is shown in eq. 5.

$$[Pt_2Me_4(\mu\text{-}SMe_2)_2] + 3HCl \longrightarrow [PtCl_2(SMe_2)_2] + 1/4[(PtMe_3Cl)_4] + CH_4 + H_2 \quad (5)$$

We have detected methane in the product mixture but not H_2. However, attempted detection of H_2 by gas chromatography was at the sensitivity limit and it may have been missed. The reaction clearly involves a methyl group transfer between platinum atoms to give the product $[(PtMe_3Cl)_4]$ and, as far as we are aware, this is unprecedented in reactions of this type [13]. It is therefore probable that the methyl group transfer occurs intramolecularly across the $Pt_2(\mu\text{-}SMe_2)_2$ unit, though the detailed mechanism is difficult to determine. In contrast, reaction of *cis*-$[PtPh_2(SMe_2)_2]$ or $[Pt_2Ph_4(\mu\text{-}SMe_2)_2]$ with hydrochloric acid gave only cleavage of phenylplatinum bonds with formation of $[PtCl_2(SMe_2)_2]$ and benzene.

Experimental

All reactions involving organolithium or organomagnesium compounds were carried out under nitrogen. A solution of PhLi (~ 1 *M*) was prepared by the standard method. Solutions of Ph_2Mg (~ 1 *M*) were prepared by the addition of dioxane to PhMgBr. $[PtCl_2(SMe_2)_2]$, as a mixture of *cis*- and *trans*-isomers, was prepared by a published method [14]. $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ was prepared by a published method [6,9]. ^1H NMR spectra were recorded by using Hitachi Perkin Elmer 60 MHz and Varian XL-200 spectrometers, and ^{31}P NMR spectrum using a Varian XL-300 spectrometer, using TMS and trimethylphosphate references, respectively. GC analysis was carried out using a Varian 1400 chromatograph with a molecular sieve column. Elemental analyses were carried out by Alfred Bernhardt Analytische Laboratorien, or by Guelph Chemical Laboratories.

Reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with HCl

$[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.05 g) was dissolved in $CDCl_3$ (2 mL) and concentrated HCl (5 drops) was added. Gas evolution occurred immediately. The gas phase contained CH_4 as indicated by GC analysis. The solvent was removed under reduced pressure and the residue dried in vacuum. The product was identified as a 1 : 1 mixture of $[PtMe_3Cl]_4$ and *trans*-$[PtCl_2(SMe_2)_2]$, by comparison of its ^1H NMR spectrum with those of authentic samples.

$[\{PtMe_3(\mu\text{-}I)\}_2(\mu\text{-}dppm)]$

$[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.1 g) was suspended in ether (20 mL) and MeI (0.5 mL) was added. The mixture was stirred overnight at room temperature, and the solvent then removed under reduced pressure. The resulting solid was dissolved in ether (40 mL) and the solution filtered. Dppm (0.15 g) was added to the filtrate with stirring. A white precipitate formed immediately. The mixture was set aside without stirring for 2 days. The white solid was isolated, washed with ether (10 mL), and dried in vacuum. It was purified by dissolving it in CH_2Cl_2 (2 mL) and layering the solution with methanol (10 mL). After 2 days the crystals which separated were washed with methanol (1 mL) and dried under high vacuum. Total yield 65%, m.p. 165–172°C

(dec.). Anal. Found: C, 33.39; H, 3.80. $Pt_2Me_6I_2$(dppm) calc.: C, 33.26; H, 3.57%. ^1H NMR ($CDCl_3$) δ 0.88 (d, $^3J(PH) = 7$ Hz, $^2J(PtH) = 73$ Hz, MePt *trans* to I); 1.97 (d, $^3J(PH) = 8$ Hz, $^2J(PtH) = 60$ Hz, MePt *trans* to P); 4.87 (t, $^2J(PH) = 11$ Hz, $^3J(PtH) = 9$ Hz, CH_2 of dppm). ^{31}P NMR ($CDCl_3$): δ −21.87 (s, $^1J(PtP) = 1056$ Hz).

Reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$

(i) With SEt_2. $[Pt_2Me_4(\mu - SMe_2)_2$ (0.05 g) dissolved in $CHCl_3$ and SEt_2 (one drop) was added. This was stirred for 5 minutes. Evaporation of the solvent gave $[Pt_2Me_4(\mu\text{-}SEt_2)_2]$ identified by its ^1H NMR spectrum.

(ii) With other ligands. Reaction of PMe_2Ph, PPh_3, or bipy (4.0 mmol) and $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (1.0 mmol) in ether led to precipitation of crystals in 80–90% yields. The crystals were isolated and identified as *cis*-$[PtMe_2L_2]$ ($L = PMe_2Ph$, PPh_3, L_2 = bipy) from their ^1H NMR spectra.

cis-*$[PtPh_2(SMe_2)_2]$*

(i) A solution of PhLi (40 mL) in ether was added at 0 °C to a stirred suspension of $[PtCl_2(SMe_2)_2]$ (1.0 g) in dry ether (40 mL). After 4 h, the solution was carefully hydrolyzed at −4 °C with H_2O (~ 10 mL). The layers were separated and the aqueous layer was twice extracted with CH_2Cl_2 (20 mL). The combined organic layers were dried over anhydrous sodium sulphate, filtered, and evaporated in air. The white residue was washed twice with 10 mL ether and dried in vacuum. Yield 0.6 g, m.p. 100 °C. Anal. Found: C, 40.54; H, 4.54. $PtPh_2(SMe_2)_2$ calc.: C, 40.58; H, 4.68%. ^1H NMR ($CDCl_3$): δ 2.11 (s, $^3J(PtH) = 24$ Hz, SMe_2); 7.36 (d, $^3J(PtH_o) = 74.0$ Hz, $^3J(H_oH_m) = 6$ Hz, H_o of Ph, 2H); 6.94 (m, H_m of Ph, 2H); 6.76 (m, H_p of Ph, 1H).

(ii) $[PtCl_2(SMe_2)_2]$ (0.3 g) was suspended in dry ether (20 mL). The mixture was cooled to 0 °C and a solution of Ph_2Mg in ether (15 mL) was added dropwise with stirring. After 1 h, an excess of Ph_2Mg was carefully hydrolyzed at 0 °C with H_2O (~ 10 mL). The desired product was recovered from the organic phase as a creamy white powder. Yield 70%.

$[Pt_2Ph_4(\mu\text{-}SMe_2)_2]$

cis-$[PtPh_2(SMe_2)_2]$ (0.1 g) was dissolved in $CHCl_3$ (120 mL). The solvent was allowed to evaporate slowly in air to leave a white solid residue. The solid was dissolved in CH_2Cl_2 (3 mL) and the solution was carefully layered with n-pentane (15 mL). Long colorless needles formed and were separated and dried under vacuum. Yield 0.06 g, m.p. = 88 °C (dec.). Anal. Found: C, 40.97; H, 4.37. $Pt_2Ph_4(SMe_2)_2$ calc.: C, 40.87; H, 3.89%. ^1H NMR ($CDCl_3$): δ 2.44 (m, $^3J(PtH) = 19$ Hz, SMe_2); 7.40 (d, $^3J(PtH_o) = 68$ Hz, $^3J(H_oH_m) = 6$ Hz, H_o of Ph, 2H); 6.94 (m, H_m of Ph, 2H); 6.80 (m, H_p of Ph, 1H).

Reaction of $[Pt_2Ph_4(\mu\text{-}SMe_2)_2]$ with HCl

$[Pt_2Ph_4(\mu\text{-}SMe_2)_2]$ (0.05 g) was dissolved in ether (15 mL), and ether (8 mL) containing concentrated HCl (3 drops) was added. The solvent was completely evaporated and the product was identified as *trans*-$[PtCl_2(SMe_2)_2]$ from its ^1H NMR spectrum.

Reaction of $[Pt_2Ph_4(\mu\text{-}SMe_2)_2]$ with donor ligands

Reaction of PMe_2Ph, bipy, and SMe_2 (4.0 mmol) and $[Pt_2Ph_4(\mu\text{-}SMe_2)_2]$ (1.0 mmol) in ether gave the monomers *cis*-$[PtPh_2L_2]$ (L = PMe_2Ph, SMe_2, L_2 = bipy), which were identified from their ^1H NMR spectra. For $[PtPh_2(bipy)]$, ^1H NMR ($CDCl_3$); δ 7.0 (m, H_m of bipy); 7.41 (m, H_p of bipy); 8.07 (d, $^3J(H_{m'}H_p) = 3$ Hz, $H_{m'}$ of bipy); 8.63 (d, $^3J(H_oH_m) = 6$ Hz, $^3J(PtH_o) = 22$ Hz, H_o of bipy); 7.47 (d, $^3J(PtH_o) = 32$ Hz, H_o of Ph]; 7.05; 6.90 (m, H_m and H_p of Ph).

Reaction of $[Pt_2Ph_4(\mu\text{-}SMe_2)_2]$ or cis-*$[PtPh_2(SMe_2)_2]$ with MeI and subsequently with bipy*

$[Pt_2Ph_4(\mu\text{-}SMe_2)_2]$ or *cis*-$[PtPh_2(SMe_2)_2]$ (0.05 g) was dissolved in $CHCl_3$ and MeI (0.1 mL) was added. The solution was set aside for 24 h. A very insoluble mixture of white and yellow solids separated. This solid mixture was treated with bipy (twofold excess) in CH_2Cl_2 (3 mL) for 24 h. A yellow precipitate formed, and was isolated, washed with CH_2Cl_2 (0.5 mL), and dried in vacuum. The product was purified by slow diffusion of n-pentane (15 mL) into a CH_2Cl_2 (6 mL) solution. Yellow crystals were obtained, and were characterized as a 2 : 1 mixture of *cis*- and *trans*-$[Pt(bipy)MePh_2I]$ respectively. ^1H NMR ($CDCl_3$) *trans* isomer: δ 1.47 (s, $^2J(PtH) = 72$ Hz, PtMe); 7.55 (m, $^3J(H_mH_o) = 6$ Hz, $^3J(H_mH_p) = 8$ Hz, H_m of bipy); 8.08 (m, $^3J(H_pH_m) = 8$ Hz, $^3J(H_pH_{m'}) = 8$ Hz, H_p of bipy); 8.26 (m, $^3J(H_m,H_p) = 8$ Hz, $H_{m'}$ of bipy); 9.03 (d, $^3J(PtH_o) = 8$ Hz, $^3J(H_oH_m) = 6$ Hz, H_o of bipy); 7.04 (m, Ph); ^1H NMR ($CDCl_3$) *cis*-isomer: 2.20 (s, $^2J(PtH) = 72$ Hz, PtMe); 7.60 (m, $H_{m'}$ of bipy); 8.04 (m, H_p of bipy); 8.20 (m, H_m of bipy); 9.15 (d, $^3J(PtH_o) = 8$ Hz, $^3J(H_oH_m) = 6$ Hz, H_o and $H_{o'}$ of bipy), 6.48 (d, $^3J(PtH_o) = 52$ Hz, $^3J(H_oH_m) = 8$ Hz, H_o of Ph); 6.8 (d, $^3J(PtH_o) = 48$ Hz, $^3J(H_oH_m) = 6$ Hz, H_o of the other Ph); 6.6–7.06 (m, other Ph protons).

Reaction of $[PtPh_2(bipy)]$ with MeI

$[PtPh_2(bipy)]$ (0.02 g) was dissolved in $CDCl_3$ (0.3 mL) in an NMR tube. One small drop of MeI was added. The ^1H NMR spectrum showed (see above) that *trans*-$[PtIMePh_2(bipy)]$ was exclusively formed in solution. When the solvent was evaporated under reduced pressure a yellow solid formed, and was identified by ^1H NMR spectroscopy as a 2 : 1 mixture of *cis*- and *trans*-$[PtIMePh_2(bipy)]$.

Acknowledgements

We thank the Shiraz University Research Council for financial support and Mr. Maleki for recording the 60 MHz NMR spectra.

References

1 J. Kuyper, R. van der Laan, F. Jeanneaus and K. Vrieze, Transition Met. Chem., 1 (1976) 199.
2 J. Kuyper and K. Vrieze, Transition Met. Chem., 1 (1976) 208.
3 B.R. Steele and K. Vrieze, Transition Met. Chem., 2 (1977) 169.
4 B.R. Steele and K. Vrieze, Transition Met. Chem., 2 (1977) 140.
5 D.P. Bancroft, F.A. Cotton, L.R. Falvellow and W. Schwotzer, Inorg. Chem., 25 (1986) 763.
6 J.D. Scott and R.J. Puddephatt, Organometallics, 2 (1983) 1643; idem, ibid., 5 (1986) 1538 and 2522.
7 R.J. Puddephatt and J.D. Scott, Organometallics, 4 (1985) 1221.
8 S. Sergi, V. Marsala, R. Pietropaolo and F. Faraone, J. Organomet. Chem., 23 (1970) 281.

9 M. Lashanizadehgan, M. Rashidi, J.E. Hux, R.J. Puddephatt and S.S.M. Ling, J. Organomet. Chem., 269 (1984) 317.
10 G. Alibrandi, G. Bruno, S. Lanza, D. Minniti, R. Romeo and M.L. Tobe, Inorg. Chem., 26 (1987) 185.
11 M.P. Brown, R.J. Puddephatt, M. Rashidi and K.R. Seddon, J. Chem. Soc., Dalton Trans., (1977) 951.
12 E.W. Abel, M.A. Beckett, P.A. Bates and M.P. Hursthouse, J. Organomet. Chem., 325 (1987) 261.
13 R.J. Puddephatt and P.J. Thompson, J. Chem. Soc., Dalton Trans., (1976) 2091.
14 L.A. Tschugaev and W. Subbotin, Chem. Ber., 43 (1910) 1200; R. Roulet and C. Barbey, Helv. Chim. Acta, 56 (1973) 2179.