Journal of Organometallic Chemistry, 269 (1984) 317–322
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE SYNTHESIS, CHARACTERIZATION AND REACTIONS OF A BINUCLEAR TETRAMETHYLPLATINUM(IV) COMPLEX

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(Received January 18th, 1984)

Summary

Reaction of excess MeLi and MeI with $[PtCl_2(SMe_2)_2]$ gives the first binuclear tetramethylplatinum(IV) complex $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$. The characterization of this complex, and its reactions with donor ligands to give *cis*-$[PtMe_4L_2]$ (L_2 = $Ph_2PCH_2PPh_2$, $Ph_2PCH_2CH_2PPh_2$, 2,2′-bipyridyl, 1,10-phenanthroline or L = PMe_2Ph, $PMePh_2$) are described.

Introduction

Although methylplatinum(IV) complexes were among the first alkyltransition metal complexes to be prepared and have played a central part in the development of the coordination chemistry of platinum(IV), very few tetramethylplatinum(IV) complexes have been isolated [1,2]. The only known derivatives are of the structure *cis*-$[PtMe_4L_2]$, where L = PEt_3, $PMePh_2$, PMe_2Ph, $AsMe_2Ph$ and L_2 = 2,2′-bipyridine [3–7]. The complexes have usually been prepared by metathesis using the powerful methylating agent methyllithium (eqs. 1,2) [3,5] but an oxidative addition route is also known (eq. 3) [7].

$$cis\text{-}[PtCl_4(PMe_2Ph)_2] + 4MeLi \rightarrow cis\text{-}[PtMe_4(PMe_2Ph)_2] + 4LiCl \quad (1)$$

$$fac\text{-}[PtIMe_3(bipy)] + MeLi \rightarrow [PtMe_4(bipy)] + LiI \quad (2)$$

$$2[PtMe_2(bipy)] + PbMe_4 \rightarrow 2[PtMe_4(bipy)] + Pb \quad (3)$$

The metathesis route (eqs. 1 and 2) is not always straightforward. For example, in the presence of iodide (either as a ligand in the platinum complex precursor or as an impurity in the methyllithium reagent), methylation followed by the usual work-up procedure may yield only the trimethylplatinum(IV) complexes *fac*-$[PtIMe_3L_2]$, for example when L = PMe_2Ph but not when L_2 = 2,2′-bipyridine.

We have developed a simple route to the first binuclear tetramethylplatinum(IV) complex, $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$, and have shown that displacement of the SMe_2 ligands by neutral ligands, L, gives a convenient synthesis of complexes $[PtMe_4L_2]$.

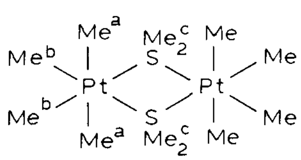
Results and discussion

Synthesis and characterization of $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$

Reaction of $[PtCl_2(SMe_2)_2]$ with methyllithium is known to give $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ [8]. In an attempted synthesis of this complex using methyllithium prepared by reaction of lithium with methyl iodide, the complex $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$ was formed. Subsequently it was shown that the binuclear tetramethylplatinum complex was formed in almost quantitative yield if methyl iodide was present during the reaction of $[PtCl_2(SMe_2)_2]$ with excess methyllithium. Methyl iodide clearly undergoes oxidative addition to a methylplatinum(II) intermediate to generate the platinum(IV) centers, and the stoichiometry is given by eq. 4.

$$2[PtCl_2(SMe_2)_2] + 6MeLi + 2MeI \xrightarrow[-2SMe_2]{-4LiCl,\ -2LiI} [Pt_2Me_8(\mu\text{-}SMe_2)_2] \quad (4)$$

The structure of $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$ is shown to be I by elemental analysis and by the ^1H NMR spectrum, which contains three resonances of equal intensity. The methylplatinum resonances were singlets with one quarter intensity satellites due to coupling with ^{195}Pt and occurred at δ 0.15 ppm, $^2J(PtH)$ 44 Hz (Me^a *trans* to Me) and at δ 0.75 ppm, $^2J(PtH)$ 72 Hz (Me^b *trans* to SMe_2), these parameters being typical of tetramethylplatinum(IV) derivatives [3–5]. The methylsulfur resonance occurs as a 1/8/18/8/1 quintet with a very low coupling constant to platinum, showing that the Me_2S ligands are bridging and *trans* to methyl ($\delta(Me^cS)$ 2.50 ppm, $^3J(PtH)$ 10 Hz) [8].



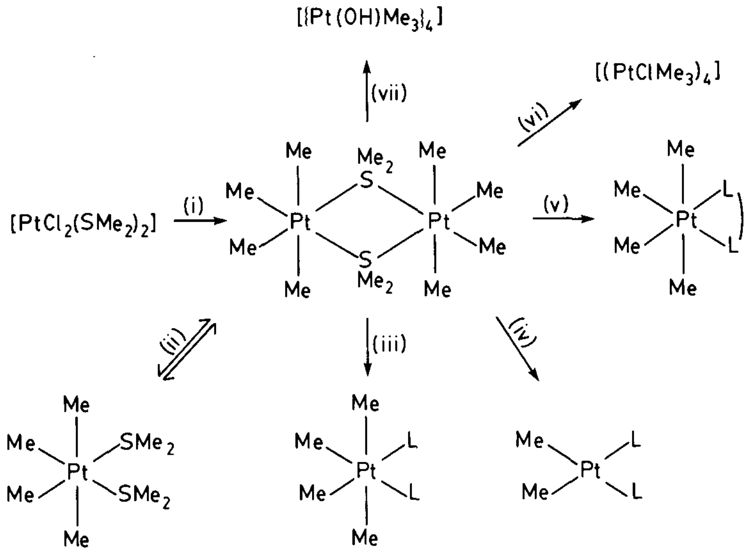
(I)

Reactions of $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$ *(I)*

Complex I decomposed only slowly when stored as a solid at room temperature. However, a solution in acetone decomposed over a period of 24 h to give $[(Me_3PtOH)_4]$ and one methylplatinum group of I was rapidly cleaved by reaction with HCl to give $[(Me_3PtCl)_4]$. Both reactions occurred with displacement of dimethylsulfide (Scheme 1).

More useful reactions occurred on reaction of I with donor ligands. Thus reactions with chelate ligands L⁀L gave rapid displacement of dimethylsulfide to give in high yield the mononuclear complexes $[PtMe_4(L⁀L)]$, where L⁀L =

$Ph_2PCH_2PPh_2$, $Ph_2PCH_2CH_2PPh_2$, 2,2'-bipyridine or 1,10-phenanthroline. With monodentate ligands, useful reactions occurred with L = PMe_2Ph or $PMePh_2$ to give the known complexes *cis*-[$PtMe_4L_2$], but in other attempted reactions the desired products *cis*-[$PtMe_4L_2$] were not obtained. The bulky ligand PPh_3 reacted with I to give *cis*-[$PtMe_2(PPh_3)_2$] and ethane, presumably involving reductive elimination from a transient intermediate [$PtMe_4(PPh_3)_2$]. Triphenylphosphine is known to promote reductive elimination from other organoplatinum(IV) complexes [9,10]. Excess dimethylsulfide reacted reversibly with I to give *cis*[$PtMe_4(SMe_2)_2$], identified in solution by the ^1H NMR spectrum. However, on evaporation of the solvent the complex lost dimethylsulfide to regenerate I. Similarly, attempts to isolate *cis*-[$PtMe_4L_2$] with L = SEt_2 or pyridine were unsuccessful. Attempted crystallization of products from reaction of I with these ligands gave only the decomposition product [$(Me_3PtOH)_4$]. Thus it seems that stable derivatives *cis*-[$PtMe_4L_2$] are formed only when the monodentate ligands, L, are reasonably compact and bind strongly to platinum (Scheme 1).



SCHEME 1. Synthesis and reactions of complex I. Reagents: (i) MeLi + MeI; (ii) Me_2S; (iii) L = PMe_2Ph or $PMePh_2$; (iv) L = PPh_3; (v) L⁀L = $Ph_2PCH_2PPh_2$, $Ph_2PCH_2CH_2PPh_2$, 2,2'-bipyridyl or 1,10-phenanthroline; (vi) HCl; (vii) H_2O.

Experimental

All the reactions involving MeLi, MeMgX, and Me_2Mg were carried out under a nitrogen atmosphere. A solution of MeMgI (~ 1 *M*) was prepared according to the standard method. A solution of MeLi (~ 1 *M*) was prepared by reacting MeI with Li in ether. Solutions of Me_2Mg (~ 1 *M*) were prepared by the addition of dioxane to MeMgX. Commercial MeLi · LiBr in ether (1.2 *M*) was used in some experiments. [$PtCl_2(SMe_2)_2$], as a mixture of *cis* and *trans* isomers was prepared by the literature method [11]. ^1H NMR spectra were recorded on Varian T60 and XL-100 instruments and ^{31}P NMR spectra on a Varian XL100, using TMS and trimethylphosphate references respectively. Elemental analyses were carried out by Alfred Bernhardt, Analytische Laboratorien, or by Guelph Chemical Laboratories.

Preparation of [$PtMe_2(SMe_2)]_2$

Me_2Mg (15 ml of the solution in ether, prepared from MeMgBr) was added slowly to a suspension of *cis*-$PtCl_2(SMe_2)_2$ (2 g) in ether (25 ml) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and subsequently hydrolysed carefully with H_2O at 0 °C. Separation of the organic layer, extraction with CH_2Cl_2 and evaporation over nitrogen gave white crystals of $[PtMe_2(SMe_2)]_2$ identified by the NMR spectrum [8].

A similar reaction used Me_2Mg, prepared from MeMgI, produced *trans*-$[PtIMe(SMe_2)_2]$ as main product. NMR in $CDCl_3$: δ (MePt) 0.7 ppm, ^2J(PtH) 76 Hz; δ(MeS) 2.63 ppm, ^3J(PtH) 54 Hz.

Preparation of [$Pt_2Me_8(\mu$-$SMe_2)_2$]

(i) A solution of MeLi (20 ml, prepared from MeI and Li) in ether was added at 0 °C to a stirred solution of *cis*-$PtCl_2(SMe_2)_2$ (0.5 g) in dry ether (20 ml). A yellow solution was obtained which turned colourless after about 5 min. After 45 min, the solution was carefully hydrolysed at 0 °C with H_2O (~ 4 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 reduced to a small volume by slow evaporation in air. The deposited white crystals were filtered, washed with ether (4 ml) and air-dried. Yield 0.2 g. The complex decomposed without melting at 105 °C (Anal. Found: C, 22.58; H, 5.53; S, 9.94. $C_{12}H_{36}S_2Pt_2$ calcd.: C, 22.6; H, 5.6; S, 10.1%).

(ii) $[PtCl_2(SMe_2)_2]$ (1.0 g) was suspended in dry ether (25 ml) with MeI (1 ml). The mixture was cooled to 0 °C and a solution of MeLi · LiBr in ether (6 ml, 1.2 *M*) was added dropwise with stirring. After 30 min, excess MeLi was hydrolysed by the cautious addition of saturated aqueous NH_4Cl. The desired product was recovered from the organic phase as a creamy white powder (0.78 g, 96%), and was identified by its NMR spectrum.

Reactions of [$Pt_2Me_8(\mu$-$SMe_2)_2$] with donor ligands

Reaction of saturated solutions of $Ph_2PCH_2PPh_2$ (2.0 mmol) and $[Pt_2Me_8(\mu$-$SMe_2)_2]$ (1.0 mmol) in ether led to precipitation of large colourless crystals over a period of 6 h. The crystals were isolated by filtration, then washed with ether and air dried. Yield of $[PtMe_4(Ph_2PCH_2PPh_2)]$ was 75%. M.p. 179 °C (decomp). Anal. Found: C, 54.6; H, 5.2; P, 9.6. $C_{29}H_{34}P_2Pt$ calcd.: C, 54.7; H, 5.3; P, 9.6%. NMR in $CDCl_3$: −0.04 (t, ^2J(PtH) 46, ^3J(PH) 7 Hz, *Me*Pt *trans* to Me); 0.87 (m, ^2J(PtH) 64 Hz, *Me*Pt *trans* to P); 4.73 (t, ^3J(PtH) 8.4, ^2J(PH) 9.4 Hz); −65.9 ppm (s, ^1J(PtP) 936 Hz, ^{31}P).

The following complexes were prepared in a similar way and were isolated in yields of 60–94%. $[PtMe_4(Ph_2PCH_2CH_2PPh_2)]$, Anal. Found: C, 55.1; H, 5.2; P, 9.3. $C_{30}H_{36}P_2Pt$ calcd.: C, 55.1; H, 5.5; P, 9.5%. NMR in $CDCl_3$: −0.56 (t, ^2J(PtH) 44, ^3J(PH) 6 Hz); 0.80 (m, ^2J(PtH) 60, ^3J(PH) + ^3J(P′H) 13.7 Hz); 2.61 ppm (t, ^3J(PtH) 8, ^2J(PH) + ^4J(P′H) 15 Hz, CH_2P). $[PtMe_4(bipy)]$, m.p. 119–122 °C, Anal. Found: C, 40.1; H, 4.75, N, 7.1. $C_{14}H_{20}N_2Pt$ calcd.: C, 40.9; H, 4.9; N, 6.8%. NMR in $CDCl_3$: −0.68 (s, ^2J(PtH) 44 Hz, *Me*Pt *trans* to Me); 0.90 ppm (s, ^2J(PtH) 73 Hz,

$MePt$ *trans* to N). [$PtMe_4$(1,10-phenanthroline)], m.p. 180 °C (decomp). NMR in C_6D_6: 0.22 (s, ^2J(PtH) 44 Hz, *Me*Pt *trans* to Me); 1.86 ppm (s, ^2J(PtH) 72.5 Hz, *Me*Pt *trans* to N]. [$PtMe_4(PMePh_2)_2$], NMR in $CDCl_3$; −0.11 (t, ^2J(PtH) 44, ^3J(PH) 6 Hz, *Me*Pt *trans* to Me); 0.38 (m, ^2J(PtH) 61, $^3J(PH)+^3J(P'H)$ 2 Hz, *Me*Pt *trans* to P); 1.67 (d, ^3J(PtH) 10, $^2J(PH)+^4J(P'H)$ 8 Hz, MeP) [6]. [$PtMe_4(PMe_2Ph)_2$], NMR in $CDCl_3$: −0.23 (t, ^2J(PtH) 44, ^3J(PH) 7 Hz, *Me*Pt *trans* to Me); 0.39 (m, ^2J(PtH) 57, $^2J(PH)+^4J(P'H)$ 2 Hz, *Me*Pt *trans* to P); 1.39 ppm (d, ^3J(PtH) 12, $^2J(PH)+ ^4J(P'H)$ 8 Hz, MeP) [3].

Reaction of [$Pt_2Me_8(\mu\text{-}SMe_2)_2$] with SMe_2

SMe_2 (3.4 μl) was added to a solution of [$Pt_2Me_8(\mu\text{-}SMe_2)_2$] (0.010 g) in $(CD_3)_2CO$ (0.7 ml) in an NMR tube. The product was *cis*-[$PtMe_4(SMe_2)_2$], as determined by the ^1H NMR spectrum: −0.30 (s, ^2J(PtH) 43, *Me*Pt *trans* Me), 0.70 (s, ^2J(PtH) 73, *Me*Pt *trans* S), 2.20 (s, ^3J(PtH) 12, SMe_2); integration 1/1/2. After evaporation of the solvent and redissolving, the NMR spectrum showed that reversion to [$Pt_2Me_8(\mu\text{-}SMe_2)_2$] had occurred.

Decomposition of [$Pt_2Me_8(\mu\text{-}SMe_2)_2$] in solution

[$Pt_2Me_8(\mu\text{-}SMe_2)_2$] decomposed (room temperature, 24 h) to give $(PtMe_3OH)_4$ in both acetone and methylene chloride solutions. The product was identified by mass spectrometry and by the characteristic ^1H NMR spectrum [12,14]. NMR in C_6D_6: δ 0.81 (s, ^2J(PtH) 79 Hz, *Me*Pt); −1.50 (septet, ^2J(PtH) 11 Hz, *H*OPt). MS: Parent ion, *m/e* 1028 (calcd. for $(Me_3{}^{195}PtOH)_4$ 1028), with the expected isotope pattern. The same product was formed in attempted reactions with Et_2S and with pyridine.

Reaction of [$Pt_2Me_8(\mu\text{-}SMe_2)_2$] with HCl

To a stirred solution of [$Pt_2Me_8(\mu\text{-}SMe_2)_2$] (0.35 g) in ether (70 ml) was added concentrated HCl solution (2 ml). Evaporation of the ether layer gave [$(Me_3PtCl)_4$], identified by its ^1H NMR spectrum [12].

Reaction of [$PtIMe_3$(dppm)], [13], dppm = $Ph_2PCH_2PPh_2$, with MeLi

[$PtMe_3I$(dppm)] (0.5 g) was suspended in ether 40 ml). MeLi (25 ml, prepared from MeI and Li) was added to the suspension at −4 °C. The reaction mixture was stirred for 10 min and was then hydrolysed carefully with H_2O at −4 °C. The clear organic layer was decanted and the aqueous layer was twice extracted with CH_2Cl_2 (10 ml). The combined organic layers were dried over anhydrous sodium sulphate, filtered and reduced to about 10 ml. This solution was then left overnight. The colourless crystals which formed were filtered, washed with ether (4 ml) and air-dried. Yield, 0.14 g. The product was identified as [$PtMe_4$(dppm)] by its ^1H NMR spectrum.

Acknowledgments

We thank the Shiraz University Research Council (Iran) and NSERC (Canada) for financial support, and Mr. Maleky for recording some of the 60 MHz NMR spectra.

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