Atomic coordinates with estimated standard deviations and hydrogen atom coordinates (Table SII), anisotropic thermal parameters for all non-hydrogen atoms (Table SIII), a complete list of bond distances and angles (Table SIV), selected least-squares planes (Table SV), and a listing of the observed and calculated structure factor amplitudes used in the refinement (Table SVI) are available as supplementary material.[16]

**Acknowledgment.** We are grateful to J.-L. Richert, D. Gesbert, and Prof. P. Granger for assistance with the $^{31}P\{^1H\}$ NMR analysis of **1**, to Prof. M. J. McGlinchey for the mass spectra, to ULP and CNRS for support, and to the Johnson Matthey Technology Center for a generous loan of $PtCl_2$.

**Registry No.** **1**, 120711-63-9; $Pt(\mu\text{-}CO)_5(CO)(PEt_3)_4$, 68875-49-0; $Na_2[Fe(CO)_4]$, 14878-31-0; *cis*-$PtCl_2(PEt_3)_2$, 15692-07-6; $Fe(CO)_4(PEt_3)$, 15078-01-0; $Fe(CO)_3(PEt)_2$, 18533-29-4; $Fe_2Pt(CO)_9(PEt_3)$, 120711-65-1; $Fe_2Pt(CO)_8(PEt_3)_2$, 120711-64-0.

**Supplementary Material Available:** Figure SI, showing a perspective view of $FePt_5(CO)_9(PEt_3)_4$ (**1**) with the complete numbering scheme, Tables SI–SV, listing crystal data and data collection parameters, fractional coordinates and hydrogen atom positions, anisotropic thermal parameters, complete bond distances and angles, and selected least-squares planes (17 pages); Table SVI, listing observed and calculated structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

---

(16) See paragraph at end of paper regarding supplementary material.

---

Contribution from the Department of Chemistry,
University of Western Ontario, London, Ontario, Canada N6A 5B7

# Synthesis and Characterization of $[Pt_2(\mu\text{-}S)(\mu\text{-}dppm)(\eta^1\text{-}dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$) and Its Use in Formation of Tetranuclear Platinum Complexes with $\mu_4$-S Ligands

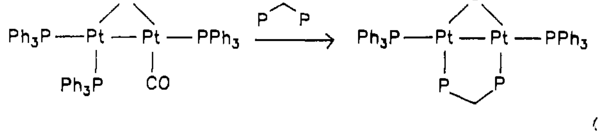
Nasim Hadj-Bagheri and Richard J. Puddephatt*

*Received November 11, 1988*

The reaction of $[Pt_2(\mu\text{-}dppm)_3]$ with COS gave a new diplatinum(I) complex $[Pt_2(\mu\text{-}S)(\mu\text{-}dppm)(\eta^1\text{-}dppm)_2]$ (**1**), where dppm = $Ph_2PCH_2PPh_2$. Complex **1** was also prepared by reaction of $[Pt_2Cl_2(\mu\text{-}dppm)_2]$ with dppm and sodium sulfide or by reaction of $[Pt_2(\mu\text{-}dppm)_3]$ with sulfur, but lower yields were obtained by these methods. Complex **1** reacted slowly with air, by oxidation of the free phosphorus atoms, to give $[Pt_2(\mu\text{-}S)(\mu\text{-}dppm)(Ph_2PCH_2P(O)Ph_2)_2]$ and with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ or $[PtPh_2(SMe_2)_2]$ to give $[Pt_4(\mu_4\text{-}S)R_4(\mu\text{-}dppm)_3]$, where R = Me or Ph, respectively. In the latter reaction, complex **1** acts as an 8-electron bis(bidentate) ligand, using the free phosphorus atoms of the $\eta^1$-dppm ligands and both lone pairs of the $Pt_2(\mu\text{-}S)$ group of **1** as donors, and the products are the first platinum complexes with the $\mu_4$-S ligand. These complexes were characterized by multinuclear NMR spectroscopy.

## Introduction

In 1967 Baird and Wilkinson reported the reaction of $[Pt(PPh_3)_3]$ with carbonyl sulfide, COS, to form the carbonyl sulfide complex $[Pt(PPh_3)_2(COS)]$, which was converted to a binuclear species, characterized soon afterwards as the diplatinum(I) complex $[Pt_2(\mu\text{-}S)(CO)(PPh_3)_3]$ having a Pt–Pt bond.[1,2] In 1981, Balch and co-workers analyzed the complex $^{31}P\{^1H\}$ NMR spectrum of this binuclear complex and studied its reactivity. It was shown that the $Pt_2S$ core in this binuclear Pt(I) complex is unreactive toward insertion of small molecules such as carbon monoxide, isocyanides, and acetylenes, but substitution reactions were observed to proceed readily at the positions trans to the sulfur bridge. In this way, a $Ph_2PCH_2PPh_2$, dppm, derivative was prepared (eq 1).[3]

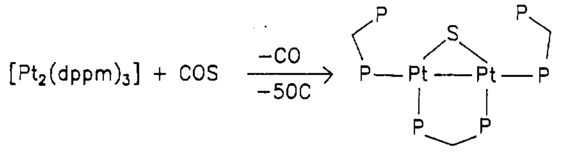


(1)

Several related complexes have been prepared, and it is clear that the $\mu_2$-S group is effective in stabilizing the Pt(I) oxidation state.[1-11] This paper reports details of the synthesis and characterization of a new useful derivative $[Pt_2(\mu\text{-}S)(\mu\text{-}dppm)(\eta^1\text{-}dppm)_2]$ (**1**). A preliminary account of parts of this work has been published.[12]

## Results and Discussion

**Synthesis of $[Pt_2(\mu\text{-}S)(\mu\text{-}dppm)(\eta^1\text{-}dppm)_2]$ (1).** When carbonyl sulfide was bubbled through a deep red solution of $[Pt_2(\mu\text{-}dppm)_3]$ (**2**) in toluene at −50 °C, a reaction occurred (eq 2) as indicated



(2)

by the color change of the solution to light orange and then yellow as the solution was allowed to warm to room temperature. Complex **1** was isolated as a stable yellow microcrystalline solid in good yield, and though this was usually unnecessary, it could

---

(1) Baird, M. C.; Wilkinson, G. *J. Chem. Soc. A.* **1967**, 865.
(2) Skapski, A. C.; Troughton, P. G. H. *J. Chem. Soc. A.* **1969**, 2772.
(3) Hunt, C. T.; Matson, G. B.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 2270.
(4) Chatt, J.; Mingos, D. M. P. *J. Chem. Soc. A.* **1970**, 1243.
(5) Hallam, M. F.; Luke, M. A.; Mingos, D. M. P.; Williams, I. D. *J. Organomet. Chem.* **1987**, *325*, 271.
(6) Werner, H.; Ebner, M.; Otto, H. *J. Organomet. Chem.* **1988**, *350*, 257.
(7) Ma, E.; Semelhago, G.; Walker, A.; Farrar, D. H.; Gukathasan, R. R. *J. Chem. Soc., Dalton Trans.* **1985**, 2595.
(8) Ebner, M.; Otto, H.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 518.
(9) Hawling, W. M.; Walker, A.; Woitzik, M. A. *J. Chem. Soc. Chem. Commun.* **1983**, 11.
(10) Browning, C. S.; Farrar, D. H.; Gukathasan, R. R.; Morris, S. A. *Organometallics* **1985**, *4*, 1750.
(11) Mason, M. G.; Swepston, P. N.; Ibers, J. A. *Inorg. Chem.* **1983**, *22*, 411.
(12) Hadj-Bagheri, N.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1269.

0020-1669/89/1328-2384$01.50/0

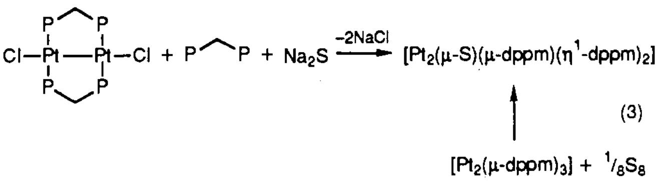
**Table I.** Selected NMR Parameters for New Complexes[a]

| complex | $\delta(P^a)$ | $\delta(P^b)$ | $\delta(P^c)$ | $\delta(Pt^a)$ | $\delta(Pt^b)$ | $^1J(PtP^a)$ | $^1J(PtP^b)$ | $^1J(PtP^c)$ | $^1J(PtPt)$[b] | $^2J(PtP^b)$ | $^2J(PtP^a)$ | $^3J(PtP^a)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | −14.1 | 13.5 | −32.0 | −3200 | | 3500 | 3200 | | 3100 | 190 | −80 | 180 |
| **4** | −13.3 | 10.7 | 18.2 | *c* | | 3510 | 3230 | | 3100 | 200 | −80 | 190 |
| **5a** | −20.5 | 7.3 | 14.9 | −3230 | −2374 | 3780 | 3300 | 1960 | 1645 | 210 | −80 | 170 |
| **5b** | −15.2 | 4.9 | 1.1 | −3443 | −2574 | 3880 | 3300 | 1800 | *c* | 200 | −80 | 160 |
| **6**[d] | −7.9 | 29.4[e] | | *c* | | 3537 | 3192[e] | | *c* | 231[e] | −108 | 175[e] |

[a] $\delta$ in ppm, $J$ in Hz. [b] For directly bonded Pt atoms in **5**. [c] Not measured. [d] **6** = $[Pt_2(\mu\text{-}S)(PPh_3)_2(\mu\text{-dppm})]$.[3] [e] $P^b = PPh_3$.

be purified by thin-layer chromatography.

Complex **1** could also be synthesized by reaction of **2** with elemental sulfur or by reaction of the binuclear Pt(I) complex, $[Pt_2Cl_2(\mu\text{-dppm})_2]$ with dppm and sodium sulfide (eq 3).



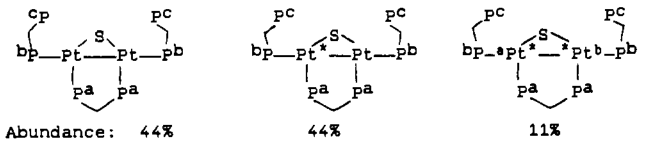
(3)

However, complex **1** formed by these reactions was contaminated with impurities, which could only be separated by thin-layer chromatography, and so eq 1 represents the preferred route to **1**.

**Characterization of Complex 1.** The formula of complex **1** was deduced by elemental analysis and by the mass spectrum, which gave a parent ion at $m/e$ = 1575 with the expected isotope distribution, and the structure was determined by NMR spectroscopy.

The $^1H$ NMR spectrum of **1** contained two resonances due to the methylene protons of the $\mu$-dppm and $\eta^1$-dppm ligands respectively, in the expected 1:2 intensity ratio. The resonance due to the $\eta^1$-dppm ligands appeared as an AB pattern, indicating that these ligands are held in a conformation in which there is no plane of symmetry containing the PCP unit.

The $^{31}P\{^1H\}$ NMR spectrum of **1** is depicted in Figure 1. This spectrum consists of resonances due to the three isotopomers containing none, one, and two $^{195}Pt$ atoms.



The resonance at $\delta$ = −32.0 ppm is assigned to the free phosphorus atoms $P^c$. The chemical shift is similar to that of free dppm, and no coupling to $^{195}Pt$ is resolved. The resonance at $\delta$ = 13.5 ppm is assigned to $P^b$, and there are satellites due to both $^1J(PtP)$ and $^2J(PtP)$ couplings. The magnitude of $^2J(PtP)$ is large, as expected for a linear P–Pt–Pt unit. The resonance due to the $P^a$ nuclei appears as a broad singlet at $\delta$ = −14.1 ppm and also has satellites due to $^1J(PtP)$ and $^2J(PtP)$ couplings. There is much fine structure due to $J(PP)$ couplings, and analysis of these signals and their $^{195}Pt$ satellites provides parameters for all the P–P and $^{195}Pt$–P couplings. The resonance due to the $P^a$ atoms gave satellites due to the isotopomer with two $^{195}Pt$ atoms, and analysis by the published method allowed the coupling $^1J(PtPt)$ to be determined.[13]

The $^{195}Pt$ NMR spectrum is shown in Figure 2. It is fully consistent with the proposed structure and gives independent measures of the PtP coupling constants measured from the $^{31}P$ NMR spectra. In addition, from the weak peaks due to the $^{195}Pt_2$ isotopomer, an independent measure of $^1J(PtPt)$ was obtained. The final parameters are given in Table I; they are comparable to similar values for $[Pt_2(\mu\text{-}S)(\mu\text{-dppm})(PPh_3)_2]$ and related compounds[3-12] and leave no doubt about the structure.

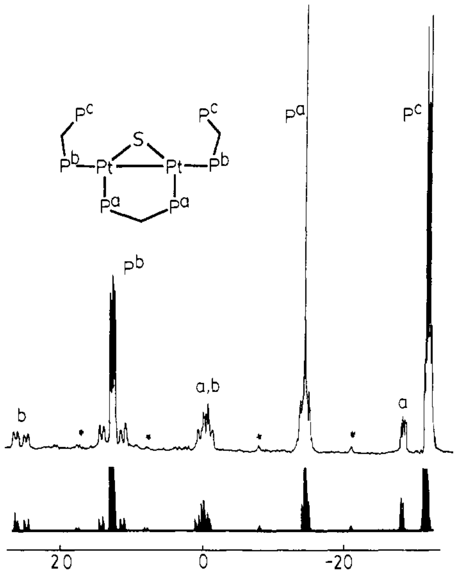


Figure 1. $^{31}P\{^1H\}$ NMR spectrum (121.5 MHz) of complex **1**. The peaks marked with an asterisk are due to the $^{195}Pt_2$ isotopomer.

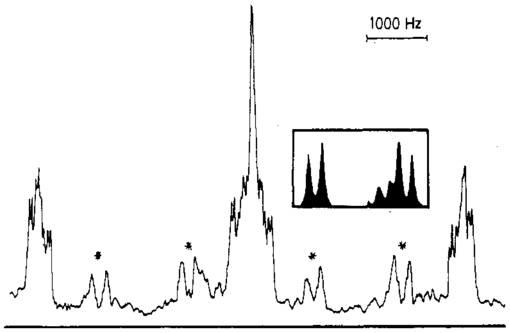


Figure 2. $^{195}Pt$ NMR spectrum (64.3 MHz) of complex **1**. The complexity of the peaks arises in part from the similar values of $^1J(PtP^a)$ and $^1J(PtP^b)$; important peaks arising from the $^{195}Pt_2$ isotopomer are marked with an asterisk. The resonance is centered at $\delta$ = −3200 ppm.

**Mechanism of Dimer Formation.** When COS was bubbled through a solution of **2** in toluene at −78 °C and the reaction mixture was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, it was observed that as the temperature was raised, the peaks due to the starting material **2** decreased and those due to **1** increased. At −50 °C the reaction was complete, and **1** was formed in essentially quantitative yield. Therefore any intermediates must be extremely short-lived.

The mechanism of reaction of COS or $CS_2$ with mononuclear platinum(0) complexes has been elucidated by the isolation of intermediates. Thus the first-formed complex $[PtL_2(COS)]$ or $[PtL_2(CS_2)]$, having side-on $\eta^2$-CS bound ligands, reacts with more platinum(0) species to give $[Pt_2L_4(\mu\text{-COS})]$ or $[Pt_2L_4(\mu\text{-}CS_2)]$, and then cleavage of the C–S bond occurs. Usually the fragment CO or CS remains in the coordination sphere of the binuclear product $[Pt_2(\mu\text{-}S)(CX)L_3]$, where X = O or S.[7-10] By analogy, the mechanism of eq 4 can be proposed for the present reaction, which is clearly much facilitated by having a binuclear precursor. It is expected that the proposed intermediate **3** would be formed

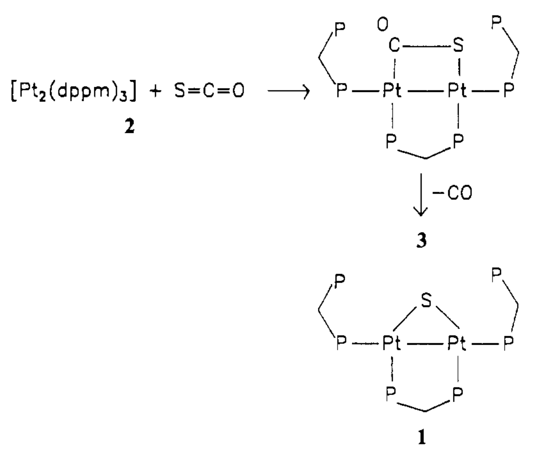
---

(13) Grossel, M. C.; Batson, J. R.; Moulding, R. P.; Seddon, K. R. *J. Organomet. Chem.* **1986**, *304*, 391.

(14) Brown, M. P.; Fisher, J. R.; Franklin, S. J.; Puddephatt, R. J.; Seddon, K. R. *J. Organomet. Chem.* **1978**, *161*, C46.

(15) Brown, M. P.; Franklin, S. J.; Puddephatt, R. J.; Thomson, M. A.; Seddon, K. R. *J. Organomet. Chem.* **1979**, *178*, 281.

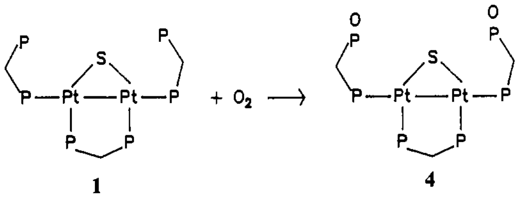
(16) Manojlović, Lj.; Muir, K. W.; Frew, A. A.; Ling, S. S. M.; Thomson, M. A.; Puddephatt, R. J. *Organometallics* **1984**, *3*, 1637.



(4)

more easily from a binuclear precursor than from a mononuclear one, but it also seems that the CS bond cleavage step is also faster in **3** than in related complexes not containing dppm.

**Reaction of Complex 1 with Air.** Complex **1** is air-stable in the solid state, but when a solution is exposed to air, the uncoordinated phosphines of the "dangling" dppm ligands are oxidized slowly to yield complex **4** (eq 5).



(5)

Complex **4** was characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. The mass spectrum contained a parent ion peak at $m/e$ = 1607, with the expected isotope pattern. The $^{31}P\{^1H\}$ NMR spectrum of **4** was similar to that of **1** except that the resonance at $\delta$ = −32.0 ppm for the free phosphorus atoms of **1** shifted to $\delta$ = 18.2 ppm for the phosphine oxide groups of **4**.

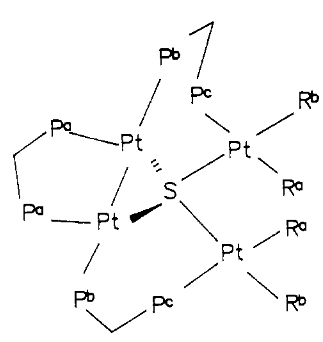
Complex **1** also reacts readily with iodomethane, but a mixture of products was formed, which we were unable to separate. This is perhaps due to competitive methylation of the free phosphine groups and the sulfur atom of **1**. Reaction of **1** with iodine led to cleavage of [PtI$_2$(dppm)]]. The major application of **1** is in the assembly of heteronuclear molecules by use of **1** as a ligand. The free phosphorus atoms and sulfur atom are available for coordination to further transition-metal acceptors, and the synthesis of trinuclear complexes has been reported earlier.[12] The synthesis of tetranuclear complexes, in which the molecule **1** acts as an 8-electron ligand, is now reported.

**Synthesis of [Pt$_4$R$_4$($\mu$-S)($\mu$-dppm)$_3$] (5a, R = Me; 5b, R = Ph).** The reaction of complex **1** with an equimolar amount of *cis,cis*-[Pt$_2$Me$_4$($\mu$-SMe$_2$)$_2$] or with 2 molar equiv of *cis*-[PtPh$_2$(SMe$_2$)$_2$] gave, by displacement of the SMe$_2$ ligands, the corresponding complex **5a** or **5b**, respectively, in high yield (eq 6).

$$\underset{\mathbf{1}}{[\mathrm{Pt_2(\mu\text{-}S)(\mu\text{-}dppm)(\eta^1\text{-}dppm)_2}]} + 2[\mathrm{PtR_2(SMe_2)_2}] \rightarrow$$

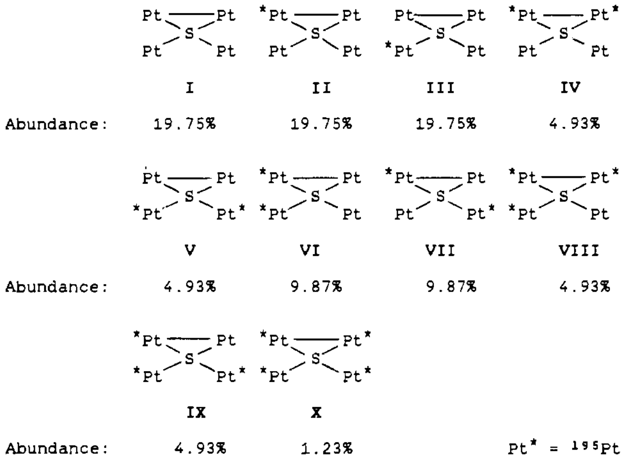
$$\underset{\mathbf{5a},\ \mathrm{R = Me};\ \mathbf{5b},\ \mathrm{R = Ph}}{[\mathrm{Pt_4R_4(\mu_4\text{-}S)(\mu\text{-}dppm)_3}]} + 4\mathrm{SMe_2} \quad (6)$$

Although attempts to grow X-ray quality crystals have been unsuccessful, the products could be characterized by NMR spectroscopy and elemental analysis. The NMR properties of **5a** will be discussed, but those of **5b** are very similar (Table I). The $^1$H NMR of **5a** gives two doublet resonances of equal intensity due to the methylplatinum protons at $\delta$ = 0.14 and 0.72 ppm, each having $^3J$(PH) = 7 Hz and with $^2J$(PtH) = 86 and 72 Hz, respectively. The $^{195}$Pt–H coupling constants indicate that the methyl groups are trans to sulfur and phosphorus, respectively.[17]



**5a**, R = Me
**5b**, R = Ph

The $^1$H NMR spectrum also contains complex multiplets at $\delta$ = 2.03, 3.58, 3.89, and 5.58 ppm in a 2:1:2:1 intensity ratio due to the methylene protons of the dppm ligands. Since a decoupling experiment has shown that the signals at 2.03 and 3.89 ppm and those at 3.58 and 5.58 ppm are coupled to each other, it is clear that the former set are due to the CH$_2$ protons of the two dppm ligands that bridge the Pt(I) and Pt(II) centers, while the latter set are due to the CH$_2$ protons of the single dppm ligand that bridges the two Pt(I) centers. There can be no plane of symmetry containing the PCP atoms of either dppm ligand. The $^{31}P\{^1H\}$ NMR spectrum of **5a** is depicted in Figure 3. This spectrum is very informative on the structure of **5a** partly because of its complexity, which arises from the presence of a number of isotopomers:



Essentially the spectrum consists of three major signals, accompanied by short- and long-range $^{195}$Pt satellites, which are attributed to the three sets of chemically inequivalent phosphorus nuclei in the proposed structure. Thus, the triplet of triplets resonance at $\delta$ = −20.5 ppm, with $^1$J(PtP) and $^2$J(PtP) values of 3780 and −80 Hz, respectively, is assigned to P$^a$, the doublet of doublets at $\delta$ = 7.3 ppm is due to P$^b$, and the doublet of doublets of triplets at $\delta$ = 14.9 ppm is due to P$^c$. Analysis of these peaks gives the $^{195}$Pt–P and P–P couplings given in Table I. There are obviously close similarities with the parameters for **1** and **4**, and in particular, the close similarity in the couplings $^2J$(PtP$^a$), $^2J$(PtP$^b$), and $^3$J(P$^b$P$^{b'}$) strongly indicates that the Pt–Pt bond of **1** is little affected on formation of **5a**. These couplings are characteristic of values through a Pt–Pt bond.[6,12–15] The chemical shift of P$^c$ and the observation of $^1J$(PtP) coupling clearly shows that these atoms are coordinated, and the low value of $^1J$(PtP) = 1960 Hz shows that P$^c$ is trans to a methylplatinum group.[16] The major difference from the spectra of **1** and **4** is the $^1J$(PtPt) value of 1646 Hz for **5a**, which is considerably smaller than the value of 3100 Hz found for both **1** and **4**. This difference probably arises from the extra rings introduced on formation of **5a** and is unlikely to be due to much weaker Pt–Pt bonding.

The $^{195}Pt\{^1H\}$ NMR spectrum of **5a** is shown in Figure 4 and confirms the proposed structure for this complex. The spectrum consists of a doublet at −2374 ppm with $^1J$(PtP) = 1960 Hz, which

---

(17) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643.

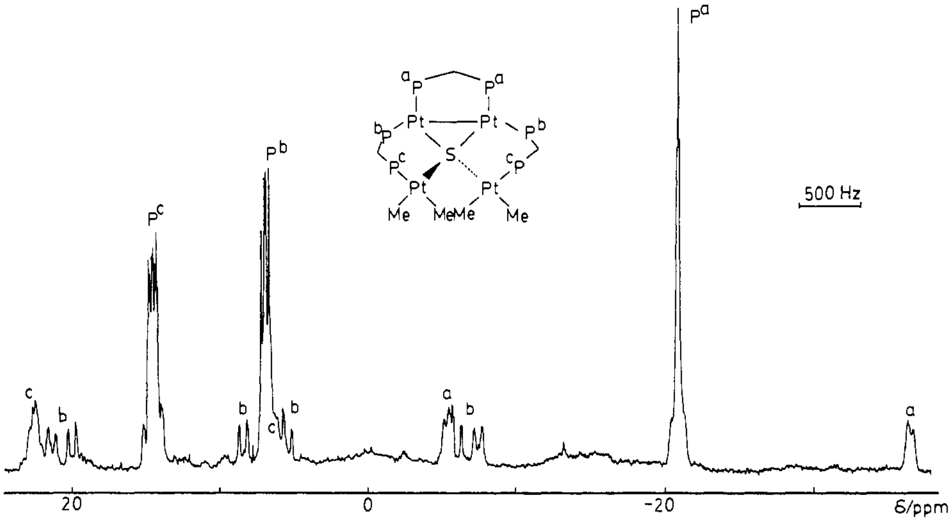


**Figure 3.** $^{31}$P NMR spectrum (121.5 MHz) of $[Pt_4(\mu_4\text{-}S)Me_4(\mu\text{-}dppm)_3]$ (**5a**).

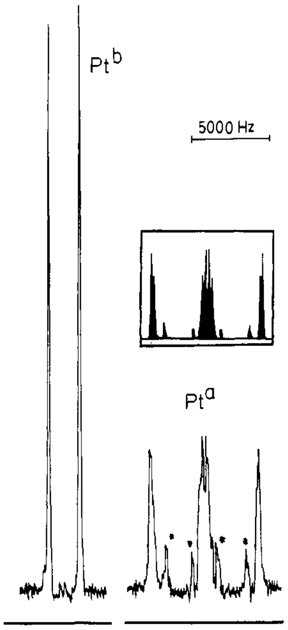


**Figure 4.** $^{195}Pt\{^1H\}$ NMR spectrum (64.3 MHz) of complex **5a**.

is assigned to Pt$^b$, and a more complex resonance at $\delta = -3231$ ppm, which is assigned to the Pt$^a$ nuclei. The latter resonance is similar to that for complex **1** (Table I).

The only connection that is not directly proved by the NMR data is the presence of the $\mu_4$-S bridge, but this is clearly required in order to give square-planar coordination at the Me$_2$Pt centers. There is also indirect evidence from the magnitude of $^2J$(PtH) = 86 Hz for one of the MePt groups, which is typical for a methylplatinum(II) group trans to sulfur.[17] These complexes are, as far as we know, the first examples of platinum clusters stabilized by a quadruply bridging sulphur ligand.[18]

In summary, complex **1** is formed readily, and the presence of free phosphine donors and a $Pt_2(\mu\text{-}S)$ group makes it particularly attractive as an assembling "ligand". In most cases it acts as a 6-electron tridentate ligand (P$_2$S donor set) in the formation of trinuclear complexes,[12] but this work has shown that it can also act as an 8-electron bis(bidentate) ligand in the formation of tetranuclear complexes. In doing so, complex **1** uses the two free phosphorus donors of the $\eta^1$-dppm ligands and *both* lone pairs of the $Pt_2(\mu\text{-}S)$ group. The sulfur thus acts as a 6-electron ligand, formally donating one electron to each Pt(I) atom and two electrons to each R$_2$Pt(II) center. The key to forming tetranuclear complexes from **1** is to add square-planar acceptors with two of the coordination sites blocked by strongly bonded ligands, which, in the present examples, are the methyl or phenyl groups in the *cis*-R$_2$Pt$^{II}$ units.

## Experimental Section

$^1$H NMR spectra were recorded by using a Varian XL-200 spectrometer and $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra by using a Varian XL-300 spectrometer. $^1$H chemical shifts were measured relative to Me$_4$Si; $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ chemical shifts were measured relative to H$_3$PO$_4$ and aqueous K$_2$[PtCl$_4$], respectively. Mass spectra were recorded on a Varian MAT8230 mass spectrometer. NMR simulations were carried out using a locally modified version of LAOCOON.

**$[Pt_2(\mu\text{-}S)(\mu\text{-}dppm)(\eta^1\text{-}dppm)_2]$ (1).** Carbonyl sulfide was bubbled through a solution of complex **2** (400 mg, 0.26 mmol) in toluene (10 mL) at −78 °C, under an atmosphere of nitrogen. The reaction mixture was stirred and allowed to warm. At −50 °C a color change from deep red to orange took place. The mixture was allowed to warm to room temperature, the solvent was removed in vacuo, and the oily residue was dissolved in acetone (5 mL). Addition of pentane (20 mL) resulted in the precipitation of the product as a yellow solid. The product was washed several times with pentane (15 mL) and dried in vacuo. In some cases when impurities were present, the product was chromatographed by using alumina TLC plates and a 1:5 mixture of acetone–toluene. Yield: 300 mg, 0.19 mmol, 73%. Mp: 115 °C dec. Anal. Calcd for $C_{75}H_{66}P_6Pt_2S$: C, 57.2; H, 4.2. Found: C, 57.2; H, 4.4%. MS: *m/e* 1575 (P). $^1$H NMR (in acetone-$d_6$): $\delta$ (ppm) = 4.2 [m, 2 H, $P_2CH^aH^b$], 4.4 [m, 2 H, $P_2CH^cH^d$], 5.2 [m, 2 H, $^3J$(PtH) = 68 Hz, $P_2CH^cH^d$], 6.9–7.3 [m, 60 H, *Ph*]. $^{31}P\{^1H\}$ NMR (in acetone-$d_6$): $\delta$ (ppm) = −32.0 [m, 2 P, $^2J(P^bP^c)$ = 41 Hz, $P^c$], −14.1 [s, 2 P, $^2J(P^aP^b)$ = 15 Hz, $^3J(P^aP^b)$ = 7 Hz, $^2J(P^aP^{a\prime})$ = 40 Hz, $^1J(PtP^a)$ = 3500 Hz, $^2J(PtP^a)$ = −80 Hz, $^1J$(PtPt) = 3100 Hz, $P^a$], 13.5 [m, 2 P, $^3J(P^bP^{b\prime})$ = 180 Hz, $^1J$(PtP) = 3200 Hz, $^2J$(PtP) = 190 Hz, $P^b$]. $^{195}Pt\{^1H\}$ NMR (in acetone-$d_6$): $\delta$ (ppm) = −3200 [m, $^1J(PtP^b)$ = 3200 Hz, $^2J(PtP^b)$ = 190 Hz, $^1J(PtP^a)$ = 3500 Hz, $^2J(PtP^a)$ = −80 Hz, $^1J$(PtPt) = 3100 Hz].

Complex **1** was also prepared in the following ways. To a yellow solution of $[Pt_2Cl_2(\mu\text{-}dppm)_2]\cdot C_6H_6$ (46 mg, 0.03 mmol) in CH$_2$Cl$_2$ (10 mL) was added dppm (13 mg, 0.03 mmol). Later Na$_2$S·9H$_2$O (8 mg, 0.03 mmol) in methanol (4 mL) was added, and the reaction mixture was stirred for several hours. The solvents were removed in vacuo, and the orange residue was extracted with CH$_2$Cl$_2$ (20 mL). The solution was filtered, and the filtrate was evaporated to dryness. Complex **1** was purified by thin-layer chromatography as described previously. Yield: 15 mg, 0.01 mmol, 27%.

To a solution of complex **2** (100 mg, 0.06 mmol), in toluene (5 mL) was added sulfur, (3 mg, 0.09 mmol). An immediate reaction was apparent from the color change to light yellow. The mixture was stirred for several hours, after which time a precipitate had formed. This was separated, washed with pentane (10 mL), and dried in vacuo. The product was purified by thin-layer chromatography as described previously. Yield: 20 mg, 0.01 mmol, 20%.

**$[Pt_2(\mu\text{-}S)(\mu\text{-}dppm)(Ph_2PCH_2P(O)Ph_2)_2]$ (4).** A solution of complex **1** (50 mg, 0.03 mmol) in acetone (10 mL) was exposed to air for a period of several days. The final product was isolated by addition of pentane (10 mL) to the solution. The yellow precipitate was separated and dried in vacuo to give the product. Yield: 40 mg, 0.02 mmol, 66%. Anal.

---

(18) Roundhill, D. M. *Comprehensive Coordination Chemistry* Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, England, 1987; Chapter 52.

Calcd for $C_{75}H_{66}O_2P_6Pt_2S$: C, 56.0; H, 4.1. Found: C, 55.9; H, 3.9%. MS: *m/e* 1607 (P), 1404 (P – P(O)Ph$_2$ = 1406), 1203 (P – 2{P(O)Ph$_2$ = 1205}). $^{31}$P{$^{1}$H} NMR (in acetone-$d_6$): $\delta$ (ppm) = –13.3 [s, 2 P, $^{1}J$(PtP) = 3510 Hz, $^{2}J$(PtP) = –80 Hz, $^{1}J$(PtPt) = 3100 Hz, $P^{a}$], 10.7 [m, 2 P, $^{3}J$(P$^{b}$P$^{b}$) = 190 Hz, $^{1}J$(PtP) = 3230 Hz, $^{2}J$(PtP) = 200 Hz, $P^{b}$], 18.2 [m, 2 P, $P^{c}$].

**Reaction of 1 with I$_2$.** To a solution of **1** (50 mg, 0.03 mmol) in acetone (5 mL) was added iodine (15 mg, 0.06 mmol). The mixture was stirred for 0.5 h. The resultant yellow precipitate was collected, washed with pentane (10 mL), and dried in vacuo to yield [PtI$_2$(dppm)]. Yield: 13 mg, 0.01 mmol, 33%. $^{31}$P{$^{1}$H} NMR (in CDCl$_3$): $\delta$ (ppm) = –68.0 [s, $^{1}J$(PtP) = 3080 Hz].

**[Pt$_4$Me$_4$($\mu_4$-S)($\mu$-dppm)$_3$] (5a).** To a solution of **1** (38 mg, 0.02 mmol) in acetone (5 mL) was added [Pt$_2$Me$_4$($\mu$-SMe$_2$)$_2$] (14 mg, 0.02 mmol) in acetone (3 mL). The reaction mixture was stirred for 0.5 h. The solvent was removed in vacuo. The yellow residue was recrystallized from CH$_2$Cl$_2$/pentane. Yield: 30 mg, 0.01 mmol, 60%. Anal. Calcd for $C_{79}H_{78}P_6Pt_4S$: C, 46.8; H, 3.9. Found: C, 46.7; H, 3.4%. MS: *m/e* 1785 (P – PtMe$_3$), $^{1}$H NMR (in CDCl$_3$): $\delta$ (ppm) = 0.14 [d, 3 H, $^{3}J$(PH) = 7 Hz, $^{2}J$(PtH) = 86 Hz, *Me*PtS], 0.72 [d, 3 H, $^{3}J$(PH) = 7 Hz, $^{2}H$(PtH) = 72 Hz, *Me*PtP], 2.03 [m, 2 H, P$_2$C$H^{a}H^{b}$], 3.58 [m, 1 H, P$_2$C$H^{c}H^{d}$], 3.89 [m, 2 H, 3$J$(PtH) = 36 Hz, P$_2$C$H^{a}H^{b}$], 5.58 [m, 1 H, $^{2}J$(PH) = 5 Hz, $^{3}J$(PtH) = 80 Hz, P$_2$C$H^{c}H^{d}$], 6.9–7.3 [m, 60 H, *Ph*]. $^{31}$P{$^{1}$H} NMR (in CD$_2$Cl$_2$): $\delta$ (ppm) = –20.5 [t of t, 2 P, $^{2}J$(P$^{a}$P$^{b}$) = 3 Hz, $^{4}J$(P$^{a}$P$^{c}$) = 10 Hz, $^{2}J$(P$^{a}$P$^{a\prime}$) = 60 Hz, $^{1}J$(PtP) = 3780 Hz, $^{2}J$(PtP) = –80 Hz, $^{1}J$(PtPt) = 1645 Hz, $P^{a}$], 7.3 [d of d, 2 P, $^{2}J$(P$^{b}$P$^{c}$) = 65 Hz, $^{4}J$(P$^{b}$P$^{c\prime}$) = 25 Hz, $^{2}J$(P$^{a}$P$^{b}$) = 3 Hz, $^{3}J$(P$^{b}$P$^{b\prime}$) = 170 Hz, $^{1}J$(PtP$^{b}$) = 3300 Hz, $^{2}J$(PtP$^{b}$) = 210 Hz, $P^{b}$], 14.9 [d of d of t, 2 P, $^{1}J$(PtP$^{c}$) = 1960 Hz, $^{3}J$(PtP$^{c}$) = 150 Hz, $P^{c}$]. $^{195}$Pt{$^{1}$H} NMR (in CD$_2$Cl$_2$): $\delta$ (ppm) = –2374 [d, $^{1}J$(PtP) = 1960 Hz, $Pt^{b}$], –3231 [m, $^{1}J$(PtP$^{b}$) = 3300 Hz, $^{1}J$(PtP$^{a}$) = 3780 Hz, $^{2}J$(PtP$^{b}$) = 210 Hz, $^{2}J$(PtP$^{a}$) = –80, $^{3}J$(PtP$^{c}$) = 150 Hz, $Pt^{a}$].

**[Pt$_4$Ph$_4$($\mu_4$-S)($\mu$-dppm)$_3$] (5b).** This was prepared similarly by using *cis*-[PtPh$_2$(SMe$_2$)$_2$]. Yield: 70%. Anal. Calcd for $C_{99}H_{86}P_6Pt_4S$: C, 52.3; H, 3.8. Found: C, 51.4; H, 3.5%. $^{1}$H NMR (in CDCl$_3$): $\delta$ (ppm) = 2.1 [m, 2 H, P$_2$C$H^{a}H^{b}$], 3.7 [m, 1 H, P$_2$C$H^{c}H^{d}$], 4.0 [m, 2 H, P$_2$C$H^{a}H^{b}$], 5.7 [m, 1 H, P$_2$C$H^{c}H^{d}$], 6.9–7.5 [m, 80 H, Ph]. $^{31}$P{$^{1}$H} NMR (in acetone-$d_6$): $\delta$ (ppm) = –15.2 [t of t, 2 P, $^{2}J$(P$^{a}$P$^{b}$) = 4 Hz, $^{4}J$(P$^{a}$P$^{c}$) = 8 Hz, $^{2}J$(P$^{a}$P$^{a\prime}$) = 60 Hz, $^{1}J$(PtP) = 3880 Hz, $^{2}J$(PtP) = –80 Hz, $P^{a}$], 1.1 [m, 2 P, $^{1}J$(PtP) = 1800 Hz, $^{3}J$(PtP) = 100 Hz, $P^{c}$], 4.6 [d of d, 2 P, $^{2}J$(P$^{b}$P$^{c}$) = 65 Hz, $^{4}J$(P$^{b}$P$^{c\prime}$) = 25 Hz, $^{2}J$(P$^{a}$P$^{b}$) = 3 Hz, $^{3}J$(P$^{b}$P$^{b\prime}$) = 160 Hz, $^{1}J$(PtP) = 3300 Hz, $^{2}J$(PtP) = 200 Hz, $P^{b}$]. $^{195}$Pt{$^{1}$H} NMR (in acetone-$d_6$): $\delta$ (ppm) = –2574 [d, $^{1}J$(PtP) = 1800 Hz, $Pt^{b}$], –3443 [m, $^{1}J$(PtP$^{b}$) = 3300 Hz, $^{1}J$(PtP$^{a}$) = 3880 Hz, $^{2}J$(PtP$^{b}$) = 200 Hz, $^{2}J$(PtP$^{a}$) = –80, $^{3}J$(PtP$^{c}$) = 100 Hz, $Pt^{a}$].

**Acknowledgment.** We thank the NSERC (Canada) for financial support.

---

Contribution from the Departamento de Química Inorgánica,
Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009-Zaragoza, Spain

# Bi- and Trinuclear PtAg Complexes with or without Pt–Ag Bonds. Molecular Structure of [PPh$_3$(C$_6$Cl$_5$)ClPt($\mu$-Cl)AgPPh$_3$]

Rafael Usón,* Juan Forniés, Milagros Tomás, Irene Ara, and José M. Casas

*Received December 7, 1988*

When (NBu$_4$)$_2$[*trans*-PtCl$_2$(C$_6$Cl$_5$)$_2$] is reacted with O$_3$ClOAgL (L = PPh$_3$, PEt$_3$; molar ratio 1:1), the binuclear (NBu$_4$)[PtAgCl$_2$(C$_6$Cl$_5$)$_2$L] (L = PPh$_3$ (I), PEt$_3$ (II)) complexes are obtained, while, for L = PPh$_2$Me, the trinuclear [Pt(C$_6$Cl$_5$)$_2${($\mu$-Cl)AgL}$_2$] (III) is obtained in low yield. The trinuclear complexes with L = PPh$_2$Me (III, in higher yield), L = PPh$_3$ (IV), and L = PEt$_3$ (V) are obtained when the above-mentioned reactions are carried out in a 1:2 molar ratio. (NBu$_4$)[*trans*-PtCl$_2$(C$_6$Cl$_5$)L] reacts with O$_3$ClOAgL′ (molar ratio 1:1 or 1:2), yielding the novel binuclear derivatives [L(C$_6$Cl$_5$)ClPt($\mu$-Cl)AgL′] (L′ = PPh$_3$, L = PPh$_3$ (VI), SC$_4$H$_8$ (VII), NC$_5$H$_5$ (VIII); L′ = PPh$_2$Me, L = PPh$_3$ (IX)). The structure of VI has been solved by single-crystal X-ray diffraction. The compound crystallizes in the monoclinic system, space group $P2_1/n$, with $a$ = 14.270 (2) Å, $b$ = 14.663 (2) Å, $c$ = 20.024 (2) Å, $\beta$ = 93.58 (1)°, $V$ = 4181.69 Å$^3$, and $Z$ = 4. The structure was refined to residuals of $R$ = 0.037 and $R_w$ = 0.037. The "PtCl$_2$(C$_6$Cl$_5$)PPh$_3$" and "AgPPh$_3$" fragments are bonded by a single chlorine bridge, Pt($\mu$-Cl)Ag (Pt–Cl1 = 2.341 (3) Å, Ag–Cl1 = 2.514 (2) Å), and a weak Pt–Ag bond (Pt–Ag = 2.945 (1) Å), and two [(PPh$_3$)(C$_6$Cl$_5$)ClPt($\mu$-Cl)Ag(PPh$_3$)] units are connected through a weak Ag′–Cl1 interaction (Ag′···Cl1 = 3.023 (2) Å). The silver atom makes a short contact with one *o*-chlorine atom of the C$_6$Cl$_5$ groups (Ag···Cl7 = 3.041 (4) Å).

## Introduction

We have recently reported[1] the synthesis, structure, and reactivity of {(NBu$_4$)[Pt(C$_6$Cl$_5$)$_2$($\mu$-Cl)$_2$Ag]}$_x$. The polymeric anion in this complex consists of trans-planar PtCl$_2$(C$_6$Cl$_5$)$_2$ units that lie on a pair of parallel planes and are linked by a central ribbon of silver atoms diagonally coordinated to two chlorine atoms, one on each plane. The long Pt–Ag distance (3.203 (1) Å) excludes any significant Pt–Ag bond, but each Ag atom interacts with four *o*-Cl atoms, since the C$_6$Cl$_5$ groups are so positioned as to bridge two adjacent silver atoms, thus completing around each silver atom a rhombically distorted octahedron of Cl atoms.

A dichloromethane suspension of this polymeric complex reacts[1] with group 15 ligands (L; Pt:L = 1:1) to give anionic binuclear (NBu$_4$)[PtAgCl$_2$(C$_6$Cl$_5$)$_2$L] (A) or neutral trinuclear [Pt(C$_6$Cl$_5$)$_2${($\mu$-Cl)AgL}$_2$] (B) complexes, depending on the neutral ligand L. The structure of one complex of each type has been established by X-ray diffraction, and in the binuclear complex (NBu$_4$)[PtAgCl$_2$(C$_6$Cl$_5$)$_2$PPh$_3$] (A),[1] the silver atom displays a bond to the platinum atom, which is singly bridged by a chloride ligand, and two short contacts to *o*-Cl atoms of the C$_6$Cl$_5$ groups (see Figure 1A). In the trinuclear compound [Pt(C$_6$Cl$_5$)$_2${($\mu$-Cl)Ag(PPh$_2$Me)}$_2$] (Figure 1B)[1] the absence of a Pt–Ag bond and *o*-Cl–Ag contacts is compensated by strong Ag–Cl and Ag–P bonds.

Since the insolubility of the polymeric starting complex precludes any meaningful change of the reaction conditions, it should be worthwhile to search for other synthetic approaches in order to ascertain whether both types of complexes would be accessible in all cases by a suitable choice of the molar ratio with soluble precursors. Both types of complexes (Figure 1) can be considered as the result of the interaction of a trans-planar "PtCl$_2$(C$_6$Cl$_5$)$_2$" fragment with one (binuclear species) or two (trinuclear species) "Ag–L" fragments. Therefore, in the present paper we study the 1:1 and 1:2 reactions between (NBu$_4$)$_2$[*trans*-PtCl$_2$(C$_6$Cl$_5$)$_2$] and O$_3$ClOAgL (L = PPh$_3$, PPh$_2$Me, PEt$_3$) as well as similar reactions of the anionic (NBu$_4$)[*trans*-PtCl$_2$(C$_6$Cl$_5$)L] with O$_3$ClOAgL′, which give a novel type of complex, as shown by the structure of the complex with L = PPh$_3$ and L′ = PPh$_3$ that has been

---

[1] Usón, R.; Forniés, J.; Tomás, M.; Casas, J. M.; Cotton, F. A.; Falvello, L. R. *Inorg. Chem.* **1986**, *25*, 4519.

0020-1669/89/1328-2388$01.50/0