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Palladium and Platinum Complexes Containing Diphenylphosphino(methylthio)methane

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Binuclear complexes containing bridging bis(diphenylphosphino)methane ligands are now well documented for a number of transition metals [1]. Analogous complexes with unsymmetrical bridging ligands, which may form head-to-head or head-to-tail isomers, are less common, although 2-(diphenylphosphino)pyridine [2] and diphenylarsino(diphenylphosphino)methane [3] examples are known. As part of our study of palladium and platinum complexes containing unsymmetrical, bidentate ligands [4] we have prepared Ph_2PCH_2SMe, diphenylphosphino(methylthio)methane, and we report here the first examples of binuclear complexes in which the metal centers are bridged by a neutral bidentate ligand containing Group 5 and Group 6 donor atoms.

The ligand Ph_2PCH_2SMe is prepared according to equation 1, and reaction of $[PtCl_2(cod)]$ with 2 mol equiv of the ligand in chloroform solution gives

$$Ph_2PCl + 2Li \xrightarrow[-LiCl]{THF} Ph_2P^-Li^+ \xrightarrow[-LiCl]{ClCH_2SMe} Ph_2PCH_2SMe \quad (1)$$

cis-$[PtCl_2(Ph_2PCH_2SMe)_2]$, δP 7.0, ^1J(Pt, P) 3680 Hz, in which the ligands are coordinated through phosphorus only. Treatment of this complex with $AgBF_4$ yields $[PtCl(Ph_2PCH_2SMe)_2]BF_4$, in which one of the ligands is chelating. The $^{31}P\{^1H\}$ NMR spectrum exhibits two resonances (with ^{195}Pt satellites) one of which appears at high field as expected for a phosphorus atom which is part of a four-membered ring [5] (Table I). No phosphorus–phosphorus coupling is observed, indicating that the phosphorus atoms are in mutually *cis*-positions. Addition of $Et_4N^+Cl^-$ to a solution of $[PtCl(Ph_2PCH_2SMe)_2]BF_4$ results in a broad $^{31}P\{^1H\}$ NMR spectrum at ambient temperature, which on cooling to −50 °C allows identification of *cis*- and *trans*-$[PtCl_2(Ph_2PCH_2SMe)_2]$ (Table I). On standing slow conversion to the *cis*-isomer occurs.

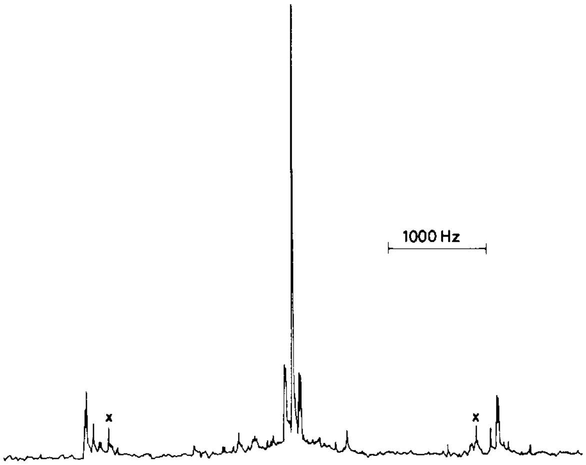

Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of $[Pt_2Cl_2(\mu\text{-}Ph_2PCH_2SMe)_2]$. Peaks marked x are ^{195}Pt satellites of the decomposition product (see text).

When $PdCl_2$ is treated with 2 mol equiv. of Ph_2PCH_2SMe a broad $^{31}P\{^1H\}$ NMR spectrum is obtained at ambient temperature, which on cooling to −50 °C reveals the presence of *cis*- and *trans*-$[PdCl_2(Ph_2PCH_2SMe)_2]$ (δP 24.6 and 29.0, relative intensities 1:1.9) in which the thioether functions remain uncoordinated. An almost identical spectrum has

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TABLE I. $^{31}P\{^1H\}$ NMR Parameters for the Platinum Complexes.

Complex	δP^a	^1J(Pt, P), Hz	Other couplings
cis-$[PtCl_2(Ph_2PCH_2SMe)_2]$	7.0	3680	
trans-$[PtCl_2(Ph_2PCH_2SMe)_2]$	16.0	2450	
$[PtCl(Ph_2PCH_2SMe)_2]BF_4$	9.2^b	3280	^2J(P,P) <2Hz
	-58.7^c	3050	
$[Pt_2Cl_2(\mu\text{-}Ph_2PCH_2SMe)_2]$	4.8	4080	^2J(Pt,P) 140 Hz, ^3J(P,P) 12 Hz, ^1J(Pt,Pt) 7750 Hz

^{a}Chemical shifts are in ppm relative to external H_3PO_4, positive shifts representing deshielding. ^{b}*trans* to S. ^{c}*trans* to Cl.

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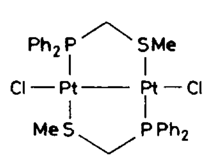
been obtained for [$PdCl_2(Ph_2Ppy)_2$] (Ph_2Ppy = 2-(diphenylphosphino)pyridine) [2c].

Refluxing *cis*-[$PtCl_2(Ph_2PCH_2SMe)_2$] with [Pt(dba)$_2$] (dba = dibenzylideneacetone) [6] in dichloromethane yields the dimeric platinum(I) complex, [$Pt_2Cl_2(\mu\text{-}Ph_2PCH_2SMe)_2$], which could be isolated as deep red crystals. The $^{31}P\{^1H\}$ NMR spectrum of this complex in chloroform solution is shown in Fig. 1, and the spectroscopic parameters are given in Table I. The dimeric nature of the complex is evident from the observation of ^2J(Pt,P) and ^3J(P,P) coupling constants, whereas the large value of ^1J(Pt, Pt) is indicative of the presence of a platinum–platinum bond. The appearance of the spectrum also indicates [2g] that the complex exists as the head-to-tail isomer, **1**. Whereas it is apparently indefinitely stable in air in the solid state, [$Pt_2Cl_2(\mu\text{-}Ph_2PCH_2SMe)_2$] decomposes slowly in solution to yield an unidentified species, δP 4.7, ^1J(Pt,P) 3640 Hz. From a similar reaction of *cis*- and *trans*-[$PdCl_2(Ph_2PCH_2SMe)_2$] with [$Pd(dba)_2$] are obtained orange crystals of [$Pd_2Cl_2(\mu\text{-}Ph_2PCH_2SMe)_2$]. This complex apparently exists as head-to-tail, **2**, and head-to-head, **3**, isomers, their relative proportions being dependent on the isolation procedure.



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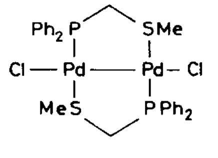

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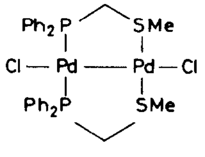

3

The two isomers exhibit single ^{31}P NMR resonances at δP 8.4 and 20.5, and we tentatively assign the latter to **3** because, where both isomers exist for Pt–Pt and Pt–Pd systems, the head-to-head isomer produces a lower field resonance [2g, 3a].

The metal–metal bond in [$Pt_2Cl_2(\mu\text{-}dppm)_2$] (dppm = bis(diphenylphosphino)methane) exhibits considerable reactivity, particularly towards the insertion of small molecules [1]. Treatment of [$Pt_2Cl_2(\mu\text{-}Ph_2PCH_2SMe)_2$] with carbon monoxide, however, provides no evidence for insertion of CO into the platinum–platinum bond, but the infrared spectrum after a few minutes exhibits absorptions at 2005 and 2030 cm^{-1} due to terminal carbonyl groups. After standing for 24 hours an intense peak appears at 2030 cm^{-1}, along with a weaker absorption at 2100 cm^{-1}. When a chloroform solution of [$Pt_2Cl_2(\mu\text{-}Ph_2PCH_2SMe)_2$] at −50 °C is reacted with ^{13}CO, the low temperature $^{13}C\{^1H\}$ NMR spectrum contains a resonance at δC 167.9, ^1J(Pt, C) 1860 Hz (no phosphorus–carbon coupling observed), which is typical of a terminal carbonyl lying *trans* to a low *trans*-influence ligand such as chloride [7]. After standing at ambient temperature for several days this resonance diminishes in intensity, and a weak resonance is detected at δC 156.0, while the $^{31}P\{^1H\}$ NMR spectrum at this stage indicates that the major phosphorus-containing species in solution is *cis*-[$PtCl_2(Ph_2PCH_2SMe)_2$]. A weak peak at δP 7.6, ^1J(Pt,P) 2985 Hz, along with the ^{13}C resonance at δC 156.0 and the infrared absorption at 2100 cm^{-1} point to *cis*-[$PtCl_2(CO)(Ph_2PCH_2SMe)$] as a minor product [7]. We suggest the initial product is obtained by cleavage of the platinum-sulfur bonds by CO (Fig. 2), followed by disproportionation of the dimeric platinum(I) species to yield products containing platinum(II) or platinum(0). The initial product of the analogous reaction of [$Pd_2Cl_2(\mu\text{-}Ph_2Ppy)_2$] with CO was suggested to be [$Pd_2Cl_2(CO)_2(Ph_2Ppy)_2$] [2c], in which the phosphine ligands were assumed to occupy the axial positions for steric reasons.

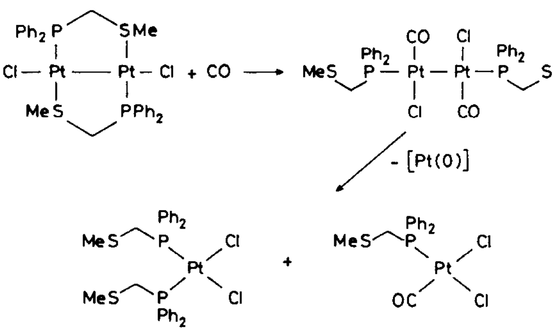

Fig. 2. Reaction of [$Pt_2Cl_2(\mu\text{-}Ph_2PCH_2SMe)$] with carbon monoxide.

It has been suggested that the inflexibility of the Ph_2Ppy ligand contributes to the lack of reactivity toward insertion reactions of the metal–metal bond in complexes spanned by this ligand [2b,c], whereas with Ph_2PCH_2SMe the ease of displacement of the thioether moiety is undoubtedly the dominant factor.

Acknowledgements

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