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Preliminary communication

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF *cis*-$Pt(SH)_2(PPh_3)_2$ AND RELATED ALKYL AND ARYL THIOLATO COMPLEXES

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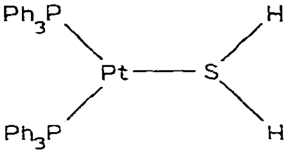
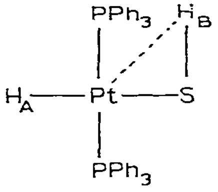
Summary

The synthesis and spectroscopic characterization of the complexes *cis*-$Pt(SR)_2(PPh_3)_2$ (R = H. Me, n-Bu and Ph) are reported, together with the single crystal X-ray crystallographic characterization of *cis*-$Pt(SH)_2(PPh_3)_2$. The ability of these complexes to act as bidentate ligands towards other metal centres is also briefly described.

In 1971 Ugo and his coworkers [1] reported that $Pt(PPh_3)_n$ (n = 2 or 3) reacts with H_2S to give an adduct $Pt(PPh_3)_2(H_2S)$, which in solution appeared to exist as a mixture of the tautomeric forms I and II.



(I)



(II)

A weak interaction between H_B and the platinum d_{z^2} orbital was initially proposed [2] to account for the high field chemical shift of H_B, although this was later discarded in favour of diamagnetic ring current effect arising from the proximity of H_B to a phenyl ring [2]. Subsequently there have been reports of other SH complexes of the platinum metals, but to date none of the complexes have been structurally characterized in the solid state [3,4].

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We have found that chloroform solution of the dioxygen complex, $Pt(O_2)(PPh_3)_2$, react readily with H_2S and RSH (R = Me, n-Bu and Ph) according to the following equation

$$Pt(O_2)(PPh_3)_2 + RSH \rightarrow \textit{cis}\text{-}Pt(SR)_2(PPh_3)_2 + H_2O_2$$

to give high yields of the *cis*-dithiolato complexes as off white (R = H) or pale yellow (R = Me, n-Bu or Ph) crystalline complexes. Crystals of *cis*-$Pt(SH)_2(PPh_3)_2 \cdot CHCl_3$ suitable for crystallographic investigation were obtained by recrystallisation from $CHCl_3$/EtOH.

Crystal data. The structure was determined from 5234 unique reflections having $I > 3\sigma(I)$ and refined to $R = 0.0450$. $C_{37}H_{33}S_2Cl_3P_2Pt$, $M = 904.5$, triclinic a 11 198(2), b 11.876(3) and c 14.462(4) Å, α 91.10(2), β 98.43(2) and γ 107.70(2)°, U 1808 Å^3, $Z = 2$, D_c 1.66 g cm^{-3}, μ(Mo-K_α) 45.4 cm^{-1}, $F(000) = 824$, Mo-K_α 0.71069 Å, Space group $P\bar{1}$.

The molecular structure of *cis*-$Pt(SH)_2(PPh_3)_2$ illustrated in Fig. 1 confirms that it has a *cis*-square planar structure with few significant distortions. The Pt, S(1), S(2), P(1) and P(2) atoms all lie within 0.06 Å of the best least squares planes through these atoms, and the deviations from 90° for S(1)—Pt—S(2) and P(1)—Pt—P(2) can be readily accounted for in terms of the very different steric requirements of SH and PPh_3. The hydrogen atoms on the SH ligands appear to be crystallographically disordered and therefore were not unambiguously located.

The ^1H and $^{31}P\{^1H\}$ NMR data for the complexes *cis*-$Pt(SR)_2(PPh_3)_2$ (R = H, Me or n-Bu) given in Table 1 confirm that they all have *cis*-geometries. The ^1H resonance associated with the SH ligands in *cis*-$Pt(SH)_2(PPh_3)_2$ occurs at

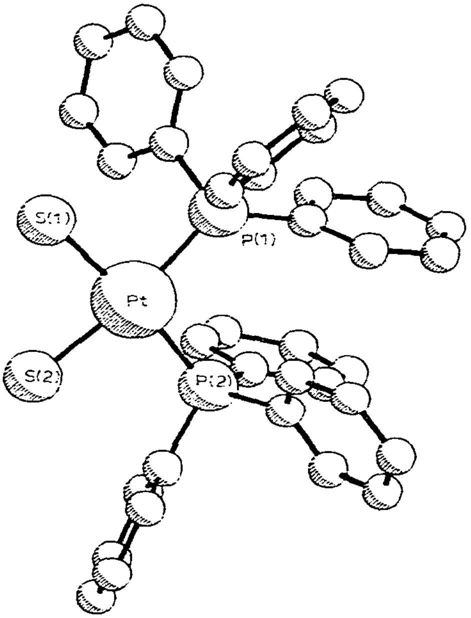

Fig. 1. Molecular structure of *cis*-$Pt(SH)_2(PPh_3)_2$, Pt—S(1) 2.360(2), Pt—S(2) 2.340(2), Pt—P(1) 2.286(2), Pt—P(2) 2.279(2) Å; S(1)—Pt—S(2) 83.14(8), S(1)—Pt—P(1) 89.28(7), S(2)—Pt—P(2) 90.06(8), P(1)—Pt—P(2) 97.65(7)°.

TABLE 1

NMR PARAMETERS[a] FOR *cis*-$Pt(SR)_2(PPh_3)_2$ IN CD_2Cl_2 AT 293 K

Complex	δ(SH)	δ(SMe)	$\delta(^{31}P)$[b]	$^2J(Pt—H)$	$^3J(P—H)$	$^3J(Pt—H)$	$^4J(Pt—H)$	$^1J(Pt—P)$
cis-$Pt(SH)_2(PPh_3)_2$	0.1		21.37	50	8.5			2981
cis-$Pt(SMe)_2(PPh_3)_2$		2.25	25.52			54	6.5	2862
cis-$Pt(SBu)_2(PPh_3)_2$			21.38					2863

[a] δ in ppm, *J* in Hz. [b] To high frequency of trimethylphosphate.

0.18 (cf. −1.58 for II [1] and *trans*-$Pt(SH)_2(PEt_3)_2$ [3] and −1.18 for *trans*-$PtH(SH)(PEt_3)_2$ [3]).

The *cis*-arrangement of dithiolato ligands in the complexes described in this paper suggests that they may be able to function as bidentate ligands towards other transition metal centres in a manner analogous to that reported previously for $M(\eta\text{-}C_5H_5)_2(SR)_2$ (M = Ti or Nb; R = Me or Ph) [5,6]. *cis*-$Pt(SPh)_2(PPh_3)_2$ reacts readily with $Mo(CO)_4(\eta^4\text{-}C_7H_8)$ in $CHCl_3$ solutions to give $(Ph_3P)_2Pt(\mu\text{-}SPh)_2Mo(CO)_4$ as a brick red crystalline solid (m.p. 134—137°C). The $\nu(CO)$ stretching frequencies for this mixed metal complex observed in $CHCl_3$ solutions at 2000, 1940, 1905, 1845 cm^{-1}, are consistent with its formulation as *cis*-bridged thiolato complex [5,6]. The complexes *cis*-$Pt(SR)_2(PPh_3)_2$ (R = n-Bu, or Ph) also react with the complexes $Pd(PhCN)_2Cl_2$ and $Pt(COD)Cl_2$ (COD = cyclooctadiene) to give the complexes $(Ph_3P)_2Pt(SR)_2MCl_2$ (M = Pd or Pt). The structural, spectroscopic and electrochemical properties of these complexes are currently being investigated. However, these preliminary results indicate that the complexes *cis*-$Pt(SR)_2(PPh_3)_2$ may prove to be important precursors for binuclear mixed metal thiolato complexes.

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