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Preliminary communication

SYNTHESIS AND STRUCTURE OF A DIMETHYL(μ-HYDRIDO)DIPLATINUM(II) COMPLEX

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Summary

The complex $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-dppm})_2][PF_6]$ (I, dppm = $Ph_2PCH_2PPh_2$) has been prepared and characterised by ^1H and ^{31}P NMR spectroscopy and by a full molecular structure determination by X-ray methods. The complex undergoes only slow reductive elimination of methane induced by added tertiary phosphine at 70°C.

Methyl(hydrido) complexes of transition metals are rare, because they frequently undergo fast reductive elimination of methane. For example, *cis*-$[PtHMe(PPh_3)_2]$ decomposes at –20°C in solution by reductive elimination of methane [1], although various complexes *trans*-$[PtHRL_2]$ (R = alkyl or aryl, L = tertiary phosphine ligand) are sufficiently stable to be isolated [2,3]. We now report a new binuclear methyl(hydrido)platinum(II) complex, which has remarkable thermal stability. The complex $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-dppm})_2][PF_6]$ (I) was prepared in good yield as a white, air stable solid by reaction of either $[Pt_2Me_3(\mu\text{-dppm})_2][PF_6]$ [4] or $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-dppm})_2][PF_6]$ [5] with sodium borohydride.

Crystals of $[Pt_2Me_2(\mu_2\text{-}H)(\mu\text{-}Ph_2PCH_2PPh_2)_2][PF_6]$ are monoclinic, space group $P2_1/c$, $a = 10.640(3)$, $b = 20.341(3)$, $c = 23.201(3)$ Å, $\beta = 91.88(2)°$ ($\lambda = 0.71069$ Å), $Z = 4$, $D_C = 1.77$ g cm^{-3}. The intensities of X-ray reflections, measured on a CAD-4F diffractometer with Mo-K_α radiation, were corrected for absorption effects. The structure was solved by the heavy atom method and refined by a full-matrix least-squares procedure. Currently R is 0.054 for 5104 reflections for which $I \geqslant 3\sigma(I)$.

The crystal structure is built of discrete cations and anions. The overall geo-

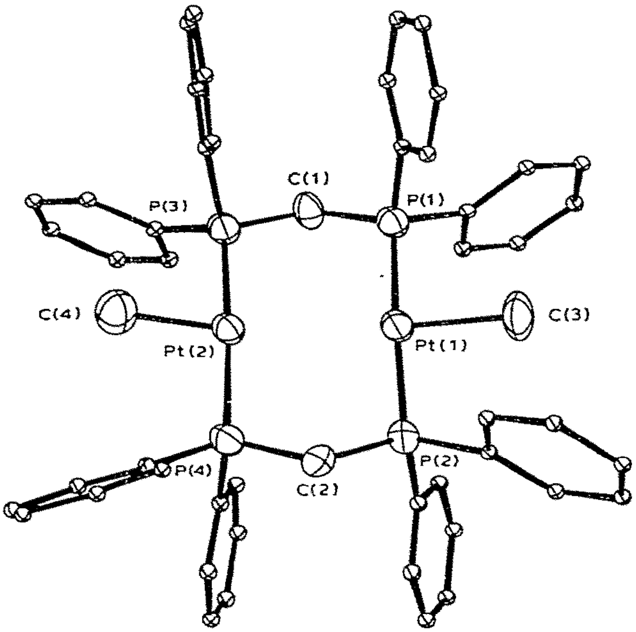

Fig. 1. A view of the structure of the $[Pt_2Me_2(\mu_2\text{-}H)(\mu\text{-}dppm)_2]^+$ cation, with hydrogen atoms omitted. Selected bond angles are: C—Pt—P 87.4(4)—92.0(4), P—Pt—P 173.1(1) and 177.1(1), P—C—P 111.2(7) and 112.3(7)°.

metry of the cation (Figure 1) is similar to that of the "A-frame" structure [6] in which the metal centres, bridged by two dppm or dpam (dpam = $Ph_2AsCH_2AsPh_2$) ligands, display square planar coordination and form a V-shaped arrangement with two terminal ligands (in this case CH_3^-) and a third ligand occupying the common coordination site. In the $[Pt_2Me_2(\mu_2\text{-}H)(\mu\text{-}dppm)_2]^+$ cation this site is available to the hydrido ligand whose position has not been revealed at this stage of the X-ray analysis. The Pt_2P_4 moiety is practically planar and perpendicular to the C(3), Pt(1), Pt(2), C(4) plane. The bond lengths involving platinum atoms are: Pt—P 2.275(3)—2.291(3) Å and Pt—C 2.05(2) and 2.13(2) Å. The C(3)—Pt(1)—Pt(2) and C(4)—Pt(2)—Pt(1) angles (169.7(7) and 162.0(6)°, respectively) and the dihedral angle between coordination planes of the Pt(1) and Pt(2) atoms (31°) are in accordance with a bent electron deficient 3-centre-2-electron Pt—H—Pt bridge. The Pt(1)—Pt(2) distance (2.933(1) Å) is appreciably longer than those usually found for Pt—Pt single bonds in binuclear complexes (2.531(1)—2.770(2) Å), [7—10] although bonding distances of 2.819(1), 2.870(3) and 2.890(2) Å have also been observed [7,8a]. On the other hand, it is considerably shorter than the Pt ... Pt separations (3.160(3) and 3.162(4) Å) in the A-frame complexes $[Pt_2Cl_2(\mu_2\text{-}CH_2)(\mu\text{-}dppm)_2]$ [11] and $[Pt_2Cl_2(\mu_2\text{-}CO)(\mu\text{-}dpam)_2]$ [12], where the metal atoms are not directly bonded to each other. It is therefore tempting to speculate on the possibility of a closed [13] Pt—H—Pt system, in which the metal atom orbitals involved in bonding with the hydrido ligand overlap significantly with one another.

The bridging nature of the hydride group was established from the ^1H NMR spectrum, which contained a signal due to the hydride at δ −7.26 ppm with the characteristic 1:8:18:8:1 quintet pattern due to coupling with ^{195}Pt expected for a hydride bridging between two ^{195}Pt atoms [14]. The ^{1}H and ^{31}P NMR data are fully consistent with the structure I and will be discussed more fully elsewhere.

Complex I remains unchanged on heating to 70°C either in the solid state or in solution in dichloromethane, and does not react at room temperature with carbon monoxide, methanethiol or ammonia. Reductive elimination of methane is induced by added dimethylphenylphosphine but this reaction is sluggish; for example reaction of I with 1.4 molar equivalents of PMe_2Ph in acetone solution at 50°C gave only 0.5 molar equivalent of methane after 3 hours. In contrast, photolysis of I in solution is rapid and yields methane and traces of ethylene (1—2%). It is likely that the high thermal stability of I is due to its rigid structure with methyl and hydrido ligands held in mutually *trans* positions so that reductive elimination cannot readily occur.

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