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Preliminary communication

PREPARATION AND X-RAY CRYSTAL STRUCTURE OF $[Pt_2(PPh_3)_2(\mu\text{-}Ph_2PCHPPh_2)(\mu\text{-}Ph_2PCH_2PPh_2)][PF_6]$, A DIPLATINUM(I) COMPLEX CONTAINING THE BIS(DIPHENYLPHOSPHINO)METHANIDE LIGAND IN A NOVEL BRIDGING ROLE

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Summary

Deprotonation of the complex cation of $[Pt_2(PPh_3)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2][PF_6]_2$ with KOH/EtOH affords $[Pt_2(PPh_3)_2(\mu\text{-}Ph_2PCHPPh_2)(\mu\text{-}Ph_2PCH_2PPh_2)][PF_6]$, the X-ray crystal structure of which shows that the bis(diphenylphosphino)-methanide ligand bridges the two platinum atoms by formation of a four-membered PtCPPt dimetallacycle.

Although there are many diplatinum complexes containing the ligand $Ph_2PCH_2PPh_2$(dppm) [1], there are no reports of diplatinum complexes containing the deprotonated form of this ligand, viz. the methanide ion $[Ph_2PCHPPh_2]^-$ (I). This is surprising since I and its methyl analogue $[Me_2PCHPMe_2]^-$ (II) are known to form several di- and poly-nuclear complexes with other transition metals. Bridging modes observed are as depicted by **A** [2], **B** [3] and **C** [4]. We now report a diplatinum complex containing I in the novel bridging mode **D**.

Previously, we prepared the mononuclear complex $[Pt(Ph_2PCHPPh_2)_2]$ (III) by, in effect, deprotonating the complex $[Pt(Ph_2PCH_2PPh_2)_2]^{2+}$ with KOH/EtOH [5]. It appears that deprotonation of this dipositively-charged complex proceeds more readily than that of similar neutral platinum/dppm complexes [6]. We now find that deprotonation of the dipositively-charged diplatinum(I) complex cation in $[Pt_2(PPh_3)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]^{2+}\cdot 2[PF_6]^-$ (IV) [7] also occurs with KOH/EtOH and affords the novel diplatinum complex $[Pt_2(PPh_3)_2\text{-}(\mu\text{-}Ph_2PCHPPh_2)(\mu\text{-}Ph_2PCH_2PPh_2)]^+[PF_6]^-$ (V) in 55% yield.

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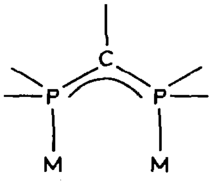
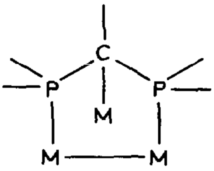


(A)



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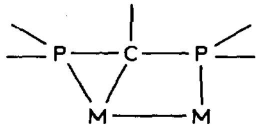

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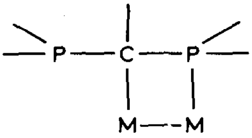
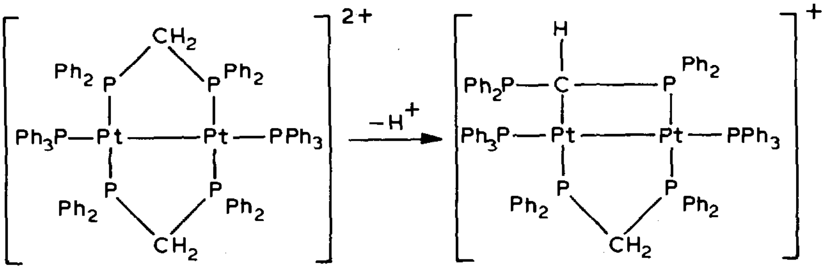


(D)



(IV) (V)

The deprotonation may also be effected in similar yield by using III as a proton acceptor:

$$\underset{}{\mathrm{IV}} + \underset{\mathrm{(III)}}{[\mathrm{Pt(Ph_2PCHPPh_2)_2}]} \rightarrow \mathrm{V} + \underset{\mathrm{(VI)}}{[\mathrm{Pt(Ph_2PCHPPh_2)(Ph_2PCH_2PPh_2)}][\mathrm{PF_6}]}$$

The "mixed" complexes V and VI are readily separated by treatment with aqueous buffer (pH = 6.8) containing $[PF_6]^-$ ion when (VI) is protonated to $[Pt(Ph_2PCH_2PPh_2)_2]^{2+}$ and precipitates in the form of its $[PF_6]^-$ salt leaving V unchanged. This demonstrates that the deprotonation IV → V is not readily reversible.

The ^1H and ^{31}P NMR spectra of V are complex and have not yet been analysed in any detail (^1H NMR (CD_2Cl_2) δ 3.46 (m, 1H, PCHP), 5.06 (m, 2H, PCH_2P) ppm) and to characterize V unambiguously we have carried out a single crystal X-ray diffraction study.

Crystallographic data: $[C_{86}H_{73}P_6Pt_2][PF_6]$, $M = 1827.5$. Monoclinic, space group $P2_1/n$, a 13.021(4), b 14.618(6), c 43.135(16) Å, β 92.81(3)°, U 8200 Å^3, $Z = 4$, D_c 1.48 g cm^{-3}. The intensities of 7078 independent reflections with $I \geqslant 3\sigma(I)$ and $2 < \theta(\text{Mo-}K_\alpha) < 21°$ have been measured, using an Enraf—Nonius CAD-4F diffractometer and Mo-K_α radiation (λ 0.71069 Å). The structure was solved by the heavy atom method. Currently R is 0.09, after a block-diagonal least-squares refinement.

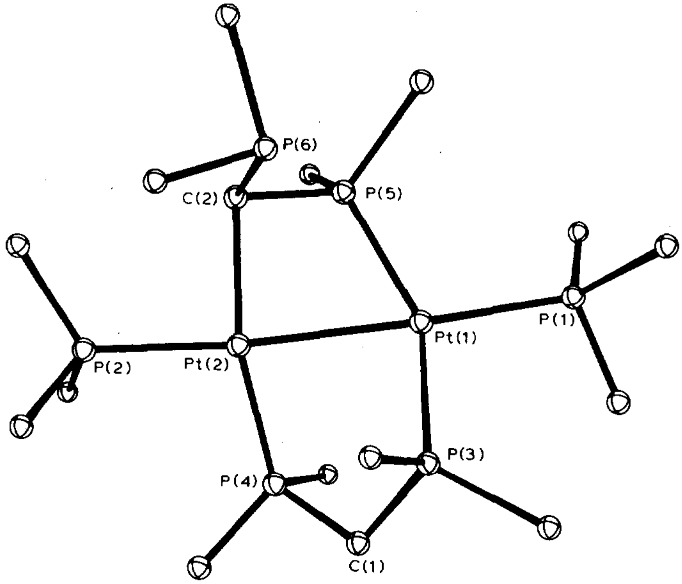


Fig. 1. A perspective view of the metal coordination polyhedra in the $[Pt_2(PPh_3)_2(Ph_2PCH_2PPh_2)(Ph_2PCHPPh_2)]^+$ cation. For clarity, each of the fourteen phenyl rings is represented by its *ipso* carbon atom only. Selected bond lengths and angles are: Pt(1)—Pt(2) 2.659(2), Pt—P 2.28(1)—2.34(1), Pt(2)—C(2) 2.18(3), P(5)—C(2) 1.82(3) Å, Pt(2)—Pt(1)—P(1) 165.2(2), Pt(2)—Pt(1)—P(3) 84.9(2), Pt(2)—Pt(1)—P(5) 67.9(2), P(1)—Pt(1)—P(3) 104.2(3), P(1)—Pt(1)—P(5) 105.9(3), P(3)—Pt(1)—P(5) 148.4(3), Pt(1)—Pt(2)—P(2) 171.9(2), Pt(1)—Pt(2)—P(4) 83.8(2), Pt(1)—Pt(2)—C(2) 83.5(7), P(2)—Pt(2)—P(4) 99.1(3), P(2)—Pt(2)—C(2) 92.5(7), P(4)—Pt(2)—C(2) 165.0(7)°.

The novel feature of the structure of V (Fig. 1) is that the anionic ligand $[Ph_2PCHPPh_2]^-$ (I) has undergone metallation at the deprotonated methylenic carbon atom. The metal centres are bridged through the Pt(2)—C(2) and Pt(1)—P(5) bonds to form a four-membered dimetallacycle, while the P(6) atom remains unattached to either platinum atom. The overall steric congestion in this highly crowded complex is therefore considerably relieved.

The other noteworthy structural feature is that both metal atoms show unusually large distortions from the ideal square planar coordination geometry, as is immediately obvious from the bond angles shown in Fig. 1. The distortion around the Pt(1) atom is tetrahedral, the Pt(2), P(5), P(1) and P(3) atoms lying alternately ca. 0.25 Å above and below their common plane with Pt(1). In contrast, the Pt(2) atom displays a pyramidal distortion and lies 0.163 Å above its coordination plane; the atoms Pt(1), P(2), P(4) and C(2) are coplanar to within 0.006 Å.

The Pt—Pt distance of 2.659(2) Å agrees well with the Pt^I—Pt^I bond lengths in dinuclear complexes $[Pt_2XX'(\mu\text{-dppm})_2]^{n+}$ (X = X' = Cl, n = 0; X = Cl, X' = CO, n = 1; X = X' = CO, n = 2) [8]. We therefore prefer to consider V as a species with a normal covalent bond between two d^9 platinum(I) ions, and to ascribe the observed distortions from square planar geometry to steric crowding. An alternative interpretation, formulating V as a mixed-valence complex with a $Pt^0 \rightarrow Pt^{II}$ donor—acceptor bond, is also tenable and has the merit of explaining the substantial tetrahedral distortion around the Pt(1) atom in terms of electronic effects.

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