$[Pt_2Me_2(\mu\text{-}Ph_2PCH_2PPh_2)_2][BF_4]_2$, a Highly Reactive and Co-ordinatively Unsaturated Di-platinum(II) Complex. Crystal Structures of $[Pt_2Me_2L_2(\mu\text{-}Ph_2PCH_2PPh_2)_2][BF_4]_2$, L = MeCN or CO

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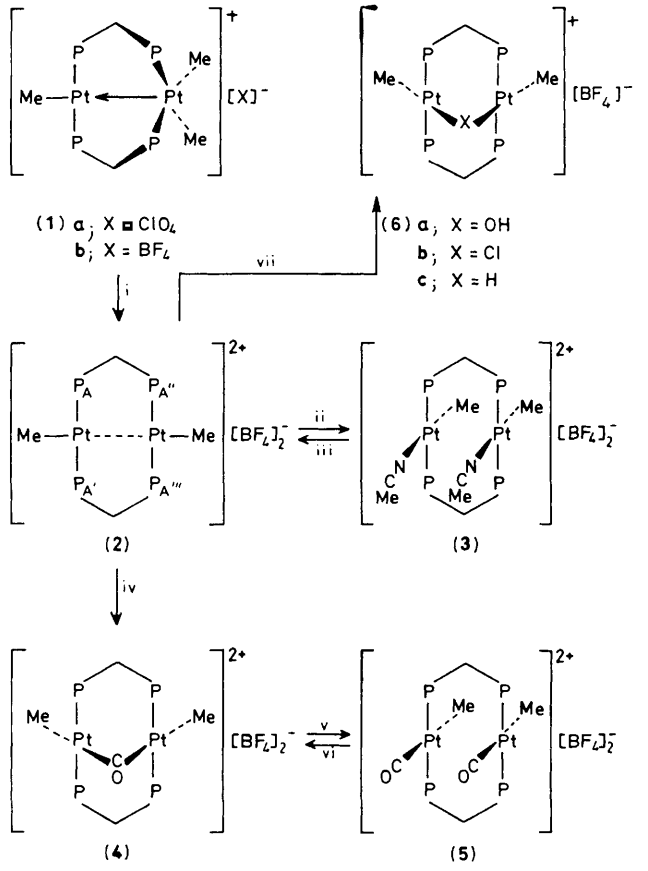
Treatment of $[Pt_2Me_3(Ph_2PCH_2PPh_2)_2][BF_4]$ with $Ph_3C^+BF_4^-$ in wet CH_2Cl_2 gives $[Pt_2Me_2(Ph_2PCH_2PPh_2)_2]^{2+}$ which reacts rapidly with MeCN, CO, OH^-, Cl^-, or MeOH to give several new complexes or adducts, including 'A-frames'.

Bis(diphenylphosphino)methane (dppm) is a versatile ligand for stabilizing several types of monometallic and bimetallic complexes.[1] Thus it gives both $[PtMe_2(dppm)]$ and the isomeric, 8-membered ring *cis-cis*-$[Pt_2Me_4(\mu\text{-dppm})_2]$ both of which, when treated with perchloric acid, give the trimethyldiplatinum cation $[Pt_2Me_3(dppm)_2]^+$, as the perchlorate, with the remarkable structure (**1a**), containing a platinum–platinum donor–acceptor bond.[2,3] We now report on the synthesis and some reactions of the dimethyldiplatinum cation $[Pt_2Me_2(dppm)_2]^{2+}$, formed by removal of a second methide ion.

We find that treatment of a dichloromethane solution of $[PtMe_2(dppm)]$ with 48% aqueous HBF_4 gives some of the required di-cation along with other (unidentified) products, but this is not a convenient synthesis. However, we find that the readily prepared $Ph_3C^+BF_4^-$ in wet (*i.e.* undried) dichloromethane is a convenient source of HBF_4 and that treatment of $[PtMe_2(dppm)]$ with 0.5 mol. equiv. of $Ph_3C^+BF_4^-$ in dichloromethane immediately gives $[Pt_2Me_3(dppm)_2][BF_4]$ (**1b**) in >95% isolated yield. Moreover further treatment of (**1b**) with a 3-fold excess of $Ph_3C^+BF_4^-$ in dichloromethane gives $[Pt_2Me_2(\mu\text{-dppm})_2][BF_4]_2$ isolated as a yellow crystalline solid in 85% yield. We formulate this complex as (**2**) from the elemental analysis (C, H, F), the electrical conductivity (Λ_M = 185 cm^2 Ω^{-1} mol^{-1} in acetone at 20 °C), the $^1H\{^{31}P\}$ n.m.r. spectrum [(CD_2Cl_2) $\delta(CH_3)$ 1.0, $^2J(PtCH_3)$ 77.7 Hz, $^3J(PtPtCH_3)$ 11.0 Hz], and the $^{31}P\{^1H\}$ n.m.r. spectrum [δ(P) 22 p.p.m., ^1J(PtP) 2693 Hz, ^2J(PtP) + ^3J(PtP) *ca.* 0 Hz, $J(P_AP_{A''})$ 45 Hz, $J(P_AP_{A'''})$ 7 Hz]. [See ref. 4 for the analysis of the $^{31}P\{^1H\}$ n.m.r. spectrum of a $Pt_2(\mu\text{-dppm})_2$ system.] The observation



Scheme 1. Synthesis and reactions of $[Pt_2Me_2(Ph_2PCH_2PPh_2)_2][BF_4]_2$; *P*-phenyl groups have been omitted for brevity. All the compounds shown have been fully characterized by elemental analysis, electrical conductivity, and by i.r. and n.m.r. spectroscopy. Some of the compounds contain solvent of crystallization but not compound (**2**). i, $[Ph_3C][BF_4]$, 3 mol. equiv., in wet CH_2Cl_2 for 2 days; ii, dissolution in MeCN; iii, dissolution in CH_2Cl_2; iv, bubble CO through solution for a few seconds; v, bubble CO through solution for 5 min; vi, warm in CH_2Cl_2; vii, (**6a**), treatment with NaF (2 min) or NaOH (2 min) in acetone; (**6b**), treatment with LiCl in acetone (2 min); (**6c**), treatment with MeOH (30 min).

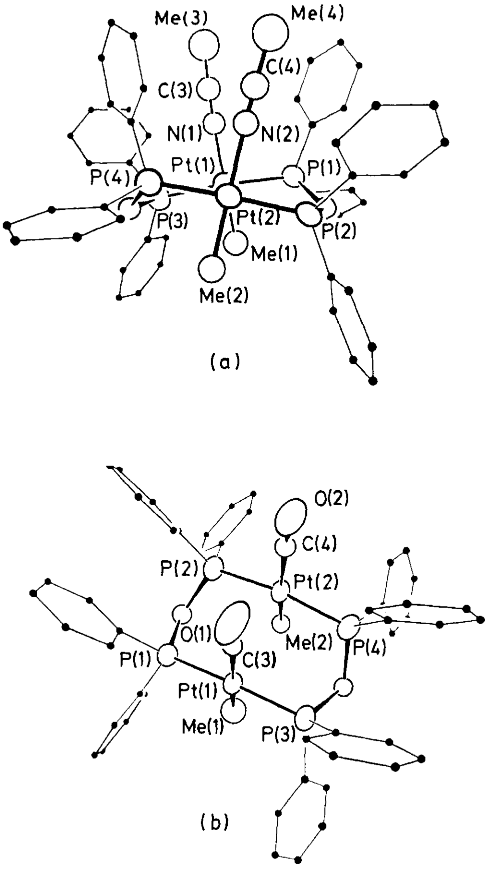


Figure 1. Molecular structures of the cation in $[Pt_2Me_2L_2(\mu\text{-}Ph_2PCH_2PPh_2)_2][BF_4]_2$ where (a) L = MeCN (**3**) or (b) L = CO (**5**). Both structures somewhat surprisingly reveal a *syn* geometry for the adducts, and while in (**5**) the CO groups eclipse each other; in (**3**) the dihedral angle between the two Pt–Pt–NCMe planes is 23°. The Pt · · · Pt distances are 3.093(1) and 3.204(1) Å in (**3**) and (**5**), respectively. There are no exceptional bond lengths in either structure.

of $^3J(Pt\text{Pt}CH_3)$ suggests a platinum – – – platinum interaction as depicted in (**2**).

We have been unable to grow crystals of (**2**) suitable for study by *X*-ray diffraction but the complex undergoes a number of reactions (summarized in Scheme 1) and two of the products have had their structures determined by crystallography.† Thus it reacts rapidly and reversibly with methyl cyanide to give an adduct $[Pt_2Me_2(NCMe)_2(\mu\text{-dppm})_2][BF_4]_2$ (**3**), the crystal structure of which is shown in Figure 1(a). It also reacts rapidly with CO to give an 'A-frame' complex, $[Pt_2Me_2(\mu\text{-CO})(\mu\text{-dppm})_2][BF_4]_2$ (**4**) (ν_{CO} 1910 cm^{-1}), further treatment giving, reversibly, the dicarbonyl complex $[Pt_2Me_2(CO)_2(\mu\text{-dppm})_2][BF_4]_2$ (**5**) (ν_{CO} 2100 cm^{-1}), the crystal structure of which is shown in Figure 1(b). Treatment of (**2**) with NaOH in acetone gives the bridging hydroxide 'A-frame' complex, $[Pt_2Me_2(\mu\text{-OH})(\mu\text{-dppm})_2][BF_4]$ (**6a**) (ν_{OH} 3550 cm^{-1}, sharp).

We found that a better method of synthesizing (**6a**) (70% isolated yield) was to treat an acetone solution of (**2**) with solid NaF and to precipitate it with ether as the fluoroborate salt. The $^1H\{^{31}P\}$ n.m.r. spectrum of (**6a**) shows a 1:8:18:8:1 quintet for O*H* [δ −0.53, ^2J(PtH) 9.5 Hz] and the resonances are sharp, *i.e.* exchange with free H_2O (present in the CD_2Cl_2 solvent) is slow on the n.m.r. time scale: the O*H* resonance disappeared on adding D_2O. Treatment of an acetone solution of (**2**) with LiCl gives the known (as Cl⁻ or PF_6^- salts)[5] chloride-bridged 'A-frame' (**6b**), and interestingly (**2**) reacts with methanol to give the hydride-bridged 'A-frame' (**6c**); the PF_6^- salt corresponding to (**6c**) has been described previously.[6]

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† *Crystal data:* (**3**)·MeCN, $C_{56}H_{56}B_2F_8N_2P_4Pt_2\cdot C_2H_3N$, monoclinic, space group $P2_1/n$, $a = 14.241(3)$, $b = 37.529(8)$, $c = 11.994(3)$ Å, $\beta = 116.42(2)°$, $Z = 4$, $\mu(\text{Mo-}K\alpha) = 50.94$ cm^{-1}. (**5**)·CH_2Cl_2, $C_{54}H_{50}B_2F_8O_2P_4Pt_2\cdot CH_2Cl_2$, orthorhombic, space group *Pbna*, $a = 23.097(5)$, $b = 37.190(11)$, $c = 13.543(3)$ Å, $Z = 8$, $\mu(\text{Mo-}K\alpha) = 51.19$ cm^{-1}. The current *R* values are respectively 0.056 and 0.069 for 4607 and 4038 independent F_o having $I > 2\sigma(I)$. Absorption corrections were applied to the data for (**5**) only. Pt, P, and O atoms were assigned anisotropic thermal parameters and hydrogen atoms were included in calculated positions. The phenyl rings were refined as rigid groups with idealized D_{6h} geometry.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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