Transformations of Methylplatinum(II) Dimers containing Bridging Cyclometallated 1,2-Bis(diphenylphosphino)ethane; *X*-Ray Crystal Structure of a Sterically Crowded Bis[methylplatinum(II)] Dimer

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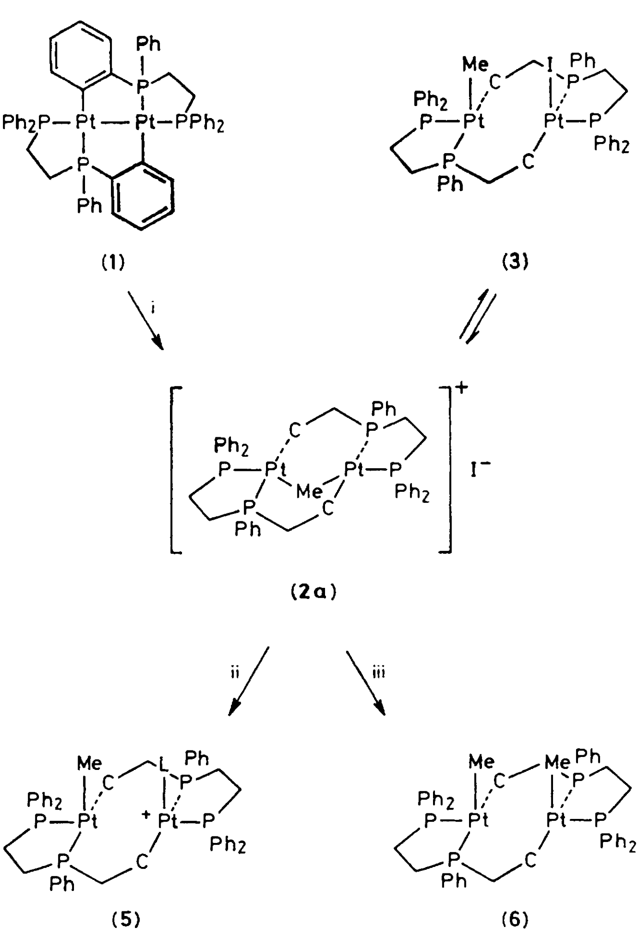
The methyl group in the 1 : 1 adduct of methyl iodide with the Pt^I–Pt^I dimer $[Pt\text{-}\mu\text{-}\{o\text{-}C_6H_4P(Ph)CH_2CH_2PPh_2\}]_2$ is either bridging or migrating rapidly on the n.m.r. time-scale between the metal atoms; the adduct reacts with methyl-lithium to give a symmetrical dimethyldiplatinum(II) complex in which the co-ordination geometry about platinum is severely distorted from planarity, as shown by single-crystal *X*-ray structural analysis.

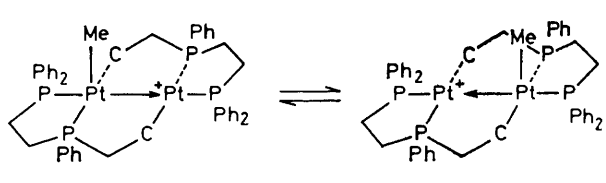
The palladium(0) complex $[Pd_2(dppm)_3]$ [dppm = 1,2-bis-(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$] was recently reported to undergo double oxidative addition of methyl halides to give A-frame bis-adducts $[Pd_2Me_2(\mu\text{-}X)(\mu\text{-}dppm)_2]^+X^-$ (X = Br, I).[1] These compounds are fluxional as a consequence of reversible co-ordination of halide ion with one of the palladium atoms, forming a non-ionic, face-to-face dimer. We now report on the oxidative addition of methyl iodide to the platinum(I)–platinum(I) dimer (**1**) containing cyclometallated 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$ (dppe)[2] which leads to a new fluxional methyldiplatinum(II) system. Subsequent reactions form other novel organoplatinum dimers whose structures are described in this and the following communication.

Methyl iodide reacts with (**1**) in toluene at room temperature to give a poorly soluble, orange, air-stable, solid 1 : 1 adduct (**2a**) in 60% yield after recrystallisation from dichloromethane–ether (Scheme 1). Two other complexes, the diiodine adduct of (**1**)[3] and the μ-methylene complex described in the following communication,[4] are formed as by-products. The



Scheme 1. *Reagents:* (i), MeI, toluene, 25 °C; (ii) Bu^tNC, $NaBF_4$, CH_2Cl_2, H_2O; (iii) MeLi, tetrahydrofuran–Et_2O, 25 °C (the bridging group from cyclometallated dppe is shown schematically for clarity).

labile iodide ion in (**2a**) is readily replaced by treatment with the appropriate sodium or silver salts to give the corresponding BF_4 (**2b**), CF_3SO_3 (**2c**), and BPh_4 (**2d**) derivatives. The conductivities of (**2a**) and (**2b**) in dichloromethane (10^{-3} M, Λ_M = 42 and 49 $ohm^{-1}\,mol^{-1}\,cm^2$ respectively) are characteristic of 1 : 1 electrolytes. The n.m.r. spectrum of (**2a**) at 20 °C† suggests that the methyl group is bound to both platinum atoms, at least on the n.m.r. time-scale. Thus, the magnitude of ^1J(Pt-CH$_3$), 193.4 Hz, is much less than the typical values found for methyl *trans* to tertiary phosphine in mononuclear platinum(II) complexes, *e.g.* 610 Hz for [$PtMe_2$(dppe)],[5] and the magnitude of ^1J(PtP) *trans* to the methyl group in (**2a**) is approximately twice that observed in [$PtMe_2$(dppe)].[5,6] The $^{31}P\{^1H\}$ n.m.r. spectrum of (**2a**) at 80.98 MHz broadens on cooling but does not reach a limit even at −112 °C, whereas the spectrum of (**2c**) is sharp and essentially independent of temperature. Addition of an excess of Bu^n_4NI to a solution of (**2c**) causes its spectrum to vary with temperature like that of (**2a**), so that the fluxional behaviour of the latter is undoubtedly due to reversible association of iodide ion; the methyl group could then exchange between bridging and terminal sites, (**2a**) ⇌ (**3**). The available data do not distinguish between the presence in (**2b**—**d**) of a static μ-methyldiplatinum cation and a pair of identical, rapidly equilibrating structures (**4a**) ⇌ (**4b**), and attempts to grow single crystals of the salts (**2b**—**d**) have been unsuccessful. Although complexes thought to contain dative M → M bonds similar to those in (**4a**) ⇌ (**4b**) have been structurally characterised,[1,7,8] intramolecular methyl group migration between platinum atoms has not been reported previously.



(**4a**) (**4b**)

Complex (**2a**) reacts with t-butyl isocyanide in the presence of $NaBF_4$ to give a pale yellow compound whose conductivity, i.r., and ^1H and $^{31}P\{^1H\}$ n.m.r. spectra‡ are consistent with the static unsymmetrical structure (**5**), in which the methyl group is attached to one platinum atom. Reaction of (**2a**) with methyl-lithium in tetrahydrofuran–ether gives a poorly soluble, pale yellow crystalline complex (**6**) in 66% yield, for which elemental analyses and spectroscopic data§ indicate a symmetrical Pt_2Me_2 structure containing a terminal methyl group on each platinum atom. Since molecular models suggested that the bridging, metallated dppe ligands must impose severe steric strain if planar co-ordination about the platinum atoms is to be maintained, an *X*-ray analysis of single crystals grown from dichloromethane–ether was undertaken.

Crystal data: $C_{54}H_{52}P_4Pt_2$, M = 1215.09, monoclinic, space group $C2/c$, a = 14.455(2), b = 19.043(2), c = 18.868(2) Å, β = 100.30(1)°, U = 5110.0 Å^3, Z = 4, D_c = 1.579 g cm^{-3}, μ(Mo-$K_{\bar{\alpha}}$) = 56.82 cm^{-1}, λ = 0.7107 Å, T = 293(1) K. The 3378 unique observed reflections [$I > 3\sigma(I)$] having $2\theta \leqslant 50°$ were measured on a Philips PW1100/20 diffractometer. The structure was solved by heavy-atom methods and refined by full-matrix least-squares (Pt and P atoms anisotropic, C isotropic, H calculated) to a current residual R of 0.050.¶

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† N.m.r. (CD_2Cl_2 or CH_2Cl_2): ^1H δ_{Me} 1.0 br ($^1H\{^{31}P\}$, t, separation of outer lines 3.5 Hz); $^{31}P\{^1H\}$ (80.98 MHz) δ_A 34.3, δ_B 29.0 (p.p.m. to high frequency of external 85% H_3PO_4), J(AA′) 51, J(AB) 0, J(AB′) 0, J(BB′) 0, J(AX) −8, J(A′X) 1609, J(BX) 367, J(B′X) 3505 Hz, J(XX′) not determined [$P_{A,A'}$ are the phosphorus atoms *trans* to the *ortho*-phenylene carbon, and the arrangement of $Pt_{X,X'}$ is B(A)X′ . . . X(A′)B′]; $^{13}C\{^1H\}$ (90% labelled) δ_{Me} −8.6 p.p.m. (9 lines observed, collapsing to 1 : 8 : 18 : 8 : 1 quintet on ^{31}P decoupling), ^1J(PtC) 193.4 Hz, ^2J(PC) (*trans*) 48.8 Hz; ^{13}C {gated-^1H} {^{31}P} all lines q, ^1J(CH) 131 Hz.

‡ Λ_M(10^{-3} M, CH_2Cl_2) 55 $ohm^{-1}\,mol^{-1}\,cm^2$; n.m.r. (CD_2Cl_2) ^1H δ 1.0 (s, 9H, Bu^t), 0.71 (tt, 3H, Pt*Me*), ^2J(PtH) 73.6 Hz, ^3J(PH), 7.4, 7.4 Hz; $^{31}P\{^1H\}$ δ_A (*trans* to Bu^t–NC) 22.7 (br), δ_B (*cis* to Bu^t–NC) 29.8, δ_C (*cis* to Me) 36.6, δ_D (*trans* to Me) 30.5 p.p.m., J(AB) 11, J(AC) 0, J(AD) 8, J(AX) 46, J(AY) 3640, J(BC) 40, J(BD) 4, J(BX) 121, J(BY) 1662, J(CD) 0, J(CX) 1696, J(CY) 52, J(DX) 1917, J(DY) *ca.* 5, J(XY) 735 Hz. [The arrangement of $Pt_{X,Y}$ is B(A)Y . . . X(C)D].

§ N.m.r. (CD_2Cl_2 or CH_2Cl_2): ^1H δ_{Me} 0.47 (complex t with 1 : 4 : 1 ^{195}Pt satellites) 'J(PH)' 7.3 Hz, ^2J(PtH) 77.3 Hz; $^{31}P\{^1H\}$ δ_A 37.6, δ_B 27.0 p.p.m., J(AA′) 37.2, J(AB) 3.7, J(AB′) 0, J(BB′) 20.4, J(AX) 144.9, J(AX′) 1873.0, J(BX) 5.9, J(BX′) 1994.4, J(XX′) 400 Hz (P_B *trans* to Me, $Pt_{X,X'}$ as above); $^{13}C\{^1H\}$ (45% labelled) δ_{Me} 8.8 p.p.m. (d with 1 : 4 : 1 ^{195}Pt satellites), ^1J(PtC) 656 Hz, ^2J(PC) (*trans*) 94 Hz, ^2J(PC)(*cis*) $\leqslant$ 5 Hz; ^{13}C {gated-^1H} all lines q, ^1J(CH) 129 Hz.

¶ Atomic co-ordinates 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.

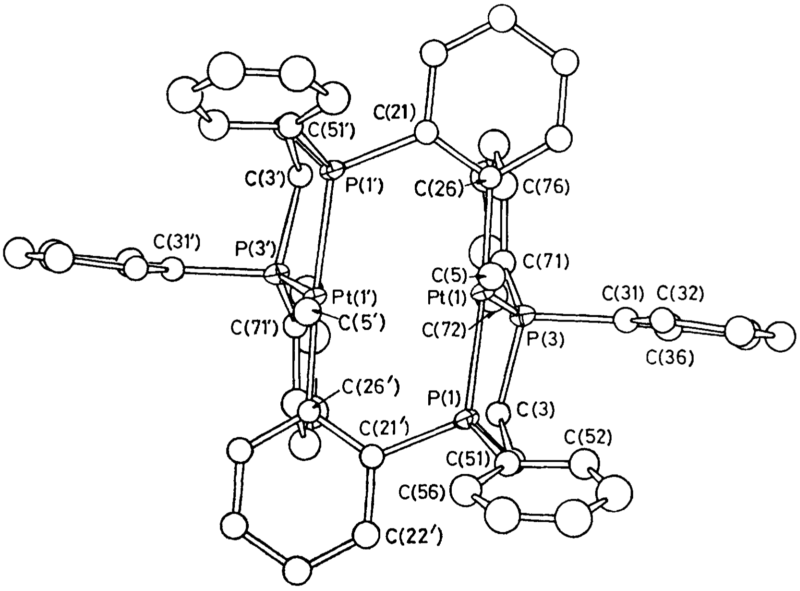

Figure 1. View of the molecule [Pt_2Me_2-μ-{*o*-$C_6H_4P(Ph)CH_2CH_2PPh_2$}$_2$] (**6**) down the 2-fold axis. Selected distances are: Pt(1)–Pt(1′) 3.010(1), Pt(1)–C(5) 2.11(1), Pt(1)–P(1) 2.286(3), Pt(1)–P(3) 2.277(3), Pt(1)–C(26) 2.05(1) Å.

The structure of the complex (Figure 1) shows two methylplatinum(II) centres related by a crystallographic two-fold axis. The Pt–Pt separation [3.010(1) Å] is significantly greater than that in (**1**) [2.628(1) Å]^2 and shows the absence of appreciable Pt–Pt interaction. The methyl carbon atoms are 3.34(3) Å apart and are almost eclipsed (dihedral angle 12°); the Pt–Me bonds are essentially normal to the Pt–Pt vector, showing that this face of the molecule is not severely strained. However, there is considerable distortion on the opposite face of the molecule owing to steric crowding involving the phenyl groups attached to P(3). The co-ordination geometry at the platinum atoms is markedly distorted from square planar to trigonal bipyramidal with a vacant site formally occupied by the other non-bonded platinum atom [angle C(5)PtP(3) = 158.4(4)°, angle C(5)PtC(26) = 84.5(5)°].

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