Formation and *X*-Ray Crystal Structure of an A-Frame μ-Methylene Diplatinum Complex containing Bridging Cyclometallated 1,2-Bis(diphenylphosphino)ethane

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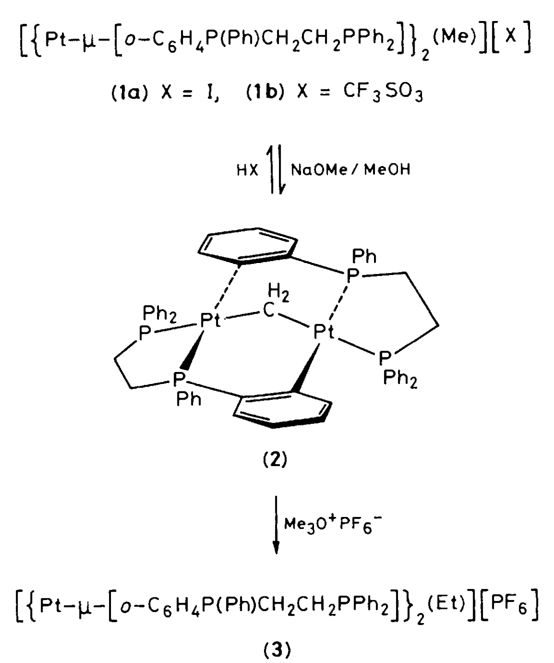
The 1 : 1 adduct of the Pt^I–Pt^I dimer $[Pt\text{-}\mu\text{-}\{o\text{-}C_6H_4P(Ph)CH_2CH_2PPh_2\}]_2$ with methyl iodide is deprotonated by sodium methoxide to give a μ-methylenediplatinum(II) complex $[Pt_2\text{-}\mu\text{-}\{o\text{-}C_6H_4P(Ph)CH_2CH_2PPh_2\}_2(\mu\text{-}CH_2)]$, characterised by single-crystal *X*-ray structural analysis; the latter complex reacts with $[Me_3O]PF_6$ to give an ethyldiplatinum(II) cation which retains the bridging cyclometallated dppe ligands.

Dinuclear μ-methylene complexes of the transition elements are attracting considerable interest,[1,2] particularly in connection with the mechanism of CO reduction on metal surfaces.[3] Most stable complexes of this type can be described as



dimetallacyclopropanes in which the methylene bridge is supported by a metal–metal bond,[2] although there are several examples in which this feature is absent. They include the dipalladium A-frame complexes $[Pd_2X_2(\mu\text{-dppm})_2(\mu\text{-}CH_2)]$ (X = Br, I; dppm = $Ph_2PCH_2PPh_2$)[4] and the digold cyclic ylide complexes $[Au_2X_2(\mu\text{-}CH_2PMe_2CH_2)_2(\mu\text{-}CH_2)]$ (X = Cl, Br, I)[5] which are formed by two-centre double oxidative addition of dihalogenomethanes to the appropriate Pd^0 and Au^I precursors. The diplatinum complex $[Pt_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}CH_2)]$ has been obtained by reaction of diazomethane with the Pt^I–Pt^I dimer $[Pt_2Cl_2(\mu\text{-dppm})_2]$.[6] The only *X*-ray structure determination of a complex of this type is that recently reported for the unsymmetrical ylide–(μ-methylene) diplatinum cation $[Pt_2Cl(\mu\text{-dppm})_2(CH_2PPh_3)(\mu\text{-}CH_2)]^+$.[7] We now report a new μ-methylenediplatinum(II) complex (**2**) obtained by deprotonation of the methyl iodide adduct (**1a**)[8] of the Pt^I–Pt^I dimer $[Pt\text{-}\mu\text{-}\{o\text{-}C_6H_4P(Ph)CH_2CH_2PPh_2\}]_2$ containing *ortho*-metallated 1,2-bis(diphenylphosphino)ethane.[9]

Treatment of a suspension of (**1a**) in dry methanol with an excess of sodium methoxide at 50 °C for 3 h gives a bright yellow, air-stable solid, which affords analytically pure (**2**) in 82% yield after recrystallisation from dichloromethane–n-hexane or dichloromethane–methanol. Complex (**2**) is also formed in low yield (*ca.* 5%) as a by-product in the preparation of (**1a**).[8] Its structure has been assigned on the basis of its ^1H, $^{31}P\{^1H\}$, and ^{13}C n.m.r. spectra† and confirmed by an *X*-ray analysis of single crystals grown from dichloromethane–methanol.

Crystal data: $C_{53}H_{48}P_4Pt_2$, M = 1199.05, monoclinic, space group $P2_1/c$, a = 13.554(1), b = 17.796(2), c = 20.668(2) Å, β = 111.83(1)°, U = 4627.8 Å^3, Z = 4, D_c = 1.721, D_m = 1.71 g cm^{-3}, $\mu(\text{Cu-}K_\alpha)$ = 128.63 cm^{-1}, λ = 1.5418 Å, T = 293(1) K. The 5441 unique observed reflections $[I > 3\sigma(I)]$ having $2\theta \leqslant 127°$ were measured on a Picker FACS1 diffractometer and corrected for absorption and crystal degradation. 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 final residual R of 0.042.‡

The molecule (Figure 1), which has almost exact two-fold symmetry, consists of two approximately planar-co-ordinated platinum(II) atoms symmetrically bridged by a methylene carbon atom and by two *ortho*-metallated dppe ligands. The overall shape corresponds to that of a typical molecular A-frame, the apical angle at the μ-methylene carbon atom being 88.9(4)°. The diminution of this angle at the formally sp^3-hybridised carbon atom from the normal tetrahedral value is probably due to the rigidity imposed by the bridging cyclometallated dppe ligands, since in the cation $[Pt_2Cl(\mu\text{-dppm})_2(CH_2PPh_3)(\mu\text{-}CH_2)]^+$ containing the more accommodating bridging dppm ligands the apical Pt–CH_2–Pt angle is 95.1(9)°.[7] In the dimethyldiplatinum complex $[Pt_2Me_2\text{-}\mu\text{-}\{o\text{-}C_6H_4P(Ph)CH_2CH_2PPh_2\}_2]$, which contains no Pt–Pt bond, the Pt–Pt separation is 3.010(2) Å and the bridging cyclometallated dppe ligands are approximately coplanar with the Pt–Pt vector.[8] The bridging methylene group in (**2**) imposes a distortion from coplanarity, the torsion angles of P(1),C(16) and of P(2),C(26) about the Pt–Pt vector being 13.3(3) and 14.8(3)°, respectively; the Pt–Pt distance is consequently reduced to 2.915(1) Å {*cf.* 3.115(1) Å in $[Pt_2Cl(\mu\text{-dppm})_2(CH_2PPh_3)(\mu\text{-}CH_2)]^+$}.[7] In $[Pt\text{-}\mu\text{-}\{o\text{-}C_6H_4P(Ph)CH_2CH_2PPh_2\}]_2$, which has an even shorter Pt–Pt distance of 2.628(1) Å, the corresponding torsion angle is 40°.[9] The Pt–C(methylene) bond length in (**2**) [2.08(1) Å] is normal and the metal–ligand distances in the *ortho*-metallated dppe moieties do not differ significantly from those in $[Pt\text{-}\mu\text{-}\{o\text{-}C_6H_4P(Ph)CH_2CH_2PPh_2\}]_2$.

In common with most μ-methylene complexes,[1,2,4] (**2**) is readily protonated at the methylene bridge, *e.g.* reaction with one equivalent of HI regenerates (**1a**) and CF_3SO_3H gives the corresponding trifluoromethanesulphonate (**1b**).[8] The nucleophilicity of the methylene carbon atom is further demonstrated by the rapid reaction of (**2**) with trimethyloxonium hexafluorophosphate in dichloromethane, which generates the fluxional ethyldiplatinum cation (**3**) in the form of its PF_6 salt. This appears to be structurally similar to the methyldiplatinum cation present in (**1a**) and (**1b**) and, as in those cases, the $^{31}P\{^1H\}$ and ^{13}C n.m.r. data§ are consistent

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† N.m.r. (CD_2Cl_2 or CH_2Cl_2): ^1H $\delta(CH)$ 3.46, complex m; $^1H\{^{31}P\}$ s with 3 sets of ^{195}Pt satellites, intensity ratio *ca.* 1:4:4:18:4:4:1, due to coincident AA′X and AA′XX′ systems, $^2J(PtH)$ 34.4 and 63.7 Hz; $^{31}P\{^1H\}$ δ_A 42.4, δ_B 41.9 (p.p.m. to high frequency of external 85% H_3PO_4), $J(AA')$ 29.4, $J(AB)$ 3.7, $J(AB')$ 0, $J(BB')$ 10.8, $J(AX)$ 182.6, $J(AX')$ 1934.2, $J(BX)$ −84.4, $J(BX')$ 2012.9, $J(XX')$ 370 Hz [P(B,B′) *trans* to CH_2, Pt(X) bonded to P(A′, B′)]; $^{13}C\{^1H\}$ (90% labelled) $\delta(CH_2)$ 46.0 p.p.m. (tt with ^{195}Pt satellites), $^1J(PtC)$ 467 Hz, $^2J(PC)$ (*trans*) 77.2 Hz, $^2J(PC)$ (*cis*) 4.9 Hz, $^1J(CH)$ 140 Hz (from ^1H spectrum).

‡ 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.

§ N.m.r. (CD_2Cl_2 or CH_2Cl_2): $^{31}P\{^1H\}$ 80.98 MHz, 20 °C, δ_A 40.7, δ_B 34.5 p.p.m., $J(AA')$ 61.2, $J(AB)$ 3.7, $J(AB')$ 0, $J(BB')$ 7.2, $J(AX)$ −63.6, $J(AX')$ 1551.4, $J(BX)$ 541.7, $J(B'X)$ 2905.2 Hz, $J(XX')$ not determined [P(A,A′) *trans* to *ortho*-metallated C atoms, Pt(X,X′) as above]; $^{13}C\{^1H\}$ (90% labelled) 50.38 MHz, 20 °C, $\delta(CH_2)$ 12.9 p.p.m. (t with ^{195}Pt satellites), $^1J(PtC)$ 220 Hz, $^2J(PC)$ (*trans*) 41.8 Hz (on ^{31}P decoupling, a triplet is observed, intensities 4:9:4, indicating equal coupling to two ^{195}Pt nuclei); ^{13}C-{gated-^1H} all lines t, $^1J(CH)$ 134 Hz.

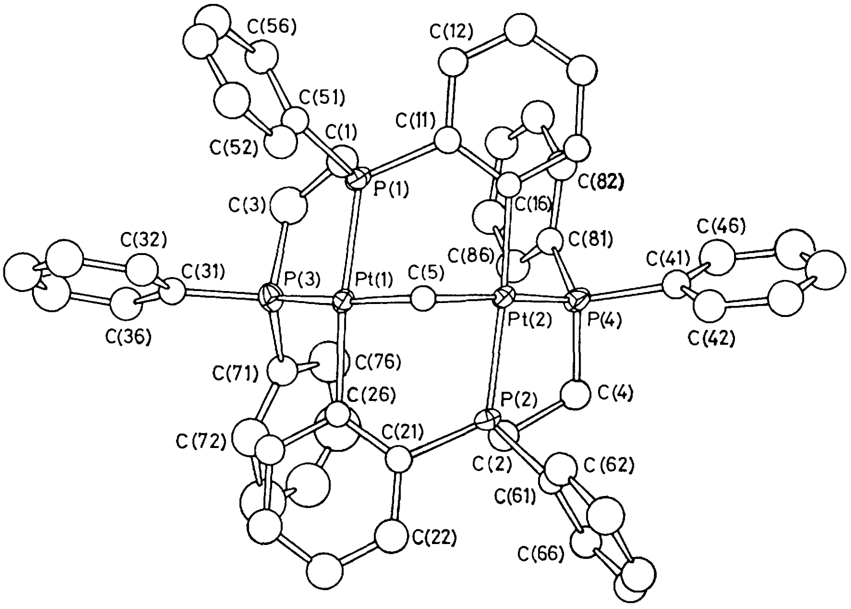

Figure 1. View of the molecule [Pt_2-μ-{*o*-$C_6H_4P(Ph)CH_2CH_2PPh_2$}$_2$(μ-CH_2)] (**2**) down the approximate 2-fold axis. Selected distances are: Pt(1)–Pt(2) 2.915(1), Pt(1)–C(5) 2.08(1), Pt(2)–C(5) 2.08(1), Pt(1)–P(1) 2.265(3), Pt(1)–P(3) 2.274(3), Pt(1)–C(26) 2.06(1), Pt(2)–P(2) 2.268(3), Pt(2)–P(4) 2.268(3), Pt(2)–C(16) 2.06(1) Å.

with the presence either of a static bridging alkyl group or of a terminal alkyl group which migrates rapidly on the n.m.r. time-scale between the platinum atoms.

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