Symmetrical η^1-, or σ–π-Acetylide Bridges in Bimetallic μ-$Ph_2PCH_2PPh_2$ (dppm) Complexes: Crystal Structures of $[MePt(\mu\text{-}\eta^1\text{-}C{\equiv}CMe)(\mu\text{-dppm})_2PtMe][BF_4]$ and $[ClPt(\mu\text{-}\sigma\text{–}\pi\text{-}C{\equiv}CMe)(\mu\text{-dppm})_2Rh(CO)][PF_6]$

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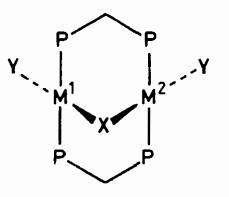
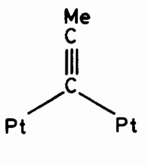
$[MePt(\mu\text{-dppm})_2PtMe]^{2+}$ [dppm = bis(diphenylphosphino)methane; $Ph_2PCH_2PPh_2$] reacts with terminal acetylenes to give a μ-η^2-HC≡CR complex, which readily deprotonates to give the symmetrically bonded μ-η^1-C≡CR complex: in contrast, in the platinum–rhodium complex, the acetylide is σ-bonded to the platinum and sideways (π) bonded to the rhodium.

There is much interest in bimetallic systems bridged by bis(diphenylphosphino)methane (dppm, $Ph_2PCH_2PPh_2$), including the so-called 'A-frames', *e.g.*, complexes of type (**1**) where M^1 and M^2 = metals, Y = various ligands, and X = H, CO, CNR, SO_2, RC≡CR *etc.*[1,2] We report here crystal structures of complexes of type (**1**) in which the bridging ligand is acetylide. In the first complex the mode of bridging is as depicted in (**2**), *i.e.*, completely symmetrical η^1, whilst in the second it is σ–π, as depicted in (**3**).

Treatment of an acetone solution of $[Pt_2Me_2(\mu\text{-dppm})_2][BF_4]_2$ (**4**)[3] with propyne gave a yellow crystalline product which, on the basis of elemental analysis (C, H, F)



(1)



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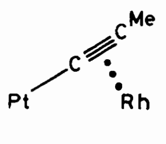

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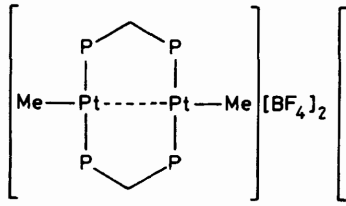

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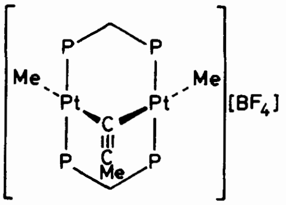

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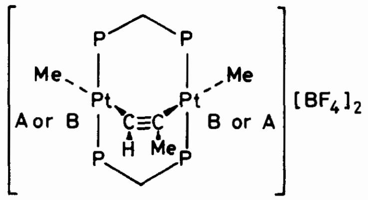

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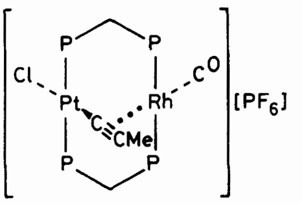

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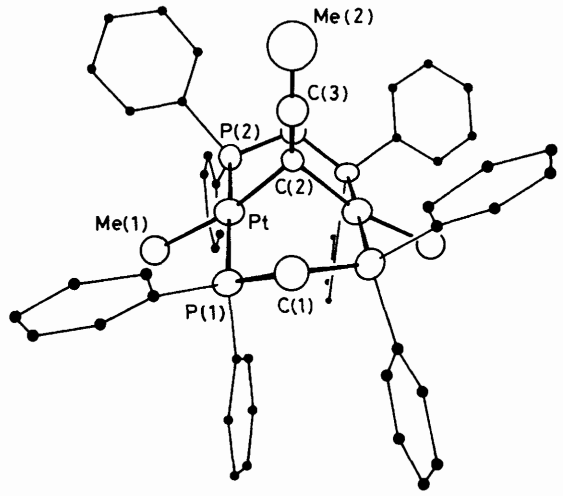

Figure 1. Molecular structure of the $[Pt_2Me_2(\mu\text{-}\eta^1\text{-}C{\equiv}CMe)(\mu\text{-}dppm)_2]^+$ cation in (**5**). Selected bond lengths: Pt–Me(1) 2.10(2); Pt–C(2) 2.11(1); C(2)–C(3) 1.20(3); and C(3)–Me(2) 1.54(4) Å. The Pt· · ·Pt′ distance is 3.025(2) Å. Selected bond angles: Pt–C(2)–C(3) 134.3(3), Pt–C(2)–Pt′ 91.4(7), and Me(1)–Pt–C(2) 165.6(5)°.

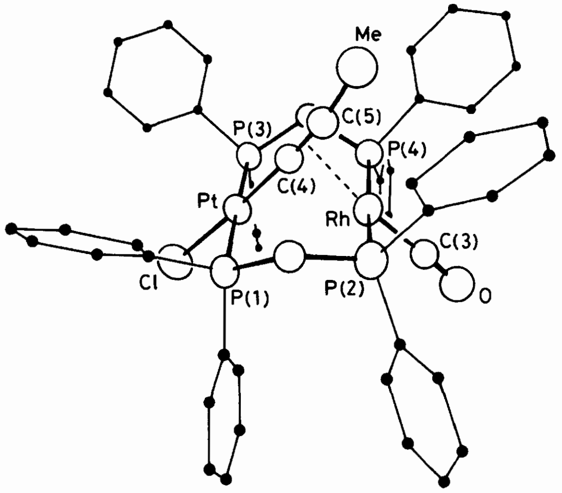

Figure 2. Molecular structure of a $[ClPt(\mu\text{-}\sigma\text{-}\pi\text{-}C{\equiv}CMe)(\mu\text{-}dppm)_2Rh(CO)]^+$ cation in (**7**). The asymmetric unit in the crystal structure comprises two virtually identical cations and two PF_6^- anions: geometric parameters are therefore given in duplicate. Selected bond lengths: Pt–C(4) 1.95(2), 1.94(2); Rh–C(4) 2.22(2), 2.29(2); Rh–C(5) 2.46(3), 2.46(2); C(4)–C(5) 1.21(3), 1.23(3); and C(5)–Me 1.48(4), 1.51(4) Å. The Pt· · ·Rh distances are 3.066(2) and 3.086(2) Å. Selected bond angles: Pt–C(4)–C(5) 176(2), 177(2); and C(4)–C(5)–Me 169(3), 169(3)°.

and ^{31}P-{^{1}H} and ^{1}H-{^{31}P} n.m.r. data,† appeared to be a symmetrical μ-η^1-bonded methylacetylide complex $[MePt(\mu\text{-}\eta^1\text{-}C{\equiv}CMe)(\mu\text{-}dppm)_2PtMe][BF_4]$ (**5**), and this was confirmed by *X*-ray crystallography.‡ The cation (Figure 1) displays crystallographically imposed C_2 symmetry, the diad axis coinciding with the MeC≡C vector, which is itself perpendicular to the Pt–Pt vector. Symmetrical μ-η^1-bonding of alkynyl groups is rare[4] although we have recently reported a related η^1 (unsymmetrical) bridge in $[(4\text{-}MeC_6H_4C{\equiv}C)\text{-}Pt(\mu\text{-}C{\equiv}CC_6H_4Me\text{-}4)(\mu\text{-}dppm)_2W(CO)_3]$.[5] In the structure of (**5**) the Pt–C–Pt′ angle of 91.4(7)° is markedly smaller than that (> 106°) found in analogous complexes with CO or CNR bridges.[6]

Treatment of acetone solutions of (**4**) with other acetylenes $[HC{\equiv}CH, HC{\equiv}CPh, HC{\equiv}CC(OH)MeEt, HC{\equiv}CC(OH)(CH_2)_5]$ gave analogues of (**5**) in isolated yields of 65—80%. We also found good evidence for the intermediacy of μ-η^2(sideways)-bonded acetylenes. Thus treatment of a dry

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† N.m.r. data for (**5**): ^{31}P-{^{1}H}, $(CD_3)_2CO$, δP 12.7 p.p.m., $^1J(PtP)$ 2859, $^3J(PtP)$ 29, $^2J(P_AP_B)$ 41, $^4J(P_AP_{B'})$ 11 Hz; ^{1}H-{^{31}P}, CD_2Cl_2, $\delta(PtCH_3)$ 0.36, $^2J(PtCH_3)$ 75 Hz, $\delta(\mu\text{-}C_2CH_3)$ 1.22, $^4J(PtCCCH_3)$ 3.4 Hz. N.m.r. data for (**6**): ^{31}P-{^{1}H}, CD_2Cl_2, δP_A 19.8 p.p.m., $^1J(PtP_A)$ *ca.* 2507 Hz, δP_B 19.4 p.p.m., $^1J(PtP_B)$ *ca.* 2424 Hz; ^{1}H-{^{31}P}, CD_2Cl_2, $\delta(Pt_ACH_3)$ 1.46, $^2J(Pt_ACH_3)$ 64 Hz, $\delta(Pt_BCH_3)$ 1.56, $^2J(Pt_BCH_3)$ 64 Hz, $\delta(C{\equiv}CCH_3)$ 2.03, $^4J(HC{\equiv}CCH_3)$ 7.4, $J(Pt\{HC{\equiv}CCH_3\})$ 7.6 Hz. We were unable to observe the HC≡C resonance owing to the complexity and lack of intensity, but its coupling to $C{\equiv}CCH_3$ was observed (7.4 Hz).

The ν(C≡C) bands in the i.r. spectra of these complexes are extremely weak (assignment uncertain) or absent altogether.

‡ *Crystal data*: (**5**), $C_{55}H_{53}BF_4P_4Pt_2$, monoclinic, space group *C*2/*c*, $a = 12.282(3)$, $b = 22.955(7)$, $c = 18.438(3)$ Å, $\beta = 101.96(2)°$, $Z = 4$. (**7**), $C_{54}H_{47}ClF_6OP_5PtRh$, orthorhombic, space group $Pn2_1a$, $a = 43.93(1)$, $b = 25.178(9)$, $c = 10.164(6)$ Å, $Z = 8$. Diffractometer data, Mo-K_α radiation ($\lambda = 0.71069$ Å). Current *R* values are respectively 0.064 and 0.058 for 2383 and 6320 independent F_o having $I > 2\sigma(I)$. Pt, Rh, Cl, and P atoms were assigned anisotropic thermal parameters. The phenyl rings were refined as rigid groups with idealised D_{6h} geometry and no hydrogen atoms were included in the calculations.

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.

dichloromethane solution of (**4**) with HC≡CMe gave an orange-red crystalline compound which we formulate as (**6**) on the basis of elemental analysis (C, H, F) and n.m.r. data.† On treating a dichloromethane solution of (**6**) with water it was immediately and completely converted into the μ-η^1-acetylide complex (**5**) on the basis of $^{31}P-\{^1H\}$ n.m.r. evidence. Complexes of the other acetylenes behaved analogously.

We have previously shown that $[Pt(dppm\text{-}PP')_2]Cl_2$ reacts with AgOAc–MeC≡CH to give [ClPt(C≡CMe)-(μ-dppm)$_2$-AgCl] which on transmetallation with $[Rh_2Cl_2(CO)_4]$ gave [ClPt(C≡CMe)(μ-dppm)$_2$Rh(CO)]$^+$ isolated as the PF_6^- salt (**7**).[7] The n.m.r. data showed that the acetylide groups bridged both metals and we tentatively formulated the bridging as η^1, *i.e.*, as in (**2**). We have now determined the structure by *X*-ray crystallography‡ and find it to be of type (**3**), with the acetylide σ-bonded to Pt and bridging the metals to form an unsymmetrical side-on π-bond to Rh (Figure 2). Since the steric requirements around the metals in (**5**) and (**7**) are similar, electronic factors presumably control the mode of bonding, *viz.* (**2**) or (**3**). We tentatively suggest that the methyl groups on Pt (high *trans*-influence) greatly weaken the σ–π bonding mode of C≡C and the η^1 (symmetrically bridging) mode is preferred. Interestingly, the metal–metal distance in both complexes are very similar, as are the C≡C distances (see captions to Figures for selected parameters).

We thank Johnson Matthey PLC for the generous loan of platinum metal salts, and the S.E.R.C. and the University of Leeds for financial assistance.

Received, 5th January 1984; Com. 017

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