Co-ordination Chemistry at a Triply Bridging Site of $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)_3]^{2+}$: the Structure of the Chloride Adduct

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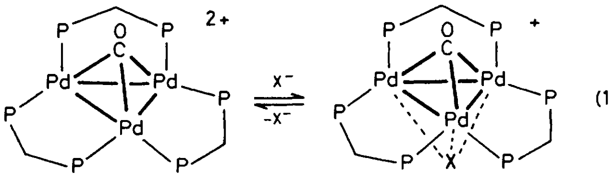
The selective attachment of halide ions to a triply bridging site in the complex cation $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ (dppm = $Ph_2PCH_2PPh_2$) has been established and the structure of the chloride adduct determined; the chloride ligand is very weakly bound to the Pd_3 unit and is shielded by a ring of phenyl groups from the dppm ligands.

In complexes containing the planar $M_3(\mu\text{-}dppm)_3$ triangular framework (dppm = $Ph_2PCH_2PPh_2$), a circle of phenyl substituents surrounds the co-ordination sites above and below the M_3 triangle, and can be expected to influence profoundly the co-ordination chemistry at the triply bridging site.[1,2] We report the first studies of such chemistry, involving the selective co-ordination of halides, X^-, to the dication (**1**),[3] even though in the $Pd_3(\mu_3\text{-}X)$ framework so formed the Pd–X distances are very long and presumably weak [equation (1)].

The complex $[(\mathbf{2b})][CF_3CO_2]\cdot H_2O$ was structurally characterized by an *X*-ray diffraction study.† The structure of the cationic cluster (**2b**) is closely similar to that previously found in the cationic part of $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3][CF_3CO_2]_2\cdot 3Me_2CO$ [(**1**) or (**2a**); see below].[3] It comprises a triangular metal core (Figure 1) in which the palladium atoms are directly bonded to each other at Pd–Pd distances of 2.584(1)—2.603(1) Å. The Pd_3 triangle is spanned by three edge-bridging dppm ligands and capped by a triply bridging carbonyl [Pd–C 2.10(2)—2.23(1) Å]. A distorted trigonal bipyramidal $Pd_3(\mu_3\text{-}C)Cl$ arrangement is completed by a chloride ion lying close to the capping site on the other side of the Pd_3 triangle, but at Pd–Cl distances of 2.741(4)—3.161(4) Å. Although these distances may be affected to some extent by the observed partial disorder of the $Pd_3(\mu_3\text{-}CO)(\mu_3\text{-}Cl)$ unit,‡ they are too long to be considered indicative of normal covalent bonding. They may be compared with the abnormally long terminal Pd–Cl bond of 2.509(4) Å in $[PdCl\{HC_8(CO_2Me)_8\}(pyridine)_2]$.[4] The complex formulated as $[(\mathbf{1})][CF_3CO_2]_2\cdot 3Me_2CO$[3] also contains one $CF_3CO_2^-$ ion lying close to the capping site of the Pd_3 unit, on the side opposite to the μ_3-CO ligand; although the Pd–O distances are very long (2.8—3.1 Å), on the basis of additional evidence given below, this compound is better formulated as $[(\mathbf{2a})][CF_3CO_2]\cdot 3Me_2CO$.

The $Pd_3(\mu_3\text{-}X)$ units in (**2**) remain intact in acetone or methanol solutions as shown by the following experiments. (i) Complexes (**2**) behaved as 1:1 electrolytes in methanol solution.§ The conductivities were much lower than for $[(\mathbf{1})][PF_6]_2$, which was prepared by anion exchange from (**2a**) in methanol. In benzene–acetone, it was not possible to displace all the $CF_3CO_2^-$ groups from (**2a**) even when using a large excess of $[PF_6]^-$. (ii) ^1H N.m.r. spectral parameters of



(1)

(1) (2)

a; X = CF_3CO_2
b; X = Cl
c; X = Br
d; X = I

PP = dppm = $Ph_2PCH_2PPh_2$

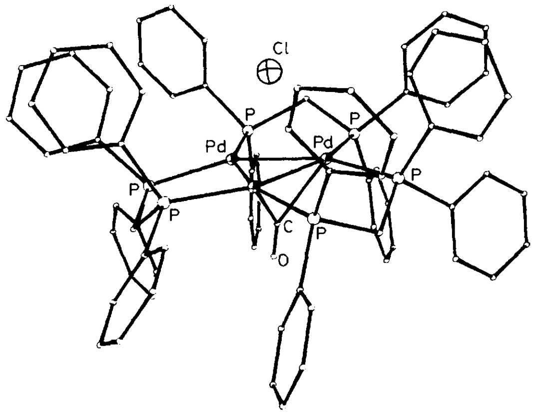


Figure 1. Geometry of the $Pd_3(PCP)_3(\mu_3\text{-}CO)(\mu_3\text{-}Cl)$ moiety in the crystal structure of $[(\mathbf{2b})][CF_3CO_2]\cdot H_2O$. Selected interatomic distances and angles are: Pd–Pd 2.584(1), 2.585(1), and 2.603(1), Pd–P 2.298(2)—2.321(2) Å, Pd–C–Pd 72.0(4)—75.6(5)°. Only one arrangement of the disordered μ_3-Cl and μ_3-CO ligands is shown for clarity.

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† *Crystal data:* $C_{78}H_{68}ClF_3O_4P_6Pd_3$, $M = 1666.9$. Triclinic, space group $P\bar{1}$, $a = 14.715(5)$, $b = 14.860(4)$, $c = 18.487(4)$ Å, $\alpha = 109.14(2)$, $\beta = 104.23(2)$, $\gamma = 96.63(3)°$, $U = 3616$ Å^3, $D_c = 1.53$ g cm^{-3}, $Z = 2$. Mo-K_α radiation, $\lambda = 0.71069$ Å, μ(Mo-K_α) = 9.52 cm^{-1}. The structure was solved by the heavy atom method and refined by a least-squares procedure to the current *R* value of 0.060, using 10 183 unique reflections with $I > 3\sigma(I)$. Intensities of these reflections were measured on a CAD 4F diffractometer and corrected for absorption effects. The atomic co-cordinates for this structure 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.

‡ The CO and Cl ligands lying on the opposite sides of the Pd_3 cluster are disordered. Their presence in $[(\mathbf{2b})][CF_3CO_2]\cdot H_2O$ has been established chemically and spectroscopically and confirmed by a successful crystallographic refinement of a structural model with 0.5C and 0.5(O + Cl) occupancy on either side of the Pd_3 triangle.

§ Molar conductivities (Λ_M, ohm^{-1} cm^2 mol^{-1} at 2×10^{-4} M) in methanol: $[(\mathbf{1})][PF_6]_2$, 328; $[(\mathbf{2a})][CF_3CO_2]$, 127; $[(\mathbf{2b})][CF_3CO_2]$, 83; $[(\mathbf{2c})][CF_3CO_2]$, 81; $[(\mathbf{2d})][CF_3CO_2]$, 81.

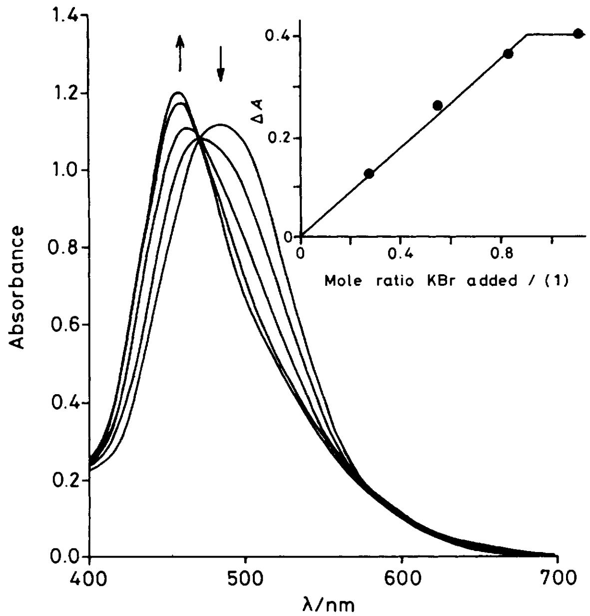

Figure 2. Spectral titration of (**2a**) with Br^- to give (**2c**). Initial concentration of (**2a**) was 4.87×10^{-5} M. Inset shows the ΔA values (λ 458 nm) as a function of added bromide. No further spectral change occurred with excess of bromide.

the complexes (**2a**—**d**) were different.¶ Exchange between (**2a**) and (**2b**) was slow on the n.m.r. time scale, since separate resonances were seen in a solution containing both. (iii) Spectral titration of (**2a**) with halide solutions showed a sharp endpoint at a 1 : 1 mole ratio (Figure 2), showing quantitative formation of (**2b**—**d**) in methanol.

There is still a question of whether the $Pd_3(\mu_3\text{-}X)$ linkage is entirely an ionic interaction or whether covalency is involved. The evidence for weak covalency in (**2b**—**d**) is as follows. (i) The equilibrium constants for formation of (**2**) follow the sequence $I^- >> Br^- >> Cl^- >> CF_3CO_2^-$, which is that expected for a covalent interaction with the soft palladium acceptor. The sequence was determined by spectral titrations similar to that of Figure 2. Thus (**2b**) reacted quantitatively with iodide to give (**2d**), but the absorption spectrum of (**2d**) was unaffected by addition of a large excess of chloride. (ii) The absorption spectra of (**2a**—**d**) are significantly different (Figure 2). The anions binding most strongly give the highest energy absorption band. ‖

The substitution reactions of equation (1) must occur by a dissociative mechanism, since the cavity defined by the phenyl groups could not accommodate two halide ions, and the ease of these reactions is clearly due to the very weak nature of the $Pd_3(\mu_3\text{-}X)$ bonds. We know of no precedents for this novel co-ordination chemistry.

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¶ N.m.r. in $[^2H_6]$acetone: $[(\mathbf{1})][PF_6]_2$ $\delta(^1H)$ 5.22 (s, CH_2P_2); $\delta(^{31}P)$ −6.9 (s) p.p.m. $[(\mathbf{2a})][CF_3CO_2]$ $\delta(^1H)$ 4.75 and 5.00 ($^2J_{HH}$ 14 Hz, $CH^aH^bP_2$); $\delta(^{31}P)$ −12.7 (s) p.p.m. $[(\mathbf{2b})][CF_3CO_2]$ $\delta(^1H)$ 4.72 and 4.89 ($^2J_{HH}$ 14 Hz, $CH^aH^bP_2$); $\delta(^{31}P)$ −12.1 (s) p.p.m. $[(\mathbf{2c})][CF_3CO_2]$ $\delta(^1H)$ 4.77 and 4.88 ($^2J_{HH}$ 14 Hz, $CH^aH^bP_2$); $\delta(^{31}P)$ −11.8 (s) p.p.m. $[(\mathbf{2d})][CF_3CO_2]$ $\delta(^1H)$ 4.84 and 4.93; $\delta(^{31}P)$ −12.0 (s) p.p.m.

‖ $\lambda_{max.}$/nm (MeOH) (**1**), 487; (**2a**), 490; (**2b**), 463; (**2c**), 459; (**2d**), 456; ε 2.3—2.9 × 10^4 l mol^{-1} cm^{-1}.