Synthesis and Structure of a Cluster Complex Containing the Dication $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)_3]^{2+}$

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Reaction of $Pd(OAc)_2$ with $Ph_2PCH_2PPh_2$ under CO in a solvent containing excess of CF_3CO_2H yields the first example of a dicationic cluster of palladium, $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)_3]^{2+}$, the structure of which has been established by *X*-ray crystallography.

There has been considerable interest in cluster complexes of palladium and platinum,[1] especially in synthesis and structure determination of high nuclearity clusters[2] and structure and bonding in low nuclearity clusters.[3] Cationic clusters are rare and no dicationic clusters appear to be known.[1,2,4] We are therefore prompted to report a simple, high yield synthesis and the molecular structure determination of a new trinuclear dicationic cluster $[Pd_3(\mu\text{-dppm})_3(\mu_3\text{-}CO)]^{2+}$, dppm = $Ph_2PCH_2PPh_2$.

The complex can be prepared (*ca.* 90% yield) by reaction of palladium(II) acetate with dppm in a 1 : 1 mol. ratio in aqueous acetone containing excess of trifluoroacetic acid under an atmosphere of CO. The mixture becomes deep red and reaction is complete after 1 day. The product is isolated by removing most of the solvent, and recrystallising the resulting oil from toluene–hexane–acetone solvent.

$[Pd_3(\mu\text{-dppm})_3(\mu_3\text{-}CO)][CF_3CO_2]_2.3Me_2CO$
(1)

$[Pd_3(\mu\text{-dppm})_3(\mu_3\text{-}CO)][PF_6]_2$
(2)

The trifluoroacetate salt crystallises with occluded solvent, one sample being characterised by elemental analysis, *X*-ray crystallography, and ^1H n.m.r. spectroscopy as $[Pd_3(\mu\text{-dppm})_3(\mu_3\text{-}CO)][CF_3CO_2]_2.3Me_2CO$, (**1**); its treatment with excess of $NH_4[PF_6]$ yields $[Pd_3(\mu\text{-dppm})_3(\mu_3\text{-}CO)][PF_6]_2$, (**2**). Complex (**1**) was characterised by its i.r. [$\nu(CO)$ 1820 cm^{-1}], ^1H n.m.r. [$\delta(CH^aH^bP_2)$ 4.75 and 5.00, $^2J(H^aH^b)$ 14 Hz], ^{31}P n.m.r. [$\delta(P)$ −14.15 p.p.m. from external $(MeO)_3PO$], and u.v.–visible spectra [λ_{max} 490 nm, ϵ 26.3 × 10^3 l mol^{-1} cm^{-1}]. Crystals of (**1**) or (**2**) are almost black while their solutions in organic solvents are dark red.

Crystal data for (**1**): $C_{89}H_{84}F_6O_8P_6Pd_3$, M = 1900.7, orthorhombic, space group $Pbc2_1$ (a non-standard setting of No. 29), a = 11.094(2), b = 28.553(5), c = 27.853(4) Å, U = 8822.9 Å^3, D_c = 1.431 g cm^{-3}, Z = 4; Mo-K_α radiation, $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 7.67 cm^{-1}.

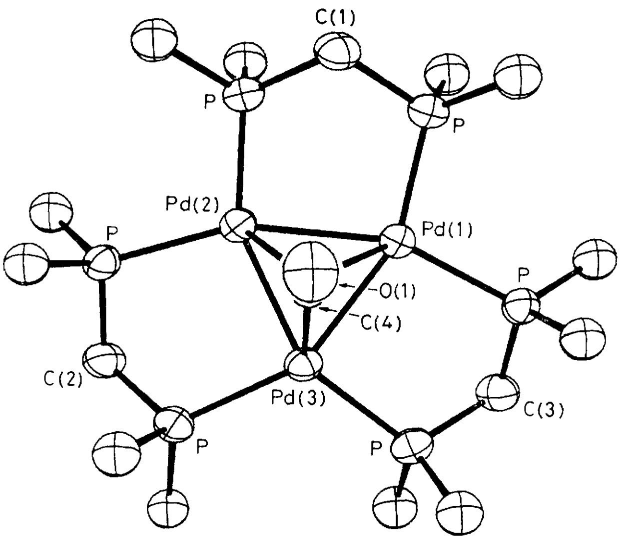

Figure 1. The structure of the $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)_3]^{2+}$ cation in (**1**), viewed along the O(1)–C(4) bond. For clarity, the twelve phenyl groups are represented by their *ipso* carbon atoms only. Selected bond lengths and angles are: Pd(1)–Pd(2) 2.576(1), Pd(1)–Pd(3) 2.607(2), Pd(2)–Pd(3) 2.610(2), Pd–P 2.296(3)—2.340(3), Pd–C(4) 2.09(1)—2.18(1) Å; Pd–Pd–Pd 59.2(1)—60.5(1), Pd–Pd–P 92.9(1)—97.7(1) and 150.3(1)—157.4(1), P–Pd–P 106.7(1)—113.1(1), Pd–C(4)–Pd 73.3(4)—76.2(4)°.

The crystal structure analysis was based on intensities of 6673 reflections with $I > 3\sigma(I)$, which were measured on a CAD4F diffractometer. The structure was solved by the heavy atom method and refined by large-block least-squares to $R = 0.076$.† The solvent of crystallisation appeared highly disordered and could not be located precisely.

The molecular structure of the cationic complex in (**1**), shown in Figure 1, contains a triangular Pd_3 cluster with all the edges spanned by bridging dppm ligands. The Pd_3P_6 unit is roughly planar, individual displacements of the palladium and phosphorus atoms from their common plane not exceeding 0.262(3) Å. The metal centres are further linked by a triply bridging carbonyl group with the donor atom, C(4), displaced by 1.64(1) Å from the Pd_3P_6 plane. The Pd–Pd distances [2.576(1)—2.610(2) Å] are comparable with those [2.586(1)—2.699(5) Å] found in the complexes $[Pd_2Br_2(\mu\text{-}dppm)_2]$, $[Pd_2Co_2(CO)_7(\mu\text{-}dppm)_2]$, and $[Pd_2Mn_2(CO)_9(\mu\text{-}dppm)_2]$,[5] and can be considered indicative of metal–metal bonding. The overall molecular geometry approximates to C_s symmetry, with the mirror plane lying normal to the Pd_3 triangle and passing through the Pd(3) and C(1) atoms (Figure 1).

In terms of bonding, we note that each palladium centre in (**1**) achieves a 16-electron count if the triangle of palladium atoms in the formal oxidation state 2/3 involves three Pd–Pd single bonds. The complex cation may also be considered to be derived from a hypothetical 'latitudinal' $[Pd_3(\mu\text{-}dppm)_3]$ cluster, as treated by Mingos,[3] by removal of two electrons from the highest energy A_1 molecular orbital, and donation of two electrons from CO into this orbital leading to the $Pd_3(\mu_3\text{-}CO)$ linkage observed. Our attempts to prepare $[Pd_3(dppm)_3]$ by reduction of (**1**) or (**2**) with sodium amalgam have been unsuccessful however.

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† 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.