Synthesis and ^{31}P Nuclear Magnetic Resonance Studies of Trinuclear Palladium Cluster Complexes; *X*-Ray Structure of $[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$

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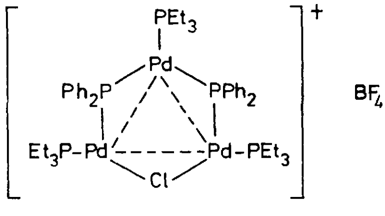
Summary Complexes $[Pd_3X(PPh_2)_2(PR_3)_3][BF_4]$ (X = Cl, Br, or SCF_3; R = Ph or Et), which are the first examples of trinuclear palladium clusters in an oxidation state other than zero, have been synthesised and characterised by ^{31}P n.m.r. spectroscopy and, in the case of (X = Cl, R = Et) (**1**), by *X*-ray diffraction.

Despite continuing efforts by several research groups, tertiary phosphine-containing cluster complexes of platinum and palladium have proved difficult to characterize.[1] The clusters $[Pt_4(CO)_5(PMe_2Ph)_4]$,[2] $[Pt_3(SO_2)_3(PPh_3)_3]\cdot C_7H_8\cdot SO_2$,[3] and $[Pt_3(CO)_3\{P(C_6H_{11})_3\}_4]$[4] are now well established as the result of *X*-ray work and very recently the confusion regarding clusters derived from $[Pt(PPh_3)_n]$ ($n = 3$ or 4) has been partially resolved by structural study of $[Pt_2(PPh_2)_2(PPh_3)_2]\cdot C_6H_6$ and $[Pt_3(Ph)(PPh_2)_3(PPh_3)_2]\cdot C_6H_6$.[5] Corresponding palladium carbonyl clusters have been prepared[6] but no structure determinations are available and the only related *X*-ray work is on $[Pd_3(\mu\text{-}SO_2)_2(CNBu^t)_5]\cdot 2C_6H_6$.[7] Moreover, no ^{31}P n.m.r. data have been obtained for the above complexes.[1] We now report that prolonged heating of $[PdCl(PPh_3)_3][BF_4]$ in tetrahydrofuran results in a red solution from which dark red diamagnetic crystals of $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$ can be isolated. Various derivatives, *e.g.* $[Pd_3X(PPh_2)_2(PR_3)_3][BF_4]$ (X = Cl, Br, or SCF_3, R = Ph or Et),† are easily prepared by metathetical and ligand exchange reactions and the compound previously formulated by Coulson[8] as a neutral complex, $[Pd_3Cl_2(PPh_2)_2(PPh_3)_3]$, evidently contains the same cationic cluster,‡ the structure proposed previously being incorrect. The clusters undergo oxidation by hydrogen peroxide in the presence of HCl to yield $[Pd_3X_4(PPh_2)_2(PR_3)_2]$ (X = Cl or Br, R = Ph or Et) but it is likely that the reaction is accompanied by gross structural change.



(1)

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† Satisfactory microanalyses have been obtained for all the complexes reported.

‡ $[Pd_3Cl(PPh_2)_2(PPh_3)_3]Cl$, synthesized by anion exchange, had an i.r. spectrum identical to the sample kindly supplied by Dr. D. R. Coulson.

A sample of $[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$ (**1**) was recrystallized from ethanol for the *X*-ray study. Crystals were monoclinic, space group $P2_1/c$ with $a = 1614(1)$, $b = 1951(1)$, $c = 1691(1)$ pm; $\beta = 97{\cdot}7(1)°$; $Z = 4$; $D_m = 1{\cdot}49$, $D_c = 1{\cdot}47$ g cm^{-3}. $R = 0{\cdot}105$ at the present stage of anisotropic least-squares refinement for 2866 independent reflections. The heavy atom skeleton is approximately planar, deviations from the least-squares plane being P(1), 11; P(2), 10; and Cl, −10 pm.§

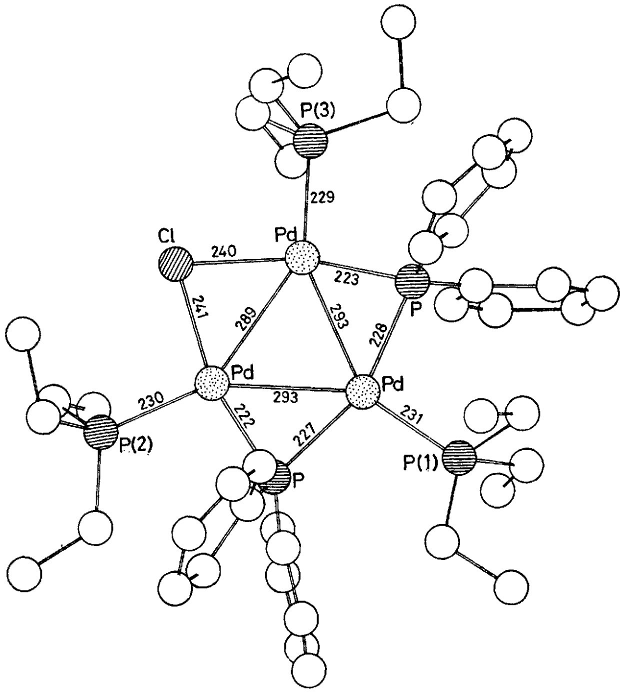

FIGURE. ORTEP plot of the cation in $[Pd_3Cl(PPh_2)_2(PEt_3)_3]$-$[BF_4]$. Bond distances are in pm.

Comparison of the metal–metal distances (see Figure) with the non-bonded, Cl-bridged, Pd–Pd distance of 347·5 pm in $[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2]$[9] indicates considerable Pd–Pd bonding in the cluster. Moreover, the equilateral nature of the Pd_3 unit is in striking contrast with $[Pt_3(Ph)(PPh_2)_3(PPh_3)_2]\cdot C_6H_6$,[5] where the metal atoms have the same average formal oxidation state ($\frac{4}{3}$) as in the present complex but in which one Pt–Pt distance is much longer (363·0 pm) than the other two (278·5 pm). The present complex is structurally similar to the Pd^0 cluster unit in $[Pd_3(\mu\text{-}SO_2)_2(CNBu^t)_5]$.[7]

The proton-decoupled ^{31}P n.m.r. spectra of $[Pd_3X(PPh_2)_2(PR_3)_3][BF_4]$ belong to the ABB′XX′ spin system (A, B, and B′ are PR_3 groups and X and X′ are PPh_2). Complete analysis by computer simulation has been achieved, and under certain circumstances, notably when $J_{XX'}$ or $J_{BB'}$ is large, a type of 'virtual coupling' prevails and the ABB′XX′ system appears like an AB_2X_2 system. The resulting parameters are very similar for all the complexes, the following data for $[Pd_3Cl(PPh_2)_2(PPh_3)_3]^+$ being typical: δ_A 128·3, δ_B 121·5, and δ_X − 81·4 p.p.m. relative to $P(OMe)_3$, positive values are upfield; J_{AB} 88·7 and J_{AX} −11·0 Hz. The other parameters are not accurately determined by the spectrum. Features unique to the cluster system are the large value of J_{AB} and the large downfield shift of the PPh_2 groups. Comparison of these values with the corresponding parameters in the absence of Pd–Pd bonding $\{J_{AA'} < 5$ Hz, δ_X +273 p.p.m. in $[Pd_2Cl_2(\mu\text{-}PPh_2)_2(PHPh_2)_2]\}$[10] emphasizes the dramatic effects of the metal–metal bonded cluster.

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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.

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