Synthesis and Structures of Re$_6$(CO)$_{18}$(μ$_4$-PMe)$_3$ and Re$_5$(CO)$_{14}$(μ$_4$-PMe)(μ-PMe$_2$)(μ$_3$-P[Re(CO)$_5$]); Two New Rhenium Cluster Geometries

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Reaction of Re$_4$Cl$_2$(CO)$_{15}${MePP(Me)PMe} with Re$_2$(CO)$_{10}$ at 230—250 °C leads to formation of the trigonal prismatic Re$_6$(CO)$_{18}$(μ$_4$-PMe)$_3$ and square pyramidal Re$_5$(CO)$_{14}$(μ$_4$-PMe)(μ-PMe$_2$){μ$_3$-P[Re(CO)$_5$]}, new rhenium cluster geometries which have been characterized by X-ray crystal analysis.

In rhenium carbonyl chemistry, polynuclear species have until recently been limited to the numerous tri- and tetra-nuclear hydridocarbonyls and hydridocarbonyl anions. Only in the last couple of years have a few large rhenium clusters based on the interstitial carbide octahedron Re$_6$C been synthesised by pyrolysis of (Et$_4$N){ReH$_2$(CO)$_4$} as the anions [Re$_6$(μ$_3$-H)$_2$-C(CO)$_{18}$]$^{2-}$,[1] mono-capped [Re$_7$C(CO)$_{21}$]$^{3-}$,[2a] and bi-capped [Re$_8$C(CO)$_{24}$]$^{2-}$.[2b] We are currently attempting to develop a chemistry associated with rhenium–phosphorus clusters.

Pyrolysis of the novel cyclometallophosphine complex Re$_4$Cl$_2$(CO)$_{15}${MePP(Me)PMe} (**1**)[3] with Re$_2$(CO)$_{10}$ under argon at 230—250 °C leads to the formation of two hexa-nuclear clusters of stoicheiometry Re$_6$(CO)$_{18}$(P$_3$Me$_3$) (**2**) and Re$_6$(CO)$_{19}$(P$_3$Me$_3$) (**3**) (Scheme 1). Total yields are essentially stoicheiometric with little decomposition, the formation of (**2**) being favoured at 230 °C, (**3**) at higher temperature.

Both compounds are dark red with relatively simple i.r. spectra: (**2**) ν(CO), tetrahydrofuran (THF): 2035s, 2028s, 2010wbr, 1980m, and 1953wbr cm^{-1}; (**3**) ν(CO), toluene: 2057sh, 2052s, 2033sh, 2024s, 2008s, 1995w, 1978m, 1966m, and 1954m cm^{-1}.

The structures of (**2**) and (**3**) have been determined by single-crystal X-ray techniques† and both proved to be new cluster geometries for rhenium. The structure of (**2**) (Figure 1) is that of a symmetrical, tri-capped trigonal prism Re$_6$(CO)$_{18}$(μ$_4$-PMe)$_3$, the three methylphosphinidene groups probably resulting from P–P bond cleavage of the MeP–P(Me)–PMe moiety in (**1**). The trigonal prism angles are fixed at 60 and 90°, the molecule possessing crystallographically imposed $\bar{6}$ symmetry. In keeping with the known trigonal prismatic clusters of group 8 {for example, [Pt$_6$(CO)$_{12}$]$^{2-}$ (ref. 4a) and [Ni$_6$(CO)$_{12}$]$^{2-}$ (ref. 4b)}, the Re–Re bonds of the triangular faces [3.092(1) Å] are somewhat shorter than the
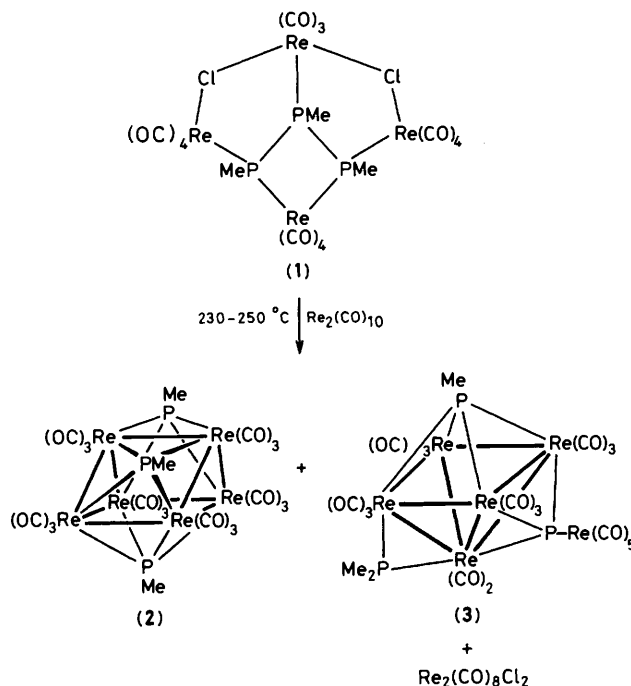
Scheme 1

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other three edges [3.156(1) Å] but the difference is much less. The deceptively simple i.r. spectrum of this compound is a reflection of its intrinsic symmetry.

The structure of (**3**) (Figure 2) is that of a pentanuclear square pyramid with the base capped by a methylphosphini-dene moiety, one triangular face capped by a –P[Re(CO)$_5$] phosphinidene-like moiety and one edge bridged by a dimethylphosphido group to give a stoicheiometry Re$_5$(CO)$_{14}$(μ$_4$-PMe)(μ-PMe$_2$){μ$_3$-P[Re(CO)$_5$]}. The variety of phosphorus ligands in this structure leads one to suggest that prior to P–P bond cleavage in (**1**), Re$_2$(CO)$_{10}$ inserts into the central Re–P bond with expulsion of Re$_2$(CO)$_8$Cl$_2$ and that in the ensuing scrambling of functionalities, methyl group migration is more favoured at higher temperatures. However, any hope of fully comprehending a mechanism for this reaction is probably unlikely in view of the drastic conditions employed. The average apical Re–Re bond length in (**3**) of 2.929 Å is markedly shorter than the average basal distances (3.044 Å) in common with other square pyramidal structures such as Ru$_5$(CO)$_{15}$(μ$_4$-PPh).[5]

Although the average Re–Re bond lengths in (**3**) (2.986 Å) are considerably shorter than those of (**2**) (3.113 Å), they are not too dissimilar to the 3.041(1) Å of Re$_2$(CO)$_{10}$[6] [Δ for (**2**) +0.072; (**3**) −0.055 Å] and are comparable to the few known large rhenium clusters [Re$_6$(μ$_3$-H)$_2$C(CO)$_{18}$]$^{2-}$ (av. 3.020 Å),[1] [Re$_7$C(CO)$_{21}$]$^{3-}$ (av. 2.992 Å),[2] and [Re$_8$C(CO)$_{24}$]$^{2-}$ (av. 2.985 Å).[3] In respect to the rhenium–phosphinidene phosphorus bond lengths, the average Re–P of 2.453 Å in (**2**) is
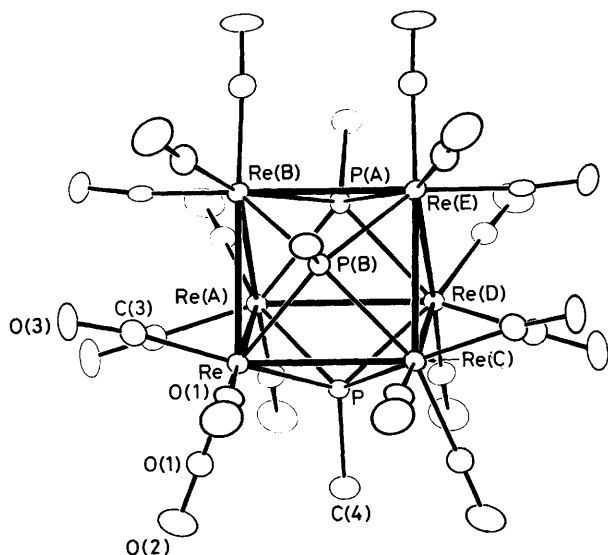
Figure 1. ORTEP plot of $RE_6(CO)_{18}(\mu_4\text{-PMe})_3$. Re–Re(A) = Re–Re(B) 3.092(1); Re–Re(C) 3.156(1); Re–P 2.432(6); Re–P(B) 2.474(6) Å; (A) = $-y,x-y,z$; (B) = $-x+y,-x,z$; (C) = $x,y,\frac{1}{2}-z$; (D) = $-y,x-y,\frac{1}{2}-z$; (E) = $-x+y,-x,\frac{1}{2}-z$.

identical to the average Re–P [Re–P(1), Re(1)–P(2), Re(4)–P(2), Re(6)–P(2)] 2.453 Å in **(3)** but with the Re(5)–P(2) bond length of 2.281(7) Å being 0.17 Å shorter, this may be viewed as a possible rhenium–phosphorus double bond.

Both these $2n$ structures conform to electron counting rules. Although **(3)** is readily recognisable as the mono-capped octahedron expected for a $14e-7$ vertex polyhedron, the tri-capped trigonal prismatic geometry of **(2)** is somewhat misleading since an $18e-9$ vertex polyhedron should be either a mono-capped square antiprism or dodecahedron. However, Figure 1 does indeed demonstrate the presence of both predicted forms with Re, Re(A), Re(C), and Re(D) half a square antiprism, Re(B), Re(E), P(A), and P(B) half a dodecahedron, and P the capping vertex.

Compounds **(2)** and **(3)** represent the first examples of high nuclearity rhenium–phosphorus clusters and are also possibly the first examples of homonuclear phosphinidene clusters outside the group 8 triad.
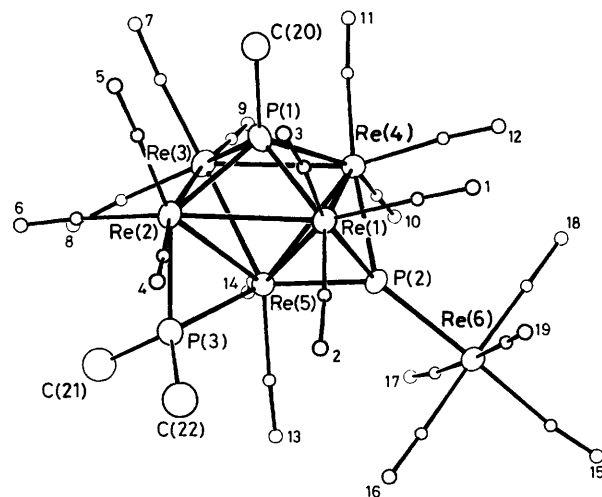

Figure 2. ORTEP plot of $Re_5(CO)_{14}(\mu_4\text{-PMe})(\mu\text{-PMe}_2)\{\mu_3\text{-P-}[Re(CO)_5]\}$. Re(1)–Re(2) 3.101(1); Re(1)–Re(4) 2.983(1); Re(1)–Re(5) 2.973(1); Re(2)–Re(3) 3.067(2); Re(2)–Re(5) 2.925(1); Re(3)–Re(4) 3.024(1); Re(3)–Re(5) 2.856(2); Re(4)–Re(5) 2.960(1); Re(1)–P(1) 2.437(7); Re(1)–P(2) 2.488(7); Re(2)–P(1) 2.436(7); Re(2)–P(3) 2.425(8); Re(3)–P(1) 2.450(7); Re(4)–P(1) 2.411(7); Re(4)–P(2) 2.465(7); Re(5)–P(2) 2.281(7); Re(5)–P(3) 2.334(8); Re(6)–P(2) 2.486(7) Å.

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