# Stepwise Addition of PtPPh$_3$ Fragments on [Re$_2$(CO)$_{10}$]. X-Ray Crystal Structures of the Complexes [Re$_2$Pt$_n$(μ-CO)$_{2n}$(CO)$_{10-2n}$(PPh$_3$)$_n$] (n = 2, 3), the First Examples of Tetra- and Penta-nuclear Rhenium–Platinum Mixed-metal Clusters

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Up to three PtPPh$_3$ fragments, originating from [Pt(PPh$_3$)$_2$(C$_2$H$_4$)], can be added to [Re$_2$(CO)$_{10}$] affording [Re$_2$Pt$_n$(μ-CO)$_{2n}$(CO)$_{10-2n}$(PPh$_3$)$_n$] (n = 1, 2, 3) mixed metal clusters, with structures based on electron short (46 valence electrons) Re$_2$Pt triangles condensed on the Re–Re hinge.

The ability of PtL$_2$ fragments to add ethylene-like molecules[1] allowed the synthesis of the triangular cluster [Re$_2$Pt(μ-H)$_2$-(PPh$_3$)$_2$(CO)$_8$], by reaction of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] 1 with [Re$_2$(μ-H)$_2$(CO)$_8$] 2.[2] We have now found that compound 1 is able to react in mild conditions with the ethane-like molecule [Re$_2$(CO)$_{10}$], 3, through a completely different pathway, leading to the addition of up to three PtPPh$_3$ fragments on [Re$_2$(CO)$_{10}$]. The reaction, at room temperature, went to completion by bubbling N$_2$ (to remove C$_2$H$_4$) through a solution of 3 and an excess of 1 (ca. 5 equiv.). Flash-

chromatography allowed the separation of the two reaction products,† a yellow and a red species, characterized by single-crystal X-ray analyses as the mixed-metal cluster complexes $[Re_2Pt_n(\mu\text{-}CO)_{2n}(CO)_{10-2n}(PPh_3)_n]$, $n = 2$, compound **4**, $n = 3$, compound **5**.‡

Compounds **4** (Fig. 1) and **5** (Fig. 2) have an approximately tetrahedral or trigonal bipyramidal metal core, respectively, but the whole hypothetical $[Re_2(CO)_{10}(PtPPh_3)_n]$ ($n = 1$ to 4) family is structurally better described when related to the parent $[Re_2(CO)_{10}]$ (which has a staggered $D_{5d}$ structure) by a sort of edge capping process of the Re–Re bond (of the eclipsed $D_{5h}$ conformers) by PtPPh$_3$ fragments. Each PtPPh$_3$ fragment is connected to the Re–Re hinge (which elongates upon successive edge-capping) by two Pt–Re bonds bridged by two equatorial, formerly terminal, carbonyl ligand. From this point of view, **4** would have a possible stereoisomer (not found, probably because the Pt$\cdots$Pt interactions slightly stabilize the observed one) with a diamond like, rather than a tetrahedral like, metal core. Each PtPPh$_3$ fragment contributes 12 electrons to the cluster valence electrons (CVEs) number; thus the $[Re_2(CO)_{10}(PtPPh_3)_n]$ ($n = 1$ to 4) compounds have $(34 + n \times 12)$ CVEs. For $n = 1$ we have a 46 CVEs species which, owing to the presence of a 16 electrons planar Pt atom, has the correct CVEs number. Moreover, using the Mingos condensed polyhedra approach,[3] we predict, for the condensation of $n$ (46 CVEs) triangles along a common edge, a CVEs number of $n \times 46 - (n-1) \times 34 = 34 + n \times 12$, which agrees with the observed values for **4** and **5** and with the previous formula. These numbers have been derived with the hypothesis of no Pt–Pt interactions, which, judging from the observed Pt$\cdots$Pt distances (ranging from 2.955 to 3.073 Å), the intertriangle dihedral angles (ranging from 82.2 to 88.5°) and the (slight) pyramidalization of the Pt(CO)$_2$P moieties (particularly evident in **5**), is only partially fulfilled.

All the Re–Pt bonds are asymmetrically bridged by carbonyl ligands, the Re–C interactions being (on average) markedly longer than the Pt–C ones (2.18 vs. 2.03 Å in **4** and 2.13 vs. 2.02 Å in **5**). We believe, judging from the reported
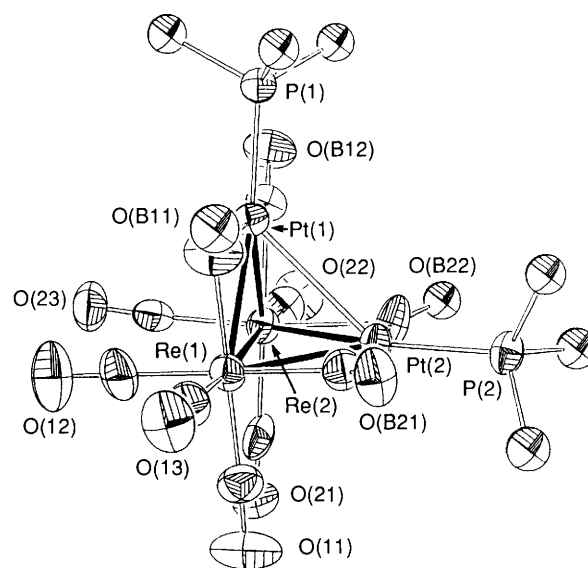


**Fig. 1** ORTEP drawing of $[Re_2Pt_2(\mu\text{-}CO)_4(CO)_6(PPh_3)_2]$, with partial labelling scheme, view along the Re–Re bond direction. For the sake of clarity the phenyl rings have been represented by the *ipso* carbon atoms only. Relevant bond lengths (Å): Pt(1)–Pt(2) 2.982(1), Pt(1)–Re(1) 2.750(1), Pt(1)–Re(2) 2.745(1), Pt(2)–Re(1) 2.734(1), Pt(2)–Re(2) 2.751(1), Re(1)–Re(2) 3.094(1). Dihedral angle between the PtRe$_2$ planes (°): 82.2.
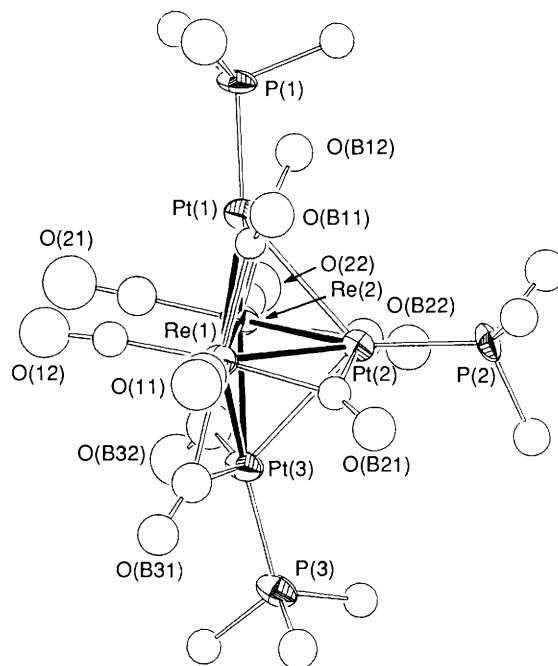
**Fig. 2** ORTEP drawing of $[Re_2Pt_3(\mu\text{-}CO)_6(CO)_4(PPh_3)_3]$, with partial labelling scheme, view along the Re–Re bond direction. For the sake of clarity the phenyl rings have been represented by the *ipso* carbon atoms only. Relevant bond lengths (Å) for molecule A and molecule B [in square brackets]: Pt(1)–Pt(2) 3.009(2) [3.073(2)], Pt(2)–Pt(3) 2.955(2) [2.962(2)], Pt(1)–Re(1) 2.732(2) [2.711(2)], Pt(1)–Re(2) 2.719(2) [2.749(2)], Pt(2)–Re(1) 2.747(2) [2.754(2)], Pt(2)–Re(2) 2.779(2) [2.744(2)], Pt(3)–Re(1) 2.778(2) [2.742(2)], Pt(3)–Re(2) 2.748(2) [2.751(2)], Re(1)–Re(2) 3.237(2) [3.258(2)]. Dihedral angles between the PtRe$_2$ planes (°): Pt(1)/Pt(2) 85.5 (88.5), Pt(2)/Pt(3) 82.6 (84.0).

average Re–C (1.936 Å) and Pt–C (1.853 Å) bond distances for terminal carbonyl ligands,[4] that this reflects the different metal size rather than an electronic effect.

The formation of these compounds is likely to proceed through the stepwise addition of the electron-rich $PtP_2$ fragment on the electrophilic equatorial carbonyls of $[Re_2(CO)_{10}]$. We have not yet been able to isolate the product of the first addition, but we have spectroscopic evidence of the presence of an intermediate,§ whose concentration always remains quite low. This could indicate that the second nucleophilic attack is as easy as the first one, for the presence in the $Re_2Pt$ intermediate of another couple of acidic (mutually-*trans*) carbonyls. The third step is, in fact, more difficult and the synthesis can be addressed selectively towards **4** by using a deficiency of **1**. The addition of **1** allows transformation of **4** into **5**.

Examples of the insertion of zero-valent Pt fragments into the single metal–metal bonds of carbonyls of the iron triad have been reported,[5] but those reactions were accompanied by other processes, such as fragmentation of the starting carbonyl complexes, CO loss or transfer of a phosphine from platinum to the other metal. In the present system the phosphines lost by the coordinated Pt atoms are mainly transferred to other $PtP_2$ groups, since $[Pt(PPh_3)_3]$ is recognized ($^{31}P$ NMR) as the dominant species in the reaction mixtures, according to the overall stoichiometry in eqn. (1).

$$[Re_2(CO)_{10}] + 2n[Pt(PPh_3)_2(C_2H_4)] \rightarrow$$
$$[Re_2(PtPPh_3)_n(CO)_{10}] + n[Pt(PPh_3)_3] + nC_2H_4 \quad (1)$$
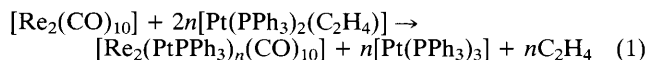
Work is in progress in order to verify if the use of different $Pt^0$ starting reagents could allow the synthesis of the missing members of this family of mixed-metal clusters.

## References

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§ A species exhibiting $\nu_{CO}/cm^{-1}$ at 2098, 2054, 1984, 1865 and 1815 and a $^{31}P$ resonance at $\delta$ 76.7 ($J_{P-Pt}$ 4450 Hz) was always observed as soon as the reagents were mixed.