Stepwise Addition of [$Re_2(\mu$-$H)_2(CO)_8$] to a Labile Pt(0) Complex. X-Ray Crystal Structures of the Bow-tie Clusters [$Re_4Pt(\mu$-$H)_{6-n}(CO)_{16}]^{n-}$ (n = 0, 1)

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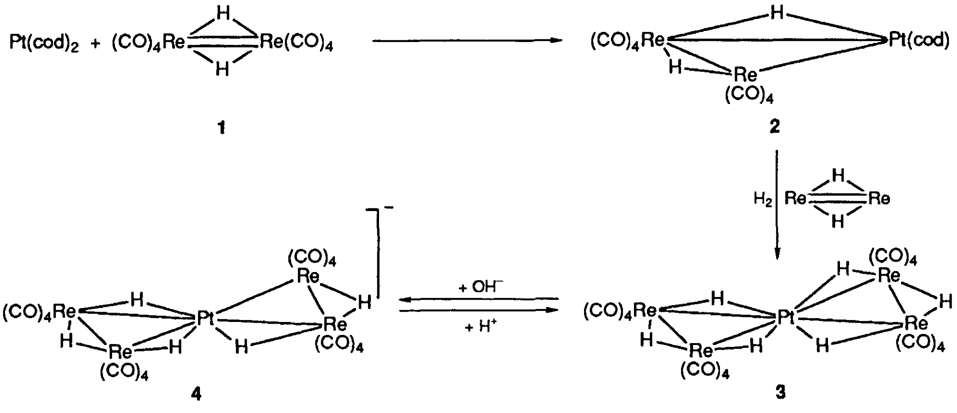
The stepwise reaction of the ethylene-like molecule [$Re_2(\mu$-$H)_2(CO)_8$] with [Pt(cod)$_2$] (cod = cycloocta-1,5-diene) affords the triangular cluster [$Re_2Pt(\mu$-$H)_2(CO)_8$(cod)] and then, under H_2, the pentanuclear species [$Re_4Pt(\mu$-$H)_6(CO)_{16}$], with a bow-tie geometry of the metal cluster, which in basic media deprotonates reversibly to [$Re_4Pt(\mu$-$H)_5(CO)_{16}]^-$.

We are currently interested in the synthesis of mixed metal Pt–Re clusters using labile Pt(0) complexes and small Re clusters as starting materials. The ability of PtL_2 fragments to add ethylene-like[1] and even ethane-like[2] molecules allowed us to obtain the [$Re_2Pt(\mu$-$H)_2(CO)_8(PPh_3)_2$][3] and [$Re_2Pt_n(\mu$-$CO)_{2n}(CO)_{10-2n}(PPh_3)_n$] ($n$ = 1,2,3)[2] clusters by reaction of [$Pt(PPh_3)_2(C_2H_4)$] with [$Re_2(\mu$-$H)_2(CO)_8$] **1** and [$Re_2(CO)_{10}$], respectively.



Scheme 1

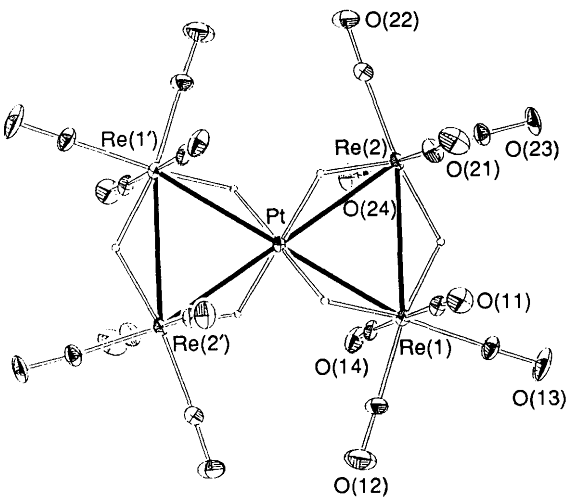


Fig. 1 ORTEP drawing of $[Re_4Pt(\mu\text{-}H)_6(CO)_{16}]$ **3**, with partial labelling scheme. The molecule lies on a crystallographic inversion centre (primed and unprimed atoms are related by the $-x$, $-y$, $-z$ symmetry operation) but the idealized symmetry is higher, namely C_{2h}. Relevant bond parameters are: Pt–Re(1) 2.901(1), Pt–Re(2) 2.911(1), Re(1)–Re(2) 3.192(1) Å; Pt–Re(2)–Re(1)–C(11) −108.9, Pt–Re(2)–Re(1)–C(14) 72.3, Pt–Re(1)–Re(2)–C(21) 109.6, Pt–Re(1)–Re(2)–C(24) −71.6, C(13)–Re(1)–Re(2)–C(23) 0.9°.

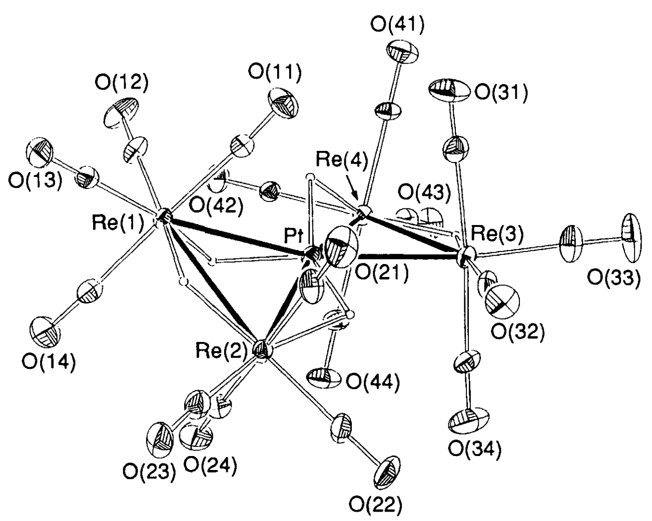


Fig. 2 ORTEP drawing of $[Re_4Pt(\mu\text{-}H)_5(CO)_{16}]^-$ **4**, with partial labelling scheme. Relevant bond parameters are: Pt–Re(1) 2.888(1), Pt–Re(2), 2.859(1), Pt–Re(3) 2.786(1), Pt–Re(4) 2.853(1), Re(1)–Re(2) 3.168(1), Re(3)–Re(4) 3.147(1) Å; Pt–Re(2)–Re(1)–C(11) −64.6, Pt–Re(2)–Re(1)–C(14) 115.5, Pt–Re(1)–Re(2)–C(21) 90.8, Pt–Re(1)–Re(2)–C(24) −83.5, Pt–Re(4)–Re(3)–C(31) −85.6, Pt–Re(4)–Re(3)–C(34) 90.4, Pt–Re(3)–Re(4)–C(41) 108.4, Pt–Re(3)–Re(4)–C(44) −69.7, C(13)–Re(1)–Re(2)–C(23) 30.6, C(33)–Re(3)–Re(4)–C(43) 24.1°.

We report now the stepwise addition of **1** to $[Pt(cod)_2]$ (cod = cycloocta-1,5-diene), which, depending on the reaction conditions and the stoichiometric ratio, affords tri- or pentanuclear species (Scheme 1).

Spectroscopic monitoring† shows that the formally unsaturated $[Re_2(\mu\text{-}H)_2(CO)_8]$ (32 valence electrons, v.e.s) reacts quantitatively and instantaneously, at 0 °C, with the electron-precise (18 v.e.s) $[Pt(cod)_2]$, giving the triangular cluster $[Re_2Pt(\mu\text{-}H)_2(CO)_8(cod)]$ (compound **2**, 46 v.e.s), with transfer of the unsaturation from the $Re_2(\mu\text{-}H)_2$ moiety to the Pt atom (16 local v.e.s). The substitution of the remaining cod with a second $[Re_2(\mu\text{-}H)_2(CO)_8]$ molecule would imply a further electron depleting of the Pt centre, as observed in the reaction of $[Rh_2(\mu\text{-}CO)_2(C_5Me_5)_2$ with $[Pt(C_2H_4)_3]$,[4] affording the 74 v.e.s species $[Rh_4Pt(\mu\text{-}CO)_4(C_5Me_5)_4]$. In the present case the reaction of **2** with a second molecule of **1** requires the presence of H_2, in order to provide the Pt atom with the two electrons lost in the substitution of the diene by $[Re_2(\mu\text{-}H)_2(CO)_8]$. The reaction between **2** and one equivalent of compound **1**, under H_2, at 0 °C, affords in fact as main product (yields *ca.* 50%) the hexahydridic pentanuclear cluster $[Re_4Pt(\mu\text{-}H)_6(CO)_{16}]$ **3**, with 76 v.e.s, as $[Fe_4Pt(CO)_{16}]$.[2–5] It appears therefore that the $(CO)_4Re(\mu\text{-}H)Re(CO)_4$ moieties are unable to furnish the steric shielding or the long range interactions usually stabilizing 14 v.e.s Pt centres (semibridging carbonyls[4] or agostic hydrogens[6]).

Compound **3** reversibly reacts with methanolic NEt_4OH transforming into its conjugate base $[Re_4Pt(\mu\text{-}H)_5(CO)_{16}]^-$ **4**, where the three Pt bound hydrides are rapidly scrambling on the four Re–Pt bonds, as shown by the presence, in the NMR spectrum, of only one signal (for these hydrides) down to 193 K.

Compounds **3** (Fig. 1) and **4** (Fig. 2) have been both structurally characterized by single crystal X-ray analysis.‡ They share the bow-tie geometry of the metal clusters. In compound **3** the central Pt atom is linked to two $(CO)_4Re(\mu\text{-}H)Re(CO)_4$ moieties *via* four $Pt(\mu\text{-}H)Re$ bonds, while, in compound **4**, all but one of the Pt–Re edges are μ_2 bridged by hydrido ligands. The presence of the hydrido ligands is evidenced by the metal–metal bond lengths pattern, the relative orientation of the four $Re(CO)_4$ units (which have their local C_2 symmetry axis not always lying in the pertinent $PtRe_2$ plane) and/or the folding of the bow-tie (the dihedral angles between the two $PtRe_2$ planes are 0 and 36.3° in **3** and **4**, respectively).§ In fact, if all the 'equatorial' carbonyl ligands and the metallic bow-tie were coplanar, the hydrides would also lie in that plane, giving unreasonable H···H contacts. Hence, in compound **3**, the $(CO)_4Re(\mu\text{-}H)Re(CO)_4$ moieties are rigidly rotated about the Re–Re vectors, in order to accommodate the four μ_2 hydrides two above and two below the $PtRe_4$ plane. Different distortions occur in compound **4**, where two out of three Pt-bound μ_2-H lie on the pertinent

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† *^1H NMR spectroscopic data* for compound **2**: (CD_2Cl_2, 233 K) δ 5.62 (4 H J_{H-Pt} 55 Hz, CH), 2.01 (8 H, CH_2), −9.17 (1 H J_{H-Pt} 745 Hz, ReH), −16.03 (1, J_{H-Pt} 22 Hz, ReH). Compound **3**: (CD_2Cl_2, 301 K) δ −13.33 (4 H, J_{H-Pt} 720 Hz, ReH), −16.14 (2 H, ReH). Compound **4**: (C_4D_8O, 298 K) δ −8.36 (3 H, J_{H-Pt} 770 Hz, ReH), −16.41 (2 H, ReH). IR ν(CO) cm^{-1} (CH_2Cl_2): compound **2** 2097m, 2056m, 2002vs, 1962s, 1918m; compound **3** 2105w, 2094m, 2032vs, 2012s, 1970m; compound **4** 2070sh, 2049m, 2006vs, 1975s, 1956sh, 1933s, 1912m. Preliminary X-ray diffraction results confirm the structure of compound **2** reported in Scheme 1.

‡ *Crystal data* for **3**: $C_{16}H_6O_{16}PtRe_4$; M = 1394.1, triclinic, space group $P\bar{1}$ (No. 2), a = 6.995(3), b = 9.659(2), c = 11.388(3) Å, α = 112.88(2), β = 96.65(3), γ = 104.96(3)°, U = 664(1) $Å^3$, $F(000)$ = 608, Z = 1, D_c = 3.484 g cm^{-3}, Mo-Kα radiation, γ = 0.71073 Å, μ(Mo-Kα) = 237.8 cm^{-1}. Intensities were measured on a CAD4 automatic diffractometer at room temperature; data were corrected for absorption and Lorentz-polarization effects. 2246 reflections, with $I>3\sigma(I)$, were used in the structure refinements. The final R value was 0.028 (R_w = 0.032).

Crystal data for **4**: $C_{24}H_{25}NO_{16}PtRe_4$; M = 1523.3, triclinic, space group $P\bar{1}$ (No. 2), a = 11.292(2), b = 12.431(4), c = 13.668(3) Å, α = 78.68(2), β = 74.43(2), γ = 86.23(2)°, U = 1812(1) $Å^3$, $F(000)$ = 1364, Z = 2, D_c = 2.792 g cm^{-3}, Mo-Kα radiation, λ = 0.71073Å, μ(Mo-Kα) = 174.5 cm^{-1}. Intensities were measured on a CAD4 automatic diffractometer at room temperature; data were corrected for absorption, Lorentz-polarization effects and decay. 4980 reflections, with $I>3\sigma(I)$, were used in the structure refinements. The final R value was 0.033 (R_w = 0.039).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the University of Bonn for structure **3** and at the Cambridge Crystallographic Data Centre for structure **4**. See Notice to Authors, Issue No. 1.

§ The hydrido ligands have been indirectly located, on the basis of the experimental heavy atoms stereochemistry, using atom pair potential computations.[7]

$PtRe_2$ planes, but the planarity of the $PtRe_4$ moiety is lost together with the local C_{2v} symmetry of the two $(CO)_4Re(\mu\text{-}H)Re(CO)_4$ moieties.

A relevant conformational parameter for bow-tie clusters M_4M' is ω, *i.e.* the dihedral angle between the two M_2M' planes. When the central atom carries many ligands, like in the series $Os_5(CO)_{19}$,[8] $Os_5(CO)_{16}\{P(OMe)_3\}_3$[9] and $Os_5(CO)_{17}(HCCH)$,[10] ω is considered to be driven by steric interactions. We have shown that the folding of the $PtRe_4$ moiety, in compound **4**, is due to steric effects, nevertheless we think that larger deviations from planarity are electronically forbidden because a value of ω close to 0 or to 90° implies a square planar or a tetrahedral central atom and then a different electron count (see for instance the structure of $[Rh_4Pt(CO)_2(CF_3C_2CF_3)_2(C_5H_5)_4]$ with ω = 90° and 78 v.e.s).[11]

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