Pseudo-raft Rhenium–Platinum Clusters. Synthesis and Crystal Structure of the Anions $[\mathrm{PtRe_3(\mu\text{-}H)(CO)_{13}}]^{2-}$ and $[\mathrm{PtRe_4(CO)_{17}}]^{2-}$, containing a Central Pt Atom surrounded by a Folded Stripe of Re Atoms

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The redox condensation between $[\{\mathrm{Pt_3(CO)_6}\}_n]^{2-}$ ($n \approx 10$) and rhenium carbonyl anions gives two novel mixed-metal species, $[\mathrm{PtRe_3(\mu\text{-}H)(CO)_{13}}]^{2-}$ and $[\mathrm{PtRe_4(CO)_{17}}]^{2-}$, containing a Pt–CO unit interacting with three and four $\mathrm{Re(CO)_4}$ moieties, respectively, arranged as a stripe folded around the Pt atom and whose formation confirms the tendency of Re atoms to cluster around Pt, giving structures based on $\mathrm{Re_2Pt}$ triangles with a low Pt : Re ratio.

The addition of mononuclear platinum(0) reactive fragments to $[\mathrm{Re_2(CO)_{10}}]$ or $[\mathrm{Re_2(\mu\text{-}H)_2(CO)_8}]$ has been previously used[1,2] to prepare several neutral Pt–Re mixed-metal clusters, most of which contain one Pt atom only, a notable exception being the complexes $[\mathrm{Re_2(CO)_{10}\{Pt(PPh_3)\}_n}]$ (n = 1, 2 or 3).[2]

We have now attempted to use preformed platinum clusters of the series $[\{\mathrm{Pt_3(CO)_6}\}_n]^{2-}$ (n = 2–10) as starting materials.[3] The redox condensation[4] between neutral rhenium species and reduced platinum clusters was unsuccessful: no reaction was observed, for example, between $[\mathrm{Re_2(CO)_{10}}]$ or $[\mathrm{Re_2(CO)_9(NCMe)}]$ and $[\mathrm{Pt_6(CO)_{12}}]^{2-}$. On the contrary, the condensation of rhenium carbonyl anions with the almost neutral platinum carbonyl clusters $[\{\mathrm{Pt_3(CO)_6}\}_n]^{2-}$ ($n > 4$) did afford heterometallic derivatives. The platinum cluster fragmented during the reactions, acting as a source of mononuclear $\mathrm{Pt(CO)}_x$ units, which in the final products are surrounded by Re atoms. Thus, the reaction between $[\{\mathrm{Pt_3(CO)_6}\}_n]^{2-}$ ($n \approx 10$) and $[\mathrm{Re_2(\mu\text{-}H)H_2(CO)_8}]^-$[5] gave in moderate yields the brown anion $[\mathrm{PtRe_3(\mu\text{-}H)(CO)_{13}}]^{2-}$ **1** (Fig. 1),[†] while the addition of $[\mathrm{Re(CO)_5}]^-$ to a suspension of $[\{\mathrm{Pt_3(CO)_6}\}_n]^{2-}$ ($n \approx 10$)[‡] produced the deep green anion $[\mathrm{PtRe_4(CO)_{17}}]^{2-}$ **2** (Fig. 2). Both anions have been characterized by X-ray analysis of their $[\mathrm{PPh_4}]^+$ salts (compounds **1a**[§] and **2a**,[¶] respectively).

A more rational preparation of compound **2** involves the addition of $[\mathrm{Re(CO)_5}]^-$ to $[\mathrm{PtCl_2(NCPh)_2}]$, in a 4:1 molar ratio (−80 °C), in line with the straightforward synthesis of Pt–Mn linear species from $[\mathrm{Mn(CO)_5}]^-$ and $[\mathrm{PtCl_2L_2}]$ (L = isonitrile or pyridine)[7] and the large number of mixed-metal platinum-containing clusters, prepared by replacement of halides bound to $\mathrm{Pt^{II}}$ with carbonyl metalates.[8]

The two derivatives have a metallic core formed by two and three $\mathrm{PtRe_2}$ triangles, respectively, fused on Pt–Re hinges. In both anions, the Pt atom bears a single terminal carbonyl, while all the Re atoms bear four carbonyls [Figs. 1(*a*) and 2(*a*)]. However, the triangles are not co-planar (hence *pseudo*-raft) [Figs. 1(*b*) and 2(*b*)] at variance from the related compound $[\mathrm{Pt_2Os_3(CO)_{14}}]$ where the metal cluster is planar.[9]

The rationale of the structures in terms of edge-sharing triangles is also supported by electronic considerations. The number of cluster valence electrons (c.v.e.s) of compounds **1** and **2** (60 and 74 respectively) agrees with the polyhedral skeletal electron pair theory,[10] if one considers that any edge-fused triangle adds 14 (48 − 34) electrons to the basic $\mathrm{PtRe_2}$ unit, which

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[†] A mixture of $[\mathrm{N(C_7H_{15})_4}]_2[\{\mathrm{Pt_3(CO)_6}\}_n]$ ($n \approx 10$) (50 mg) and $[\mathrm{NEt_4}][\mathrm{Re_2H_3(CO)_8}]$ (60 mg, Pt and Re about equimolar) was refluxed in tetrahydrofuran (thf) for 2 h, giving a brown solution containing the mixed-metal cluster $[\mathrm{PtRe_3(\mu\text{-}H)(CO)_{13}}]^{2-}$ **1** in moderate amount (30–50%, according to IR and NMR monitoring). The product was purified by precipitation with $[\mathrm{PPh_4}]\mathrm{Br}$, from MeOH solution, and crystallization from thf–propan-2-ol; ν_{CO}(acetone) 2004s, 1980(sh), 1964s, 1956s, 1931m, 1910m, 1888m (br), 1868mw and 1845w cm^{-1}; ^{1}H NMR ([^{2}H$_6$]acetone), δ −10.5.

[‡] A solution of $\mathrm{Na[Re(CO)_5]}$ (*ca.* 0.05 mol dm^{-3} in thf, 20 cm^3) was added dropwise to a suspension of $[\mathrm{NEt_4}]_2[\{\mathrm{Pt_3(CO)_6}\}_n]$ ($n \approx 10$) (90 mg), up to a Re : Pt ratio of 3 : 1, giving a deep green solution. Precipitation with $[\mathrm{PPh_4}]^+$ and crystallization from $\mathrm{CH_2Cl_2}$–diisopropyl ether afforded well shaped crystals of $[\mathrm{PPh_4}]_2[\mathrm{PtRe_4(CO)_{17}}]$ (yields 20–40%); ν_{CO}(thf) 2015s, 1997vs, 1978s, 1964vs, 1936m, 1926s, 1894m and 1867w cm^{-1}.

[§] Crystal data for compound **1a**: $\mathrm{C_{61}H_{41}O_{13}P_2PtRe_3}$, M = 1797.6, triclinic, space group $P\bar{1}$ (no. 2), a = 13.733(4), b = 19.991(4), c = 11.769(4) Å, α = 106.58(2), β = 106.86(2), γ = 89.93(2)°, U = 2952(3) Å^3, $F(000)$ = 1688, Z = 2, D_c = 2.02 g cm^{-3}, Mo-Kα radiation, λ = 0.710 73 Å, μ(Mo-Kα) = 87.2 cm^{-1}. 8176 Intensities were measured on a dark red crystal of dimensions 0.20 × 0.17 × 0.12 mm with a CAD4 automatic diffractometer at room temperature with θ ranging from 3 to 23.5°; data were corrected for absorption (maximum, minimum relative transmission factors 1.00, 0.69), Lorentz-polarization effects and decay (1.00–1.60). 3508 Reflections with $I > 3\sigma(I)$ were used in the structure refinements. The structure was solved by Patterson methods and refined by full-matrix least squares {the weighting scheme adopted was $w = 1.679/[\sigma^2(F_o) + 0.000\,32F_o^2]$} using the SHELX program.[6] The hydrido ligand was placed in idealized positions on the basis of the experimental heavy-atoms stereochemistry, using atom pair potential computations. The final R value was 0.048 (R' = 0.045).

[¶] Crystal data for compound **2a**: $\mathrm{C_{65}H_{40}O_{17}P_2PtRe_4{\cdot}CH_2Cl_2}$, M = 2137.3, monoclinic, space group $C2/c$ (no. 15), a = 12.975(3), b = 22.060(7), c = 46.706(9) Å, β = 96.01(2)°, U = 13 295(10) Å^3, $F(000)$ = 7960, Z = 8, D_c = 2.13 g cm^{-3}, Mo-Kα radiation, λ = 0.710 73 Å, μ(Mo-Kα) = 96.3 cm^{-1}. 11 942 Intensities were measured on a dark green crystal of dimensions 0.16 × 0.13 × 0.07 mm with a CAD4 automatic diffractometer at room temperature with θ ranging from 3 to 25°; data were corrected for absorption (maximum, minimum relative transmission factors 1.00, 0.50), Lorentz-polarization effects and decay (1.00–1.17). 5345 Reflections with $I > 3\sigma(I)$ were used in the structure refinements. The structure was solved by Patterson methods and refined by full-matrix least squares {the weighting scheme adopted was $w = 1.387/[\sigma^2(F_o) + 0.000\,36\,F_o^2]$} using the SHELX program.[6] The final R value was 0.037 (R' = 0.035).

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

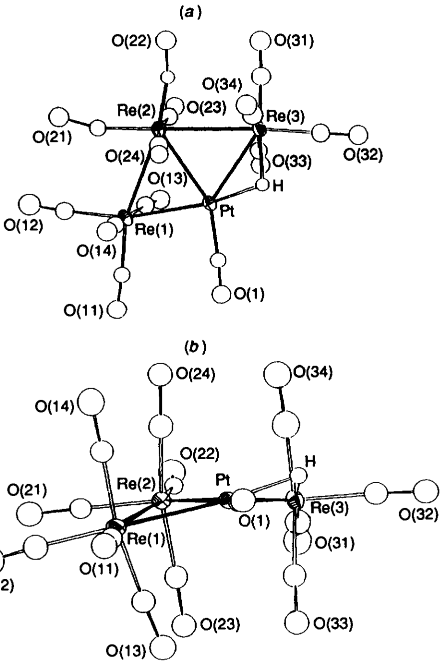

Fig. 1 The structure and labelling scheme for the $[\mathrm{PtRe_3(\mu\text{-}H)(CO)_{13}}]^{2-}$ anion. The molecule is viewed along (*a*) the normal to the Pt, Re(2), Re(3) plane and (*b*) the vector passing through Pt and bisecting the Re(2)–Re(3) bond. Relevant bonding parameters are: Pt–Re(1) 2.706(1), Pt–Re(2) 2.798(2), Pt–Re(3) 2.799(1), Re(1)–Re(2) 3.046(1), Re(2)–Re(3) 3.091(1) Å; C(21)–Re(2)–C(22) 100(1), Re(1)–Pt–C(1) 87.6(7)°

requires only 46 c.v.e.s. Obviously, $[\mathrm{Pt_2Os_3(CO)_{14}}]$, having one more 'planar' Pt atom, has two c.v.e.s less (72).

Triangles of $\mathrm{PtRe_2}$ are the building blocks of all the Re–Pt clusters so far synthesized,[1,2] which fall into two different classes. In $[\mathrm{Re_2(CO)_{10}\{Pt(PPh_3)\}_{\mathit{n}}}]$ (n = 1, 2 or 3)[2] the triangles share a common Re–Re bond, while in $[\mathrm{\{Re_2Pt(\mu\text{-}H)_2(CO)_8\}(\mu\text{-}H)Re(CO)_5}]$, in the bow-tie $[\mathrm{\{Re_2(\mu\text{-}H)(CO)_8\}_2Pt(\mu\text{-}H)_{4-\mathit{n}}}]^{n-}$ (n = 0 or 1)[1b] and in clusters **1** and **2** there is a common Pt atom. In the latter class, the metal framework of compounds **1** and **2** can be related, respectively, to the previously known spike and bow-tie geometries by breaking a Re–Re bond.

Compounds **1** and **2** differ mainly because the μ-H of **1** is replaced by a μ-$\mathrm{Re(CO)_4}$ group in **2**. The two fragments are similarly bound to the central $\mathrm{PtRe_2}$ unit, with no major stereochemical changes, apart from a shrinking of the C(21)–Re(2)–C(22) and Re(1)–Pt–C(1) angles [Figs. 1(*b*) and 2(*b*)] in the latter. We can thus envisage a series of structurally related $[\mathrm{PtRe_2(CO)_9\{\mu\text{-}Re(CO)_4\}_{\mathit{m}}(\mu\text{-}H)_{2-\mathit{m}}}]^{2-}$ anions (the term m = 0 still missing), where both the μ-$\mathrm{Re(CO)_4}$ and μ-H ligands formally contribute one c.v.e. to the central $\mathrm{PtRe_2}$ moiety (which so attains 46 c.v.e.s). The two fragments, however, cannot be considered isolobal because they use a different number of frontier orbitals in their interactions. As a result, on the basis of a local electron book-keeping, the central $\mathrm{PtRe_2}$ moiety bears all the negative charge of the cluster when $m = 0$, but it is neutral when $m = 2$.

A first attempt to interconvert the members of this family has been performed using oxidative cluster degradation,[11] which allows the removal of cluster vertices as cationic fragments, such as $[\mathrm{Re(CO)_3(NCMe)_3}]^+$. The protonation of compound **2** (m = 2) with $\mathrm{CF_3SO_3H}$ in acetonitrile gave a complex mixture, which however contained **1** (m = 1) in about 20% yield (NMR monitoring). Research in this area, as well as on rational ways to prepare the dihydride species (m = 0), is in progress.

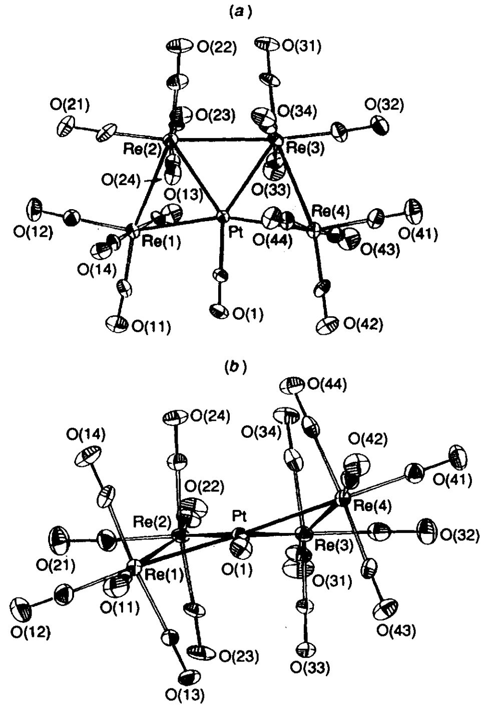

Fig. 2 The structure and labelling scheme for the $[\mathrm{PtRe_4(CO)_{17}}]^{2-}$ anion. The molecule is viewed along (*a*) the normal to the Pt, Re(2), Re(3) plane and (*b*) the idealized C_2 symmetry axis passing through Pt and bisecting the Re(2)–Re(3) bond. Relevant bonding parameters are: Pt–Re(1) 2.7640(8), Pt–Re(2) 2.7354(8), Pt–Re(3) 2.7428(9), Pt–Re(4), 2.7583(8), Re(1)–Re(2) 3.0351(9), Re(2)–Re(3) 3.0495(8), Re(3)–Re(4) 3.0115(9) Å; C(21)–Re(2)–C(22) 89.3(8), Re(1)–Pt–C(1) 80.7(5)°

Acknowledgements

We thank the Progetto Finalizzato Chimica Fine II of the Consiglio Nazionale delle Ricerche and the Ministero Università e Ricerca Scientifica e Tecnologica for financial and instrumental support.

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Received 24*th August* 1992; *Communication* 2/04558C