Synthesis, Characterization and Crystal Structures of $Os_4Pt_2(CO)_{18}$ and $Os_2Pt(CO)_{10}$. The Reversible Formation of a Hexanuclear Puckered Raft Cluster from a Triangular Cluster

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The triosmium cluster $H_2Os_3(CO)_{10}$ reacts with dicarbonyldimethylplatinum, $(CO)_2PtMe_2$, to give one major product in good yield, $Os_4Pt_2(CO)_{18}$, a compound with a novel puckered raft structure, which upon addition of carbon monoxide splits into two triangular clusters of $Os_2Pt(CO)_{10}$.

The ability of platinum to adopt 16 and 18 electron configurations has led us to study the synthesis of mixed metal clusters containing platinum, including clusters which do not contain phosphine ligands, since phosphine ligands are more firmly bound to platinum than other common ligands. Only a few osmium–platinum mixed metal cluster compounds without phosphine ligands have been isolated; these contain cyclooctadiene or carbonyl ligands co-ordinated to platinum.[1] Such cluster compounds would probably show different reactivity patterns and adopt different structures than complexes containing more strongly bonded ligands. Our previously reported synthetic route[1b] gives a hexanuclear osmium–plati-

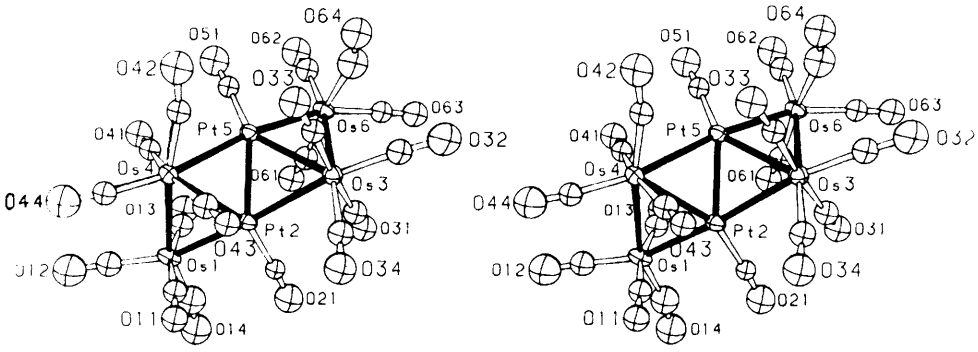

Figure 1. Stereoscopic view of (**1**). Angles between planes: Os(1)Pt(2)Os(4)–Pt(2)Os(4)Pt(5) 38.2, Pt(2)Os(4)Pt(5)–Pt(2)Os(3)Pt(5) 48.1, Pt(2)Os(3)Pt(5)–Os(3)Pt(5)Os(6) 46.1°; important metal–metal distances (Å); Os(1)–Pt(2) 2.652(3), Os(1)–Os(4) 2.906(2), Pt(2)–Os(3) 2.916(4), Pt(2)–Os(4) 2.816(4), Pt(2)–Pt(5) 2.667(2), Os(3)–Pt(2) 2.849(4), Os(3)–Os(6) 2.876(3), Os(4)–Pt(5) 2.869(4), Pt(5)–Os(6) 2.658(4).

num cluster with novel properties, this puckered hexanuclear raft structure being formed reversibly from a triangular cluster.

The reaction between $(CO)_2PtMe_2$, prepared from $(C_8H_{12})PtMe_2$, [(C_8H_{12}) = cyclo-octa-1,5-diene] and $H_2Os_3(CO)_{10}$ in dichloromethane, gave two products which could be separated on a silica gel column with hexane–dichloromethane (3:1) as eluant. The major product (**1**), with an intense red colour, was obtained in 55—60% yield. It showed no ^1H n.m.r. signals, and elemental analyses also indicated the absence of hydride. ESCA data were recorded in the regions of Os4f, Pt4f, C1s, and O1s, and the intensities of the Os and Pt signals indicated a *ca.* 2:1 molar ratio of osmium to platinum. Crystals of good quality were obtained by cooling a saturated dichloromethane solution, and the crystal structure of (**1**) was determined (Figure 1).†

The hexanuclear core consists of two edge-sharing butterflies. The osmium–platinum distances of *ca.* 2.65 Å are as found in $OsPt_2(CO)_5(PPh_3)_2(C_2Me_2)$ (mean 2.67 Å),[2] and also in compound (**2**) (*vide infra*). Osmium–osmium distances close to 2.9 Å are as found in most osmium clusters.[1] The platinum–platinum distance of 2.67 Å is as found in similar systems, *e.g.* in $Fe_3Pt_3(CO)_{15}^-$, 2.66[3] and $Pt_3(CO)_3(\mu\text{-}CO)_3^{2-}$, 2.66 Å,[4] both of which contain a central platinum triangle. There are four elongated metal–metal bond distances in the compound: the platinum–osmium distances defining the central butterfly, 2.82–2.92 Å. $Os_6(CO)_{20}[C{=}C(H)R]$[5] has a similar but more planar core and shows the same pattern of elongated metal–metal distances. Generally the angles between two adjacent planes in (**1**) are *ca.* 40°, whereas in $Os_6(CO)_{20}[C{=}C(H)R]$ the three triangles are essentially coplanar, while the triangle co-ordinating the alkyne ligand is orientated out of the plane by 34°.

In both (**1**) and $Os_6(CO)_{20}[C{=}C(H)R]$ there are two electrons in excess of the number based on the 18-electron rule, when nine two-centre two-electron (2c–2e) bonds are assigned to the structure. However, it is known that 2c–2e bonds are a simplification in many of these systems. Two electrons in excess were also found for $Fe_3Pt_3(CO)_{15}^{2-}$,[6] a planar platinum-containing mixed metal cluster. The two extra electrons in $Fe_3Pt_3(CO)_{15}^{2-}$ are found in an antibonding orbital.[6]

Treatment of the red solution of (**1**) with carbon monoxide (50 atm) gave a yellow solution of another cluster compound (**2**), which is not stable under ambient conditions. If left in air at room temperature, the yellow solution of (**2**) quickly darkens, and the resultant solution contains up to 30% of (**1**), indicating reversible behaviour. Crystals of (**2**) were obtained by cooling a dichloromethane solution. So far the crystal structure of (**2**) has not been successfully refined,† probably owing to disorder or unsuccessful correction for the absorption effects. However, it is clear that this cluster has a triangular metal core and ten terminal carbonyl ligands, *i.e.* $Os_2Pt(CO)_{10}$ (Figure 2). This result is in agreement with ESCA and i.r. data,‡ and elemental analysis.

The ^{195}Pt n.m.r. spectra‡ of (**1**) showed only one signal; the coupling constant of *ca.* 1800 Hz was also found in the ^{13}C n.m.r. spectrum indicating a Pt–CO group. The rather complicated ^{13}C n.m.r. spectrum showed six major sharp signals and one broad signal, and the number of signals did not correspond to the number of chemically inequivalent carbonyl groups found in the structure. A spectrum recorded at −50 °C was different, but no less complicated. These ^{13}C n.m.r. data are consistent with some kind of fluxional process within the cluster. No further attempts were made here to assign the ^{13}C signals of (**1**) nor to study this fluxional process.

† *Crystal data* for (**1**): $C_{18}O_{18}Os_4Pt_2$, M = 1655.2, orthorhombic, space group $P2_1cn$ (alternative setting of $Pna2_1$, No. 33), a = 10.325(2), b = 15.549(3), c = 17.748(3) Å, U = 2849.2(5) Å^3, Z = 4, μ(Mo-K_α) = 277.5 cm^{-1}, R = 0.068, (R_w = 0.083) for 2242 intensities. Data were collected on a CAD4 diffractometer in the ω–2θ mode with ω scan width = 0.70 + 0.50 tan θ, 3630 intensities measured ($3 \leq \theta \leq 27°$, $+h$, $+k$, $+l$), 3252 unique intensities, corrected for Lorentz, polarization, and absorption effects, giving 2242 intensities with $I > 2\sigma(I)$. Direct methods for Os and Pt followed by difference Fourier to locate carbon and oxygen; full-matrix least-squares refinement, Pt and Os only were refined anisotropically.

Crystal data for (**2**): $C_{10}O_{10}Os_2Pt$, M = 855.6, triclinic, space group $P\bar{1}$, a = 7.081(2), b = 9.004(2), c = 12.888(4) Å, α = 98.46(2), β = 98.54(2), γ = 74.36(2)°, U = 777.6(2) Å^3, Z = 2, μ(Mo-K_α) = 254.8 cm^{-1}, R = 0.11 (R_w = 0.14) for 2687 intensities. Data were collected on a CAD4 diffractometer in the ω–2θ mode with ω scan width = 1.00 + 0.50 × tan θ; 3830 intensities measured ($3 \leq \theta \leq 27°$, $+h$, $\pm k$, $\pm l$), 3364 unique intensities, corrected for Lorentz, polarization, and absorption effects, giving 2687 intensities with $I > 2\sigma(I)$. Refinement as for (**1**) gave residual electron density ($\approx \pm 14$ e/Å^3) near (~0.9 Å) the Os and Pt atoms in the difference Fourier map. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the University of Bonn. See Notice to Authors, Issue No. 1.

‡ *I.r. data* for (**1**): $\nu(CO)_{max.}$ cm^{-1}: 2091s, 2067vs, 2033s, 2008m; (**2**): $\nu(CO)_{max.}$ cm^{-1}: 2069vs, 2025s, 1998m, 1981m. N.m.r. ($CDCl_3$, room temp.) for (**1**): ^{13}C, δ: 168.2, 172.2, 173.6, 174.6, 178.5br., 178.8 ($J_{Pt\text{-}C}$ 1802 Hz), 180.3 (poor S/N ratio; treasure height: 20% of max. height, *i.e.* peaks less than 20% of max. height were omitted); ^{195}Pt (preliminary spectra of ^{13}C enriched sample, no internal reference): multiplet, 2:1:15:1:2 ($J_{unassigned}$ 916, $J_{Pt\text{-}C}$ 1819 Hz).

The triangular compound (**2**) easily dimerizes to give the pleated core of (**1**). The reaction can be reversed in an autoclave charged with carbon monoxide [equation (1)]. This reversible dimerization of two triangular units, together with the metal–metal distances found in (**1**), is consistent with the structure found. The pleated structure could be viewed as two triangles held together by one strong interaction, the platinum–platinum bond. The two weaker interactions, *i.e.* the elongated osmium–platinum distances, allow (**1**) to adopt a pleated structure. These weak elongated osmium–platinum bonds can be understood in terms of an occupied antibonding molecular orbital. The deviation from a planar structure is due to nonbonded repulsions between the carbonyl groups, analogous to that of the twisted 'bow-tie' clusters. In these nonplanar 'bow tie' clusters, *e.g.* $Os_5(CO)_{19}$, the twisted conformation is merely a consequence of the finding that the orbitals in the central, T-shaped $Os(CO)_3$ fragment favour planar configurations to a lesser degree than $Os(CO)_4$ fragments.[6]

$$2\ Os_2Pt(CO)_{10} \rightleftharpoons Os_4Pt_2(CO)_{18} + 2\ CO \qquad (1)$$

This dimerization can be compared to similar reactions of other platinum clusters. The formation of $Fe_4Pt_6(CO)_{22}^{2-}$, a decanuclear structure with a central tetrahedral platinum unit,[3] is thought to take place by dimerization of two planar $Fe_2Pt_3(CO)_{11}^{-}$ units. The platinum anion $Pt_3(CO)_6^{2-}$ also tends to dimerize by forming anions with stacked platinum triangles. Several anions of the general formula $Pt_{3n}(CO)_{6n}^{2-}$ (n = 1—6, ≈ 10) have been characterized.[4]

The core structure found in (**1**) has not been observed in cluster compounds previously prepared. This core resembles a step or a disorder of a surface. As such positions on a surface are often considered to be catalytically active,[7] this cluster might be used as a model system to study such interactions. The key question then would be if the core remains intact upon co-ordination of, say, alkyne ligands.

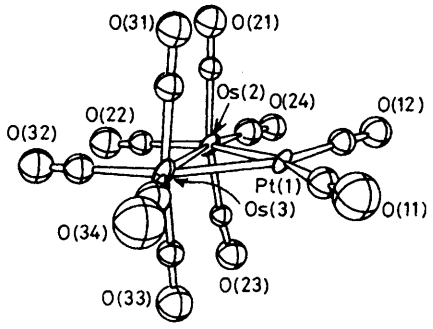

Figure 2. The structure of $Os_2Pt(CO)_{10}$, (**2**). Preliminary bond distances (Å): Os–Os: 2.860(2); Os–Pt: 2.669(2) and 2.689(2); Os–C(range): 1.81(5)—1.97(4); Pt–C: 1.86(4) and 1.87(4); C–O (range): 1.05(5)—1.26(6).

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