

Reversible Addition of Hydrogen and Carbon Monoxide to a *closo*-Triosmiumplatinum Cluster: X-Ray Crystal Structures of $[\text{Os}_3\text{Pt}(\mu\text{-H})_4(\text{CO})_{10}\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$ and $[\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{11}\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$

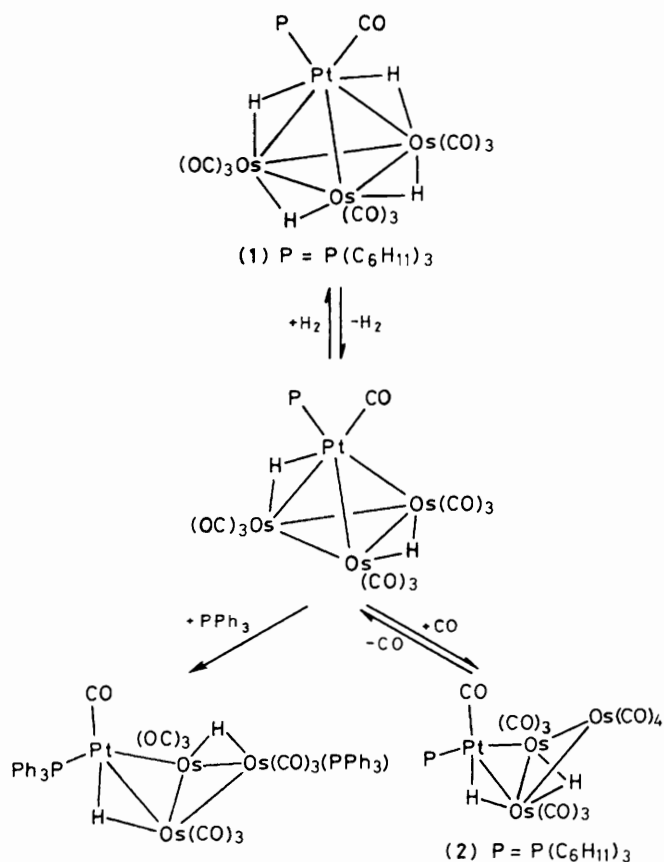
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Treatment of $[\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$ with either H_2 or CO results in 1 : 1 adduct formation affording $[\text{Os}_3\text{Pt}(\mu\text{-H})_4(\text{CO})_{10}\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$ and $[\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{11}\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$, respectively, both of which revert to the starting complex under N_2 purge; the structures of the adducts have been determined by X-ray crystallography, the tetrahydrido-species adopting a *closo*-structure and the CO complex a butterfly structure for the metal atom core.

The reversible addition of CO to metal atom clusters is becoming well established but that of H_2 is a rare phenomenon.¹⁻³ Hitherto there seem to have been no examples of a cluster complex which shows well authenticated reversible reactivity

towards both H_2 and CO, although such processes have obvious implications for catalysis.

The 58-electron triosmiumplatinum cluster $[\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$,³ which is formally unsaturated, readily



Scheme 1

reacts with H₂ (200 atm) in diethyl ether affording a yellow solution and yellow crystals of (1). Removal of H₂ pressure and purging the system with N₂ allowed recovery of the parent complex (ca. 70% after one cycle of H₂ uptake and loss).

An X-ray diffraction study of (1) established^{†‡} that there were two crystallographically independent molecules in the unit cell, differing only in the conformations of the cyclohexyl groups. One molecule is shown in Figure 1. The metal atom core is *closo*, and the hydrido-ligands bridge two Pt-Os and two Os-Os edges, as inferred from the molecular geometry and potential energy calculations.⁴ As in the isoelectronic compound [Os₄(μ-H)₄(CO)₁₂],⁵ four metal-metal distances in (1) are 'long' and two are 'short' the Os₃Pt framework being distorted from *T_d* to approximate *D_{2d}* symmetry. Co-ordination about the platinum atom is approximately trigonal bipyramidal

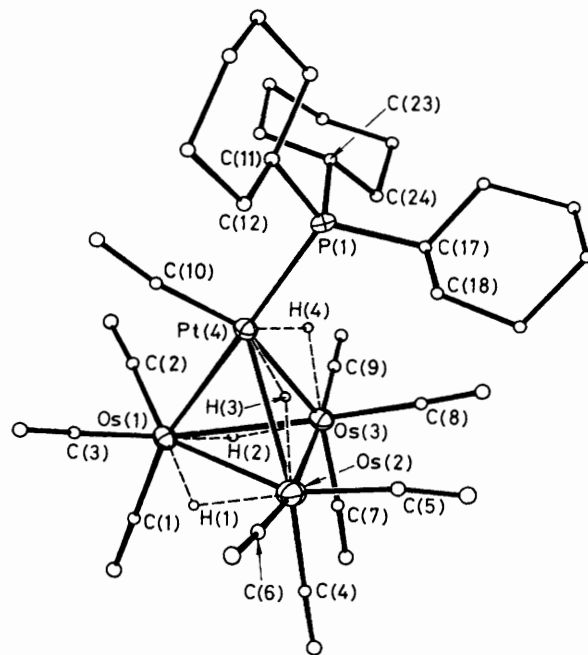


Figure 1. Molecular geometry of one of the two independent molecules of (1). Important interatomic averaged distances are: Os(1)-Os(2) 2.998(4), Os(1)-Os(3) 2.976(4), Os(1)-Pt(4) 2.717(4), Os(2)-Os(3) 2.867(4), Os(2)-Pt(4) 3.009(4), Os(3)-Pt(4) 2.935(4), Pt(4)-P(1) 2.373(11) Å.

with the phosphine ligand in one apical site, and an osmium atom, Os(1), in the other, with the CO and H ligands in equatorial sites. The ¹H n.m.r. spectrum (CD₂Cl₂, -80 °C) showed signals at δ -15.5 [s, 2H, μ-HPtOs, *J*(PtH) 570 Hz] and -20.77 [s, 2H, μ-HOs₂], consistent with a structure in solution the same as that established in the solid state.

Thus the parent *closo*-Os₃Pt 58-electron cluster reacts reversibly with molecular hydrogen to give a *closo*-Os₃Pt tetrahydrido-60-electron species. In view of the interesting retention of a closed structure it became important to establish what geometrical changes were involved in the reaction of CO, an alternative source of two electrons, with *closo*-[Os₃Pt(μ-H)₂(CO)₁₀{P(C₆H₁₁)₃}. This reaction had been previously observed to form a 1:1 adduct (2) [Os₃Pt(μ-H)₂(CO)₁₁{P(C₆H₁₁)₃}.³ Recrystallisation (CH₂Cl₂) of (2) under a CO atmosphere afforded yellow crystals suitable for single-crystal X-ray diffraction studies.^{†§}

The molecular structure (Figure 2) established that an Os(CO)₄ fragment had been generated, and that one of the original Os-Pt contacts had become non-bonding [Os(2)-Pt 3.775(1) Å]. The resulting 60-electron 'butterfly' complex (2) is thus analogous to the previously characterised triphenylphosphine complex [Os₃Pt(μ-H)₂(CO)₁₀(PPh₃)₂], which also has a non-bonded Os-Pt vector [Os-Pt 3.530(1) Å].³ The position of the hydrido-ligands in (2), and in the analogous PPh₃ adduct, were deduced from the molecular geometry and

[†] The atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[‡] *Crystal data* for (1): C₂₈H₃₇O₁₀Os₃Pt, *M* = 1330.3, orthorhombic, space group *Pccn*, *a* = 20.848(11), *b* = 36.254(26), *c* = 18.350(9) Å, *U* = 13 870(14) Å³, *Z* = 16, *D_e* = 2.55 g cm⁻³, *F*(000) = 9 689, Mo-*K*_α X-radiation (graphite monochromator), λ = 0.710 69 Å, μ(Mo-*K*_α) = 151.4 cm⁻¹. Data for (1) were collected at 210 K on a Nicolet P3m diffractometer by an ω scan technique in the range 4 ≤ 2θ ≤ 45°. The structure was solved by direct and Fourier methods, and refined by least-squares to give residual indices *R* 8.1% (*R_w* 7.6%) for 5 559 unique, absorption corrected, observed intensity data [*I* ≥ 2σ(*I*)]. All hydrogen atoms were placed in calculated positions in the final refined model.

[§] *Crystal data* for (2): C₂₉H₃₅O₁₁Os₃Pt, *M* = 1355.6, triclinic, space group *P1̄*, *a* = 10.158(5), *b* = 15.097(7), *c* = 12.007(5) Å, α = 94.06(3), β = 86.66(4), γ = 105.26(4)°, *U* = 1 770(1) Å³, *Z* = 2, *D_e* = 2.54 g cm⁻³, *F*(000) = 1 236, Mo-*K*_α X-radiation (graphite monochromator), λ = 0.710 69 Å, μ(Mo-*K*_α) = 148.3 cm⁻¹. Data were collected at 295 K in the range 3 ≤ 2θ ≤ 50°. The structure was solved and refined as for (1) to give residual indices *R* 4.8% (*R_w* 4.7%) for 3 652 unique, absorption corrected, observed intensity data [*I* ≥ 2.5σ(*I*)]. All hydrogen atoms were included in calculated positions in the final model.

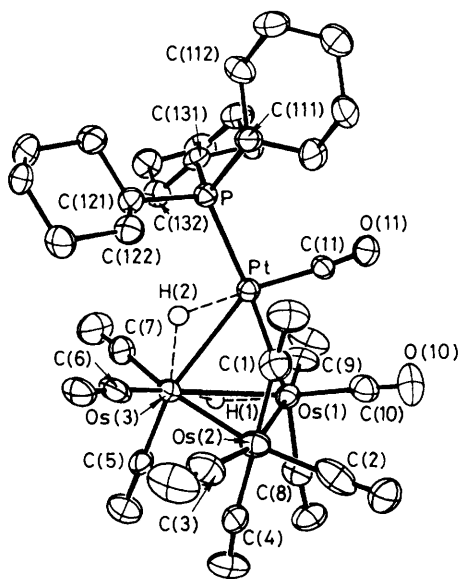


Figure 2. Molecular geometry of (2). Important interatomic distances are: Os(1)–Os(2) 2.877(1), Os(1)–Os(3) 2.869(1), Os(1)–Pt 2.729(1), Os(2)–Os(3) 2.882(1), Os(2)–Pt 3.775(1), Os(3)–Pt 2.914(1), Pt–P 2.346(4) Å.

potential energy calculations, and it is interesting that they have different arrangements, as illustrated in Scheme 1. However, in both $[\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{11}\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$ and $[\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}(\text{PPh}_3)_2]$ there is a distinct preference for a *cis*-Pt(H)(PR₃) group.

The breaking of a metal–metal bond upon CO addition to cluster molecules has been observed previously. In cyclohexane

solution, in the presence of dissolved CO, (2) is the only species present, but Fourier-transform i.r. studies showed that under an N₂ purge bands due to the parent cluster rapidly appear, there being no evidence for the formation of other carbonyl species. Thus as in the reaction with H₂, reversible adduct formation can occur. However, in contrast with the hydrogen reaction, a *closo* to 'butterfly' rearrangement of the Os₃Pt core takes place.

The different processes involve the ability of platinum to behave as a 16-electron square planar centre in (2), or as an 18-electron trigonal bipyramidal centre in (1), treating the Os–(μ-H)Pt bridge bonds as occupying one co-ordination site on platinum. Flexibility of electronic and co-ordinative properties is fundamental to chemical reactivity at mononuclear metal ion centres, particularly in homogeneous catalysis, and is here shown to pertain to cluster chemistry.

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