Synthesis of Cluster Compounds *via* Nucleophilic Metal Complexes; *X*-Ray Crystal Structures of $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{(C_6H_{11})_3P\}]$ and $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(Ph_3P)_2]$

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Summary The dihydrido complex $[H_2Os_3(CO)_{10}]$ reacts with $[Pt(C_2H_4)_2(R_3P)]$, $[Ni(C_2H_4)(Ph_3P)_2]$, $[AuMe(Ph_3P)]$, and $[Rh(acac)(C_2H_4)_2]$ to afford, respectively, $[H_2Os_3Pt(CO)_{10}(R_3P)]$ ($R = C_6H_{11}$ or Ph), $[H_2NiOs_3(CO)_{10}(Ph_3P)_2]$, $[HAuOs_3(CO)_{10}(Ph_3P)]$, and $[H_2Os_3Rh(acac)(CO)_{10}]$, while $[H_2Os(CO)_4]$ and $[Pt(C_2H_4)_2(Ph_3P)]$ yield $[H_2Os_2Pt_2(CO)_8(Ph_3P)_2]$; *X*-ray diffraction studies have established the structures of the osmium–platinum compounds.

Electron-rich d^{10} metal complexes undergo oxidative insertion reactions with electron deficient carbaboranes.[1] Several *closo*- and *nido*-platinacarbaboranes have been obtained in this manner *via* formal addition of an electron-pair metal-centre to the cage structures.[2] This approach to the synthesis of cluster[3] compounds might be applicable to the preparation of heteronuclear transition metal complexes by judicious combination of electron-deficient and electron-rich species. Herein we describe reactions of the electronically unsaturated dihydride $[H_2Os_3(CO)_{10}]$[4] with d^8 and d^{10} complexes.

Pentane solutions of $[H_2Os_3(CO)_{10}]$ react at room temperature with the complexes $[Pt(C_2H_4)_2(R_3P)]$ ($R = Ph$ or C_6H_{11}) to afford (60—80%) dark green crystalline compounds $[H_2Os_3Pt(CO)_{10}(R_3P)]$ [**1**, R = Ph, m.p. 140—145 °C (decomp.), ν_{CO}(cyclohexane) 2 079m, 2 053sh, 2 045s, 2 029vw, 2 019s, 1 989s, 1 975m, 1 963w, and 1 947w cm^{-1}; **2**, R = cyclo-C_6H_{11}, m.p. 176—178 °C (decomp.), ν_{CO}(cyclohexane) 2 075m, 2 043s, 2 017s, 1 985m, 1 973m, 1 959w, 1 943m, and 1 913vw cm^{-1}]. Examination of the ^1H n.m.r. spectra revealed that the complexes undergo dynamic behaviour in solution. Thus the ^1H spectrum ($CDCl_3$) of (**1**) at room temperature showed a broad hydride signal at *ca.* τ 17 which at −60 °C changed to two sharp resonances at τ 16·16 [s, ^2J(PtH) 8 Hz] and 17·52 [d, ^2J(PH) 16, ^1J(PtH) 590 Hz]. In order to establish the molecular structure of the complexes $[H_2Os_3Pt(CO)_{10}(R_3P)]$ a single crystal *X*-ray diffraction study was carried out on compound (**2**).†

Crystal data: $C_{28}H_{35}O_{10}Os_3PPt$, *M* 1328·2, monoclinic, space group $P2_1/c$, $a = 11{\cdot}822(4)$, $b = 16{\cdot}584(5)$, $c = 17{\cdot}763(9)$ Å, $\beta = 108{\cdot}10(4)°$, $U = 3310(3)$ Å^3, $Z = 4$, $D_m = 2{\cdot}55$, $D_c = 2{\cdot}67$ g cm^{-3}, $F(000) = 2416$, $\mu(\text{Mo-}K_\alpha) = 166{\cdot}6$ cm^{-1}. Current *R* 0·046 (R′ 0·048) for 6586 absorption corrected intensities [200 K, $2\theta \leqslant 60°$, $I \geqslant 2\sigma(I)$, Syntex $P2_1$ diffractometer, Mo-K_α ($\lambda = 0{\cdot}71069$ Å)].

The molecular structure (Figure 1) shows that the osmium atoms form an essentially isosceles triangle to which the platinum atom is asymmetrically bonded [Pt–Os(1), 2·863(2); Pt–Os(2), 2·791(2); and Pt–Os(3), 2·832(2) Å]. The *X*-ray study also reveals that a carbonyl ligand has migrated onto the platinum atom, which also carries the tricyclohexyl phosphine group. Evidence for the presence of bridging hydrogen atoms between Os(1)–Pt and between

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† The atomic co-ordinates for this work 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.

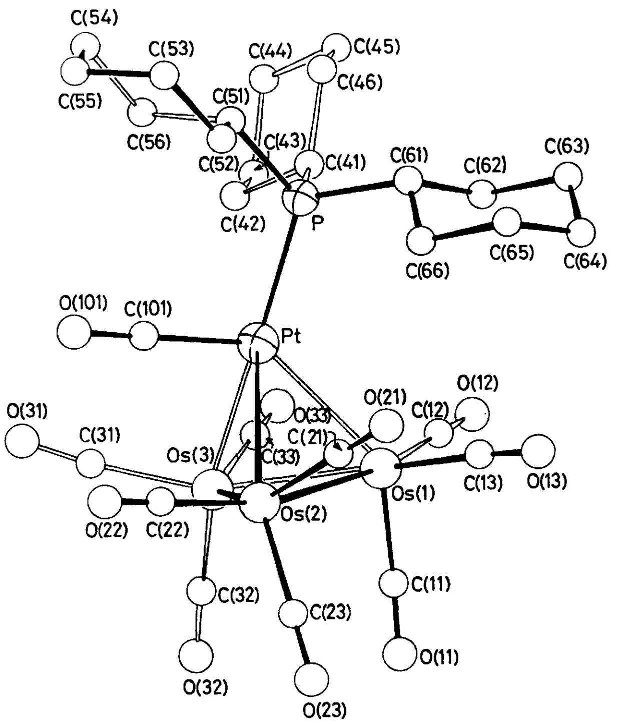

FIGURE 1. Molecular structure of $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{(C_6H_{11})_3P\}]$; Pt–Os distances are given in the text, Os(1)–Os(2), 2·778(2); Os(2)–Os(3), 2·789(2); Os(1)–Os(3), 2·741(2); and Pt–P, 2·373(4) Å

Os(2)–Os(3), the two longest edges of their type, is given in the electron-density difference maps. The usual associated widening of the equatorial Os–Os–CO angles is also observed [∠Os(2)–Os(3)–C(31), 110°; ∠Os(3)–Os(2)–C(22), 112°; the other *cis* Os–Os–C angles range from 81 to 105°]. A resonance in the ^1H n.m.r. spectrum of (**2**) at τ 16·9 is assigned to the [Os(μ-*H*)Os] bridge. The other high field signal at τ 18·4 [*J*(PtH) 583 Hz] is ascribed to [Os(μ-*H*)Pt].

The complexes (**1**) and (**2**) are '58-electron' clusters and as such are formally unsaturated.[3] Accordingly, compound (**1**) reacts with CO, Ph_3P, or Ph_3As to afford quantitatively the '60-electron' species $[H_2Os_3Pt(CO)_{10}(Ph_3P)L]$ [L = CO (**3**), Ph_3P (**4**), and Ph_3As (**5**)]. Acetylene also readily reacts with (**1**). The entering ligands L in (**3**)—(**5**) are bonded to either Os(2) or Os(3). Thus the ^{31}P (^1H decoupled, room temperature, $CDCl_3$ solution) n.m.r. spectrum of (**4**) showed two singlet resonances at 7·33 and −30·76 p.p.m. [rel. to H_3PO_4 (external)] with only the latter having platinum satellites [*J*(PPt) 2501 Hz].‡ Partial decoupling experiments revealed that each phosphorus nucleus was coupled with only one hydrido ligand, and the ^1H n.m.r. spectrum ($CDCl_3$, −60 °C) showed two doublets at τ 18·55 [*J*(PH) 20; *J*(PtH) 590 Hz] and 27·55 [*J*(PH) 15 Hz].

The unsaturated complex $H_2Os_3(CO)_{10}$ also reacts with the compounds $[Ni(C_2H_4)(Ph_3P)_2]$, $[AuMe(Ph_3P)]$, and $[Rh(acac)(C_2H_4)_2]$ to afford, respectively, $[H_2NiOs_3(CO)_{10}(Ph_3P)_2]$ (**6**), $[HAuOs_3(CO)_{10}(Ph_3P)]$ (**7**), and $[H_2Os_3Rh(acac)(CO)_{10}]$ (**8**).

The orange complex (**6**) is not isostructural with (**4**) since the i.r. spectrum shows bridging (1 855m and 1 821m cm^{-1}) as well as terminal (2 073s, 2 065m, 2 037vs, 2 015s, 1 999s, 1 985m sh, 1 973m, and 1 959w sh cm^{-1}) carbonyl stretching bands. The ^{31}P (^1H decoupled, $CDCl_3$) n.m.r. spectrum established that one Ph_3P ligand is attached to nickel and the other to osmium {−63·6 [d, Ni*P*, *J*(PP) 6 Hz] and −2·6 p.p.m. [d, Os*P*, *J*(PP) 6 Hz]}. The ^1H spectrum showed two high field signals [τ 23·63, *J*(PH) 16 Hz; 30·20, *J*(PH) 11 Hz]. The exchange of Ph_3P for CO between the two metals also occurs in the formation of (**4**) from the related reaction of $[H_2Os_3(CO)_{10}]$ with $[Pt(C_2H_4)(Ph_3P)_2]$.

The green gold–osmium complex (**7**), m.p. 168—173 °C (decomp.) [^1H n.m.r.: τ 22·1, {Os(μ-*H*)Os}], isoelectronic with (**1**), is evidently formed *via* elimination of methane. The black crystalline rhodium–osmium cluster (**8**), m.p 130—134 °C (decomp.) has a ^1H n.m.r. spectrum [$CDCl_3$, room temperature, τ 4·50 (s, 1H, C*H*), 7·96 (s, 6 H, *Me*), 20·10 (s, 1H), and 25·55 (s, 1H)] in which the two high-field signals sharpen on cooling to −50 °C, indicating dynamic behaviour in solution, but the absence of ^{103}Rh–^1H coupling implies that rhodium–hydride bonding does not occur.

Reaction of the complexes $[Pt(C_2H_4)_2(R_3P)]$ (R = Me, C_6H_{11},Ph) with the mono-nuclear dihydride $[H_2Os(CO)_4]$ affords diplatinum–diosmium compounds $[H_2Os_2Pt_2(CO)_8(R_3P)_2]$ [**9**; R = Ph, m.p. 185—189 °C (decomp.), i.r. (cyclohexane): ν_{CO} 2 059s, 2 031vs, 2 011w, 1 981s, 1 963w, and 1 943m cm^{-1}; n.m.r.: ^{31}P (^1H decoupled, $CDCl_3$), −33·83 p.p.m. {s, ^1J(PPt) 2741, ^2J(PPt) 53·7, ^1J(PtPt) 1744 Hz}; ^1H ($CDCl_3$, room temperature), τ 2·68—2·78 (m, 30H, Ph) and 17·72 {d of d, 2H, ^2J(PH) 20, ^3J(PH) 2·5, ^1J(PtH) 520 Hz}, at 130 °C the hydride signal collapses to a triplet {*J*(PH) 11, *J*(PtH) 260 Hz}].§ An *X*-ray crystallographic study of (**9**) was undertaken.†

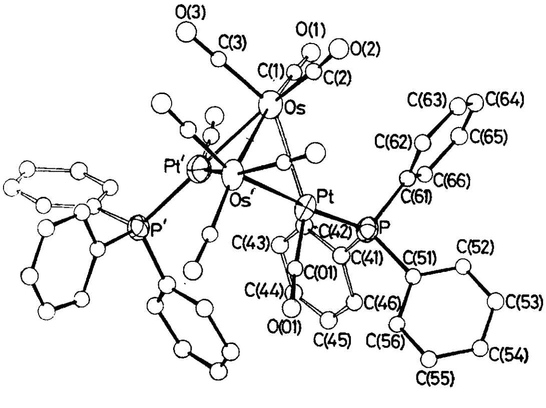

FIGURE 2. Molecular structure of $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(Ph_3P)_2]$; metal–metal distances are given in the text, Pt–P, 2·319(2) Å.

‡The down-field satellite and central peak were broadened at room temperature but sharpened at −50 °C. Moreover, at the lower temperature new low-intensity peaks appeared at −34·4 and 6·54 p.p.m. Thus the complex is stereochemically non-rigid.

§ Complex (**9**) has been observed previously (M. I. Bruce, G. Shaw, and F. G. A. Stone, *J.C.S. Dalton*, 1972, 1781) as one product of the reaction of $[H_2Os(CO)_4]$ with $[Pt(C_2H_4)(Ph_3P)_2]$.

Crystal data: $C_{44}H_{32}O_8Os_2P_2Pt_2$, M 1521·3, monoclinic, space group $C2/c$, $a = 15{\cdot}488(4)$, $b = 12{\cdot}949(3)$, $c = 21{\cdot}364(5)$ Å, $\beta = 93{\cdot}71(2)°$, $U = 4276(4)$ Å^3, $Z = 4$, $D_m = 2{\cdot}35$, $D_c = 2{\cdot}37$ g cm^{-3}, $F(000) = 2792$, $\mu(\text{Mo-}K_\alpha) = 132{\cdot}7$ cm^{-1}. Current R 0·037 (R' 0·042) for 4427 absorption-corrected intensities [200 K, $2\theta \leqslant 60°$, $I \geqslant 2\sigma(I)$].

The X-ray study reveals a 'butterfly' arrangement for the four metal atoms (Figure 2). The molecule lies astride a crystallographic two-fold axis with the Pt atoms 3·206(1) Å apart. We take this distance to indicate the absence of direct Pt–Pt bonding. The two osmium atoms (Os, Os') are asymmetrically bonded to the platinum atoms [Os–Pt, 2·8626(7); Os'–Pt, 2·7086(7) Å] and it is reasonable to suggest (μ-H) bonding along the Os–Pt and Os'–Pt' edges, an inference supported by electron density difference maps. The Os–Os' distance [2·7803(9) Å] is 0·097 Å shorter than in $[Os_3(CO)_{12}]$.[5]

We thank the S.R.C. for support.

(*Received*, 28*th December* 1977; *Com.* 1304.)

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