Notes

Preparation of Two Mixed-metal Carbonyl Clusters based on the Platinumtriosmium Core. *X*-Ray Crystal Structure of $[Os_3PtH_2(cod)(CH_2)(CO)_9]$ (cod = Cyclo-octa-1,5-diene)†

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Two saturated platinumtriosmium clusters, $[Os_3PtH_2(cod)(CH_2)(CO)_9]$ (**1**) and $[Os_3PtH_2(CH_2)(CO)_{11}]$ (**2**), have been prepared in 10—20% yield, by refluxing $[Os_3H_2(CO)_{10}]$ and $[PtMe_2(cod)]$ (cod = cyclo-octa-1,5-diene) in toluene. The crystal structure was solved for (**1**); it comprises a saturated tetrahedral Os_3Pt core bridged by two hydrides and a methylene group. The platinum atom is η^4-co-ordinated by the cod ligand. The other cluster, (**2**), has the cod ligand substituted by two carbonyls but is expected to be similar to (**1**) in all other respects. The bridging methylene group probably originates from the starting methylplatinum complex. The co-ordinated cod ligand of (**1**) has been substituted quantitatively, by treatment with carbon monoxide, to give (**2**).

The unsaturated mixed-metal cluster $[Os_3PtH_2(PR_3)(CO)_{10}]$, originally prepared by Stone and co-workers,[1] shows several interesting properties. One is the reversible addition of carbon monoxide; this results in an opening of the metal core from a tetrahedral to a 'butterfly' structure. This generation of vacant co-ordination sites is interesting from a catalytic point of view.

The aim of the present work was to produce novel carbonyl clusters, based on the platinumtriosmium core containing no phosphine ligand. For example, the synthetic route using mononuclear transition metal–cyclo-octa-1,5-diene (cod) complexes has previously been used successfully in the synthesis of $[Os_3MH_3(CO)_{12}]$ (M = Ir or Rh); the cod ligands were substituted with carbon monoxide to give the novel carbonyl cluster compounds.[2]

One method of generating metal–metal bonds is to use a metal alkyl compound and a metal hydride as reactants. This method has been employed to give metal clusters based on the platinumtetraosmium core in high yield (80%), by the reaction of $[Os_4H_4(CO)_{12}]$ with $[PtMe_2(dppe)]$ [dppe = 1,2-bis-(diphenylphosphino)ethane], as briefly reported by Lewis and co-workers.[3]

In this paper we wish to report the synthesis of two novel non-phosphine-containing platinumtriosmium clusters, prepared by refluxing $[Os_3H_2(CO)_{10}]$ and $[PtMe_2(cod)]$ in toluene. These clusters were shown to be saturated, *i.e.* all four metal atoms have 18-electron configurations.

Results and Discussion

The reaction studied in this case gave two novel mixed-metal clusters; both are believed to have the same core arrangement. A suitable crystal could not be obtained for one of them, $[Os_3PtH_2(CH_2)(CO)_{11}]$ (**2**). For the other compound, $[Os_3PtH_2(cod)(CH_2)(CO)_9]$ (**1**), single crystals of high quality were prepared and the crystal structure was determined. The structure of the platinumtriosmium core is tetrahedral, with a pseudo-mirror plane defined by Os(3)–Pt–C(methylene) (Figure). Selected bond distances and angles are collected in Table 1. Each osmium atom co-ordinates three terminal carbonyl ligands. The cyclo-octadiene ligand is η^4-co-ordinated to the platinum atom; the co-ordinating double bonds in cod are situated in a plane parallel to the basal plane of the tetrahedron (through the osmium atoms). The platinum–osmium distances are not equal nor are all the Pt–C co-ordination bond distances. A methylene group bridges Os(1)–Os(2), while two hydrides are believed to bridge Os(1)–Os(3) and Os(2)–Os(3), respectively. The assignment of the hydrides for these positions was based on spectroscopic data (^{1}H n.m.r.) and it is further supported by the elongated metal–metal bonds.

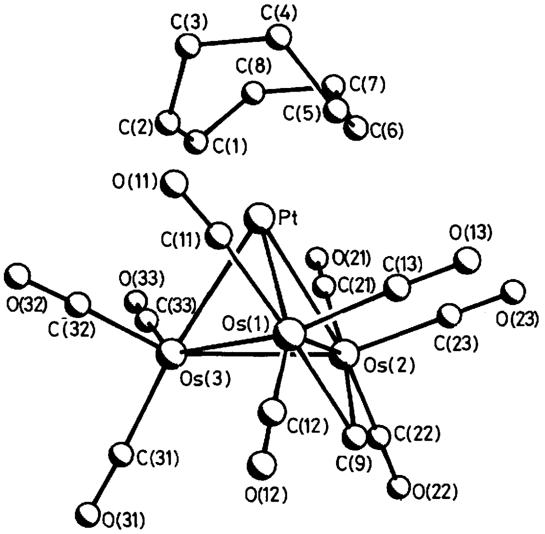

Figure. Perspective view of $[Os_3PtH_2(cod)(CH_2)(CO)_9]$ (**1**), showing the atom labelling scheme. Hydrogen atoms are omitted for clarity

The only expected change of (**2**) from the structure of (**1**) is the substitution of the cod ligand by two carbonyl groups. As the

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† 2,2,2,3,3,3,4,4,4-Nonacarbonyl-1-(η^4-cyclo-octa-1,5-diene)-di-μ-hydrido-2,3-μ-methylene-*tetrahedro*-platinumtriosmium(3 *Pt–Os*)(3 *Os–Os*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: atm = 101 325 Pa.

Table 1. Selected distances and angles for (**1**)

Distances (Å)			
Pt–Os(3)	2.712(1)		
Pt–Os(1)	2.788(1)	Pt–Os(2)	2.785(1)
Os(3)–Os(1)	2.936(2)	Os(3)–Os(2)	2.940(1)
Os(1)–Os(2)	2.833(1)		
Pt–C(1)	2.20(1)	Pt–C(2)	2.20(2)
Pt–C(5)	2.28(2)	Pt–C(6)	2.27(2)
C(9)–Os(1)	2.17(1)	C(9)–Os(2)	2.17(1)
Os(1)–C(11)	1.96(1)	Os(2)–C(21)	1.95(2)
Os(1)–C(12)	1.92(1)	Os(2)–C(22)	1.88(2)
Os(1)–C(13)	1.89(1)	Os(2)–C(23)	1.90(2)
Os(3)–C(31)	1.89(1)		
Os(3)–C(32)	1.89(1)	Os(3)–C(33)	1.91(1)
Os–C (mean)	1.91		
C–O (mean)	1.15		
Angles (°)			
Pt–Os(3)–Os(1)	59.00(2)	Pt–Os(3)–Os(2)	58.88(2)
Os(1)–Os(3)–Os(2)	57.64(3)		
Os(1)–Pt–Os(2)	61.09(3)		
Os(1)–C(9)–Os(2)	81.6(5)		
Os(1)–C(11)–O(11)	170(1)	Os(2)–C(21)–O(21)	169(1)
Os(1)–C(12)–O(12)	177(1)	Os(2)–C(22)–O(22)	178(1)
Os(1)–C(13)–O(13)	177(1)	Os(2)–C(23)–O(23)	178(1)
Os(3)–C(31)–O(31)	177(1)		
Os(3)–C(32)–O(32)	176(1)	Os(2)–C(33)–O(33)	178(2)

cluster (**1**) is saturated, no other structural changes are expected. The removal of the cod ligand is observed from ^1H n.m.r. measurements. This method of synthesis thus produces two saturated similar clusters, based on a tetrahedral platinum-triosmium core. The formation of the bridging methylene groups here is analogous to that of a bridging chlorine atom reported in $[Os_3IrH_2(\mu\text{-}Cl)(PR_3)(CO)_{10}]$.[4] In both cases a ligand migrates from the mononuclear starting complex to an osmium–osmium bridging position in the mixed-metal cluster. An identical methylene bridge is formed when the unsaturated complex $[Os_3H_2Pt(PR_3)(CO)_{10}]$ reacts with diazomethane.[1] The methylene groups in clusters (**1**) and (**2**) are not reactive towards hydrogen (50 atm, 80 °C). The methylene-bridged iron dimer, $[\{Fe(CO)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}CH_2)]$, on the other hand produces methane under even milder conditions (11 atm, 60 °C).[5] Several attempts to produce novel clusters from (**1**) and (**2**), either by removing the methylene group or by transforming it into carbido or methylidyne species, have so far failed. By small changes in reaction conditions other clusters are produced which do not appear to contain such a methylene group. Preliminary results indicate that these clusters might be unsaturated.

Experimental

The reactions were performed using standard Schlenk-tube techniques under an atmosphere of dry oxygen-free nitrogen. The solvents used, toluene and hexane, were distilled with CaH_2 and stored over molecular sieves. Separations were performed using t.l.c. plates of silica gel 60 (Merck). The i.r. spectra were recorded with a Perkin-Elmer PE580 spectrophotometer, using CaF_2 cells. At an early stage of the characterisation, ESCA (electron spectroscopy for chemical analysis) spectra were measured in order to establish the metal composition of the core; these were recorded on an AEI 200 electron spectrometer. Proton n.m.r. spectra were measured on a Varian XL300 spectrometer.

Preparation of Complexes.—In a typical reaction, $[Os_3H_2(CO)_{10}]$ (80 mg) and $[PtMe_2(cod)]$ (60 mg) were mixed in toluene and refluxed under nitrogen for 10 min. The solvent was removed under vacuum, and the residue was dissolved in hexane. Here some precipitate appeared. The precipitate was washed with dichloromethane and identified as $[Os_4H_4(CO)_{12}]$ by ^1H n.m.r., ESCA, and i.r. (*cf.* ref. 6 for i.r. data). The hexane and dichloromethane solutions were applied to a t.l.c. plate and separated using hexane as eluant to give several compounds. Two yellow compounds having R_f values greater than 0.5 were collected in 17% [(**1**)] and 12% yield [(**2**)]. Compounds (**1**) and (**2**) were recrystallised in order to give crystals suitable for *X*-ray diffraction analysis. Only crystals of (**1**) have been obtained in good quality, by cooling a filtered dichloromethane solution of the cluster compound to −20 °C, giving red-orange crystals. I.r.: $\nu_{max.}$(CO) (CH_2Cl_2) 2 082m, 2 060vs, 2 046s, 1 999s, and 1 957m cm^{-1}. N.m.r.: δ_H($CDCl_3$) 6.9 (2 H, m, μ-CH_2), 5.5 (4 H, m, CH, cod), 2.6—2.1 (8 H, m, CH_2, cod), and −20.6 p.p.m. (2 H, m, Os–H–Os).* The ESCA spectrum of (**1**) showed a molar ratio Os:Pt of 3:0.9. Compound (**2**) (that of the highest R_f value) is not stable on dry silica but decomposes to a brownish spot within 30 min. This compound was obtained as thin, fragile yellow crystals. I.r.: $\nu_{max.}$(CO) (CH_2Cl_2) 2 110w, 2 082s, 2 061vs, 2 030w, 2 015m, and 1 986w cm^{-1}. N.m.r.: δ_H($CDCl_3$) 7.3 (2 H, m, μ-CH_2) and −21.3 p.p.m. (2 H, m, Os–H–Os). The ESCA spectrum was as for (**1**) (Found: C, 13.1; H, 0.3. Calc. for $C_{12}H_4O_{11}Os_3Pt$: C, 13.2; H, 0.4%).

Reactions of Complexes (**1**) *and* (**2**).—(*a*) *Complex* (**1**) *with carbon monoxide.* Treatment of the cod complex (**1**) under carbon monoxide (1 atm) for 20 h produced some of the carbonyl complex (**2**); no other products were observed (t.l.c., i.r.). In an autoclave charged with carbon monoxide at 50 atm and room temperature, full conversion to (**2**) took place.

(*b*) *Complex* (**1**) *with hydrogen.* A toluene solution of the cod complex (**1**) was treated in an autoclave under hydrogen (70 °C, 50 atm H_2, 20 h). No products were identified (t.l.c., i.r.).

(*c*) *Complex with triphenylphosphine.* No products were observed (t.l.c., i.r.) when the cod complex (**1**) was treated in CH_2Cl_2 with an equimolar amount of triphenylphosphine (room temperature, 20 h).

(*d*) *Complex* (**2**) *with cyclo-octa-*1,5*-diene.* When the carbonyl complex (**2**) was treated with an excess of cod in CH_2Cl_2 for several days at room temperature, no substitution occurred. Immediate reaction occurred if NMe_3O in methanol was added (molar ratio 2:1). The major product formed was the cod complex (**1**), obtained in 30% yield and identified by t.l.c. and i.r.

Crystal Structure Determination of (**1**).—*Crystal data.* $C_{18}H_{16}O_9Os_3Pt$, M = 1 142, monoclinic, space group $P2_1/c$, a = 15.546(6), b = 10.015(5), c = 15.814(2) Å, β = 114.89(3)°, Z = 4, U = 2 233.4(6) Å^3 (by least-squares refinement of 25 θ values), $F(000)$ = 2 008, μ(Mo-K_α) = 246.5 cm^{-1}; red-orange air-stable crystals, dimensions 0.2 × 0.3 × 0.05 mm.

Data collection and processing. CADA diffractometer, $\omega/2\theta$ mode with ω-scan width 0.70 + 0.50 tanθ, graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å); 4 301 reflections measured ($3 \leqslant \theta \leqslant 25°$; $+h$, $+k$, $+l$), 4 151 unique reflections, corrected for Lorentz, polarisation, and absorption effects[7] (transmission range 0.014—0.175), giving 2 769 reflections with $I > 3\sigma(I)$. No systematic variation in the intensity of the standard reflections was found.

Structure analysis and refinement. Direct methods for osmium

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* Upon decoupling of the bridging hydrides, the resonance collapsed to a quartet.

Table 2. Final fractional atomic co-ordinates, with estimated standard deviations in parentheses, for $[Os_3PtH_2(cod)(CH_2)(CO)_9]$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Os(1)	0.356 64(3)	0.458 61(5)	0.837 48(3)	C(22)	0.245 2(11)	0.338 5(15)	0.545 4(11)
Os(2)	0.270 53(3)	0.466 35(5)	0.640 08(3)	C(23)	0.378 2(11)	0.533 2(15)	0.626 1(11)
Os(3)	0.148 88(3)	0.450 22(5)	0.740 39(3)	C(31)	0.093 4(9)	0.281 1(13)	0.737 3(10)
Pt	0.246 04(3)	0.676 38(5)	0.743 32(3)	C(32)	0.123 0(10)	0.512 3(16)	0.840 1(10)
C(1)	0.134 2(11)	0.829 7(13)	0.701 4(10)	C(33)	0.038 7(10)	0.530 2(14)	0.646 4(10)
C(2)	0.179 6(11)	0.827 2(14)	0.797 5(10)	O(11)	0.342 8(8)	0.656 7(11)	0.980 5(7)
C(3)	0.248 0(13)	0.929 6(20)	0.856 7(13)	O(12)	0.442 9(8)	0.238 0(11)	0.980 1(7)
C(4)	0.345 2(15)	0.934 7(19)	0.852 8(11)	O(13)	0.548 0(8)	0.561 9(12)	0.854 6(8)
C(5)	0.361 7(10)	0.834 9(15)	0.787 8(12)	O(21)	0.134 3(8)	0.673 8(11)	0.504 5(7)
C(6)	0.317 4(14)	0.840 4(14)	0.696 5(14)	O(22)	0.231 5(8)	0.256 7(13)	0.489 9(9)
C(7)	0.250 6(16)	0.938 8(20)	0.643 3(12)	O(23)	0.443 8(8)	0.572 5(14)	0.620 0(9)
C(8)	0.152 7(20)	0.938 1(19)	0.640 7(14)	O(31)	0.059 2(9)	0.180 0(10)	0.738 7(9)
C(11)	0.342 9(10)	0.593 2(14)	0.921 9(9)	O(32)	0.110 5(9)	0.544 4(12)	0.905 2(8)
C(12)	0.411 8(9)	0.321 9(14)	0.929 4(9)	O(33)	−0.025 6(8)	0.579 4(12)	0.588 5(8)
C(13)	0.475 5(9)	0.524 3(15)	0.850 1(10)	C(9)	0.354 2(10)	0.312 3(14)	0.735 2(9)
C(21)	0.186 8(19)	0.605 7(16)	0.562 0(9)				

and platinum followed by difference-Fourier synthesis to locate C and O; full-matrix least-squares refinement for these atoms. In the final refinement non-hydrogen atoms were made anisotropic. Hydrogens bound to carbon were placed in calculated positions, r(C–H) = 0.95 Å, and the thermal parameter, U_H (not refined), was 0.08 Å^2. The weighting function $w = [(\sigma_c^2/4|F_o|)^2 + (0.035|F_o|)^2]^{-1}$ was used. Final R and R' values were 0.030 and 0.040, respectively. Computer programs used and sources of scattering factor data are given in ref. 7. Final atomic co-ordinates are given in Table 2.

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