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The synthesis of Os_3Pt clusters. X-ray crystal structure of $Os_3Pt(CO)_{11}(PPh_3)_2$

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Abstract

The new clusters $Os_3Pt(CO)_{11}L_2$, where L = PPh_3 or P^tBu_2Ph, have been obtained as major products of the reaction of $Os_3(CO)_{11}(NCMe)$ with sources of PtL_2. A single crystal X-ray crystallographic investigation of the structure where L = PPh_3 indicates that the molecules consist of an equilateral triangle of osmium atoms, one edge of which is bridged by a PtL fragment. A second phosphine ligand occupies an equatorial site on the unique osmium atom. Each Os–Pt edge is bridged by a carbonyl ligand, while the remaining nine carbonyl ligands are terminally bound to osmium atoms. The minor products from the reaction of $Os_3(CO)_{11}(NCMe)$ and PtL_2 are phosphine-substituted derivatives of $Os_3(CO)_{12}$ and the raft clusters $Os_6(CO)_{21-n}(NCMe)_n$, (n = 1,2).

Introduction

There has been speculation that the incorporation of different metals within the same metallic framework may lead to reactivity quite unlike that of the known homometallic clusters. Before heterometallic cluster reactivity can be explored in detail it is necessary to devise synthetic strategies that provide selective, high-yield routes to their synthesis. One such route involves the use of the electronically or coordinatively unsaturated clusters, $H_2Os_3(CO)_{10}$ and $Os_3(CO)_{12-n}(NCMe)_n$ (n = 1 or 2) [1–4]. Typical examples are the reaction of $H_2Os_3(CO)_{10}$ with $Pt(C_2H_4)_2(PCy_3)$ to give $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)$ [2] and the reaction of $Os_3(CO)_{10}(NCMe)_2$ with $HW(Cp)(CO)_3$ which yields $Os_3WH(Cp)(CO)_{12}$ [4]. We now report the synthesis of planar triosmium–platinum cluster complexes by the reaction of $Os_3(CO)_{11}(NCMe)$ with zero-valent platinum complexes.

Results and discussion

The cluster complex $Os_3Pt(CO)_{11}(PPh_3)_2$ is obtained as the major product (over 80% yield) from the reaction of $Os_3(CO)_{11}(NCMe)$ [5] with one equivalent of $Pt(C_2H_4)(PPh_3)_2$. The structure of this complex has been determined by single crystal X-ray crystallography. The molecule consists of an equilateral triangle of osmium atoms, one edge of which is bridged by a Pt–PPh_3 fragment, with a second PPh_3 ligand occupying an equatorial site on the unique osmium atom. A perspective view of the molecule is given in Fig. 1 and some selected bond distances and angles are presented in Table 1.

The four metal atoms in cluster complex $Os_3Pt(CO)_{11}(PPh_3)_2$ adopt a planar arrangement; the largest deviation from a least-squares plane containing Pt, Os1, Os2 and Os3 is 0.023(6) Å (Pt). The two phosphorus atoms also lie in the plane defined by the metal atoms as their distances from this plane are 0.030(7) and 0.109(8) Å for P1 and P2, respectively. Each Os–Pt bond is bridged by a carbonyl ligand, with the distances between the plane defined by the metal atoms and C–O atoms being

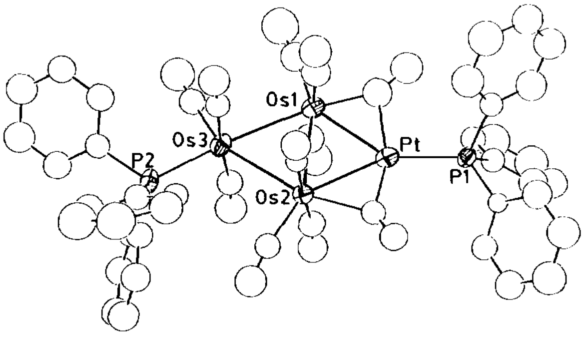

Fig. 1. An ORTEP drawing of $Os_3Pt(CO)_{11}(PPh_3)_2$ plotted as 50% probability thermal ellipsoids, with H atoms omitted.

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TABLE 1. Selected bond distances (Å) and bond angles (°)

Bond	Distance	Bond	Distance
Pt–Os1	2.715(2)	Pt–Os2	2.705(2)
Os1–Os2	2.910(2)	Os1–Os3	2.910(2)
Os2–Os3	2.900(2)	Pt–P1	2.268(7)
Pt–C11	2.17(4)	Pt–C21	2.09(3)
Os1–C11	1.93(4)	Os2–C21	2.14(3)
C11–O11	1.21(6)	C21–O21	1.15(4)
Atoms	**Angle**	**Atoms**	**Angle**
Os1–Pt–Os2	64.95(7)	Pt–Os1–Os2	57.36(10)
Pt–Os2–Os1	57.70(18)	Os2–C21–O21	142(3)
Os1–C11–O11	150(4)	Pt–C21–O21	138(3)
Pt–C11–O11	127(3)		

0.05(4) and 0.11(3) Å for C11 and O11, and 0.30(3) and 0.63(2) Å for C21 and O21. The two μ-carbonyl ligands and the two phosphorus atoms all lie on the same side of the plane defined by the metal atoms. The remaining nine carbonyl ligands are terminally bonded to the three osmium atoms, three ligands to each osmium atom, with the following average values: Os–C, 1.89(3) Å, C–O, 1.16(4) Å and Os–C–O, 172(3)°.

The Os–Os bond distances range from 2.900(2) to 2.910(2) Å (3.5σ) with an average value of 2.907(3) Å. This average distance is just statistically different (7σ) from the value reported for $Os_3(CO)_{12}$ (average value 2.877(3) Å) [6]. The Pt–Os1 and Pt–Os2 bond distances, 2.715(2) and 2.705(2) Å, respectively, are comparable with one of the values reported for the isoelectronic butterfly cluster $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2$ [7], 2.717(1) Å, but not the other, 2.848(1) Å. An Os–Pt bond distance of 2.772(4) Å is reported for the cluster $Os_3Pt(CO)_{11}(\mu\text{-}CH_2)(PPh_3)_2$ [8].

The other products from the reaction of $Os_3(CO)_{11}(NCMe)$ with one equivalent of $Pt(C_2H_4)(PPh_3)_2$ are the phosphine-substituted derivatives $Os_3(CO)_{11}(PPh_3)$ (10% yield) and $Os_3(CO)_{10}(PPh_3)_2$ (5% yield) together with traces of the raft clusters $Os_6(CO)_{21-n}(NCMe)_n$, ($n = 1,2$). The cluster $Os_3(CO)_{11}(PPh_3)$ probably results from direct reaction of $Os_3(CO)_{11}(NCMe)$ with free phosphine ligand [5] while $Os_3(CO)_{10}(PPh_3)_2$ is assumed to come from some decomposition of $Os_3Pt(CO)_{11}(PPh_3)_2$ rather than phosphine substitution on $Os_3(CO)_{11}(PPh_3)$ which requires more forcing conditions. Solutions of $Os_3Pt(CO)_{11}(PPh_3)_2$ do decompose slowly to $Os_3(CO)_{11}(PPh_3)$, $Os_3(CO)_{10}(PPh_3)_2$, and other unidentified products, on prolonged standing at 25 °C. The formation of the raft clusters $Os_6(CO)_{21-n}(NCMe)_n$, ($n = 1,2$), is consistent with the observation that $Os_3(CO)_{11}(NCMe)$ undergoes coupling reactions to generate the raft clusters in the presence of catalytic amounts of $PdCl_2$ [9]. The mechanism of this coupling reaction has not been reported. It appears that Pt(0) complexes also catalyze this reaction.

The synthetic approach can be applied to other Pt(0) complexes. The reaction of $Os_3(CO)_{11}(NCMe)$ with one equivalent of $Pt(P^tBu_2Ph)_2$ [10], yields a product distribution which is similar to that observed for $Pt(C_2H_4)(PPh_3)_2$. Spectroscopic data for the mixed metal cluster compounds are presented in Table 2. The major product formed is $Os_3Pt(CO)_{11}(P^tBu_2Ph)_2$ with $Os_3(CO)_{11}(P^tBu_2Ph)$, $Os_3(CO)_{10}(P^tBu_2Ph)_2$ and $Os_6(CO)_{21-n}(NCMe)_n$, $n = 1$ and 2, also being observed. The IR spectra of $Os_3Pt(CO)_{11}(P^tBu_2Ph)_2$, $Os_3(CO)_{11}(P^tBu_2Ph)$ and $Os_3(CO)_{10}(P^tBu_2Ph)_2$ are indistinguishable from their Ph_3 analogues in the CO stretching region. The ^{31}P NMR spectra of $Os_3Pt(CO)_{11}(PPh_3)_2$ and $Os_3Pt(CO)_{11}(P^tBu_2Ph)_2$ exhibit resonances at 7 and 31 ppm, respectively, assigned to the Os-bond P nuclei. The downfield resonances at 97 and 116 ppm with large Pt–P coupling constants are assigned to the P nuclei of

TABLE 2. ^{31}P NMR[a] and IR[b] data for the Os_3Pt products

Compound	$\delta(^{31}P)$ (ppm)	$\lvert ^1J(P\text{–}Pt)\rvert$ (Hz)	$\nu(CO)$ (cm^{-1})
$Os_3Pt(CO)_{11}(PPh_3)_2$	97 7	5146	2107w, 2092w, 2054sh, 2042m, 2026sh, 2011s, 1978m, 1843w, 1803w(br)
$Os_3Pt(CO)_{11}(P^tBu_2Ph)_2$	116 31	5533	2107w, 2092w, 2054sh, 2042m, 2026sh, 2011s, 1978m, 1843w, 1803w(br)

[a] Relative to 85% H_3PO_4, recorded in CH_2Cl_2. [b] Recorded as CH_2Cl_2 solutions.

TABLE 3. Positional and thermal parameters and their e.s.d.s.

Atom	x	y	z	U_{eq} (Å^2)
Pt	0.88342(4)	0.2500(10)	0.21501(11)	0.0454(8)
Os1	0.91918(4)	0.07144(15)	0.30668(12)	0.0474(8)
Os2	0.83502(4)	0.11489(14)	0.29118(10)	0.0381(7)
Os3	0.87022(4)	−0.07587(13)	0.39833(10)	0.0399(7)
P1	0.89431(25)	0.3990(6)	0.1254(7)	0.039(4)
P2	0.82214(27)	−0.1857(6)	0.4520(7)	0.042(5)
O11	0.9712(9)	0.2221(27)	0.2084(25)	0.091(9)
O12	0.9930(12)	−0.058(3)	0.358(3)	0.125(13)
O13	0.8962(8)	−0.0273(25)	0.0611(24)	0.083(8)
O14	0.9433(11)	0.1801(29)	0.548(3)	0.109(11)
O21	0.7949(7)	0.2981(20)	0.1337(20)	0.062(6)
O22	0.8523(8)	0.2402(25)	0.5169(25)	0.080(8)
O23	0.8091(8)	0.0054(21)	0.0620(21)	0.066(7)
O24	0.7526(9)	0.0850(24)	0.3415(23)	0.080(8)
O31	0.9415(11)	−0.2112(29)	0.5046(28)	0.101(10)
O32	0.8568(8)	−0.1898(22)	0.1674(23)	0.074(8)
O33	0.8801(9)	0.0479(26)	0.6279(26)	0.092(9)
C11	0.9429(13)	0.184(3)	0.238(4)	0.074(11)
C12	0.9643(14)	−0.004(4)	0.332(4)	0.080(12)
C13	0.9064(12)	0.013(3)	0.154(4)	0.070(11)
C14	0.9332(13)	0.127(4)	0.457(4)	0.079(12)
C21	0.8212(10)	0.2522(28)	0.1882(26)	0.048(8)
C22	0.8508(12)	0.195(3)	0.432(3)	0.063(10)
C23	0.8212(9)	0.0400(24)	0.1491(25)	0.037(7)
C24	0.7835(10)	0.0887(27)	0.3219(27)	0.052(8)
C31	0.9138(11)	−0.163(3)	0.468(3)	0.058(9)
C32	0.8622(10)	−0.1463(27)	0.2536(28)	0.047(8)
C33	0.8788(11)	0.004(3)	0.537(3)	0.060(9)
C112	0.9405(7)	0.4414(16)	−0.0341(20)	0.081(12)
C113	0.9561(7)	0.4197(16)	−0.1303(20)	0.083(12)
C114	0.9448(7)	0.3294(16)	−0.1945(20)	0.077(12)
C115	0.9179(7)	0.2607(16)	−0.1623(20)	0.098(15)
C116	0.9024(7)	0.2824(16)	−0.0661(20)	0.084(13)
C111	0.9136(7)	0.3727(16)	−0.0019(20)	0.045(8)
C122	0.8287(7)	0.5115(18)	0.1449(14)	0.056(9)
C123	0.7977(7)	0.5829(18)	0.1103(14)	0.071(11)
C124	0.7897(7)	0.6244(18)	−0.0016(14)	0.092(13)
C125	0.8127(7)	0.5944(18)	−0.0789(14)	0.084(13)
C126	0.8436(7)	0.5230(18)	−0.0443(14)	0.069(11)
C121	0.8516(7)	0.4816(18)	0.0676(14)	0.033(6)
C132	0.9241(7)	0.5989(19)	0.1930(20)	0.076(12)
C133	0.9514(7)	0.6704(19)	0.2547(20)	0.089(14)
C134	0.9853(7)	0.6359(19)	0.3351(20)	0.111(17)
C135	0.9919(7)	0.5300(19)	0.3538(20)	0.115(18)
C136	0.9646(7)	0.4584(19)	0.2921(20)	0.059(9)
C131	0.9307(7)	0.4929(19)	0.2117(20)	0.052(8)
C212	0.7667(7)	−0.1586(16)	0.2418(18)	0.048(8)
C213	0.7320(7)	−0.1831(16)	0.1583(18)	0.078(12)
C214	0.7075(7)	−0.2641(16)	0.1780(18)	0.103(15)
C215	0.7177(7)	−0.3206(16)	0.2812(18)	0.104(16)
C216	0.7523(7)	−0.2961(16)	0.3647(18)	0.066(10)
C211	0.7768(7)	−0.2151(16)	0.3450(18)	0.052(8)
C222	0.8666(7)	−0.3616(18)	0.4335(17)	0.062(10)
C223	0.8824(7)	−0.4597(18)	0.4654(17)	0.064(10)
C224	0.8728(7)	−0.5115(18)	0.5588(17)	0.080(12)
C225	0.8474(7)	−0.4652(18)	0.6202(17)	0.080(12)
C226	0.8316(7)	−0.3670(18)	0.5883(17)	0.065(10)
C221	0.8411(7)	−0.3152(18)	0.4950(17)	0.049(8)
C232	0.8291(6)	−0.1349(22)	0.6861(21)	0.071(11)
C233	0.8145(6)	−0.1083(22)	0.7828(21)	0.076(11)
C234	0.7742(6)	−0.0830(22)	0.7693(21)	0.075(11)
C235	0.7485(6)	−0.0842(22)	0.6590(21)	0.079(12)
C236	0.7631(6)	−0.1108(22)	0.5623(21)	0.070(11)
C231	0.8034(6)	−0.1362(22)	0.5758(21)	0.061(10)

(continued)

TABLE 3. (continued)

the phosphine ligands coordinated to the platinum atoms.

Experimental

Reaction of [Os$_3$(CO)$_{11}$(NCMe)] with [Pt(C$_2$H$_4$)(PPh$_3$)$_2$]

Pt(C$_2$H$_4$)(PPh$_3$)$_2$ (32 mg, 0.04 mmol) was added to a frozen dichloromethane solution of Os$_3$(CO)$_{11}$(NCMe) (40 mg, 0.04 mmol). As the solution warmed up to room temperature the colour gradually turned a deep red. The solvent was removed under vacuum and separation of the mixture was carried out by thin layer chromatography using 30% dichloromethane/70% hexanes as eluent. R_f values are not given as the plates were continuously eluted until acceptable separation was achieved. All products were characterized by comparison of their IR spectra with authentic samples, with the exception of Os$_3$Pt(CO)$_{11}$(PPh$_3$)$_2$ which was studied by single crystal X-ray diffraction. The products, with approximate yields, in the order that they separate on a TLC plate are: Os$_3$(CO)$_{11}$(PPh$_3$) (10%), Os$_3$(CO)$_{10}$(PPh$_3$)$_2$ (5%), Os$_3$Pt(CO)$_{11}$(PPh$_3$)$_2$ (80%), Os$_6$(CO)$_{20}$(NCMe) (5%) and traces of Os$_6$(CO)$_{19}$(NCMe)$_2$.

Reaction of [Os$_3$(CO)$_{11}$(NCMe)] with [Pt(P^{t}Bu$_2$Ph)$_2$]

The reaction was performed in an analogous manner to that given above except using [Pt(P^{t}Bu$_2$Ph)$_2$] (26 mg, 0.04 mmol) in place of Pt(C$_2$H$_4$)(PPh$_3$)$_2$. An identical product distribution was observed.

X-ray study of Os$_3$Pt(CO)$_{11}$(PPh$_3$)$_2$

Crystal data

C$_{47}$H$_{30}$O$_{11}$P$_2$Os$_3$Pt, $M = 1598.38$, monoclinic space group $C2$ with $a = 34.370(5)$, $b = 12.899(4)$, $c = 11.834(2)$ Å, $\beta = 103.47(1)°$, $V = 5102$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.71069$ Å), $Z = 4$, $D_c = 2.10$ g cm^{-3}; μ(Mo Kα) = 99.75 cm^{-1}.

Red crystals of Os$_3$Pt(CO)$_{11}$(PPh$_3$)$_2$ were obtained by recrystallization from diethylether at −15 °C. A crystal (approximate crystal dimensions 0.012 × 0.040 × 0.002 cm) was mounted on an Enraf-Nonius CAD4 diffractometer (graphite-monochromated Mo $K\alpha$ radiation) and cell constants and an orientation matrix were determined using the SEARCH and INDEX routines [11]. Data was collected using a $\theta/2\theta$ mode with scan width $0.80+0.35 \tan \theta$, scan speed 0.5–10.0° min^{-1}. A total of 4772 reflections was measured ($1<2\theta<50°$, $\pm h$, $+k$, $+l$). The crystal faces were identified as {100}, (010), $(0\bar{1}0)$ and {001}. The data were then corrected for absorption effects using the Gaussian method (8×16×4 grid) [11], with transmission coefficients varying from 0.346 to 0.858 and the symmetry related reflections were averaged ($R=2.0\%$ on F_{obs}). The positional coordinates for the Os and Pt atoms were obtained using the direct methods routines in the program SHELX [12]. A series of difference Fourier syntheses and least-squares refinements revealed the positions of the remaining 60 non-hydrogen atoms. After several cycles of full-matrix least-squares refinement on F, the model converged at $R=\Sigma||F_c|-|F_o||/\Sigma|F_o|| = 0.0493$ and $R_w=(\Sigma w(|F_c|-|F_o|)^2/\Sigma wF_o^2)^{1/2} = 0.0527$ (3147 unique reflections having $F_o^2>3\sigma(F_o^2)$ and 214 variables) [12]. H atoms were included in idealized positions but not refined. Pt, Os and P atoms refined with anisotropic thermal parameters and all remaining atoms refined isotropically. In the final cycle no shift exceeded 0.01 of its standard deviation. A total difference Fourier synthesis calculated from the final structure factors contained no features of chemical significance with the highest peak, of electron density 1.87 e Å^{-3}, associated with Os(2) at fractional coordinates (0.863, 0.116, 0.298). Final positional and U_{iso} thermal parameters for the atoms are given in Table 3.

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