The reactions of [HOs$_3$(CO)$_{11}$]$^-$ with main group halide species; a route to terminal and bridged mixed metal clusters. Crystal structure of [(μ-H)Os$_3$(CO)$_{10}$(μ-SbPh$_2$)]

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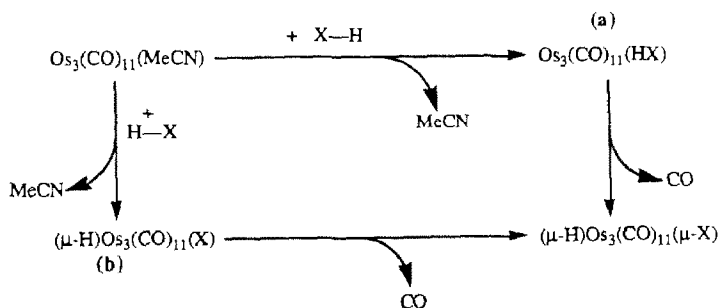(Received October 17th, 1988; in revised form January 10th, 1990)

Abstract

The trinuclear hydrido-anion [HOs$_3$(CO)$_{11}$]$^-$ (**1**) reacts with EPh$_2$Cl (E = P or Sb) to give the bridged species, (μ-H)Os$_3$(CO)$_{10}$(μ-EPh$_2$), and with I$_2$ to give initially HOs$_3$(CO)$_{11}$I and then the iodo-bridged species (μ-H)Os$_3$(CO)$_{10}$(μ-I). In contrast, reaction of **1** with SnPh$_3$Cl yields the complex, HOs$_3$(CO)$_{11}$(SnPh$_3$). The crystal structure of [(μ-H)Os$_3$(CO)$_{10}$(μ-SbPh$_2$)] is reported. Also reported are preliminary results from the reactions of [HOs$_3$(CO)$_{11}$]$^-$ with group 15 trihalide species, EX$_3$ (E = Sb, Bi).

Introduction

A number of clusters of the type [(μ-H)M$_3$(CO)$_{10}$(μ-X)] (M = Ru or Os; X = main group, three electron donor) have been reported. [1] Such species are commonly prepared from the reaction of the triosmium cluster [Os$_3$(CO)$_{12}$], or a related activated cluster (e.g., [Os$_3$(CO)$_{11}$(MeCN)]), with the appropriate main group species, X–H. Two possible reaction routes may be proposed. The first (Scheme 1a), which has been observed for compounds of the type, ER$_1$R$_2$H (E = N, P, As), involves ligand substitution to produce Os$_3$(CO)$_{11}$(X–H), followed by CO loss and the concomitant insertion of an adjacent metal atom into the X–H bond. For the species AsR$_1$R$_2$H (R$_1$,R$_2$ = Me; Ph; R$_1$,R$_2 \neq$ H), the initial substitution is rapidly followed by a metal insertion into the As–H bond. In this case, however, no
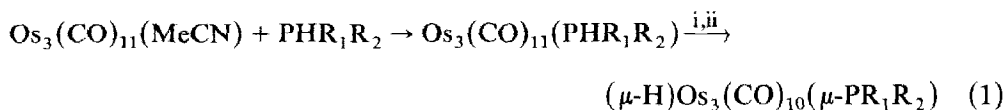

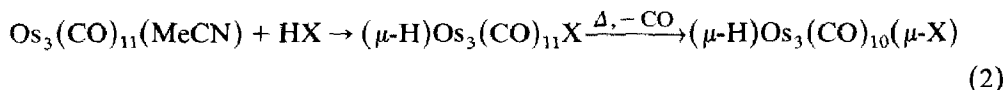* Present address: Department of Chemistry, University of Alabama, University, Alabama 35486 (U.S.A.)

$Os_3(CO)_{11}(MeCN)$ $\xrightarrow{+ \ X—H}$ $Os_3(CO)_{11}(HX)$ **(a)**

$+$
$H—X$

MeCN

MeCN

$(\mu\text{-}H)Os_3(CO)_{11}(X)$ $\longrightarrow$ $(\mu\text{-}H)Os_3(CO)_{11}(\mu\text{-}X)$
(b)

CO

CO

Scheme 1. Reaction routes resulting in $[(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}X)]$ species from $[Os_3(CO)_{11}(MeCN)]$.

carbonyl loss is observed but a metal–metal bond is ruptured [2]. The alternate route (Scheme 1b), which is the reverse of the first, has, as the initial step, the insertion of a metal atom into the X–H bond to give a one-electron-donating terminal X species, with a hydride migration to the metal triangle. The X moiety in this case has a lone pair of electrons, which can then replace a ligand on an adjacent metal atom to form the three-electron-donating bridged species.

The first route was utilised by Colbran et al. [1a] who, by a stepwise deprotonation/reprotonation pathway, prepared the phosphinidene bridged species, $[(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}PR_1R_2)]$ in high yields, from the cluster $[Os_3(CO)_{11}(PHR_1R_2)]$ (Eq. 1). The second route is that observed in the reaction of hydrogen halide species (HX) with $[Os_3(CO)_{11}(MeCN)]$ [3]. When X is chloride or bromide, the proposed undecacarbonyl intermediate in the reaction, $[(\mu\text{-}H)Os_3(CO)_{11}X]$, can be isolated [3]. Gentle thermolysis of these species results in carbonyl loss and the formation of the halo-bridged species (Eq. 2). To date there have been no reports of a reaction between a triosmium cluster and a group 15 hydride species that has been found to proceed by a route 2 type pathway.

$$Os_3(CO)_{11}(MeCN) + PHR_1R_2 \rightarrow Os_3(CO)_{11}(PHR_1R_2) \xrightarrow{i,ii}$$

$$(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}PR_1R_2) \quad (1)$$

(i: $NaCO_3/MeOH$; ii: CF_3COOH/CH_2Cl_2)

$$Os_3(CO)_{11}(MeCN) + HX \rightarrow (\mu\text{-}H)Os_3(CO)_{11}X \xrightarrow{\Delta,\ -\ CO} (\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}X)$$

$$(2)$$

X = Cl, Br and I (but proposed intermediate not isolated for X = I)

Reports of the reaction between $[HM_3(CO)_{11}]^-$ (M = Os, Ru) (1) and NO^+ to give the complexes, $[(\mu\text{-}H)M_3(CO)_{10}(NO)]$ [4], suggest that 1 may be an alternative starting material for the synthesis of bridged species. A likely intermediate in this reaction is a neutral undecacarbonyl species similar to that observed in the hydrogen halide reactions with $[Os_3(CO)_{11}(MeCN)]$ (Fig. 1). In a complex of this type the lone pair on the nitrogen should then be sufficiently basic to displace a carbonyl ligand from a neighbouring metal atom. A recent report of the synthesis of the bridged clusters, $[Fe_3(CO)_9(\mu_3\text{-}SR)(\mu\text{-}X)]$ (X = PR_2, AsR_2, SbR_2, SR and SeR) [5], from the reactions of $[Fe_3(CO)_9(\mu_3\text{-}SR)]^-$ with XCl, suggested that main group species of this type might be useful reagents for reaction with the hydrido-anion
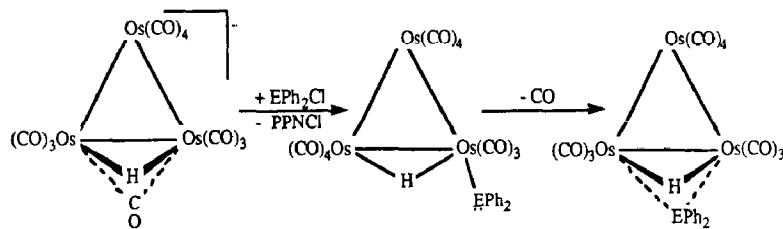
Scheme 2. Proposed route of reaction of **1** with main group halide species.

$[HOs_3(CO)_{11}]^-$ (Scheme 2). It was considered likely that the reaction between **1** and group 15 halide species would allow the isolation of a terminally bonded group 15 moiety.

Results and discussion

The reaction of $[HOs_3(CO)_{11}]^-$ (**1**) with Ph_3SnCl gives, in low yields, a compound identified as $(\mu$-$H)Os_3(CO)_{11}(SnPh_3)$ (**2**) by spectroscopic comparison (Table 1) with an authentic sample prepared as described previously [6] by the reaction of $[Os_3(CO)_{11}(MeCN)]$ with Ph_3SnH.

The reaction of **1** with I_2 in thf at reduced temperature gave two yellow compounds. The first was identified, by IR and mass spectrometry as the iodo-bridged species $[HOs_3(CO)_{10}(\mu$-$I)]$. The second, and major, product was identified as the previously proposed undecacarbonyl species, $(\mu$-$H)Os_3(CO)_{11}I$ (**3**) on the basis of a comparison of its spectroscopic data (Table 1) with those for the chloro- and bromo-analogues [3]. Compound **3** readily loses CO in solution to give the iodo-bridged species, but can be crystallised from hexane at $-30\,^{\circ}C$. As might be expected, the mass spectrum of **3** shows only the parent ion of the iodo-bridged species. In the ^1H NMR spectrum there is a singlet at a similar chemical shift to those found for the Cl and Br analogues. Microanalysis is also consistent with the formulation.

These results suggest that the initial product from this reaction is $(\mu$-$H)Os_3(CO)_{11}X$. The IR spectrum of this type of compound is distinctive, and so in subsequent reactions with group 15 halide species the progress of the way reaction mixtures monitored during the course of the reaction to try and obtain evidence for such intermediates.

In the reaction of **1** with Ph_2PCl in thf, the red solution (the colour arising from the anion) rapidly turns yellow. The reaction was monitored by IR spectroscopy and analytical TLC, and this indicated that the reaction was complete within 10 min, and that the most likely product was the phosphinidene-bridged cluster, $(\mu$-
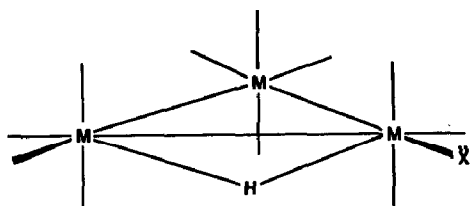

Fig. 1. Proposed intermediate in reaction of $[HM_3(CO)_{11}]^-$ with main group halide compounds.

Table 1

Infrared data for the products of $[HOs_3(CO)_{11}]^-$ and main group halides compounds

No.	Complex	IR spectrum ($\nu(CO)$) [a]	Ref.
	$HOs_3(CO)_{11}Cl$	2142vw, 2099s, 2079vs, 2066vs, 2052s, 2043vs, 2026s, 2023s, 2013m, 1990w, 1976.	3
	$HOs_3(CO)_{11}Br$	2143vw, 2100s, 2081vs, 2068s, 2056s, 2037vs, 2026m, 2016m, 1996m, 1978w.	3
3	$HOs_3(CO)_{11}I$	2141vw, 2097s, 2077vs, 2065vs, 2055s, 2038vs, 2026s, 2023s, 2015ms, 1996m, 1978w.	
2	$HOs_3(CO)_{11}(SnPh_3)$	2134vw, 2083s, 2054vs, 2048m(sh), 2031ww, 2019m, 2005ms, 1996m, 1973vw.	6
4	$HOs_3(CO)_{10}(\mu\text{-}PPh_2)$	2104w, 2057vs, 2053m, 2021vs, 2015mw, 1991m, 1978vw.	1a
5	$HOs_3(CO)_{10}(\mu\text{-}SbPh_2)$	2102mw, 2068w, 2054vs, 2022s, 2012ms, 1988mw, 1990m.	
	$[HOs_3(CO)_{11}]^- + SbCl_3$	2138w, 2087m, 2057s, 2008m.	
	$[HOs_3(CO)_{11}]^- + SbI_3$	(2 min) 2136vw, 2084m, 2053vs, 2027mw(sh), 2003m.	
	$[HOs_3(CO)_{11}]^- + BiCl_3$	(2 min) 2139vw, 2087m, 2054vs, 2005m.	
	$[HOs_3(CO)_{11}]^- + (PhH)BiCl_2 + [AlCl_4]^-$	(As for $BiCl_3$).	
	$[HOs_3(CO)_{11}]^- + BiBr_3$	(2 min) 2139vw, 2087s, 2055vs, 2034w, 2006m.	

[a] s = strong, m = medium, w = weak, v = very, sh = shoulder.

Table 2

Selected bond lengths (Å) and angles (°) for $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}SbPh_2)$ (5)

Bond lengths

Os(1)–Os(2)	2.975(1)	Os(1)–Os(3)	2.877(1)
Os(2)–Os(3)	2.894(1)	Os(1)–Sb(1)	2.633(1)
Os(2)–Sb(2)	2.638(1)	Os(1)–H(1)	1.92(3)
Os(2)–H(1)	1.94(3)		
Os(1)–C(1)	1.88(1)	Os(1)–C(2)	1.89(1)
Os(1)–C(3)	1.89(1)	Os(2)–C(4)	1.91(1)
Os(2)–C(5)	1.88(1)	Os(2)–C(6)	1.91(2)
Os(3)–C(7)	1.94(1)	Os(3)–C(8)	1.93(1)
Os(3)–C(9)	1.89(1)	Os(3)–C(10)	1.89(1)
C–O (av.)	1.14(2)		
Sb(1)–C(11)	2.112(9)	Sb(1)–C(17)	2.131(9)
C–C (Ph-rings, av.)	1.37(s)		

Bond angles

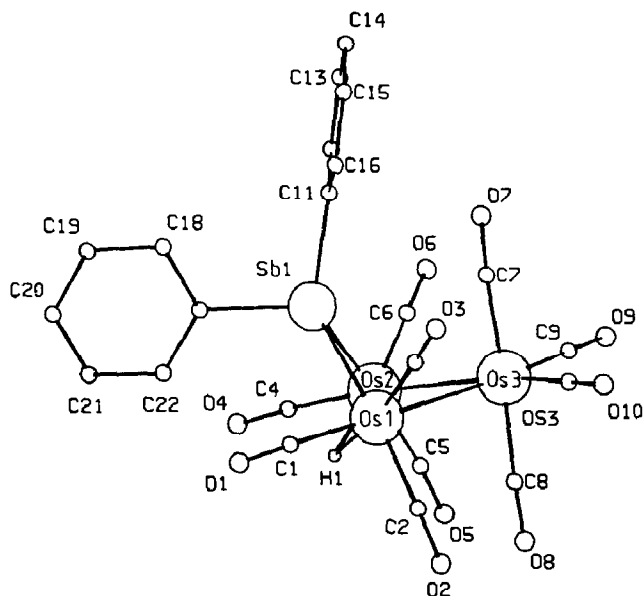|			
Os(2)–Os(1)–Os(3)	59.26(1)	Os(2)–Os(1)–Sb(1)	55.71(2)
Os(3)–Os(1)–Sb(1)	88.58(2)	Os(2)–Os(1)–H(1)	40(1)
Os(3)–Os(1)–H(1)	92 (1)	Sb(1)–Os(1)–H(1)	74(1)
Os(1)–Os(2)–Os(3)	58.68(1)	Os(1)–Os(2)–Sb(1)	55.57(2)
Os(3)–Os(2)–Sb(1)	88.12(2)	Os(1)–Os(2)–H(1)	39(1)
Os(3)–Os(2)–H(1)	91 (1)	Sb(1)–Os(2)–H(1)	74(1)
Os(1)–Os(3)–Os(2)	62.06(1)	Os(1)–H(1)–Os(2)	101(1)
Os(1)–Sb(1)–Os(2)	68.72(2)	Os(1)–Sb(1)–C(11)	129.2(3)
Os(2)–Sb(1)–C(11)	126.9(3)	Os(1)–Sb(1)–C(17)	114.3(3)
Os(2)–Sb(1)–C(17)	117.4(3)	C(11)–Sb(1)–C(17)	99.9(4)

Fig. 2. Molecular structure of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-SbPh}_2)$ (5).

H)$Os_3(CO)_{10}(\mu\text{-PPh}_2)$ (3) [1a]. Spectra taken at intermediate times gave no indication of the presence of significant quantities of a terminal-PPh_2 containing intermediate. The product was purified by TLC to give good (70–80%) yields of 4. Complex 4 was identified by spectroscopic comparison (Table 1) with an authentic sample [1a].

The analogous reaction of 1 with Ph_2SbCl gave comparable isolable yields of the unknown complex [$(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-SbPh}_2)$] (5). Again no evidence was obtained for the presence of an intermediate terminally-bonded EPh_2 species in solution. After purification by TLC, complex 5 was obtained from hexane as yellow/orange crystals, and was characterised by IR, ^1H NMR, and mass spectroscopy and microanalysis (Table 1). The data obtained were consistent with the cluster's having a structure similar to that proposed for the analogous complex 4. Complex 5 is the first reported cluster containing osmium and antimony in which the antimony moiety is not a σ-donating SbR_3 ligand.

In order to confirm the structural assignment, an X-ray crystallographic study of 5 was carried out. The molecular structure of 5, along with the atom numbering scheme is shown in Fig. 2, and selected bond lengths and angles in Table 2.

The structure of 5 is similar to those reported for [$(\mu\text{-H})M_3(CO)_{10}(\mu\text{-PHPh})$] (M = Ru [7], Os [1c,8]). The triosmium framework defines an isosceles triangle with the non-bridged edges having M–M distances, of 2.877(1) Å [Os(1)–Os(3)] and 2.894(1) Å [Os(2)–Os(3)], which are on average, 0.09 Å shorter than the M–M distance of the bridged edge. This effect is similar to, but more pronounced than, that observed in [$(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-PHPh})$] (2.88 Å (av.) non-bridged; 2.917(1) Å bridged edge) [1c,8]. We suggest that in 5 the increased steric bulk of the μ-$SbPh_2$ moiety causes a greater bond extension than that in [$(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-PHPh})$]. The inclusion of the antimony produces an Os_3Sb butterfly with a hinge angle of 112°. The antimony atom is equidistant from both Os(1) and Os(2), and the

Table 3

Atom coordinates of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-SbPh}_2)$ (5)

Atom	x	y	z	U(eq)
Os(1)	1189.7(4)	2737.2(3)	1041.0(3)	323
Os(2)	450.3(4)	3787.3(3)	2988.8(3)	358
Os(3)	3287.4(4)	4435.7(4)	2465.0(3)	388
Sb(1)	566.8(6)	1428.3(5)	2604.4(5)	308
C(1)	−292(11)	1658(11)	173(8)	433
O(1)	−1158(10)	1017(8)	−405(7)	706
C(2)	1372(12)	3910(11)	39(8)	463
O(2)	1424(10)	4575(10)	−618(8)	681
C(3)	2685(12)	1955(11)	737(8)	439
O(3)	3613(11)	1481(10)	614(7)	770
C(4)	−1488(14)	3370(11)	3187(10)	555
O(4)	−2630(11)	3203(11)	3315(10)	814
C(5)	389(14)	5488(11)	2959(10)	567
O(5)	241(12)	6519(9)	2932(11)	880
C(6)	1239(15)	3948(12)	4421(11)	643
O(6)	1714(13)	4013(12)	5260(8)	943
C(7)	3871(11)	3042(11)	3136(10)	466
O(7)	4340(9)	2302(8)	3543(9)	633
C(8)	2567(12)	5727(11)	1736(11)	512
O(8)	2220(10)	6523(8)	1302(8)	706
C(9)	4170(17)	5533(13)	3628(11)	674
O(9)	4665(14)	6205(10)	4334(10)	997
C(10)	4796(13)	4521(15)	1676(13)	586
O(10)	5670(14)	4564(14)	1194(12)	1156
C(11)	1809(10)	371(8)	3505(7)	339
C(12)	1872(12)	453(11)	4552(8)	490
C(13)	2616(17)	−271(16)	5147(10)	765
C(14)	3371(13)	−1064(12)	4699(10)	581
C(15)	3293(13)	−1137(12)	3645(9)	503
C(16)	2535(12)	−415(10)	3056(8)	468
C(17)	−1396(10)	127(9)	2289(8)	391
C(18)	−1429(11)	−1089(10)	2525(10)	490
C(19)	−2715(16)	−1934(12)	2311(12)	724
C(20)	−3923(15)	−1568(14)	1881(11)	650
C(21)	−3873(12)	−383(13)	1652(10)	605
C(22)	−2594(11)	492(10)	1842(9)	489
H(1)	−337	3364	1545	500

Os–Sb–Os angle of 68.7(2)° in 5 is significantly more acute than the Os–P–Os angle of 76.1(3)° in [$(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-PHPh})$], reflecting the greater steric bulk of the antimony atom. The hydride ligand was located directly from the electron density map, and was refined to a position 1.92(3) and 1.94(3) Å from Os(1) and Os(2), respectively. The carbonyl groups are all linear with normal bond lengths and angles. The usual feature that the M–C bonds to the equatorial ligands are slightly shorter than those to the axial ligands is observed for the carbonyls attached to Os(3).

The Sb–Ph bond distances (2.112(9), 2.131(9) Å) are in the normal range for Sb–C bonds, [9–11] and the C(11)–Sb(1)–C(17) angle of 99.9(4)° is similar to the corresponding angle in [$Ph_2Sb\text{-}O\text{-}SbPh_2$] [11], but more acute than that in the

[$-SbPh_2-$] linking moiety in [$(SbPh_3)(Ph)Fe(CO)_3 \cdot SbPh_2 \cdot Fe(CO)_4$] (C–Sb–C 102.5°) [9]. In this iron complex there is no bond between the two iron atoms (Fe–Sb–Fe 117°). In **5** the phenyl rings are normal, with all angles close to 120°. The phenyl protons were placed in calculated positions and not refined.

Although the synthesis of the bridged group 15 moiety clusters did not show any evidence suggesting the existence of a terminally bonded ER_2 species (E = group 15 element), the products of the Ph_3SnCl and I_2 reactions indicate that the most likely route is through an intermediate of this type. It is noteworthy that in route 1, the initial substituted products generally require further activation, either chemical [1a] or thermal [1c], to give the bridged species, whereas, by the method described here, only the bridged species is formed. Some insight into the relative rates of substitution and metal insertion (oxidative addition) may be drawn from this result, and the rate differences may explain why group 15 hydride species preferentially react via route 1.

It is assumed that the lone pair basicity on the main group atoms is responsible for the activity of the proposed terminally bonded ER_2 species, and so decreasing the electron density at the main group atom might allow the isolation of the terminal species. With this in mind, the reactions of **1** with the group 15 trihalides, EX_3 (E = Sb, X = Cl, I; E = Bi, X = Cl, Br) were examined. In all cases, the reaction went rapidly and the initially formed products had IR spectra consistent with the presence of a terminally bonded main group moiety. However, these species reacted further to give products that are as yet uncharacterised. Further work on these species is in progress.

Experimental

All reaction were carried out under nitrogen by standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled under nitrogen before use. The starting materials, [$HOs_3(CO)_{11}$]$^-$ [12] and $SbPh_2Cl$ [13] were prepared by published methods. Other chemicals were used as received from the various suppliers. TLC separations were carried out on silica plates (20 × 20, Merck Kieselgel $60F_{254}$, 0.25 mm thick) with mixtures of CH_2Cl_2/hexane as eluents.

(a) Reaction of [HOs_3(CO)_{11}]⁻ with Ph_3SnCl, preparation of 2

To a solution of PPN$^+$[$HOs_3(CO)_{11}$]$^-$ (9 mg, 0.006 mmol) was dissolved in Et_2O (4 ml) was added $SnPh_3Cl$ (3 mg, 0.008 mmol). The mixture was stirred and during 20 min the colour of the solution changed from red to yellow. The solvent was removed in vacuo and the residue dissolved in CH_2Cl_2 to give a bright yellow solution, which was reduced in volume to 1–2 ml and subjected to TLC. Two bands were observed with hexane/CH_2Cl_2 (60/40) as eluant:

Band 1: (minor) $HOs_3(CO)_{11}(SnPh_3)$ (**2**) by spectroscopic comparison with the reported spectrum [6] (^{1}H NMR ($CDCl_3$): −18.6 ppm).

Band 2: (moved only in 100% CH_2Cl_2); IR (CH_2Cl_2): 2109w, 2069s, 2059s, 2011vs, 1966m.

(b) Reaction of [HOs_3(CO)_{11}]⁻ with I_2, preparation of 3

A solution of PPN$^+$[$HOs_3(CO)_{11}$]$^-$ (10 mg, 0.007 mmol) in thf (3 ml) was cooled to −78°C in a dry ice/acetone bath and a solution of I_2 (1.8 mg, 0.007 mmol) in

thf (3 ml) was added slowly. The mixture was allowed to warm to room temperature, to give a yellow solution. The IR spectrum of this solution showed that all starting material had been consumed. TLC on silica plates gave two bands:

Band 1: identified by IR spectroscopy as $HOs_3(CO)_{10}(\mu\text{-I})$.

Band 2: 3 identified by IR spectroscopy (by comparison with the chloro- and bromo-analogues), ^1H NMR (-16.66 ppm) and microanalysis (Anal. Found: C, 12.96; H, 0.14. $C_{11}HIO_{11}Os_3$ calcd.: C, 13.10; H, 0.10%).

(c) Reaction of $[HOs_3(CO)_{11}]^-$ with Ph_2PCl, preparation of 4

To a solution of $PPN^+[HOs_3(CO)_{11}]^-$ (11 mg, 0.008 mmol) in thf (5 ml) was added an excess of Ph_2PCl. The mixture was stirred. An IR spectrum taken immediately after mixing indicated that no terminal $HOs_3(CO)_{11}PPh_2$ had been formed. The reaction was complete within 10 min, after which the solvent was removed in vacuo and the residue pumped to remove the surplus Ph_2PCl. The residue was dissolved in CH_2Cl_2 (1–2 ml) and purified by TLC with hexane/CH_2Cl_2 (80/20) as eluant. The only band observed on the TLC was identified as $HOs_3(CO)_{10}(\mu\text{-PPh}_2)$ (4) by comparison of its IR spectroscopic data with those previously reported [1a].

(d) Reaction of $[HOs_3(CO)_{11}]^-$ with Ph_2SbCl, preparation of $HOs_3(CO)_{10}(\mu\text{-SbPh}_2)$ (5)

To a solution of $PPN^+[HOs_3(CO)_{11}]^-$ (50 mg, 0.035 mmol) in thf (10 ml) was added an excess of Ph_2SbCl (18 mg, 0.058 mmol). The mixture was stirred and reaction found to be complete within 10 min, after which the solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 (1–2 ml) and purified by TLC with hexane/CH_2Cl_2 (80/20) as eluant. Three bands were observed by TLC but only one was identified. The major compound was characterised as $HOs_3(CO)_{10}(\mu\text{-SbPh}_2)$ (5) by comparison of its IR spectrum with that of $HOs_3(CO)_{10}(\mu\text{-PPh}_2)$, mass spec. ($M^+$ m/e 1134), ^1H NMR ((CD_2Cl_2): δ -19.79 ppm (1H, hydride), 7.95 (m, 2H), 7.55 (m, 3H), 7.35 (m, 3H), 7.12 (m, 2H)) and by X-ray crystallography (Anal. Found: C, 23.67; H, 0.98. $C_{22}H_{11}O_{10}Os_3Sb$ calcd.: C, 23.43; H, 0.98%).

(e) Reaction of $[HOs_3(CO)_{11}]^-$ with $SbCl_3$

A solution of $PPN^+[HOs_3(CO)_{11}]^-$ (11 mg, 0.008 mmol) in thf (5 ml) was added to a stirred solution of an excess of $SbCl_3$ in thf (5 ml). There was an immediate colour change from red to bright yellow and the IR spectrum recorded immediately after the addition indicated the presence of a species of the type $HOs_3(CO)_{11}X$ (2138w, 2087m, 2057s, 2008m). This was judged to be $HOs_3(CO)_{11}(SbCl_2)$. The spectrum changed rapidly with time and after 1 h, the spectrum indicated that all the initial product had reacted further. The positions of the peaks indicated that the terminal chloro-complex $HOs_3(CO)_{11}Cl$ was now the major species in solution.

(f) Reaction of $[HOs_3(CO)_{11}]^-$ with SbI_3

A solution of $PPN^+[HOs_3(CO)_{11}]^-$ (11 mg, 0.008 mmol) in thf (5 ml) was added to a stirred solution of an excess of SbI_3 in thf (5 ml). There was an immediate colour change from red to orange. The IR spectrum of the solution recorded immediately after the addition ((thf): 2036w, 2084m, 2052s, 2003m) indicated that a species of the type $HOs_3(CO)_{11}X$ was present. This was judged to be

$HOs_3(CO)_{11}SbI_2$. When the reaction was allowed to continue a precipitate was formed, the IR spectrum of which indicated that it was not pure. The IR spectrum of the supernatant solution showed that $HOs_3(CO)_{11}I$ was present, but when the solution was kept overnight this lost carbon monoxide to form $HOs_3(CO)_{10}(\mu\text{-I})$.

(g) Reaction of [HOs_3(CO)_{11}]⁻ with BiCl_3

A solution of $PPN^+[HOs_3(CO)_{11}]^-$ (11 mg, 0.008 mmol) in thf (5 ml) was added to a stirred solution of an excess of $BiCl_3$ in thf (5 ml). There was an immediate colour change from red to bright yellow. The IR spectrum of the solution, recorded immediately after the addition ((thf): 2039w, 2087m, 2054s, 2005m), indicated that a species of the type, $HOs_3(CO)_{11}X$ was present, and this was judged to be $HOs_3(CO)_{11}BiCl_2$. This initial product could not be isolated, and the IR spectrum of the solution continued to change on stirring overnight. The only products that could be isolated were small amounts of $HOs_3(CO)_{10}(\mu\text{-Cl})$ (Identified by IR spectroscopy).

(h) Reaction of [HOs_3(CO)_{11}]⁻ with BiBr_3

A solution of $PPN^+\{HOs_3(CO)_{11}]^-$ (11 mg, 0.008 mmol) in thf (5 ml) was added to a stirred solution of an excess of $BiBr_3$ in thf (5 ml). There was an immediate colour change from red to bright yellow. The IR spectrum of the solution recorded immediately after the addition. ((thf): 2039w, 2087m, 2055s, 2006m), indicated that a species of the type $HOs_3(CO)_{11}X$ was present, and this judged to be $HOs_3(CO)_{11}BiBr_2$. This initial product could not be isolated, and the IR spectrum of the solution changed on continued stirring. The products could not be purified by TLC, and the only product isolated after continued reaction was $HOs_3(CO)_{10}(\mu\text{-Br})$.

(i) Reaction of [HOs_3(CO)_{11}]⁻ with [(C_6H_6)BiCl_2]⁺ [AlCl_4]⁻

$[(C_6H_6)BiCl_2]u + [AlCl_4]^-$ was prepared by the published method [14]. A solution of (11 mg, 0.008 mmol) was in thf (5 ml) was added to a stirred solution of an excess of $[(C_6H_6)BiCl_2]^+[AlCl_4]^-$ in thf (5 ml). There was an immediate colour change from red to bright yellow. The IR spectrum of the solution, recorded immediately after the addition ((thf): 2139w, 2086m, 2054s, 2005m), indicated that $HOs_3(CO)_{11}BiCl_2$ was present. In this preparation, the complex decomposed more slowly than was the case in (g), but had completely decomposed after overnight standing.

X-ray crystallography

A light brown single crystal of dimensions $0.08 \times 0.23 \times 0.35$ mm was mounted in a glass capillary and transferred to the goniometer head on an Enraf–Nonius CAD4 diffractometer. Final unit cell dimensions, calculated from a least-squares treatment of the angles of 24 accurately determined reflections were: a 9.692(2), b 10.973(5), c 13.091(6) Å, α 92.94(4), β 97.89(4), γ 100.72(3)° and V 1351 Å³. Other parameters are: $Z = 2$, space group $P\bar{1}$ (No. 2), $D_c = 2.78$ g cm⁻³, $F(000) = 1004$, $\mu(Mo\text{-}K_\alpha)$ 151.33 cm⁻¹. 3147 reflections were collected by $\omega/2\theta$ scans (scan width $0.9 + 0.35\tan\theta$) using graphite-monochromated Mo-K_α radiation, of which 2638 with $F > 4\sigma(F)$ were considered observed and unique ($R_{merg} = 0.013$). These were corrected for Lorentz and polarisation effects, as well as for absorption (max/min correction, 2.25/0.99).

The structure was solved by routine Patterson and Fourier methods and refinement was effected through full matrix least squares methods, anisotropic thermal parameters being assigned to all non-hydrogen atoms. The bridging hydride was located from a difference map and its positional and thermal parameters refined for two cycles before it was constrained to ride upon the attached osmiums. All other hydrogens were geometrically positioned and not refined. A Chebyshev weighting scheme with coefficients 9.68, -4.36 and 7.03 gave satisfactory agreement analyses. The R and R' values were 0.0304 and 0.0349, respectively. The highest residual electron density in the difference map was 0.7 $e^-/\text{Å}^3$ near Os(3).

A table of thermal parameters and a list of observed and calculated structure factors are available from S.G.B.

Acknowledgements

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