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Preparation of $[Os_3(CO)_{11}]^{2-}$ and its reactions with $Os_3(CO)_{12}$; structures of $[Et_4N][HOs_3(CO)_{11}]$ and $H_2Os_4(CO)_{13}$

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Abstract

The dianion $[Os_3(CO)_{11}]^{2-}$ has been prepared by stoichiometric reduction of $Os_3(CO)_{12}$ with potassium-benzophenone ketyl. Infrared and ^{13}C NMR spectra (−120°C) of $[Os_3(CO)_{11}]^{2-}$ reveal the presence of a bridging carbonyl. Monoprotonation of $[Os_3(CO)_{11}]^{2-}$ with HCl gives $[HOs_3(CO)_{11}]^-$ in high yield. Reactions of $[Os_3(CO)_{11}]^{2-}$ with $Os_3(CO)_{12}$ in 3:1 and 1:1 molar ratios followed by protonation steps give mixtures of clusters: $H_2Os_4(CO)_{13}$, $H_4Os_4(CO)_{12}$, $H_2Os_3(CO)_{10}$, $H_2Os_5(CO)_{16}$, and $H_2Os_7(CO)_{20}$. The structure of $[Et_4N][HOs_3(CO)_{11}]$ was determined from a single crystal X-ray analysis. The anion structure consists of an Os_3 triangle. One Os atom is bound to four terminal carbonyls, while the other two osmiums are each bound to three terminal carbonyls and are bridged by a CO unit and apparently the H atom. Crystal data for $[Et_4N][HOs_3(CO)_{11}]$: space group $P2_1/c$, $a = 12.439(2)$ Å, $b = 11.819(9)$ Å, $c = 17.629(4)$ Å, $\beta = 97.34(1)°$, $V = 2570.4$ Å^3, $Z = 4$, mol wt = 1009.6, $\rho_{calcd} = 2.61$ g cm^{-3}, $\mu = 148.69$ cm^{-1} for Mo Kα radiation. $R_f = 0.041$, $R_{wf} = 0.063$ for 3558 independent reflections with $I \geqslant 3\sigma(I)$. $H_2Os_4(CO)_{13}$ was prepared by the reaction of $K_2[Os_3(CO)_{11}]$ with $Os(CO)_5$, generated *in situ* by the reduction of a CO_2 with $M_2[Os(CO)_4]$ (M = Na or K), followed by protonation. The structure of $H_2Os_4(CO)_{13}$ was determined from a single crystal X-ray analysis. Its molecular structure is similar to that of $H_2Ru_4(CO)_{13}$. It consists of a tetrahedral core of Os atoms. There are two semi-bridging carbonyls and two terminal carbonyls bound to the apical Os atom while the three basal Os atoms are each bound to two terminal carbonyls. These basal Os atoms are bridged by two single μ-H atoms. Crystal data for $H_2Os_4(CO)_{13}$: space group $P\bar{1}$, $a = 9.129(4)$ Å, $b = 26.551(6)$ Å, $c = 9.025(5)$, $\alpha = 91.95(4)°$, $\beta = 112.27(4)°$, $\gamma = 81.76(3)°$, $V = 2003.1$ Å^3, $Z = 4$, mol wt = 1126.8, $\rho_{calcd} = 3.74$ g cm^{-3}, $\mu = 53.98$ cm^{-1} for Mo Kα radiation. $R_f = 0.044$, $R_{wf} = 0.062$ based upon 7077 independent reflections with $I \geq 3\sigma(I)$.

1. Introduction

An earlier study from this laboratory showed that $[Ru_3(CO)_{11}]^{2-}$ will undergo redox reactions with $Ru_3(CO)_{12}$ to give higher nuclearity anions with the products determined by the stoichiometric ratios of reactants [1]. The following reactions were observed. Potassium salts of the $[Ru_4(CO)_{13}]^{2-}$ and $[Ru_6(CO)_{18}]^{2-}$ ions were isolated in over 80% yields.

$$3[Ru_3(CO)_{11}]^{2-} + Ru_3(CO)_{12} \rightarrow 3[Ru_4(CO)_{13}]^{2-} + 6CO \quad (1)$$

$$[Ru_3(CO)_{11}]^{2-} + Ru_3(CO)_{12} \rightarrow [Ru_6(CO)_{18}]^{2-} + 5CO \quad (2)$$

It was of interest to determine if the related dianion $[Os_3(CO)_{11}]^{2-}$, which was reported in a preliminary communication [2], would undergo parallel specific syntheses of higher nuclearity osmium clusters. Reported here are details of the synthesis of $[Os_3(CO)_{11}]^{2-}$, its reactions with $Os_3(CO)_{12}$, and the structures of $[Et_4N][HOs_3(CO)_{11}]$ and $H_2Os_4(CO)_{13}$.

2. Experimental details

2.1. General

All manipulations were carried out on a standard high vacuum line or in a glovebox. Solvents used were dried and degassed according to standard methods [3]. Benzophenone (J.T. Baker), $Os_3(CO)_{12}$ (Strem Chemical Co.) and carbon monoxide, 99% ^{13}C enriched (Monsanto Research Corp.) were used as received. HCl and CO_2 (Matheson Scientific Products) were

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TABLE 1. Crystallographic data for $[Et_4N][HOs_3(CO)_{11}]$ and $H_2Os_4(CO)_{13}$

Chemical formula	$C_{19}H_{21}NO_{11}Os_3$	$C_{13}H_2O_{13}Os_4$
Crystal color	Deep red	Orange-yellow
Crystal dimensions (mm^3)	0.6 × 0.4 × 0.3	0.5 × 0.9 × 0.3
Molecular weight	1009.6	1126.8
Space group	$P2_1/c$	$P\bar{1}$
Z	4	4
Temperature (°C)	25	25
a (Å)	12.439(2)	9.129(4)
b (Å)	11.819(9)	26.551(6)
c (Å)	17.629(4)	9.025(5)
α (°)		91.95(4)
β (°)	97.34(1)	112.27(4)
γ (°)		81.76(3)
Volume ($Å^3$)	2570.4	2003.1
ρ_c ($g\ cm^{-3}$)	2.61	3.74
μ (cm^{-1})	148.69	253.98
Radiation Mo Kα (Å)	0.710730	0.710730
Scan mode	$\omega-2\theta$	$\omega-2\theta$
Data collectn limits (°)	4–50	4–50
No. unique reflections	4886	8579
No. reflections with $I \geq 3\sigma(I)$	3558	7077
$R_f = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$	0.041	0.044
$R_{wf} = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma\lvert F_o\rvert^2]^{1/2}$	0.063	0.062
$w = [\sigma(I)^2 + (kI)^2]^{-1/2}$	0.06	0.03

TABLE 2. Positional parameters and e.s.d.s for $[Et_4N][HOs_3(CO)_{11}]$

Atom	x	y	z	B_{eq} ($Å^2$) [a]
Os1	0.26945(4)	0.81246(4)	0.30511(3)	3.328(9)
Os2	0.34479(4)	0.63597(4)	0.21893(3)	3.58(1)
Os3	0.11701(3)	0.67278(4)	0.21306(3)	3.442(9)
C11	0.3879(9)	0.8863(9)	0.3607(7)	3.5(2)
C12	0.1832(9)	0.8070(9)	0.3852(7)	3.7(2)
C13	0.2077(9)	0.944(1)	0.2533(7)	3.9(2)
C21	0.4942(8)	0.6365(9)	0.2307(6)	3.2(2)
C22	0.329(1)	0.651(1)	0.1083(7)	4.4(3)
C23	0.3360(8)	0.6541(8)	0.3344(6)	3.0(2)
C24	0.329(1)	0.482(1)	0.2255(7)	4.8(3)
C31	0.1373(9)	0.780(1)	0.1350(7)	3.6(2)
C32	0.0798(9)	0.558(1)	0.1449(7)	4.0(2)
C33	0.1216(9)	0.579(1)	0.3009(7)	3.8(2)
C34	−0.0127(9)	0.743(1)	0.2310(7)	4.0(3)
O11	0.4588(7)	0.9277(8)	0.3955(6)	5.6(2)
O12	0.1318(7)	0.8007(8)	0.4333(5)	5.3(2)
O13	0.1694(8)	0.9750(8)	0.2310(6)	5.9(2)
O21	0.5856(7)	0.6356(8)	0.2615(5)	4.9(2)
O22	0.3291(9)	0.646(1)	0.0460(6)	7.3(3)
O23	0.3606(7)	0.6027(7)	0.3917(4)	3.9(2)
O24	0.3220(8)	0.3830(8)	0.2307(7)	6.8(3)
O31	0.1445(8)	0.8429(8)	0.0915(5)	5.3(2)
O32	0.0569(8)	0.4857(9)	0.1017(7)	6.9(3)
O33	0.1177(7)	0.5191(8)	0.3532(5)	5.5(2)
O34	−0.0927(8)	0.7789(8)	0.2617(7)	6.8(3)
N1	0.2790(7)	0.2002(7)	0.0060(5)	2.7(2)
C1	0.332(1)	0.327(1)	0.4345(7)	5.1(3)
C2	0.344(1)	0.156(1)	0.0770(7)	4.3(3)
C3	0.1680(9)	0.145(1)	−0.0080(8)	4.7(3)
C4	0.365(1)	0.028(1)	0.0780(9)	5.0(3)
C5	0.271(1)	0.171(1)	0.5153(8)	5.3(3)
C6	0.210(2)	0.112(1)	0.4476(9)	7.2(4)
C7	0.446(1)	0.285(1)	0.4382(9)	6.7(3)
C8	0.098(1)	0.165(2)	0.062(1)	6.8(4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + abB_{1,2}\cos\gamma + acB_{1,3}\cos\beta + bcB_{2,3}\cos\alpha]$.

purified by fractionation through successive U-traps at −111°C and −126°C, and stored at −78°C. $K_2[Os(CO)_4]$ [4a] or $Na_2[Os(CO)_4]$ [4b] were prepared by previously reported methods. $Os(CO)_5$ was generated *in situ* by the reduction of CO_2 with $[Os(CO)_4]^{2-}$ in a reaction similar to that described by Maher and Cooper [5].

Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer. Proton NMR spectra (δ(TMS) = 0.00 ppm) were recorded on Bruker WM-200 and Bruker AM-500 spectrometers. Carbon-13 NMR spectra (δ(TMS) = 0.00 ppm) were recorded on a Bruker AM-500 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

X-Ray diffraction data were collected with an Enraf-Nonius CAD4 diffractometer. Crystallographic computations were carried out on a PDP 11/44 computer using the Structure Determination Package (sdp) [6*]. Table 1 gives crystallographic data for $[Et_4N][HOs_3(CO)_{11}]$ and $H_2Os_4(CO)_{13}$. Data were corrected for Lorentz and polarization effects. The intensities were also corrected for absorption by applying an empirical method based on the crystal orientation and measured psi scans.

The structure was solved by a combination of the direct method MULTAN 11/82 and the difference Fourier technique, and was refined by full-matrix least squares. Analytical atomic scattering factors were used throughout the structure refinement with both the real and imaginary components of the anomalous dispersion included. Final positional and isotropic thermal parameters for the atoms are given in Tables 2 and 3.

2.2. $[Os_3(CO)_{11}]^{2-}$

In a controlled atmosphere box, K (45.8 mg, 1.17 mmol), benzophenone (212 mg, 1.16 mmol), and $Os_3(CO)_{12}$ (506 mg, 0.558 mmol) were placed in a 250 ml flask which contained a Teflon-coated magnetic stirbar. The bulb was then attached to a vacuum line extractor and the apparatus placed on the vacuum line, evacuated and 10 ml of dry THF was condensed into the flask at −78°C. The contents of the vessel were

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* Reference number with asterisk indicates a note in the list of references.

TABLE 3. Positional parameters and e.s.d.s for $H_2Os_4(CO)_{13}$

Atom	x	y	z	B_{eq} (Å^2) [a]
Os11	0.06447(7)	0.12622(3)	0.2071(7)	2.34(1)
Os12	0.31941(7)	0.04961(2)	0.21965(7)	2.03(1)
Os13	0.39229(6)	0.14310(2)	0.40389(6)	2.01(1)
Os14	0.2811(1)	0.14294(4)	0.0694(1)	2.27(2)
Os21	−0.42912(6)	0.38136(2)	−0.32220(6)	3.10(1)
Os22	−0.18408(6)	0.31120(2)	−0.36289(6)	2.91(1)
Os23	−0.10010(6)	0.38043(2)	−0.09133(6)	2.77(1)
Os24	−0.19280(9)	0.41516(3)	−0.40850(9)	2.89(2)
O111	−0.171(2)	0.0937(6)	−0.108(2)	4.6(4)
O112	0.030(1)	0.4380(6)	−0.405(1)	5.0(3)
O113	−0.167(2)	0.2159(7)	0.247(2)	6.9(5)
O121	0.884(1)	0.9911(5)	0.099(1)	3.6(3)
O122	0.231(2)	−0.0258(5)	0.406(1)	4.2(3)
O123	0.620(2)	0.9772(6)	0.254(2)	5.0(4)
O131	0.480(2)	0.1375(7)	0.765(1)	5.0(4)
O132	0.334(2)	0.2588(6)	0.393(2)	6.2(5)
O133	0.734(2)	0.1424(8)	0.437(2)	5.9(4)
O141	0.107(2)	0.1251(7)	−0.289(1)	5.2(4)
O142	0.450(2)	0.2288(7)	0.034(2)	9.0(4)
O143	0.036(2)	0.2355(6)	0.045(2)	5.1(4)
O144	0.592(1)	0.0804(6)	0.086(2)	4.6(3)
O211	−0.669(1)	0.3810(5)	−0.664(1)	5.3(3)
O212	−0.547(1)	0.2905(5)	−0.229(2)	6.2(3)
O213	−0.658(1)	0.4548(5)	−0.222(2)	7.1(3)
O221	−0.390(2)	0.3028(6)	−0.717(2)	7.2(4)
O222	−0.277(2)	0.2181(5)	−0.271(2)	7.5(5)
O223	0.116(1)	0.2462(5)	−0.376(2)	6.9(4)
O231	−0.044(2)	0.3303(5)	0.225(1)	5.2(3)
O232	−0.153(2)	0.4902(5)	0.021(2)	6.3(4)
O233	0.249(1)	0.3809(6)	−0.030(2)	6.4(4)
O241	−0.345(2)	0.4241(5)	−0.778(1)	5.8(4)
O242	−0.060(2)	0.5154(5)	−0.360(2)	8.7(5)
O243	−0.410(1)	0.5007(4)	−0.321(1)	4.3(2)
O244	0.121(1)	0.3645(5)	−0.418(1)	5.2(3)
C111	−0.084(2)	0.1052(7)	0.011(2)	3.0(4)
C112	0.009(2)	0.0810(7)	0.333(2)	3.4(4)
C113	−0.082(2)	0.1819(7)	0.234(2)	3.3(4)
C121	0.192(2)	0.2336(6)	0.021(2)	2.6(3)
C122	0.261(2)	0.0030(7)	0.339(2)	2.7(3)
C123	1.008(2)	1.0047(7)	0.243(2)	3.2(4)
C131	0.447(2)	0.1375(7)	0.635(2)	3.2(4)
C132	0.352(2)	0.2156(6)	0.396(2)	3.2(4)
C133	0.608(2)	0.1413(8)	0.424(2)	3.6(4)
C141	0.172(2)	0.1311(8)	−0.159(2)	3.4(4)
C142	0.388(2)	0.1978(8)	0.045(2)	4.3(4)
C143	0.104(2)	0.1955(7)	0.070(2)	2.9(4)
C144	0.471(2)	0.0960(7)	0.092(2)	2.8(3)
C211	−0.582(2)	0.3810(6)	−0.536(2)	3.4(3)
C212	−0.497(2)	0.3236(7)	−0.264(2)	4.3(4)
C213	−0.583(2)	0.4304(7)	−0.269(2)	5.2(4)
C221	−0.315(2)	0.3070(7)	−0.582(2)	4.3(4)
C222	−0.242(2)	0.2524(6)	−0.310(3)	6.5(6)
C223	0.000(2)	0.2725(6)	−0.372(2)	4.8(4)
C231	−0.058(2)	0.3468(6)	0.109(2)	3.6(3)
C232	−0.127(2)	0.4484(7)	−0.023(2)	4.7(4)
C233	0.122(2)	0.3806(7)	−0.052(2)	4.3(4)
C241	−0.295(2)	0.4219(5)	−0.636(2)	3.7(3)
C242	−0.103(2)	0.4779(6)	−0.369(2)	5.5(5)
C243	−0.363(2)	0.4612(5)	−0.352(2)	3.7(3)
C244	−0.004(2)	0.3762(7)	−0.409(2)	4.0(3)
H11	0.18(3)	0.15(1)	0.42(3)	2.75
H12	0.46(3)	0.07(1)	0.44(3)	2.75
H21	−0.32(3)	0.39(1)	−0.08(3)	2.75
H22	−0.05(3)	0.31(1)	−0.13(3)	2.75

[a] Anisotropically refined atoms are given in the form of the isotropic thermal parameter defined as: $(4/3)[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + abB_{1,2}\cos\gamma + acB_{1,3}\cos\beta + bcB_{2,3}\cos\alpha]$.

stirred at room temperature for 3 h. During this time the potassium was consumed, a clear orange solution formed and CO gas was produced. THF was pumped away at room temperature. Me_2O (approx. 2 ml) was distilled into the flask along with 10 ml of dry CH_2Cl_2 at −196°C. This mixture was warmed to room temperature and stirred for about 1 h. The Me_2O was pumped away at −78°C causing the product to precipitate as a yellow-orange powder, which was filtered, washed with several portions of fresh CH_2Cl_2, and dried under vacuum. A yield of 467 mg (0.488 mmol, 87.5%) of $K_2[Os_3(CO)_{11}]$ was isolated. IR spectrum of $K_2[Os_3(CO)_{11}]$ ν(CO) (THF): 2040m, 1970s, 1950vs, 1890m,sh, 1665vw, 1625m cm^{-1}. Anal. Found: K, 8.02; C, 13.60; Os, 59.27. $K_2[Os_3(CO)_{11}]$ calcd.: K, 8.17; C, 13.80; Os, 59.62%. ^{13}C-enriched $K_2[Os_3(CO)_{11}]$ was obtained by equilibration with ^{13}CO (1 atm) over a period of 15 h. ^{13}C NMR spectrum (THF-d_8/Me_2O, −120°C): δ 185.7, 202.7, 282.0 ppm. The Na salt of $[Os_3(CO)_{11}]^{2-}$ is synthesized in a similar manner. The PPN salt of $[Os_3(CO)_{11}]^{2-}$ as well as other complex cation salts are generated by a room temperature metathesis reaction of the alkali metal cluster with a suitable salt in THF/CH_2Cl_2. IR spectrum of $[PPN]_2[Os_3(CO)_{11}]$ ν(CO) (THF): 2061w,sh, 2046w,sh, 2024s, 2006m,sh, 1994vs, 1980vs, 1958s, 1953vs,sh, 1884w,sh, 1693m cm^{-1}.

2.3. $[HOs_3(CO)_{11}]^-$

A flask containing $K_2[Os_3(CO)_{11}]$ (150 mg, 0.157 mmol) and THF was attached to an extractor. The solution was frozen at −196°C and HCl (0.173 mmol) was condensed onto it. With continuous stirring, the reaction mixture was slowly warmed to room temperature and stirred for 1 h. The mixture was filtered leaving KCl on the frit. THF was removed from the filtrate and CH_2Cl_2 was distilled onto it. The brown precipitate of $K[HOs_3(CO)_{11}]$ was stirred, filtered, washed with CH_2Cl_2 and dried under vacuum. IR and

^1H NMR spectra of the isolated $K[HOs_3(CO)_{11}]$ (129 mg, 0.141 mmol, 89% yield) are in agreement with the previously reported spectra [7] for the anion. IR spectrum ν(CO) (THF): 2080w, 2020s, 1990s, 1950s, 1700w, 1660w cm^{-1}. ^1H NMR spectrum (THF-d_8, 25°C): δ -13.8 ppm.

2.4. $[Et_4N][HOs_3(CO)_{11}]$

A 50-ml reaction flask was loaded with $K[HOs_3(CO)_{11}]$ (110 mg, 0.109 mmol) and $[Et_4N]Br$ (21.0 mg, 0.100 mmol) and a Teflon-coated stirbar and then connected to a vacuum line extractor in a controlled atmosphere box. This unit was transferred to the vacuum line and evacuated. THF and CH_2Cl_2 (5 ml each) were condensed into the flask at -196°C. The flask was warmed to room temperature and stirred for 1 h during which time a white precipitate formed. The mixed solvent was pumped away at room temperature and fresh CH_2Cl_2 (5 ml) was distilled into the reaction vessel at -196°C. The system was then warmed to room temperature in order to dissolve the $[Et_4N][HOs_3(CO)_{11}]$ and the resulting solution was filtered and KCl remained on the filter frit. The flask containing the filtrate was transferred under N_2 to another extractor. Addition of Et_2O caused precipitation of $[Et_4N][HOs_3(CO)_{11}]$. The mixture was filtered, washed with fresh Et_2O and dried under vacuum at room temperature overnight. $[Et_4N][HOs_3(CO)_{11}]$ was isolated in 90.9 mg, 0.090 mmol, 90% (based on $[Et_4N]Br$) yield. IR spectrum ν(CO) (THF): 2080w, 2020s, 1995s, 1950s, 1703w, 1680w cm^{-1}. ^1H NMR spectrum (CD_2Cl_2, 25°C): δ 3.30 (q, 8H); 1.27 (t, 12H); -13.6 (s, 1H) ppm. The spectra of the anion agree well with earlier data for the PPN salt [7]. Crystals were grown by slowly condensing Et_2O into a CH_2Cl_2 solution of the salt at room temperature.

2.5. Reactions of $K_2[Os_3(CO)_{11}]$ with $Os_3(CO)_{12}$

A 3 : 1 molar ratio mixture of $K_2[Os_3(CO)_{11}]$ (95.4 mg, 0.0997 mmol) and $Os_3(CO)_{12}$ (28.9 mg, 0.0319 mmol) was allowed to react in THF at 55°C for 2 days. The system was cooled to -196°C and HCl (0.0997 mmol) was condensed into the reaction vessel which was then warmed to room temperature and stirred for 2 h. Products were extracted with CH_2Cl_2 followed by separation using TLC (1 : 3 CH_2Cl_2/hexane) and identification by comparison with the reported [8–11] IR and ^1H NMR spectra. $H_2Os_3(CO)_{10}$ (1.2 mg, 0.0014 mmol, 1% yield), $H_4Os_4(CO)_{12}$ (1.7 mg, 0.0015 mmol, 2% yield), $H_2Os_4(CO)_{13}$ (14.6 mg, 0.0130 mmol, 13%).

A 1 : 1 molar ratio mixture of $K_2[Os_3(CO)_{11}]$ (214.2 mg, 0.2238 mmol) and $Os_3(CO)_{12}$ (203.9 mg, 0.2254 mmol) gave $H_2Os_3(CO)_{10}$ (12.1 mg, 0.0142 mmol, 3% yield), $H_4Os_4(CO)_{12}$ (21.4 mg, 0.0194 mmol, 6% yield), $H_2Os_4(CO)_{13}$ (28.6 mg, 0.0254 mmol, 7.5% yield), and a mixture of $H_2Os_5(CO)_{16}$ and $H_2Os_7(CO)_{20}$ (22 mg).

2.6. Preparation of $H_2Os_4(CO)_{13}$

A two-neck reaction vessel equipped with a magnetic stirbar, stopcock adaptor and a drip tube containing $K_2[Os_3(CO)_{11}]$ (200 mg, 0.209 mmol) in 10 ml of THF, was loaded with $Na_2[Os(CO)_4]$ (75 mg, 0.215 mmol). $K_2[Os(CO)_4]$ can be substituted for the $Na_2[Os(CO)_4]$. The vessel was evacuated and 10 ml of dry THF was distilled into it at -78°C. Dry CO_2 (0.645 mmol) was then condensed into the vessel at -196°C. The reaction mixture was allowed to warm to -78°C, stirred for 10 h, and then warmed to -22°C and stirred for 2 h. The excess CO_2 was removed by cooling the reaction mixture again to -78°C and pumping for 15 min. The $K_2[Os_3(CO)_{11}]$ solution was added slowly into the reaction mixture from the drip tube. The reaction mixture was stirred at -22°C for 2 h, warmed up to room temperature, placed in a 55°C oil bath and stirred for 8 h to ensure the complete reaction between $Os(CO)_5$ and $[Os_3(CO)_{11}]^{2-}$, and finally protonated by condensing a 50% molar excess of dry HCl gas (0.627 mmol) onto the reactants at -196°C. With continuous stirring this solution was slowly warmed to room temperature and allowed to stir for 2h. The protonated mixture was dried and CH_2Cl_2 was added to the flask; however, the major product was an insoluble red-brown solid with an IR spectrum [7] of $[HOs_4(CO)_{13}]^-$. This solid product was separated by filtration, dissolved in dry THF (10 ml) and protonated a second time with a large excess of dry HCl. The solution changed from deep orange-red to light orange within 10 min. The mixture was dried, dissolved in CH_2Cl_2 and chromatographed on a TLC plate. Elution with 1 : 3 CH_2Cl_2/hexane gave two bands. In order of decreasing R_f values, the first yellow band was identified as $H_4Os_4(CO)_{12}$ and the second orange-yellow band was identified as $H_2Os_4(CO)_{13}$ (147 mg, 0.131 mmol, 63% yield) based on comparison of the ^1H NMR and IR spectra reported in the literature [10]. IR spectrum ν(CO) (THF): 2080s, 2062s, 2052s, 2020s, 1990w, 1875br cm^{-1}. ^1H NMR spectrum (THF-d_8, 25°C): δ -21.2 ppm; ($CDCl_3$, 25°C): δ -21.4 ppm. The FT-ICR mass spectrum contains a molecular ion at 1134 (calcd. 1134 for $^1H_2\,^{192}Os_4\,^{12}C_{13}\,^{16}O_{13}$) with peaks accounting for the loss of 13 carbonyl groups. A peak of maximum intensity at m/e 1128 and the distribution of peak intensities in the envelope are in accord with that predicted [12*] for the natural abundance isotopic distribution. ^{13}C-enriched $H_2Os_4(CO)_{13}$ was obtained by equilibrating 1 atm ^{13}CO with the reaction mixture for 10 h prior to protonation. ^{13}C NMR spectrum

(d_8-THF, −110°C): δ 165.6, 167.5, 168.5, 170.9, 172.7, 184.2 ppm.

2.7. *Deprotonation of $H_2Os_4(CO)_{13}$*

Reaction of $H_2Os_4(CO)_{13}$ (75 mg, 0.066 mmol) and PPNCl (38 mg, 0.066 mmol) in THF resulted in a color change from orange to pink-red. After stirring the reaction mixture at room temperature for 30 min, hexane was added to precipitate $[PPN][HOs_4(CO)_{13}]$ which was filtered and washed with additional hexane (82 mg, 0.049 mmol, 75% yield). The IR spectrum ν(CO) (THF): 2069w, 2029s, 2014vs, 2003s, 1972m, 1937w, 1850w,br cm^{-1}. ^1H NMR spectrum ($CDCl_3$, 25°C): δ −19.1 ppm. These values are in good agreement with those in the literature [13].

3. Results and discussion

3.1. *$[Os_3(CO)_{11}]^{2-}$ and $[HOs_3(CO)_{11}]^-$*

From the following reduction reaction, (3), $K_2[Os_3(CO)_{11}]$ was isolated as a bright yellow-orange powder:

$$2K[C_6H_5COC_6H_5] + Os_3(CO)_{12} \rightarrow K_2[Os_3(CO)_{11}] + 2C_6H_5COC_6H_5 \quad (3)$$

It is sensitive to air and moisture but can be stored indefinitely in an inert atmosphere or in a vacuum. It is soluble in ethers, such as THF or glyme, and insoluble in CH_2Cl_2 and alkanes. $K_2[Os_3(CO)_{11}]$ can be converted to the $[PPN]^+$, $[Ph_4P]^+$ and $[Ph_4As]^+$ salts by the reaction with [PPN]X, $[Ph_4P]X$ and $[Ph_4As]X$ (X = halide), respectively, in THF/CH_2Cl_2.

Salts of the $[HOs_3(CO)_{11}]^-$ anion were obtained (*ca.* 90% yields) according to reactions (4) and (5).

$$K_2[Os_3(CO)_{11}] + HCl \rightarrow K[HOs_3(CO)_{11}] + KCl \quad (4)$$

$$K[HOs_3(CO)_{11}] + [ER_4]X \rightarrow [ER_4][HOs_3(CO)_{11}] + KX \quad (5)$$

$$[ER_4]X = [NEt_4]Br, \quad [PPN]Cl$$

The complex cation salts of $[HOs_3(CO)_{11}]^-$ appear to be significantly more air stable than the alkali metal salts. Procedures reported earlier for the preparation of this anion involve reaction of $NaBH_4$ with $Os_3(CO)_{12}$ [14] in refluxing THF and reaction of alcoholic KOH with $Os_3(CO)_{12}$ [7], with yields between 55 and 70%.

X-Ray crystal structure $[HOs_3(CO)_{11}]^-$ and the proposed structure of $[Os_3(CO)_{11}]^{2-}$

From a single crystal X-ray analysis, the molecular structure of $[Et_4N][HOs_3(CO)_{11}]$ was determined. The molecular configuration of the $[HOs_3(CO)_{11}]^-$ anion is shown in Fig. 1. Selected bond distances and bond angles are listed in Tables 4 and 5, respectively.

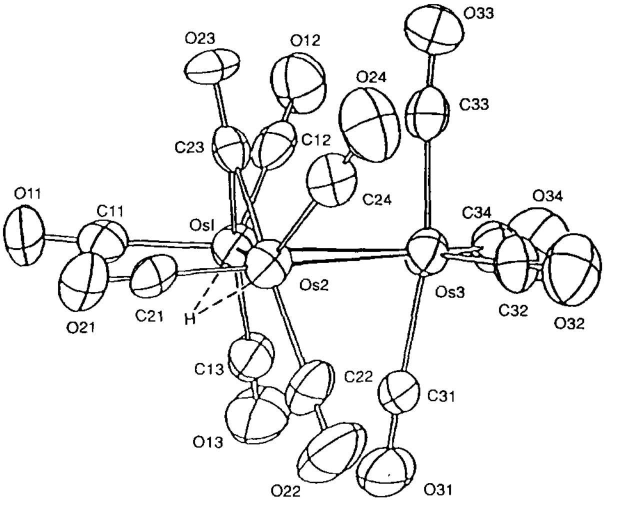

Fig. 1. Molecular structure of $[Et_4N][HOs_3(CO)_{11}]$ showing 50% probability thermal ellipsoids.

The structure consists of discrete $[HOs_3(CO)_{11}]^-$ anions and $[Et_4N]^+$ cations. The anion structure is consistent with that proposed [7] in solution based upon NMR data, and is also structurally close to $[HFe_3(CO)_{11}]^-$ [15] and $[HRu_3(CO)_{11}]^-$ [16]. It consists of an Os_3 isosceles triangle with four terminal carbonyls bound to Os(3) while Os(1) and Os(2) are linked to three terminal carbonyls and one bridging carbonyl. The hydrogen atom was not located. Its NMR chemical shift (−13.8 ppm) is consistent with that

TABLE 4. Selected bond distances (Å) and e.s.d.s for $[Et_4N][HOs_3(CO)_{11}]$

A. Metal – metal distances			
Os(1)–Os(2)	2.813(2)	Os(1)–Os(3)	2.860(3)
Os(2)–Os(3)	2.856(2)		
B. Metal – carbon distances			
Os(1)–C(11)	1.88(1)	Os(2)–C(21)	1.84(1)
Os(1)–C(12)	1.88(2)	Os(2)–C(22)	1.94(1)
Os(1)–C(13)	1.92(2)	Os(2)–C(23)	2.07(1)
Os(1)–C(23)	2.09(1)	Os(2)–C(24)	1.84(2)
Os(3)–C(31)	1.91(1)	Os(3)–C(32)	1.83(1)
Os(3)–C(33)	1.90(1)	Os(3)–C(34)	1.88(1)
C. Carbon – oxygen distances			
C(11)–O(11)	1.12(1)	C(21)–O(21)	1.13(2)
C(12)–O(12)	1.13(1)	C(22)–O(22)	1.11(2)
C(13)–O(13)	1.12(2)	C(23)–O(23)	1.18(2)
C(24)–O(24)	1.18(2)	C(31)–O(31)	1.08(1)
C(32)–O(32)	1.16(2)	C(33)–O(33)	1.16(1)
C(34)–O(34)	1.10(1)		
D. Cationic bond distances			
N(1)–C(1)	1.537(6)	C(1)–C(5)	1.492(7)
N(1)–C(2)	1.496(7)	C(2)–C(6)	1.532(6)
N(1)–C(3)	1.516(8)	C(3)–C(7)	1.600(5)
N(1)–C(4)	1.542(8)	C(4)–C(8)	1.503(4)

TABLE 5. Selected bond angles (°) and e.s.d.s for $[Et_4N][HOs_3(CO)_{11}]$

A. Metal angles			
Os(2)–Os(1)–Os(3)	60.44(2)	Os(1)–Os(2)–Os(3)	60.60(3)
Os(1)–Os(3)–Os(2)	58.96(2)		
B. Carbon – metal – carbon angles			
C(11)–Os(1)–C(12)	96.1(4)	C(11)–Os(1)–C(13)	96.4(7)
C(11)–Os(1)–C(23)	91.6(6)	C(12)–Os(1)–C(13)	99.0(4)
C(12)–Os(1)–C(23)	91.7(3)	C(13)–Os(1)–C(23)	165.9(4)
C(21)–Os(2)–C(22)	94.7(5)	C(21)–Os(2)–C(24)	94.0(9)
C(21)–Os(2)–C(24)	96.2(6)	C(22)–Os(2)–C(23)	165.9(7)
C(22)–Os(2)–C(24)	98.9(3)	C(23)–Os(2)–C(24)	92.2(4)
C(31)–Os(3)–C(32)	93.5(7)	C(31)–Os(3)–C(33)	168.9(9)
C(31)–Os(3)–C(34)	91.5(6)	C(32)–Os(3)–C(33)	94.7(7)
C(32)–Os(3)–C(34)	106.6(5)	C(33)–Os(3)–C(34)	93.2(7)
C. Carbon – metal – metal angles			
C(11)–Os(1)–Os(2)	109.6(7)	C(11)–Os(1)–Os(3)	170.0(6)
C(12)–Os(1)–Os(2)	129.9(7)	C(12)–Os(1)–Os(3)	90.4(8)
C(13)–Os(1)–Os(2)	119.0(5)	C(13)–Os(1)–Os(3)	90.1(6)
C(23)–Os(1)–Os(3)	80.5(9)	C(21)–Os(2)–Os(1)	109.7(6)
C(22)–Os(2)–Os(1)	118.5(5)	C(24)–Os(2)–Os(1)	131.0(7)
C(21)–Os(2)–Os(3)	170.1(8)	C(22)–Os(2)–Os(3)	88.7(5)
C(23)–Os(2)–Os(3)	81.0(5)	C(24)–Os(2)–Os(3)	92.3(8)
C(31)–Os(3)–Os(1)	83.6(7)	C(31)–Os(3)–Os(2)	84.6(5)
C(32)–Os(3)–Os(1)	153.4(6)	C(32)–Os(3)–Os(2)	153.8(4)
C(33)–Os(3)–Os(1)	85.8(5)	C(33)–Os(3)–Os(2)	87.4(6)
C(34)–Os(3)–Os(1)	99.9(5)	C(34)–Os(3)–Os(2)	158.8(7)
D. Metal – carbon – oxygen angles			
Os(1)–C(11)–O(11)	178(1)	Os(3)–C(31)–O(31)	177(1)
Os(1)–C(12)–O(12)	178(1)	Os(3)–C(32)–O(32)	180(1)
Os(1)–C(13)–O(13)	172(1)	Os(3)–C(33)–O(33)	176(1)
Os(2)–C(21)–O(21)	179.0(9)	Os(3)–C(34)–O(34)	175(1)
Os(2)–C(22)–O(22)	170(1)	Os(1)–C(23)–O(23)	138.3(9)
Os(2)–C(24)–O(24)	178(1)	Os(2)–C(23)–O(23)	138.3(8)
E. Cationic bond angles			
C(1)–N(1)–C(2)	111.8(3)	C(5)–C(1)–N(1)	113.9(5)
C(1)–N(1)–C(3)	104.9(5)	C(6)–C(2)–N(1)	115.3(7)
C(1)–N(1)–C(4)	109.0(4)	C(7)–C(3)–N(1)	112.5(7)
C(2)–N(1)–C(3)	112.0(9)	C(8)–C(4)–N(1)	114.5(9)
C(2)–N(1)–C(4)	107.3(8)		
C(3)–N(1)–C(4)	111.9(6)		

of the bridging H atom (−12.8 ppm) [16] in $[HRu_3(CO)_{11}]^-$. This hydrogen is assigned a bridging position between Os(1) and Os(2) based upon the close correspondence of C–metal–metal and C–metal–C angles involving Os(1) and Os(2) with the angles for the equivalent cluster fragments [16] in $[HRu_3(CO)_{11}]^-$ (Os(1)–Os(2)–C(22) = 118.5(5)°, Os(2)–Os(1)–C(13) = 119.1(5)° and Ru(1)–Ru(2)–C = 117.5(3)°, Ru(2)–Ru(1)–C = 119.8(3)°). The distance Os(1)–Os(2) (2.813(3) Å) is comparable to Ru(1)–Ru(2) (2.815(2) Å) for $[HRu_3(CO)_{11}]^-$. The metal–metal distances for the unbridged osmiums are comparable to those found in $Os_3(CO)_{12}$ (2.866(3) Å ave) [17]. They are *ca.* 0.02 Å longer than the unbridged Ru–Ru distances in $[HRu_3(CO)_{11}]^-$. The ten terminal carbonyls of $[HOs_3(CO)_{11}]^-$ show normal bond distances and angles ranging from 1.08(1) to 1.18(2) Å and 170(1) to 180(1)°.

The infrared spectrum of $K[HOs_3(CO)_{11}]$ in THF contains a band at 1659 cm^{-1} that can only be assigned to the edge-bridging carbonyl that is observed in the X-ray structure of the anion. Due to contact ion-pairing of K^+ with the bridging carbonyl, this band occurs at a significantly lower frequency than is observed, 1705 cm^{-1} (THF), when $[PPh_4]^+$ is the counterion and solvent separated ion-pairing predominates [18]. Similar differences in the frequency of the edge-bridging carbonyl as a function of ion-pairing ability of the counterion are observed in salts of $[HRu_3(CO)_{11}]^-$ ($[PPN][HRu_3(CO)_{11}]$, 1733 cm^{-1} (THF) [19]; $K[HRu_3(CO)_{11}]$, 1680 cm^{-1} (THF) [20]).

Contact ion-pairing also affects the infrared spectrum of $[Os_3(CO)_{11}]^{2-}$. A band that is assigned to an edge-bridging carbonyl is shifted from 1693 cm^{-1} (THF) for $[PPN]_2[Os_3(CO)_{11}]$ to 1625 cm^{-1} (THF) for $K_2[Os_3(CO)_{11}]$.

The ^{13}C NMR spectrum of $K_2[Os_3(CO)_{11}]$ in THF-d_8/Me_2O consists of a single signal at 196.7 ppm from room temperature down to about −50°C. At −100°C the spectrum consists of a sharp signal at 185.7 ppm and satellite signals at 193.0 and 198.0 ppm. At −120°C the ^{13}C NMR spectrum of $K_2[Os_3(CO)_{11}]$ consists of three signals. There is a broad signal at 282.0 ppm (1C) which is assigned to a bridging carbonyl, a sharp signal at 202.7 ppm (2C), and a broadened signal at 185.7 ppm (8C), which are assigned to terminal carbonyls.

The resonance at 282.0 ppm is consistent with an edge-bridging carbonyl, *e.g.* 273 ppm for $[PPN][HOs_3(CO)_{11}]$ [7] and 282 ppm for $K[HRu_3(CO)_{11}]$ [1]. The possibility that $[Os_3(CO)_{11}]^{2-}$ has a capping carbonyl [21] as in $[Fe_3(CO)_{11}]^{2-}$ has been considered. In $[Fe_3(CO)_{11}]^{2-}$ the carbonyl is asymmetrically situated, being significantly closer (1.85(2) Å) to one iron than the other two (2.21(1) Å). In view of the decreased proclivity of a carbonyl to bridge metals proceeding down the iron subgroup [22], we believe that if capping occurs at all it is highly asymmetric. Note that while $[Fe_4(CO)_{13}]^{2-}$ has a face capping carbonyl [23], $[Ru_4(CO)_{13}]^{2-}$ does not [24]. Figure 2 depicts the proposed structure of $[Os_3(CO)_{11}]^{2-}$ and the known structure of $[Fe_3(CO)_{11}]^{2-}$ [21].

3.3. Reactions of $[Os_3(CO)_{11}]^{2-}$ with $Os_3(CO)_{12}$

Unlike the stoichiometric reactions [1] of $[Ru_3(CO)_{11}]^{2-}$ with $Ru_3(CO)_{12}$ which give $[Ru_4(CO)_{13}]^{2-}$ and $[Ru_6(CO)_{18}]^{2-}$, the reactions of $[Os_3(CO)_{11}]^{2-}$ with $Os_3(CO)_{12}$ give mixtures of osmium clusters. With a 3 : 1 molar ratio of $[Os_3(CO)_{11}]^{2-}$ to $Os_3(CO)_{12}$, $H_2Os_3(CO)_{10}$ (1%), $H_4Os_4(CO)_{12}$ (4%), $H_2Os_4(CO)_{13}$

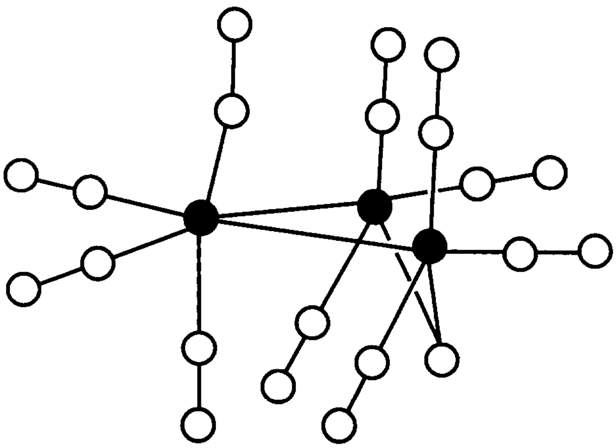

Fig. 2. Proposed structure of $[Os_3(CO)_{11}]^{2-}$.

(25%) and $H_2Os_5(CO)_{16}$ (15%) are obtained. A 1:1 molar ratio of $[Os_3(CO)_{11}]^{2-}$ to $Os_3(CO)_{12}$, gives the mixture $H_2Os_3(CO)_{10}$ (3%), $H_4Os_4(CO)_{12}$ (6%), $H_2Os_4(CO)_{13}$ (7.5%), $H_2Os_5(CO)_{16}$ (15%) and $H_2Os_7(CO)_{20}$ (20%).

3.4. $H_2Os_4(CO)_{13}$

From the reaction of $K_2[Os_3(CO)_{11}]$ with $Os(CO)_5$, $H_2O_4(CO)_{13}$ was obtained in 62% yield. This is a significant improvement from earlier pyrolysis [7] or alcoholic base [8] reactions and is a good alternative to the most recently reported syntheses employing the reaction of $Os_3(CO)_{10}(CH_3CN)_2$ with $H_2Os(CO)_4$ [11] or $Na_2Os(CO)_4$ [10].

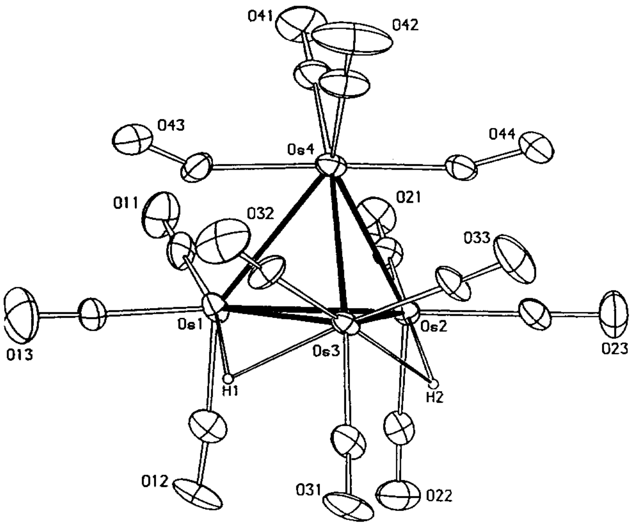

Fig. 3. Molecular structure of $H_2Os_4(CO)_{13}$ showing 50% probability thermal ellipsoids.

TABLE 6. Selected bond distances (Å) and e.s.d.s for $H_2Os_4(CO)_{13}$

	Molecule 1	Molecule 2
A. Metal – metal distances		
Os(1)–Os(2)	2.836(1)	2.828(1)
Os(1)–Os(3)	2.936(1)	2.936(1)
Os(1)–Os(4)	2.796(1)	2.818(1)
Os(2)–Os(3)	2.954(1)	2.936(1)
Os(2)–Os(4)	2.780(1)	2.792(1)
Os(3)–Os(4)	2.795(1)	2.806(1)
B. Metal – carbon distances		
Os(1)–C(11)	1.91(1)	1.91(1)
Os(1)–C(12)	1.94(1)	1.89(1)
Os(1)–C(13)	1.920(9)	1.97(1)
Os(1)–C(43)	2.40(1)	2.335(9)
Os(2)–C(21)	1.90(1)	1.89(1)
Os(2)–C(22)	1.920(9)	1.85(1)
Os(2)–C(23)	1.90(1)	1.87(1)
Os(2)–C(44)	2.56(1)	2.69(1)
Os(3)–C(31)	1.958(9)	1.922(9)
Os(3)–C(32)	1.906(9)	1.90(1)
Os(3)–C(33)	1.963(9)	1.92(1)
Os(4)–C(41)	1.95(1)	1.91(1)
Os(4)–C(42)	1.92(1)	1.93(1)
Os(4)–C(43)	1.98(1)	2.05(1)
Os(4)–C(44)	1.93(1)	1.88(1)
C. Carbon – oxygen distances		
C(11)–O(11)	1.13(2)	1.13(2)
C(12)–O(12)	1.09(2)	1.15(3)
C(13)–O(13)	1.14(3)	1.06(2)
C(21)–O(21)	1.13(2)	1.16(3)
C(22)–O(22)	1.12(3)	1.12(2)
C(23)–O(23)	1.14(2)	1.19(2)
C(31)–O(31)	1.09(2)	1.10(3)
C(32)–O(32)	1.14(3)	1.19(2)
C(33)–O(33)	1.11(2)	1.10(3)
C(41)–O(41)	1.12(3)	1.18(2)
C(42)–O(42)	1.09(2)	1.11(3)
C(43)–O(43)	1.14(3)	1.14(2)
C(44)–O(44)	1.14(2)	1.16(2)
D. Metal – hydride distances		
Os(1)–H(1)	1.9(1)	2.1(1)
Os(2)–H(2)	2.0(1)	2.0(1)
Os(3)–H(1)	2.0(1)	2.0(1)
Os(3)–H(2)	2.0(1)	1.9(1)

The molecular structure of $H_2Os_4(CO)_{13}$ is shown in Fig. 3. Selected bond distances and bond angles are collected in Tables 6 and 7. The cluster $H_2Os_4(CO)_{13}$ is found to be isostructural with $H_2Ru_4(CO)_{13}$ [25], $H_2FeRu_3(CO)_{13}$ [26], $H_2FeOs_3(CO)_{13}$ [27], and $H_2RuOs_3(CO)_{13}$ [28–30].

The unbridged Os(1)–Os(2) bond lengths of 2.836(1) and 2.828(1) Å are comparable to those observed in $H_2FeOs_3(CO)_{13}$ [27] and $H_2RuOs_3(CO)_{13}$ [28–30] and other neutral Os_4 tetrahedral clusters [31]. The hydrogen-bridged Os–Os distances ranging from 2.936(1) to 2.954(1) Å for Os(1)–Os(3) and Os(2)–Os(3) are longer than the distance for Os(1)–Os(2) ranging from 2.828(1) to 2.836(1) Å. These distances are comparable to those

TABLE 7. Selected bond angles (°) and e.s.d.s for $H_2Os_4(CO)_{13}$

	Molecule 1	Molecule 2
A. Metal angles		
Os(2)–Os(1)–Os(3)	61.52(1)	61.29(1)
Os(2)–Os(1)–Os(4)	59.15(2)	59.27(2)
Os(3)–Os(1)–Os(4)	58.31(2)	58.33(2)
Os(1)–Os(2)–Os(3)	60.90(2)	61.16(2)
Os(1)–Os(2)–Os(4)	59.71(2)	60.18(2)
Os(3)–Os(2)–Os(4)	58.26(2)	58.56(2)
Os(1)–Os(3)–Os(2)	57.58(2)	57.55(2)
Os(1)–Os(3)–Os(4)	58.35(2)	58.73(2)
Os(2)–Os(3)–Os(4)	57.77(2)	58.09(2)
Os(1)–Os(4)–Os(2)	61.15(2)	60.55(2)
Os(1)–Os(4)–Os(3)	63.35(2)	62.94(2)
Os(2)–Os(4)–Os(3)	63.98(2)	63.35(2)
B. Metal–metal–carbon angles		
Os(2)–Os(1)–C(11)	95.36(2)	97.81(2)
Os(2)–Os(1)–C(12)	87.09(2)	85.32(2)
Os(2)–Os(1)–C(13)	170.10(2)	173.57(2)
Os(2)–Os(1)–C(43)	103.12(3)	104.7(3)
Os(3)–Os(1)–C(11)	149.00(2)	151.77(2)
Os(3)–Os(1)–C(12)	105.41(3)	104.38(2)
Os(3)–Os(1)–C(13)	109.20(2)	112.72(2)
Os(3)–Os(1)–C(43)	76.84(2)	74.9(3)
Os(4)–Os(1)–C(11)	92.80(3)	95.36(2)
Os(4)–Os(1)–C(12)	146.15(2)	144.51(2)
Os(4)–Os(1)–C(13)	120.26(3)	120.53(2)
Os(4)–Os(1)–C(43)	43.99(2)	45.6(4)
Os(1)–Os(2)–C(21)	91.20(2)	89.16(2)
Os(1)–Os(2)–C(22)	93.08(2)	98.04(2)
Os(1)–Os(2)–C(23)	172.34(2)	170.70(2)
Os(1)–Os(2)–C(44)	101.70(2)	99.9(2)
Os(3)–Os(2)–C(21)	144.54(2)	143.50(2)
Os(3)–Os(2)–C(22)	109.70(2)	111.12(2)
Os(3)–Os(2)–C(23)	111.52(2)	110.39(2)
Os(3)–Os(2)–C(44)	73.73(2)	71.4(2)
Os(4)–Os(2)–C(21)	89.64(2)	89.20(2)
Os(4)–Os(2)–C(22)	152.77(2)	158.14(2)
Os(4)–Os(2)–C(23)	116.24(2)	112.79(2)
Os(4)–Os(2)–C(44)	42.21(2)	40.1(2)
Os(1)–Os(3)–C(31)	114.5(4)	113.8(4)
Os(1)–Os(3)–C(32)	96.7(3)	96.6(3)
Os(1)–Os(3)–C(33)	148.9(4)	148.8(5)
Os(2)–Os(3)–C(31)	116.5(3)	112.5(3)
Os(2)–Os(3)–C(32)	145.1(3)	146.1(4)
Os(2)–Os(3)–C(33)	99.12(4)	99.8(4)
Os(4)–Os(3)–C(31)	172.2(3)	169.7(3)
Os(4)–Os(3)–C(32)	89.4(4)	90.6(4)
Os(4)–Os(3)–C(33)	92.5(5)	91.7(5)
Os(1)–Os(4)–C(41)	104.6(4)	102.4(4)
Os(1)–Os(4)–C(42)	138.1(4)	131.5(6)
Os(1)–Os(4)–C(43)	57.2(5)	54.6(4)
Os(1)–Os(4)–C(44)	123.6(4)	126.9(4)
Os(2)–Os(4)–C(41)	104.9(3)	101.2(4)
Os(2)–Os(4)–C(42)	145.2(4)	153.8(4)
Os(2)–Os(4)–C(43)	118.3(5)	114.9(4)
Os(2)–Os(4)–C(44)	62.81(4)	67.1(4)
Os(3)–Os(4)–C(41)	166.1(3)	162.1(4)
Os(3)–Os(4)–C(42)	96.6(4)	99.4(6)
Os(3)–Os(4)–C(43)	87.1(5)	82.2(4)
Os(3)–Os(4)–C(44)	87.2(6)	86.9(3)

TABLE 7 (continued)

	Molecule 1	Molecule 2
C. Metal–carbon–oxygen angles		
Os(1)–C(11)–O(11)	178.2(6)	177.5(7)
Os(1)–C(12)–O(12)	175.9(6)	175.6(6)
Os(1)–C(13)–O(13)	177.8(9)	171.7(6)
Os(1)–C(43)–O(43)	128.7(8)	131(1)
Os(2)–C(21)–O(21)	178.8(6)	177.1(8)
Os(2)–C(22)–O(22)	176.8(8)	176.8(7)
Os(2)–C(23)–O(23)	178.6(7)	177.9(7)
Os(2)–C(44)–O(44)	125.1(6)	125.1(9)
Os(3)–C(31)–O(31)	175.4(7)	174(1)
Os(3)–C(32)–O(32)	177.7(1)	176(1)
Os(3)–C(33)–O(33)	177(2)	180(1)
Os(4)–C(41)–O(41)	178.6(7)	174(1)
Os(4)–C(42)–O(42)	178.8(7)	174(2)
Os(4)–C(43)–O(43)	152(1)	149(1)
Os(4)–C(44)–O(44)	159(2)	162(1)
D. Metal–CO–metal and metal–H–metal angles		
Os(4)–C(43)–Os(1)	78.8(4)	79.7(4)
Os(4)–C(44)–Os(2)	74.9(8)	72.8(4)
Os(1)–H(11)–Os(3)	97(1)	92(1)
Os(2)–H(12)–Os(3)	96(1)	98(1)

reported for $H_2FeOs_3(CO)_{13}$ [27] and $H_2RuOs_3(CO)_{13}$ [28–30].

Two semi-bridging carbonyls are associated with the Os(4) atom which exhibit typical metal–carbon and carbon–oxygen bond distances and bond angles. Os(4)–C(34) = 1.98(1)–2.05(1) Å, Os(4)–C(44) = 1.88(1)–1.93(1) Å, C(43)–O(43) = 1.14(2)–1.14(3) Å, C(44)–O(44) = 1.14(2)–1.16(2) Å. Os(4)–C(43)–O(43) = 149(1)–152(1)° and Os(4)–C(44)–O(44) = 159(2)–162(1)°.

Carbon-13 NMR spectra of $H_2Os_4(CO)_{13}$ in THF-d_8 are shown in Fig. 4. The room temperature ^{13}C NMR spectrum consists of three signals at 179.1, 169.4, 167.6 ppm. As the temperature is lowered to −110°C, the spectrum resolves into six terminal carbonyl resonances. A signal at 184.2 ppm is assigned to the apical carbonyls (a and b) that are rotating as an $Os(CO)_4$ group. Proton decoupling from ^{13}C sharpens signals at 168.5 and 167.5 ppm. These signals are assigned to the radial carbonyls f and c *trans* to the bridging hydrogens. Resonances at 172.7 and 170.9 ppm are assigned to the axial carbonyls g and e since axial carbonyls resonate at lower field than equatorial or radial carbonyls [32]. The signal 165.6 ppm is assigned to the radial carbonyl d. This spectrum at −110°C is similar to that of $H_2Ru_4(CO)_{13}$ at −72°C [33] except that greater resolution in the present spectrum permits assignment of the unique axial carbonyl g.

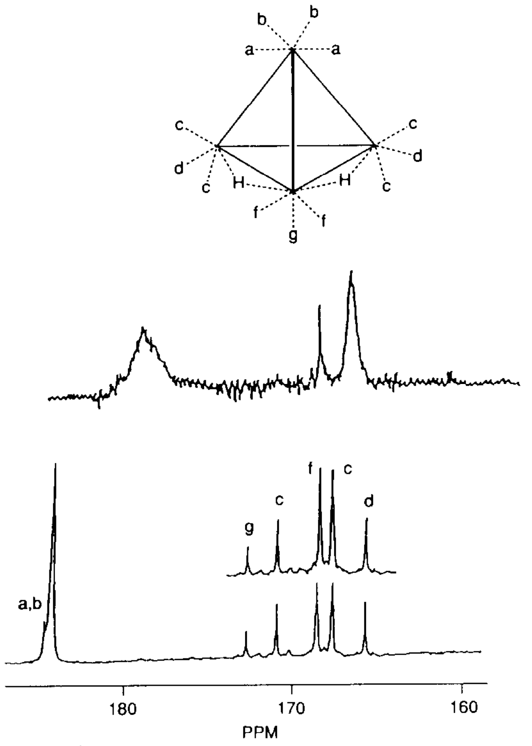

Fig. 4. ^{13}C NMR spectra of $H_2Os_4(CO)_{13}$.

Deprotonation of $H_2Os_4(CO)_{13}$ with NaH in THF resulted in the formation of a mixture of anions. To overcome this problem, deprotonation reactions were carried out using [PPN]Cl, which has been shown [34] to be successful in deprotonating $H_4Ru_4(CO)_{12}$. A 75% yield of $[PPN][HOs_4(CO)_{13}]$ was obtained within a few minutes.

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