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The $ReOs_4(\mu\text{-}H)(CO)_n$ ($n = 19, 18, 16$) Clusters

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Addition of $Re(CO)_5(H)$ to $Os_4(CO)_{14}$ in solution at room temperature affords $ReOs_4(\mu\text{-}H)(CO)_{19}$ (**1**). Careful pyrolysis of **1** in hexane at 85 °C initially yields $ReOs_4(\mu\text{-}H)(\mu\text{-}CO)(CO)_{17}$ (**2**), which on further heating gives $ReOs_4(\mu\text{-}H)(CO)_{16}$ (**3**). There was no evidence for $ReOs_4(\mu\text{-}H)(CO)_{17}$. The four osmium atoms in **1** have a planar kite arrangement with the $Re(CO)_5$ in an equatorial site, that is, a spiked kite metal skeleton. The H ligand is believed to bridge the OsOs bond (length 2.892(1), 2.904(1) Å; two independent molecules) that is cis to the Re atom, rather than one of the longer OsOs bonds. Cluster **2** has a distorted tetrahedral Os_4 nucleus with the $Re(CO)_5$ again acting as a spike ligand (i.e., a spiked tetrahedral metal skeleton). Compound **3** has the expected trigonal bipyramidal core of metal atoms with the $Re(CO)_4$ unit in the equatorial plane. The structures of **1**−**3** are compared to those of the analogous $Os_5(CO)_n$ ($n = 19, 18, 16$) clusters. The solution behavior of the new clusters was also investigated by variable-temperature ^{13}C NMR spectroscopy.

Introduction

Unlike $Os_3(CO)_{12}$, $Os_4(CO)_{14}$ readily reacts in solution at room temperature with donor molecules. Of particular relevance to this study is the addition of $Os(CO)_4(L)$ (L = CO, PMe_3, Bu^tNC) to $Os_4(CO)_{14}$ in solution at or below room temperature to give $Os_5(CO)_{18}(L)$.[1−3] Upon mild pyrolysis, the pentanuclear derivatives undergo stepwise decarbonylation to give the corresponding $Os_5(CO)_{17}(L)$ and $Os_5(CO)_{15}(L)$ clusters. (There was no evidence for $Os_5(CO)_{16}(L)$.)[1−3]

Here we report the corresponding reaction of $Os_4(CO)_{14}$ with $Re(CO)_5(H)$ to give the $ReOs_4(\mu\text{-}H)(CO)_n$ (n = 19, 18, 16) clusters. There were two reasons for undertaking this study. The rational synthesis of metal clusters, particularly heteronuclear clusters, remains a challenge in metal carbonyl cluster chemistry, although several syntheses have been reported recently.[4,5] Furthermore, it has been previously observed that the replacement of a carbonyl ligand with two H ligands in a metal carbonyl cluster often causes a rearrangement of the metal skeleton. For example, $Os_4(CO)_{14}(PMe_3)$ has a planar kite Os_4 unit, whereas in $Os_4(\mu\text{-}H)_2(CO)_{13}(PMe_3)$ the osmium atoms have a nonplanar butterfly geometry.[6,7] The binary carbonyl $Os_7(CO)_{21}$ has a capped octahedral Os_7 nucleus, whereas the metal unit in $Os_7(\mu\text{-}H)_2(CO)_{20}$ consists of a capped trigonal bipyramidal Os_6 polyhedron with the seventh Os atom bridging the OsOs edge directly opposite the capping Os atom.[8,9] It was therefore of interest to compare structures of the $ReOs_4(\mu\text{-}H)(CO)_n$ clusters with the known structures of the $Os_5(CO)_n$ analogues.[1,10−12] Significant changes to metal skeletal geometry upon relatively minor changes in ligand and metal composition provide insight into metal cluster bonding.

Experimental Section

Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere with the use of standard Schlenk techniques. Hydrocarbon solvents were refluxed over potassium, distilled, and stored over molecular sieves before use. Dichloromethane was dried in a similar manner except that P_2O_5 was employed as the drying agent. The following precursory compounds were prepared by literature procedures: $Re(CO)_5(H)$, $Os(CO)_5$,

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$Os_3(CO)_{10}(CH_3CN)_2$.[13–15] An improved preparation for $Os_4(CO)_{14}$ (and $Os_4(CO)_{15}$) is given below. Samples used for $^{13}C\{^1H\}$ NMR spectra were enriched to ~25–30% ^{13}CO and were prepared from ^{13}CO-enriched $Os_4(CO)_{14}$ and/or ^{13}CO-enriched $Re(CO)_5(H)$ (see text). The ^{13}CO-enriched $Os_4(CO)_{14}$ was made from ^{13}CO-enriched $Os_3(CO)_{12}$;[16] ^{13}CO-enriched $Re(CO)_5(H)$ was synthesized from ^{13}CO-enriched $Re(CO)_5(Br)$.[17] NMR spectra were recorded on a Bruker AMX400 spectrometer at the appropriate operating frequencies for ^1H and ^{13}C NMR spectra.

Improved Preparation of $Os_4(CO)_{14}$. To a solution of $Os_3(CO)_{10}(CH_3CN)_2$ (200 mg, 0.214 mmol) in CH_2Cl_2 (20 mL) was added an excess of $Os(CO)_5$ in hexane. The resulting solution was stirred at room temperature for 4 h, then stored at −29 °C overnight to precipitate $Os_4(CO)_{15}$. The mother solution was decanted, and the remaining dark red-green solid was washed with two 15 mL portions of hexane and then dried to give pure $Os_4(CO)_{15}$ (140 mg, 55%). IR (hexane) ν(CO) $Os_4(CO)_{15}$: 2086 (s), 2073.5 (m), 2045 (vs), 2023 (m), 2002 (sh), 1939 (m, br) cm^{-1}.[18] To a round-bottom flask (250 mL) equipped with a water-cooled reflux condenser was added $Os_4(CO)_{15}$ (90 mg, 0.076 mmol) in toluene (40 mL). The solution was heated to 90 °C and nitrogen bubbled through it for 3.5 h. The solution was transferred to a Schlenk tube, and the volume of toluene was reduced to ~30 mL and stored overnight at −29 °C to yield crystals of $Os_4(CO)_{14}$. The solution was removed from the crystals, which were washed with hexane (2 × 15 mL) and dried to give pure $Os_4(CO)_{14}$ (76 mg, 86%) as brown crystals that are air stable. IR (hexane) ν(CO) $Os_4(CO)_{14}$: 2058 (s, br), 2018 (m, br) 1938 (vw, br) cm^{-1}.[19]

Preparation of $ReOs_4(\mu\text{-}H)(CO)_{20}$. To a solution of $Os_4(CO)_{15}$ (20 mg, 0.017 mmol) in toluene (20 mL) was added an excess of $Re(CO)_5(H)$ in hexane at 0 °C. The reaction was stirred for 15 min, during which time the green solution turned bright yellow. An infrared spectrum of this solution indicated the presence of $ReOs_4(\mu\text{-}H)(CO)_{20}$ and $ReOs_3(\mu\text{-}H)(CO)_{16}$ in an approximate 1:1 ratio. The solution was reduced to approximately half its initial volume and stored overnight at −29 °C, to yield orange crystals of $ReOs_4(\mu\text{-}H)(CO)_{20}$ (4 mg, 16%). (The crystals were not suitable for X-ray crystallography.) In a second preparation the solution after the reaction period was evaporated to dryness and the solid subjected to chromatography on a silica gel column (1 × 10 cm). Elution with hexane/CH_2Cl_2 (99:1 by volume) gave a yellow band of $ReOs_3(\mu\text{-}H)(CO)_{16}$ immediately followed by an orange band of the desired product. Collection of the orange band gave a sample of $ReOs_4(\mu\text{-}H)(CO)_{20}$ that was almost pure by IR spectroscopy. The compound decomposes in solution at room temperature; one of the decomposition products has been identified by IR and ^1H and ^{13}C NMR spectroscopy as the known $ReOs_3(\mu\text{-}H)(CO)_{16}$.[20] $ReOs_4(\mu\text{-}H)(CO)_{20}$: IR (hexane) ν(CO) 2135 (w), 2114 (m), 2081 (s), 2055 (vs), 2029 (sh), 2022 (s), 2009 (vs), 1995 (w), 1979 (s), 1968 (sh), 1950 (w), 1932 (w) cm^{-1}; even in the spectra of the best samples there were weak bands due to $ReOs_3(\mu\text{-}H)(CO)_{16}$ (ν(CO) 2136 (w), 2104 (m), 2075 (s), 2055 (vs), 2029 (m), 2020 (m), 2005 (s), 2001 (s), 1994 (w), 1977 (m), 1969 (w), 1948 (w) cm^{-1}); ^1H NMR (benzene-d_6) δ −18.9 (s); $^{13}C/^{13}C\{^1H\}$ NMR (CD_2Cl_2, −50 °C) δ 193.8 (2C, *ax*-Os-*C*), 191.2 (4C, Os(*C*O)$_4$), 189.6 (br, 4C, Re-*C*), 183.0 (2C, *ax*-Os-*C*), 182.5 (br, 1C Re-*C*), 180.9 (1C, *eq*-Os-*C*), 174.4 (br, >2C, *ax*-Os-*C*, degenerate with signal of $ReOs_3(\mu\text{-}H)(CO)_{16}$), 170.8 (1C, *eq*-Os-*C*), 169.6 (1C, *eq*-Os-*C*), 164.4 (1C, *eq*-Os-*C*), 162.9 (1C, J_{HC} = 9.2 Hz, *eq*-Os-*C*); weak signals at δ 195.8, 190.9, 183.5, 181.6, 171.1, 169.8, 164.8, 163.4 were attributed to $ReOs_3(\mu\text{-}H)(CO)_{16}$ by comparison with the spectrum of a pure sample; MS (FAB) *m/z* 1507.6 (M^+) (calcd for M^+ = 1510 (100%), 1508 (98.2%)).

Preparation of $ReOs_4(\mu\text{-}H)(CO)_{19}$ (1). To a stirred solution of $Os_4(CO)_{14}$ (25 mg, 0.017 mmol) in CH_2Cl_2 (25 mL) at room temperature was added an excess amount of $Re(CO)_5(H)$ in hexane. The color of the solution immediately changed from brown-red to deep red. The solution was evaporated to dryness and the resulting solid recrystallized from CH_2Cl_2. The analytical sample of **1** was obtained in a greater than 95% yield as air-stable, deep red crystals: IR (hexane) ν(CO) 2108 (m), 2075 (m), 2058 (m), 2042 (vs), 2036 (sh), 2019 (s, br), 1995 (w), 1984 (m), 1978 (sh), 1966 (w) cm^{-1}; ^1H NMR (CD_2Cl_2) δ −14.5 (s); $^{13}C/^{13}C\{^1H\}$ NMR (CD_2Cl_2, RT, see text) δ 198.1 (2C, *ax*-Os-*C* J_{CH} = 2.6 Hz), 192.2 (2C, *ax*-Os-*C* J_{CH} = 3.4 Hz), 188.0 (2C, *ax*-Os-*C*), 186.7 (4C, Re-*C*), 184.0 (1C, *eq*-Os-*C*, J_{CH} = 6.9 Hz), 180.4 (1C, Re-*C*) 178.7 (1C, *eq*-Os-*C*, J_{CH} = 2.7 Hz), 173.4 (1C, *eq*-Os-*C* J_{CH} = 2.7 Hz), 173.0 (1C, *eq*-Os-*C*), 172.6 (2C, *ax*-Os-*C*), 169.9 (1C *eq*-Os-*C*), 163.2 (1C *eq*-Os-*C*); MS (FAB) *m/z* 1481.6 (M^+) (calcd for M^+ = 1482 (100%), 1480 (98.3%)). Anal. Calcd for $C_{19}HO_{19}Os_4Re$: C, 15.42; H, 0.07. Found: C, 15.54; H, 0.08.

Preparation of $ReOs_4(\mu\text{-}H)(\mu\text{-}CO)(CO)_{17}$ (2). To a flame-dried Carius tube (fitted with a Teflon valve) was added $ReOs_4(\mu\text{-}H)(CO)_{19}$ (16 mg, 0.011 mmol) and hexane (25 mL). The tube was cooled to −196 °C, the solution degassed with three freeze−pump−thaw cycles, and the vessel sealed under vacuum. The reaction mixture was then heated at 85 °C for 24 h, during which time a yellow-orange precipitate formed. The mixture was cooled to room temperature and the mother solution decanted from the precipitate. The precipitate was washed with hexane (2 × 10 mL) and dried on the vacuum line to give **2** (13 mg, 83%). The analytical sample of **2** was obtained as air-stable, orange crystals by recrystallization from CH_2Cl_2: IR (hexane) ν(CO) 2127 (w), 2096 (m), 2063 (vs), 2029 (s), 2025 (sh), 2007 (w), 1991 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ −18.8 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, RT) δ 188.9 (m, Re-*C*), 185.9 (vs, Re-*C*), 178.9 (w), 173.4 (w), 164.8 (w/broad); MS (FAB) *m/z* 1451.7 (M^+) (calcd for M^+ = 1454 (100%), 1452 (98.2%)). Anal. Calcd for $C_{18}HO_{18}Os_4Re$: C, 14.88; H, 0.07. Found: C, 15.01; H, 0.09.

Preparation of $ReOs_4(\mu\text{-}H)(CO)_{16}$ (3). A flame-dried Carius tube (fitted with a Teflon valve) was charged with $ReOs_4(\mu\text{-}H)(CO)_{19}$ (20 mg, 0.014 mmol) and hexane (20 mL). The vessel was cooled to −196 °C, the solution degassed with three freeze−pump−thaw cycles, and the tube sealed under vacuum. This solution was then heated at 95 °C for 4 days; the solution was degassed as described above and the vessel resealed under vacuum every 24 h. Over this period the red solution turned orange (due to formation of **2**) and then red-brown at the completion of the reaction. After the reaction was complete the solvent was removed on the vacuum line and the remaining solid recrystallized from CH_2Cl_2 to give **3** (9 mg, 48%) as analytically pure, air-stable, dark red (almost black) crystals: IR (hexane) ν(CO) 2106 (w), 2096 (w), 2072 (vs), 2060 (vs), 2040 (vs), 2022 (w), 2010 (w), 2000 (m), 1984 (w), 1970 (w), 1955 (w); ^1H NMR (CD_2Cl_2) δ −20.4 (s); ^{13}C NMR (CD_2Cl_2, RT) δ 181.4 (s, br); $^{13}C/^{13}C\{^1H\}$ NMR (CD_2Cl_2, −90 C) δ 180.4 (2C), 179.6 (1C), 175.6 (2C), 172.0 (1C), 167.9 (1C, d, J_{CH} = 6.9 Hz); ^{13}C NMR ($CD_2Cl_2/CHFCl_2$, −125 °C) δ 191.9 (2C), 188.8 (2C), 184.4 (~1C), 180.7 (2C), 179.9 (1C), 176.0 (2C), 172.6 (2C), 172.1 (1C), 170.6 (2C), 168.1 (~1C); MS (FAB) *m/z* 1397.8 (M^+) (calcd for M^+ = 1398 (100%), 1396 (98.6%)). Anal. Calcd for $C_{16}HO_{16}Os_4Re$: C, 13.75; H, 0.07. Found: C, 13.83; H, 0.09.

X-ray Analyses of 1, 2, and 3. Suitable crystals were selected, mounted on thin, glass fibers using paraffin oil, and cooled to the data collection temperature (−70 °C in each case). Data were collected on a Bruker AXS SMART 1k CCD diffractometer using 0.3° ω-scans at 0°, 90°, and 180° in ϕ.

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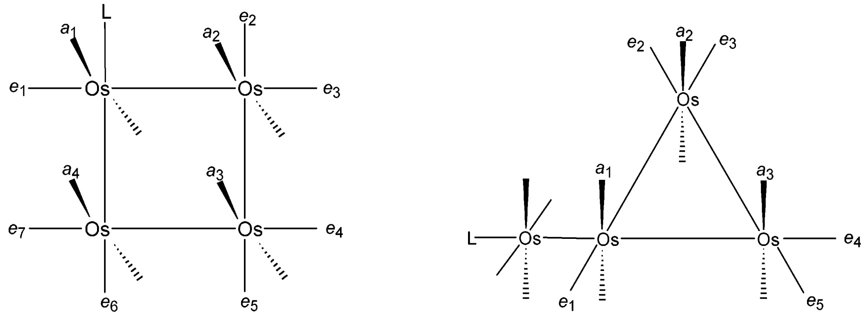
Table 1. Crystal Structure Data for $ReOs_4(\mu\text{-}H)(CO)_{19}$ (1), $ReOs_4(\mu\text{-}H)(CO)_{18}$ (2), and $ReOs_4(\mu\text{-}H)(CO)_{16}$ (1)

	1	2	3
empirical formula	$C_{19}HO_{19}Os_4Re$	$C_{18}HO_{18}Os_4Re$	$C_{16}HO_{16}Os_4Re$
fw	1480.20	1452.19	1396.17
color	deep red	orange	dark red
cryst syst	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$
a (Å)	12.762(1)	8.5656(8)	9.634(1)
b (Å)	15.661(2)	9.0159(8)	11.498(1)
c (Å)	16.031(2)	17.734(2)	21.581(2)
α (deg)	72.652(2)	94.118(2)	90
β (deg)	67.689(2)	102.929(2)	90
γ (deg)	87.151(2)	100.287(2)	90
V (Å^3), Z	2822.0(5), 4	1304.4(2), 2	2390.6(4), 4
D(calcd) (Mg m^{-3})	3.484	3.697	3.879
abs coeff (mm^{-1})	22.301	24.117	26.304
no. of ind reflns	11 240 [R(int) = 0.0861]	5915 [R(int) = 0.0800]	5631 [R(int) = 0.0438]
R_F[a]	0.0504	0.0632	0.0289
R_{wF}[b]	0.1134	0.1415	0.0505

[a] $R_F = \Sigma|(|F_o| - |F_c|)|/\Sigma|F_o|$. [b] $R_{wF} = [\Sigma(w(|F_o| - |F_c|)^2)/\Sigma(wF_o^2)]^{1/2}$. $w = [\sigma^2(F_o)^2 + kF_o^2]^{-1}$.

Chart 1



Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[21]

Systematic absences in the diffraction data and unit-cell parameters were uniquely consistent with the reported space group for **3**. No symmetry higher than triclinic was observed for **1** or **2**; solution in the centrosymmetric space group option yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. Two symmetry unique but chemically identical compound molecules were located in the asymmetric unit of **1**. The absolute structure parameter refined to nil, indicating that the true hand of the data for **3** was established. Hydride ligands were placed in calculated positions by use of the XHYDEX program.[22] For **1** the OsH distances were constrained to be the same and refined. For **2** and **3** the H positions are those given by the XHYDEX program (i.e., they were not refined). All non-hydrogen atoms were refined with anisotropic displacement coefficients. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 6.12 program library.[23] Crystal structure data can be found in Table 1; selected bond lengths and angles are given in Tables 2, 3, and 4 for **1**, **2**, and **3**, respectively.

Results and Discussion

$ReOs_4(\mu\text{-}H)(CO)_{20}$. The reaction of $Re(CO)_5(H)$ with $Os_4(CO)_{15}$ in solution at 0 °C gave a yellow precipitate, the mass spectrum of which indicated it was $ReOs_4(\mu\text{-}H)(CO)_{20}$. It decomposed in solution at room temperature over a period of 3 h; one of the decomposition products was identified as the known $ReOs_3(\mu\text{-}H)(CO)_{16}$.[20] (The binary carbonyl $Os_4(CO)_{16}$ readily decomposes in solution at room temperature to give $Os_3(CO)_{12}$.[24]) The instability of $ReOs_4(\mu\text{-}H)(CO)_{20}$ prevented its complete characterization.

Clusters of the type $Os_4(CO)_{15}(L)$ are found to adopt either a puckered square (L = CO, PF_3) or a spiked triangular (L = $P(OCH_2)_3CMe$, PMe_3) configuration of metal atoms as shown diagrammatically in Chart 1.[24] The $^{13}C/^{13}C\{^1H\}$ NMR of ^{13}CO-enriched $ReOs_4(\mu\text{-}H)(CO)_{20}$ was complicated by signals due to a small amount of $ReOs_3(\mu\text{-}H)(CO)_{16}$; nevertheless, the NMR data are consistent with a spiked triangular structure for $ReOs_4(\mu\text{-}H)(CO)_{20}$. In particular, a signal of intensity 4 at δ 191.2 is in the region expected for the resonance of an $Os(CO)_4$ unit. Furthermore, there are only five signals of intensity 1 in the shift range for signals due to equatorial carbonyls attached to osmium.[16] In the ^1H-coupled ^{13}C NMR spectrum only one signal (due to an equatorial carbonyl on Os) was split into a doublet. This suggests the H ligand bridges the OsOs bond trans to the spike Os atom. The structures of $(OC)_5ReOs_3(\mu\text{-}H)(CO)_{10}(CH_3CN)$ and $[(OC)_5Re]_2Os_3(\mu\text{-}H)_2(CO)_{10}$, however, indicate the hydride ligands bridge OsOs bonds cis to the $Re(CO)_5$ substituents.[25,26] It is believed that the H ligand in $ReOs_4(\mu\text{-}H)(CO)_{20}$ bridges the OsOs cis

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $ReOs_4(\mu\text{-}H)(CO)_{19}$ (1)

molecule 1		molecule 2	
Re(1)−Os(1)	2.953(1)	Re(2)−Os(5)	2.947(1)
Os(1)−Os(2)	3.038(1)	Os(5)−Os(6)	3.014(1)
Os(1)−Os(4)	2.892(1)	Os(5)−Os(8)	2.904(1)
Os(2)−Os(3)	2.961(1)	Os(6)−Os(7)	2.960(1)
Os(2)−Os(4)	2.945(1)	Os(6)−Os(8)	2.928(1)
Os(3)−Os(4)	2.802(1)	Os(7)−Os(8)	2.813(1)
Re(1)−C(1)	1.88(2)	Re(2)−C(20)	1.94(2)
Re−C(*rad.*) range	1.95(2)−2.03(2)		1.97(2)−2.01(2)
Os−C range	1.87(2)−1.99(2)		1.83(2)−1.98(2)
Os(1)−H(1)	2.0(1)	Os(5)−H(2)	2.0(1)
Os(4)−H(1)	2.0(1)	Os(8)−(2)	2.0(1)
		Os(4)···C(4)[a]	2.84(1)
Re(1)−Os(1)−Os(4)	111.50(3)	Re(2)−Os(5)−Os(8)	109.57(3)
Re(1)−Os(1)−Os(2)	169.82(3)	Re(2)−Os(5)−Os(6)	168.69(3)
Os(2)−Os(1)−Os(4)	59.49(2)	Os(6)−Os(5)−Os(8)	59.27(2)
Os(3)−Os(2)−Os(4)	56.65(3)	Os(5)−Os(6)−Os(7)	115.55(3)
Os(1)−Os(2)−Os(3)	114.43(3)	Os(5)−Os(6)−Os(8)	58.49(2)
Os(1)−Os(2)−Os(4)	57.78(2)	Os(7)−Os(6)−Os(8)	57.09(2)
Os(2)−Os(3)−Os(4)	61.39(2)	Os(6)−Os(7)−Os(8)	60.88(3)
Os(1)−Os(4)−Os(2)	62.74(3)	Os(5)−Os(8)−Os(6)	62.25(2)
Os(1)−Os(4)−Os(3)	124.70(3)	Os(5)−Os(8)−Os(7)	124.24(3)
Os(2)−Os(4)−Os(3)	61.96(3)	Os(6)−Os(8)−Os(7)	62.03(2)

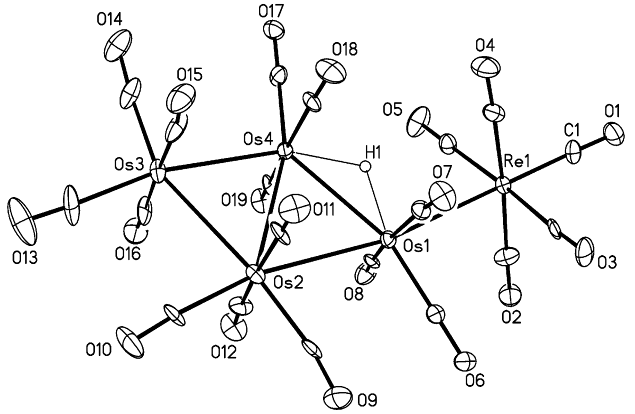

Figure 1. Molecular structure of molecule A of $ReOs_4(\mu\text{-}H)(CO)_{19}$ (**1**).

to the spike Os atom and one of the CH couplings is small because the HOsC angle to this C atom is not near 180°. This is also observed for $ReOs(\mu\text{-}H)(CO)_{19}$ discussed immediately below.

$ReOs_4(\mu\text{-}H)(CO)_{19}$ (1). Compound **1** was prepared by the addition of $Re(CO)_5(H)$ to $Os_4(CO)_{14}$ in CH_2Cl_2 at room temperature (eq 1). The complex was isolated as deep red, air-stable crystals in almost quantitative yield.

$$Os_4(CO)_{14} + Re(CO)_5(H) \xrightarrow{25\ ^\circ C} \underset{\mathbf{1}}{ReOs_4(\mu\text{-}H)(CO)_{19}} \quad (1)$$

The structure of **1** has two crystallographically independent molecules in the unit cell; a view of one of the molecules is given in Figure 1. Selected bond lengths and angles for **1** are given in Table 2. Rhenium and osmium atoms cannot, of course, be distinguished reliably by X-ray crystallography. The site of the Re atom is however confidently assigned on the basis of the method of synthesis of **1**, the 18-electron rule, and the bond length and spectroscopic data.

Unbridged ReOs bonds reported in the literature range in length from 2.931 to 3.006 Å, whereas unbridged OsOs bonds in chain complexes are typically in the range 2.871−2.918 Å.[27] The ReOs lengths in the independent molecules of **1** of 2.947(1) and 2.953(1) Å are therefore within the range reported for unbridged ReOs bonds.

The metal framework in **1** consists of a planar Os_4 rhomboid, which is also found in $Os_4(CO)_{15}$, with the $Re(CO)_5$ unit bound in an equatorial site to one Os atom. We have dubbed the Os_4 arrangement in $Os_4(CO)_{15}$ and some of its derivatives as a kite arrangement.[18] The metal skeleton in **1** may therefore be described as a "spiked kite". There are several reports in the literature of metal carbonyl cluster complexes with a spiked butterfly arrangement, that is, where the rhomboid is nonplanar. Two examples are $Ru_5(\mu_5\text{-}C_2Ph_2)(\mu\text{-}PPh_2)(dppm)(CO)_{12}$ and $(\eta^5\text{-}C_5Me_5)RhRu_4(\mu\text{-}H)[\mu_5\text{-}B(\mu\text{-}H)_2](\mu\text{-}CO)_2(CO)_{11}$.[28,29] To our knowledge however there has been only one previous report of a pentanuclear cluster in which the rhomboid is flat, and that is $Os_5(\mu\text{-}H)(\eta^2\text{-}C_6F_5NNNC_6F_5)(CO)_{17}$.[30]

The OsOs lengths in $Os_4(CO)_{15}$ are unusual in that the peripheral bonds consist of two long (about 3.00 Å) bonds between $Os(CO)_4$ units and two short bonds (about 2.77 Å) that involve the $Os(CO)_3$ fragment.[18] Bonds between osmium atoms in open cluster compounds are usually within 0.5 Å of 2.877 Å, the average OsOs distance in $Os_3(CO)_{12}$.[31] We have rationalized the lengths of $Os_4(CO)_{15}$ in terms of 3c−2e bonds as shown Chart 2.[18] (MO calculations give an alternative view.[32]) In **1** the peripheral OsOs bonds that involve the Os atom of the hinge $Os(CO)_4$ unit are likewise long at 3.038(1) and 2.961(1) Å (molecule 1) and 3.014(1) and 2.960(1) Å (molecule 2). The OsOs bonds that include the Os atom of the $Os(CO)_3$ grouping are 2.802(1) and 2.892(1) Å (molecule 1) and 2.802(1) and 2.904(1) Å (molecule

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Chart 2

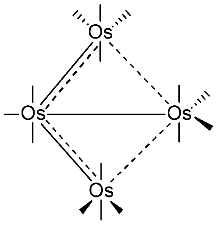
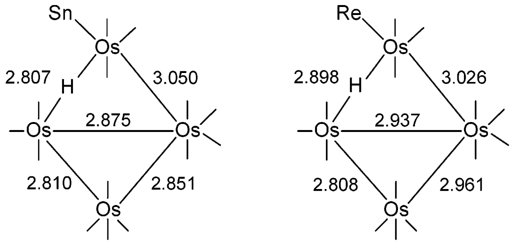
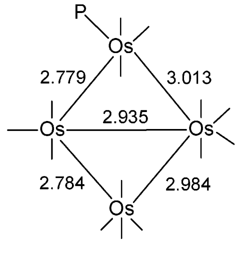


Chart 3



$Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$		$Os_4(\mu\text{-}H)(CO)_{14}[Re(CO)_5]$ (**1**)



$Os_4(CO)_{14}(PMe_3)$

2). The longer bond in each pair is believed to be bridged by the hydride ligand rather than one of the long OsOs bonds (see below). The presence of a single bridging hydride ligand usually causes an elongation of about 0.12 Å to an OsOs bond in Os cluster compounds.[33] The lengthening Os(1)Os(4) bond in **1** caused by the presence of the bridging hydride ligand is therefore slightly less than this value. The hinge OsOs bond (2.945(1), 2.928(1) Å) although somewhat long is more typical of a single OsOs bond.

The hydride ligand in **1** and the other structures described here was placed by the use of the XHydex program.[22] Placement of the H ligand across the Os(1)-Os(4) bond gave a "site energy" of 1.2 by the program. This is in the range of 0.2−10.6 previously found for bridging hydride ligands. Support for this placement also comes from the Os(2)Os(4)C(17) angle, which is 163.7(6)°. The corresponding angle in $Os_4(CO)_{15}$ (Chart 2) is 180° by crystallography. The next lowest site energy was for the hydride ligand in a terminal position on Os(4) at 10.5, which is outside the range (2.2−7.5) previously determined for terminal metal hydride site energies.[22] As implied above, it might have been expected that the H ligand bridges one of the long OsOs bonds in the molecule. However, the site energies determined for these positions (33.5 and 42.8 for bridging Os(1)Os(2) and Os(2)Os(4), respectively) clearly indicate the H ligand is not located across either of these bonds.

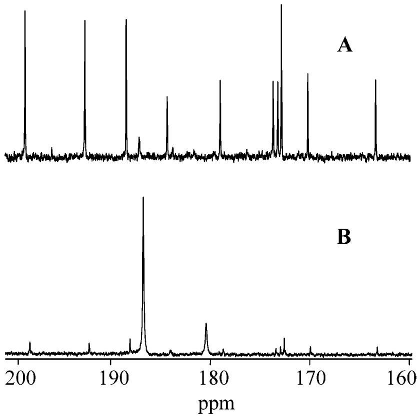


Figure 2. $^{13}C\{^1H\}$ NMR spectra of **1** (in CH_2Cl_2/CD_2Cl_2): (A) sample prepared from ^{13}C-enriched $Os_4(CO)_{14}$; (B) sample prepared from ^{13}C-enriched $Re(CO)_5(H)$.

Cluster **1** is similar to $Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$ that was prepared by the addition of $HSnMe_3$ to $Os_4(CO)_{14}$.[34] The tin derivative has the same configuration as **1**, but with the $SnMe_3$ unit replacing the $Re(CO)_5$ grouping. Persuasive structural and spectroscopic evidence indicates that, like **1**, the H ligand bridges the OsOs bond cis to the noncarbonyl ligand in $Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$, which is unusually short for a $Os(\mu\text{-}H)Os$ grouping. As shown in Chart 3, the OsOs distances in the tin compound show interesting differences from the corresponding distances in **1**. (The distances for **1** are the mean of the distances found in the independent molecules in the unit cell.) Also shown in Chart 3 are the OsOs lengths in $Os_4(CO)_{14}(PMe_3)$, which has the same electron count as **1** and $Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$, but lacks a bridging hydride.[6] It is our view that the OsOs bond lengths in these clusters cannot be readily explained by using simple bonding arguments. It is well known however that metal−metal bonds are soft and sensitive to crystal packing forces.[35] The differences in analogous OsOs lengths of the molecules shown in Chart 3 might therefore simply be the result of different packing forces within the crystals. On the other hand, in a study from this laboratory an analysis of 18 crystal structures of the type $Os_3(CO)_{11}(PR_3)$ indicated crystal packing forces were small and rarely accounted for more than a difference of 0.02 Å in the OsOs lengths.[36]

The $^{13}C\{^1H\}$ NMR spectrum of **1** prepared from ^{13}C-enriched (~30%) $Os_4(CO)_{14}$ and unenriched $Re(CO)_5(H)$ displayed signals consistent with the solid-state structure of **1** with the exception that the signals due to the carbonyls attached to the Re atom were very weak (Figure 2A). This could be due to the absence of CO exchange in **1** or to quadrupolar broadening of these signals due to the rhenium atom (both naturally occurring isotopes of Re have spin 5/2). To distinguish between the two possibilities, **1** was prepared from unenriched $Os_4(CO)_{14}$ and ^{13}CO-enriched $Re(CO)_5(H)$. The $^{13}C\{^1H\}$ NMR spectrum of this sample is shown in Figure 2B and clearly shows strong signals due to the

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for $ReOs_4(\mu\text{-}H)(\mu\text{-}CO)(CO)_{17}$ (2)

Re−Os(1)	2.970(1)	Os(2)−Os(3)	2.837(1)
Os(1)−Os(2)	2.963(1)	Os(2)−Os(4)	2.804(1)
Os(1)−Os(3)	2.873(1)	Os(3)−Os(4)	2.733(1)
Os(1)−Os(4)	2.860(1)	Os(3)−C(15)	2.19(2)
Re−C(5)	1.89(2)	Os(4)−C(15)	2.10(2)
Re−C(*rad.*) range	1.99(2)−2.02(2)	Os−C(term.) range	1.84(2)−1.96(2)
Os(1)−H	1.83	Os(2)−H	2.14
Re−Os(1)−Os(2)	115.82(3)	Os(3)−Os(2)−Os(4)	57.96(2)
Re−Os(1)−Os(3)	148.32(3)	Os(1)−Os(3)−Os(2)	62.51(2)
Re−Os(1)−Os(4)	150.65(3)	Os(1)−Os(3)−Os(4)	61.27(2)
Os(2)−Os(1)−Os(3)	58.15(2)	Os(2)−Os(3)−Os(4)	60.41(2)
Os(2)−Os(1)−Os(4)	57.55(3)	Os(1)−Os(4)−Os(2)	63.08(3)
Os(3)−Os(1)−Os(4)	56.95(2)	Os(1)−Os(4)−Os(3)	61.78(2)
Os(1)−Os(2)−Os(3)	59.34(2)	Os(2)−Os(4)−Os(3)	61.63(2)

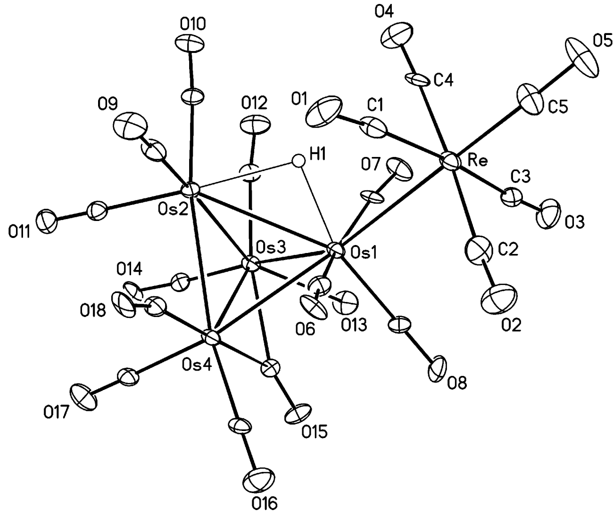

Figure 3. Molecular structure of $ReOs_4(\mu\text{-}H)(CO)_{18}$ (**2**).

Re carbonyls, but weak resonances due to the Os carbonyls. The spectrum was also recorded after the sample had been allowed to stand at room temperature for 5 days. The signals due to the Os carbonyls had significantly increased in intensity, but were still not of the expected intensity for complete scrambling of the ^{13}CO ligands over all the available carbonyl sites. Carbonyl exchange between the $Re(CO)_5$ grouping and the rest of the cluster is thus slow on the synthetic time scale at room temperature. In this respect it resembles the CO exchange in $(OC)_5MnRe(^{13}CO)_5$.[37]

The ^{13}C NMR resonances for the Os carbonyls of **1** consist of four signals of intensity 2 and five with intensity 1, which is as predicted from the solid-state structure (Figure 1). One of the former signals is shifted to high field such that it is in the region where peaks due the equatorial carbonyls occur. This was also observed in the $^{13}C\{^1H\}$ NMR spectra of $Os_4(CO)_{14}(PMe_3)$ and $Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$ and probably reflects the usual bonding in these derivatives.[6,34]

The H-coupled ^{13}C NMR spectrum of **1** showed coupling to two resonances due to axial carbonyls and three resonances attributed to equatorial carbonyls. The couplings were in the range 2.6−3.4 Hz except that to the signal at δ 184.0, which was 6.7 Hz. The resonance at δ 184.0 can be confidently assigned as due to C(6) (Figure 1), as it is directly trans to the H atom. The coupling pattern might be considered to be more consistent with placement of the H ligand across the long Os(1)Os(2) or the Os(2)Os(3) bond. It is believed the H ligand does indeed bridge the Os(1)Os(4) bond and that one of the small couplings to a signal attributed to an equatorial carbonyl is the all-trans, three-bond coupling to C(13) (Figure 1) and is larger than normal because of the delocalized bonding in the molecule. The C−H couplings observed in the spectrum of **1** are similar to the corresponding couplings in $Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$, where the evidence for the positioning of the H ligand is stronger.[34]

$ReOs_4(\mu\text{-}H)(\mu\text{-}CO)(CO)_{17}$ (2). Careful heating of **1** in hexane at 85 °C for 24 h produced as a precipitate compound **2** (eq 2). The complex was isolated as orange

$$ReOs_4(\mu\text{-}H)(CO)_{19} \xrightarrow{85\ °C} \underset{\mathbf{2}}{ReOs_4(\mu\text{-}CO)(CO)_{17}} \qquad (2)$$

air-stable crystals upon recrystallization from CH_2Cl_2. The structure of **2** consists of a spiked tetrahedral arrangement of metal atoms (Figure 3). (Selected bond lengths and angles for **2** are given in Table 3.) There is a bridging carbonyl present in the molecule, which is rare for Os carbonyl cluster complexes, although a bridging carbonyl is present in $Os_5(\mu\text{-}CO)(CO)_{17}$, a cluster with the same 76-electron count as **2**.[1,11,38] As before, the spike metal atom is confidently assigned as the Re atom on the basis of the metal−metal lengths. The spike metal−metal length of 2.970(1) Å is typical of an unsupported ReOs bond.[27] The XHYDEX program indicated that the hydride ligand bridges Os(1)Os(2), and consistent with this view is that the OsOs vector is long at 2.963(1) Å. The other OsOs lengths are significantly shorter and are in the range 2.733(1)−2.873(1) Å. The shortest OsOs distance is associated with the bridging carbonyl group; the other two short metal−metal distances involve the Os atom of the $Os(CO)_3$ grouping. These lengths are typical of the OsOs lengths found in the more condensed Os carbonyl clusters such as $Os_5(CO)_{16}$, $Os_6(CO)_{18}$, and $Os_7(CO)_{21}$.[12,38,39]

The spiked tetrahedral arrangement of metal atoms is extremely rare in metal carbonyl cluster chemistry. It is found in $Os_6(\mu\text{-}H)(\eta^2\text{-}C_6F_5NNNC_6F_5)(\mu\text{-}CO)(CO)_{19}$, which has the same $Os_4(\mu\text{-}H)(\mu\text{-}CO)(CO)_{12}$ unit as **2**.[40]

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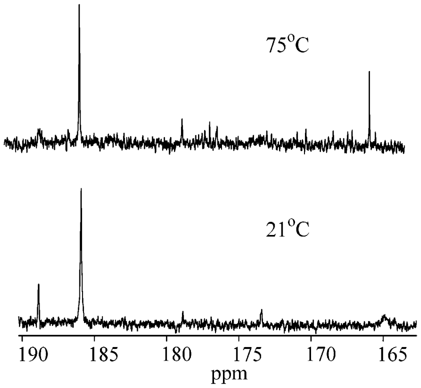


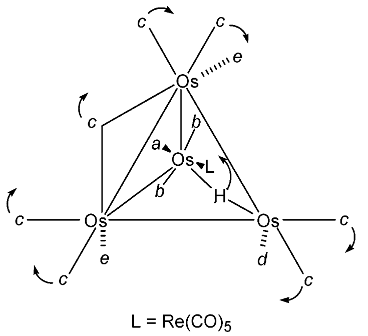
Figure 4. $^{13}C\{^1H\}$ NMR spectra of **2**. The solvent for the room-temperature spectrum was CH_2Cl_2/CD_2Cl_2; for the spectrum at 75 °C it was $C_2H_2Cl_4/C_2D_2Cl_4$.

The arrangement is also present in $RuOs_4(\mu\text{-}H)_3(\mu_3\text{-}\eta^6\text{-}C_6H_5)(CO)_{12}[P(OMe)_3]$ and $Ru_2Os_3(\mu\text{-}H)(\mu_3\text{-}\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)(CO)_{11}[P(OMe)_3]$; in each case the spike metal−metal bond is bridged by ligands.[41,42] In the dianion $[Ir_8(CO)_{22}]^{2-}$ two Ir_4 tetrahedra are fused by an unbridged IrIr bond.[43]

Cluster **2** is much less soluble than the other pentanuclear clusters reported here and those mentioned in the Introduction.[1−3] The calculated densities for the $ReOs_4(\mu\text{-}H)(CO)_n$ clusters (Table 1) do not suggest any unusually strong intramolecular forces present in **2**. The shortest intermolecular separations are five O···O contacts around 2.9 Å.

The insolubility of **2** prevented its study by $^{13}C\{^1H\}$ NMR spectroscopy below room temperature. The spectrum at ambient temperature in CH_2Cl_2/CD_2Cl_2 was obtained with difficulty (~30% ^{13}CO enriched in all sites; 37 000 scans) and is shown in Figure 4. As such, the spectrum consisted of two intense signals (at δ 188.9 and 185.1) in an approximate 1:4 ratio that are confidently assigned as due to the carbonyls of the $Re(CO)_5$ unit. Of much weaker intensity were two resonances at δ 178.9 and 173.4 in a 1:2 ratio and a broad signal centered at δ 165. (The same spectrum was obtained on samples from two different preparations.) In the spectrum at 75 °C ($C_2H_2Cl_4/C_2D_2Cl_4$, 31,623 scans; Figure 4) the signal originally at δ 188.1 had broadened (at δ 188.9). Because the peak width of the signal originally at δ 185.9 appeared unchanged (δ 185.9), the broadening is attributed to quadrupolar coupling to Re rather than the result of CO exchange. In the Os−CO region there was a relatively strong signal at δ 165.3 plus several other signals that were hardly discernible above the background (Figure 4). The most intense of the weak signals was at δ 178.9; this signal was attributed to $ReOs_4(\mu\text{-}H)(CO)_{16}$, the thermal decomposition product of **2** (see below). The presence of this product was confirmed by a $^{13}C\{^1H\}$ NMR spectrum (in CH_2Cl_2/CD_2Cl_2, RT) of the sample recovered after the spectrum at 75 °C had been determined.

Chart 4



The NMR results are interpreted as follows. The carbonyls attached to the Re atom are rigid on the NMR scale. The carbonyls bound to the Os atom of the $Os(CO)_3[Re(CO)_5]$ grouping (i.e., carbonyls *a* and *b* in Chart 4) are rigid at room temperature but undergo mutual exchange at 75 °C such that the ^{13}C signals are broadened into the baseline or such that the coalesced signal is not sufficiently above background to be confidently assigned. The carbonyls in the Os_3 plane that contain the bridging carbonyl (i.e., the carbonyls labeled *c* in Chart 4) undergo exchange to give the broad signal at δ 165 that sharpens in the spectrum at 75 °C. Cluster compounds with a single bridging CO ligand typically undergo rapid merry-go-round CO exchange in the plane containing the $M(\mu\text{-}CO)M$.[44] (Maintaining equivalent electronic configurations between the different states requires the hydride ligand to move counter to the motion of the CO exchange as shown in Chart 4.) The ^{13}C NMR chemical shifts of bridging carbonyls are typically 30 ppm to low field of the shifts of terminal carbonyls.[45] Coalescence of two signals due to the two different types of carbonyls would require a rate of exchange of $\sim 7 \times 10^3\ s^{-1}$.

It is unclear why the signals due to the carbonyls on the Os atoms were of low intensity. It is tentatively attributed to partial saturation due to long T_1 relaxation times of the C atoms of these ligands. The intensity of these signals, however, did not change when the spectrum was recorded with the relaxation agent $Cr(acac)_3$ added to the solution.[46]

$ReOs(\mu\text{-}H)(CO)_{16}$ (3). Heating of **1** (or a suspension of **2**) in hexane at 95 °C for 4 days gave **3** after workup (eq 3). The complex was isolated as dark red, almost

$$ReOs_4(\mu\text{-}H)(CO)_{19} \xrightarrow[\text{4 days}]{95\ ^\circ C} \underset{\mathbf{3}}{ReOs_4(\mu\text{-}H)(CO)_{16}} \qquad (3)$$

black, air-stable crystals. The structure of **3** is shown in Figure 5; selected bond lengths and angles are collected in Table 4. The Re atom once again is placed in the site shown on the basis of the metal−metal bond lengths: the (unbridged) lengths involving this metal atom are significantly longer than those between the other metal atoms (2.8911(6)−2.9978(6) Å versus 2.7468(6)−2.8209(6) Å). As indicated by the XHYDEX pro-

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for $ReOs_4(\mu\text{-}H)(CO)_{16}$ (3)

Re−Os(1)	3.0840(6)	Os(1)−Os(2)	2.8209(6)
Re−Os(2)	2.8911(6)	Os(1)−Os(4)	2.7978(6)
Re−Os(3)	2.9978(6)	Os(2)−Os(3)	2.7776(6)
Re−Os(4)	2.9170(6)	Os(2)−Os(4)	2.7995(6)
		Os(3)−Os(4)	2.7468(6)
Re−C (range)	1.96(1)−2.01(1)	Os−C (range)	1.88(1)−1.94(1)
Re−H	1.83	Os(1)−H	1.82
Os(2)···C(2)[a]	2.69(1)	Os(4)···C(4)[a]	2.84(1)
Os(3)···C(3)[a]	2.82(1)		
Os(1)−Re−Os(2)	56.23(1)	Os(1)−Os(2)−Os(3)	112.95(2)
Os(1)−Re−Os(3)	100.24(2)	Os(1)−Os(2)−Os(4)	59.71(1)
Os(1)−Re−Os(4)	55.50(1)	Os(3)−Os(2)−Os(4)	59.01(1)
Os(2)−Re−Os(3)	56.25(2)	Re−Os(3)−Os(2)	59.93(1)
Os(2)−Re−Os(4)	57.63(1)	Re−Os(3)−Os(4)	60.85(1)
Os(3)−Re−Os(4)	55.32(1)	Os(2)−Os(3)−Os(4)	60.89(2)
Re−Os(1)−Os(2)	58.43(1)	Re−Os(4)−Os(1)	65.28(2)
Re−Os(1)−Os(4)	59.23(2)	Re−Os(4)−Os(2)	60.72(1)
Os(2)−Os(1)−Os(4)	59.77(2)	Re−Os(4)−Os(3)	63.83(2)
Re−Os(2)−Os(1)−	65.34(2)	Re−Os(4)−Os(3)	63.83(2)
Re−Os(2)−Os(3)	63.82(2)	Os(1)−Os(4)−Os(2)	60.53(1)
Re−Os(2)−Os(4)	61.65(2)	Os(1)−Os(4)−Os(3)	114.65(2)
		Os(2)−Os(4)−Os(3)	60.10(1)

[a] Weak interaction.

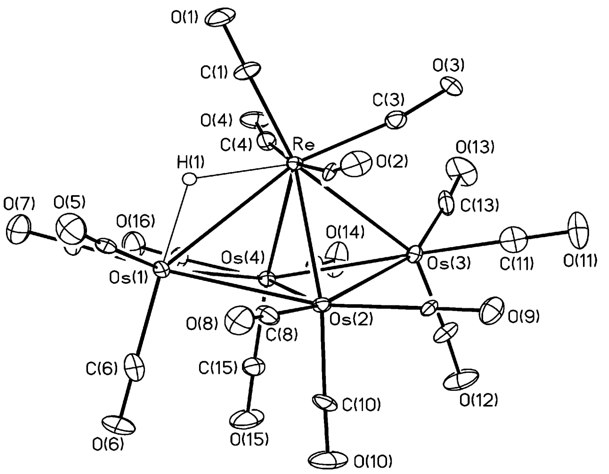

Figure 5. Molecular structure of $ReOs_4(\mu\text{-}H)(CO)_{16}$ (**3**).

gram, the H ligand bridges the longest metal−metal vector (3.0840(6) Å). The trigonal bipyramidal arrangement of metal atoms in **3** is the structure expected for a 72-electron cluster and is the skeleton found for the isoelectronic $Os_5(CO)_{16}$.[12,38,47] The Re-bound CO ligands that are not cis to the H atom (i.e., CO(2), CO(3), and CO(4)) show weak bridging interactions with the neighboring osmium atom (Table 4). The shortest of these interactions is Os(2)···C(2) at 2.69(1) Å. Furthermore, whereas the ReCO(1) angle is 179.5(10)°, the other ReCO angles are in the range 167.7(9)−169.8(10)°. In other words, the CO ligands other than CO(1) are showing incipient bridging character which is consistent with the CO exchange described below.

The $^{13}C\{^1H\}$ NMR spectrum of **3** (^{13}CO enriched) in CH_2Cl_2/CD_2Cl_2 at room temperature consisted of a somewhat broadened singlet at δ 181.4 (Figure 6). This is indicative of rapid carbonyl exchange over the entire $ReOs_4$ unit. (In unpublished work we find $Os_5(CO)_{16}$ exhibits similar behavior.) The spectrum at −90 °C consisted of five sharp signals in a 2:1:2:1:1 ratio plus some barely discernible broad peaks (Figure 6). Only the resonance at highest field (i.e., that at δ 167.5) exhibited hydrogen coupling (of 6.9 Hz). This indicates the hydride ligand is rigid at this temperature and that the signal can be confidently assigned to the CO trans to the H atom (i.e., C(6) in Figure 5). That this carbonyl is rigid implies that the other two (chemically equivalent) carbonyls on Os(1) are also rigid and accounts for a signal of intensity 2. The remaining sharp signals in a 2:1:1 intensity ratio are readily assigned to the carbonyls of the $Re(CO)_4$ grouping because a rigid $Os(CO)_3$ unit would not give resonances with this intensity pattern. It is believed that the carbonyls of each of the $Os(CO)_3$ units not involved with the bridging H ligands are undergoing mutual exchange within the particular $Os(CO)_3$. (There is probably no exchange between carbonyls on different Os atoms at this temperature, but this cannot be ruled out.)[48,49] This causes broadening

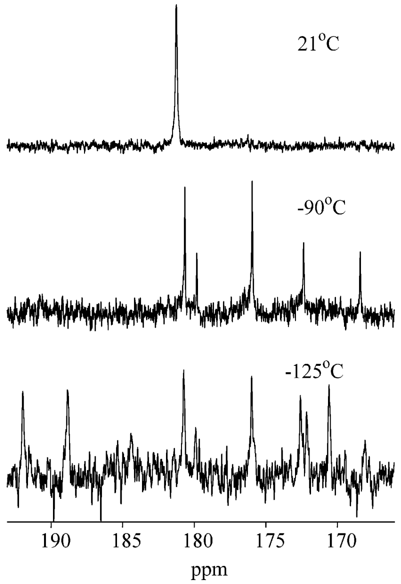

Figure 6. $^{13}C\{^1H\}$ NMR spectra of **3**. The solvent for the room-temperature spectrum and that at −90 °C was CH_2Cl_2/CD_2Cl_2; for the spectrum at −125 °C it was $CHFCl_2/CD_2Cl_2$.

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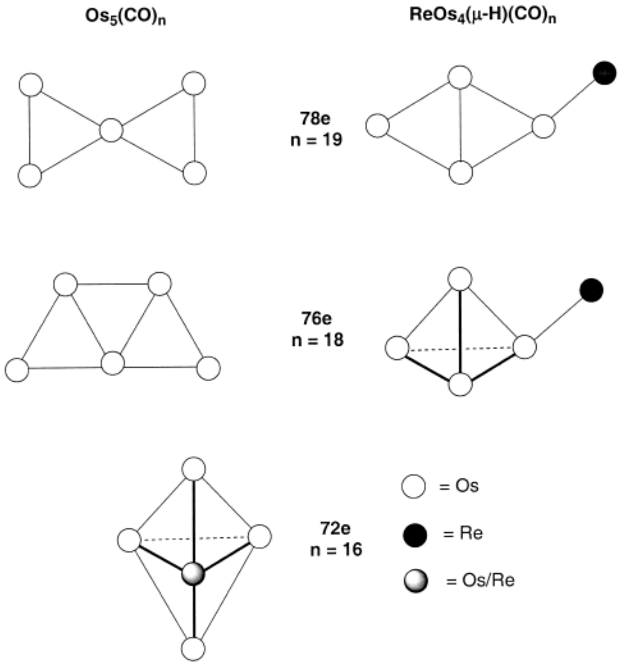
Chart 5



of the signals of these $Os(CO)_3$ groups into the baseline. Exchange of carbonyls within individual $Os(CO)_3$ units is a feature of hexanuclear Os carbonyl clusters.[48,49] The ^{13}C NMR spectrum at −125 °C (in $CHFCl_2/CD_2Cl_2$) although not of high quality (Figure 6) is consistent with the solid-state structure (i.e., all carbonyls rigid on the NMR time scale).

Conclusions

Compound **1** can be considered a cluster of the type $Os_4(CO)_{14}(L)$ where L is $Re(CO)_5$ and with an H ligand associated with the Os_4 nucleus. As such, the Os_4 skeleton resembles the Os framework in $Os_4(CO)_{14}(L)$ (L = CO, $CNBu^t$,[18] PMe_3[6]) allowing for a slight expansion of the skeleton due to the presence of the hydride ligand. Likewise, compound **2** has a similar Os_4 unit found in $Os_4(CO)_{13}(L)$ (L = CO,[19] PMe_3[6]). In other words, the presence of a single bridging hydride ligand does not cause a major change in the geometry in these clusters.

In Chart 5 are shown the metal skeletons found for the $Os_5(CO)_n$ clusters[1,10−12] along with the corresponding skeletons reported here for the $ReOs_4(\mu\text{-}H)(CO)_n$ molecules. As can be seen, the metal skeleton found for $Os_5(CO)_{19}$ differs from that in **1** even though both have six metal−metal bonds expected from electron counting rules. The same situation is observed for the structures of $Os_5(\mu\text{-}CO)(CO)_{17}$ and **2** in that both compounds have seven metal−metal bonds, but the connectivity is different in each molecule.

It has not been established that these clusters are the thermodynamically stable forms for the clusters. It may be that the $Re(CO)_5$ unit is kinetically inert under the preparative conditions employed and prevents the conversion of **1** and **2** to the isomeric forms of their $Os_5(CO)_n$ analogues. (There was no infrared evidence in the conversion of **1** to **2** and from **2** to **3** for any other compounds other than those isolated.) It is noted that the metal frameworks found for **1** and **2** maximize the number of OsOs bonds in the cluster. There is only one ReOs bond in the structures of **1** and **2**, whereas if these clusters assumed the skeletons in the $Os_5(CO)_n$ analogues, there would be a minimum of two ReOs bonds (Chart 5). The differences in the structures might therefore be rationalized if an OsOs bond is stronger than a similar ReOs bond. As discussed above OsOs bonds are significantly shorter than comparable ReOs bonds, which is consistent with this view.[50] On the other hand, in **3** the $Re(CO)_4$ grouping occupies an equatorial rather than axial position in the trigonal bipyramidal metal skeleton that maximizes the number of ReOs bonds. The formation of **3** from **2** must involve breaking of an OsOs bond in the Os_4 tetrahedron of **2**. In $Os_5(CO)_{16}$ the Os atom with four carbonyl ligands (shaded circle Chart 5) has a formal 20-electron count. A referee has pointed out that with the Re atom in this site in **3** the electron density in the cluster is more evenly distributed because rhenium has one less electron than osmium.

This study provides further evidence for skeletal variability in open metal carbonyl clusters that is not readily predicted from current bonding theories.[51]

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Supporting Information Available: Figure showing both independent molecules of **1**; tables of crystal structure and refinement data, atomic coordinates, thermal parameters, and bond lengths and angles for compounds **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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