A), 2.34 (s, $CH_3C_6H_4$, B), 2.45 (s, $CH_3C_6H_4$, A); ^{13}C NMR ($CDCl_3$) δ 223.2 (WCO, B), 222.2 (WCO, A), 205.3 (CCO, A + B), 198.2 (CCO, A), 198.0 (CCO, B), 138.8–137.0 (Tol, A + B), 133.2–126.9 (dppe, A + B), 94.4 (Cp, B), 94.2 (Cp, A), 21.8 (Tol, A), 21.5 (Tol, B), 29.5 (t, J_{P-C} = 16 Hz, dppe, B), 27.9 (t, J_{P-C} = 16 Hz, dppe, A). Anal. Calcd: C, 55.37; H, 3.98. Found: C, 55.85; H, 4.01.

Conversion of 8 into 7. A CH_2Cl_2 solution of 8 (60 mg, 0.049 mmol) was treated with dppe (20 mg, 0.05 mmol) at room temperature to give an immediate color change from purple-red to orange-red. An IR spectrum showed that the mixture contained a 1:1 mixture of 7 and 8. Continued stirring at room temperature for 1 h showed no further changes in the IR spectrum so additional dppe (80 mg, 0.20 mmol) was added. An IR spectrum of the now orange solution showed only carbonyl bands attributable to 7.

Crystallographic Characterization of $[Cp(CO)_2W]_2(\mu\text{-}TolCC\{O\}CTol)$ (2). Table I provides the crystal parameters and details of the data collection and refinement processes. The data crystal was cleaved from a larger specimen grown from CH_2Cl_2/pentane. The unit-cell parameters were obtained from the angular settings of 25 reflections (26° ≤ 2θ ≤ 31°) which included Friedel-related sets to inspect optical and diffractometer alignment. The centosymmetric triclinic space group $P\bar{1}$ was indicated correct by the successful and computationally stable refinement of the structure. Delauney reduction indicated that no higher symmetry existed. Owing to the platelike crystal shape and evidence for large edge-effect intensity deviations, the empirical correction for absorption ignored those reflections making a glancing angle of ≤3° to the major face (001). Of the 216 ψ-scan reflections used, 12 were ignored, and 368 data were similarly discarded from the full data set. For the remaining 204 ψ-scan reflections R(int) was reduced from 10.7% to 1.6% with T(max)/T(min) = 0.68/0.36.

The W atoms were located by an autointerpreted Patterson synthesis. Subsequent difference Fourier synthesis provided the remaining non-hydrogen atoms. Hydrogen atoms were idealized (d(C–H) = 0.96 Å) and updated. All non-hydrogen atoms were refined anisotropically.

All software routines are contained in the SHELXTL (5.1) program library (Nicolet Corp., Madison, WI). Tables of complete bond lengths and angles, anisotropic thermal parameters, calculated hydrogen atom positions, and structure factors for 2 were provided as supplementary material to ref 9.

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Registry No. 1, 60260-15-3; 2, 95029-84-8; 5, 102615-19-0; 6, 102615-20-3; 7, 111189-61-8; 8 (isomer 1), 111265-70-4; 8 (isomer 2), 111189-59-4; *trans*-$Cl(CO)_4W{\equiv}CTol$, 68480-95-5; *trans*-$Cl(CO)_2(TMEDA)W{\equiv}CTol$, 111189-60-7.

Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom positions for 2 (5 pages); a listing of structure factors for 2 (22 pages). Ordering information is given on any current masthead page.

Synthesis, Structure, and Fluxional Properties of the Novel Tetranuclear Osmium Clusters $Os_4(CO)_n(PMe_3)$ (n = 15, 14, 13)[1]

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Addition of $Os(CO)_4(PMe_3)$ to $Os_3(CO)_{11}(CH_3CN)$ or to $Os_3(\mu\text{-}H)_2(CO)_{10}$ affords $Os_4(CO)_{15}(PMe_3)$ (1) as the major product. Treatment of 1 in CH_2Cl_2 with Me_3NO gives $Os_4(CO)_{14}(PMe_3)$ (2) which in turn can be converted to $Os_4(CO)_{13}(PMe_3)$ (3) by heating in hexane at 90 °C under vacuum or by UV irradiation in hexane. The structures of 1, 2, and 3 have been determined by X-ray crystallography: Compound 1 crystallizes in the space group $P\bar{1}$, with a = 12.473 (2) Å, b = 13.325 (2) Å, c = 17.547 (2) Å, α = 109.05 (1)°, β = 90.44 (1)°, γ = 94.60 (1)°, and Z = 4; R = 0.037 and R_w = 0.041 for 5172 observed reflections. Compound 2 crystallizes in the space group $P2_1/a$, with a = 13.525 (5) Å, b = 12.969 (6) Å, c = 14.825 (5) Å, β = 99.14 (3)°, and Z = 4; R = 0.039 and R_w = 0.048 for 2424 observed reflections. Compound 3 crystallizes in the space group $P2_1/c$, with a = 15.470 (2) Å, b = 10.193 (1) Å, c = 16.527 (2) Å, β = 113.45 (1)°, and Z = 4; R = 0.047 and R_w = 0.060 for 2060 observed reflections. In 1, the $Os(CO)_4(PMe_3)$ acts as a ligand to an $Os_3(CO)_{11}$ fragment via an unbridged dative Os–Os bond of lengths 2.939 (1) and 2.937 (1) Å for the two independent molecules in the unit cell. The Os–Os bond lengths within the Os_3 triangle are 2.849 (1) and 2.855 (1) Å (trans to the Os–Os dative bond), 2.923 (1) and 2.930 (1) Å (cis to the Os–Os dative bond), and 2.894 (1) and 2.894 (1) Å. In CD_2Cl_2/CH_2Cl_2, 1 is rigid at −67 °C by ^{13}C NMR spectroscopy. However, at ambient temperature all the carbonyl ligands of 1 undergo exchange. Cluster 2 has a planar Os_4 skeleton with two adjacent short Os–Os bonds (of lengths 2.779 (2) and 2.784 (2) Å) and two long Os–Os bonds (of lengths 2.982 (2) and 3.013 (2) Å); the diagonal Os–Os bond is normal at 2.935 (2) Å. The unusual structure of 2 is rationalized in terms of three-center–two-electron metal–metal bonds to give Os–Os bonds of orders 1.5 and 0.5 and achieves an 18-electron configuration for each osmium atom. The cluster is also fluxional in solution, even at −89 °C. A novel mechanism that involves cleavage of the weakest Os–Os bond is proposed to account for the nonrigidity. Cluster 3 has a tetrahedral framework with an $Os(CO)_4$, an $Os(CO)_3(PMe_3)$, and two $Os(CO)_3$ units; the Os–Os bond lengths range from 2.765 (1) to 2.869 (1) Å. Weak semibridging interactions are present for four of the carbonyl ligands. The cluster is highly fluxional, exhibiting a singlet for the carbonyl ligands in the ^{13}C NMR spectrum even at −120 °C in $CHFCl_2/CD_2Cl_2$. This is believed to be the first report of a 64-electron cluster that has been successively converted to a 62- and then to a 60-electron cluster.

One of the challenges of modern inorganic chemistry is the rational synthesis of transition-metal cluster compounds.[2,3] Several strategies have been adopted for this purpose. These include the reaction of a transition-metal

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hydride or other mononuclear (or multinuclear) species with clusters that contain easily displaced ligands,[4-8] reactions of metal complexes with unsaturated metal clusters (especially $Os_3(\mu\text{-}H)_2(CO)_{10}$),[9-11] the so-called redox condensation reactions for cluster syntheses,[3] the reaction of unsaturated metal fragments with metal carbene and carbyne compounds,[12] and the use of clusters with bridging ligands such as sulfur to build clusters of higher nuclearity.[13,14]

Recent work from this laboratory has demonstrated that neutral 18-electron complexes can act as ligands to give bimetallic compounds with unbridged, donor–acceptor metal–metal bonds. Two examples of compounds of this type are $(Me_3P)(OC)_4OsW(CO)_5$[15] and $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$.[16] Here we report the use of this concept in the synthesis of the novel tetranuclear clusters of osmium $Os_4(CO)_n(PMe_3)$ (n = 15, 14, 13) (eq 1–3). Part of this study has appeared in communications.[17,18]

$$Os_3(CO)_{11}(CH_3CN)\ (Os_3(\mu\text{-}H)_2(CO)_{10}) + Os(CO)_4(PMe_3) \rightarrow Os_3(CO)_{11}[Os(CO)_4(PMe_3)] \quad (1)$$

$$Os_3(CO)_{11}[Os(CO)_4(PMe_3)] \xrightarrow{Me_3NO} Os_4(CO)_{14}(PMe_3) \quad (2)$$

$$Os_4(CO)_{14}(PMe_3) \xrightarrow[\text{or } h\nu]{\Delta} Os_4(CO)_{13}(PMe_3) \quad (3)$$

Experimental Section

Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. Hexane was refluxed over potassium, distilled, and stored under nitrogen before use. Dichloromethane was treated similarly except that P_2O_5 was used as the drying agent. The osmium complexes, $Os(CO)_4(PMe_3)$,[19] $Os_3(\mu\text{-}H)_2(CO)_{10}$,[20] $Os_3(CO)_{11}(MeCN)$,[21] and $Os_3(CO)_{10}(MeCN)_2$,[21] were prepared by literature methods or by minor modification thereof. The ^{13}CO-enriched compounds were obtained from ^{13}CO-enriched $Os_3(CO)_{12}$ ($\sim$35% ^{13}C). This in turn was prepared by heating $Os_3(CO)_{12}$ in toluene at 125 °C under $\sim$1.5 atm ^{13}CO (99% ^{13}C) for 3 days. The Me_3NO, as obtained commercially, was sublimed before use.

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer; the internal calibration of the instrument was periodically checked against the known absorption frequencies of gaseous CO. Electron-impact (70 eV) mass spectra were obtained on a Kratos-MS-50 instrument (University of British Columbia, regional facility); the pattern of the envelope of ions at highest mass for each compound matched that simulated by computer for the species involved. NMR spectra were recorded on a Brucker WM400 spectrometer. Melting points were determined on samples sealed in capillaries under nitrogen by use of a Gallenkamp apparatus. Microanalyses were performed by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

Preparation of $Os_4(CO)_{15}(PMe_3)$ (1). Method 1. A solution of $Os_3(\mu\text{-}H)_2(CO)_{10}$ (200 mg, 0.27 mmol) and $Os(CO)_4(PMe_3)$ (230 mg, 0.60 mmol) in hexane (25 mL) was stirred at room temperature for 2 h during which time an orange precipitate formed. The mother solution was then removed from the precipitate which was washed with hexane (3 × 5 mL). The precipitate was then dissolved in a minimum volume of hot CH_2Cl_2 ($\sim$10 mL), the resulting solution filtered, and the product $Os_4(CO)_{15}(PMe_3)$ (194 mg, 57%) reprecipitated with hexane. The analytical sample was recrystallized from CH_2Cl_2: mp 148 °C; IR(CH_2Cl_2) ν(CO) 2115 (vw), 2086 (m), 2048 (s), 2033 (s), 2005 (m, asym), 1974 (w), 1961 (w), 1916 (w, br) cm^{-1}; ^1H NMR (C_6D_6) δ 0.57 (d, J_{P-H} = 10.4 Hz); $^{13}C\{^1H\}$ NMR (CH_2Cl_2/CD_2Cl_2, 4:1; –67 °C) δ 198.4, 187.7, 184.0 (ax-CO's), 181.6 (J_{P-C} = 4.1 Hz, $Os(CO)_4(PMe_3)$), 183.9, 180.1, 173.0, 171.6, 171.0 (eq-CO's) 21.9 (J_{P-C} = 38 Hz, $P(CH_3)_3$); MS(EI) m/z 1202 (M^+ – 2CO). Anal. Calcd for $C_{18}H_9O_{15}POs_4$: C, 17.20; H, 0.72. Found: C, 17.09; H, 0.76.

Method 2. A hexane solution of $Os_3(CO)_{11}(MeCN)$ (130 mg, 0.130 mmol) and $Os(CO)_4(PMe_3)$ (55 mg 0.145 mmol) was stirred at 60 °C for 2 h. The supernatant liquid was then removed from the orange precipitate of $Os_4(CO)_{15}(PMe_3)$ which was washed with hexane and dried on the vacuum line. The yield was somewhat lower (about 40%) than that obtained by method 1; the yield was not improved by longer reaction times.

Preparation of $Os_4(CO)_{14}(PMe_3)$ (2). Method 1. To a solution of $Os_4(CO)_{15}(PMe_3)$ (100 mg, 0.079 mmol) in CH_2Cl_2 (25 mL) a solution of Me_3NO in MeOH was added dropwise until all the $Os_4(CO)_{15}(PMe_3)$ had been consumed (the progress of the reaction was monitored by the disappearance of the band at 2086 cm^{-1} in the infrared spectrum of the solution). During the addition the color of the solution changed from orange to deep red. The solution was filtered through a short column of silica (10 × 2.5 cm) and evacuated to dryness. The resulting solid was extracted with hot hexane (3 × 20 mL). The hexane extracts were combined and the solvent removed on the vacuum line to yield dark red crystals of $Os_4(CO)_{14}(PMe_3)$ (80 mg, 80%). The analytical sample was obtained by recrystallization from hexane: mp 128 °C; IR (hexane) ν(CO), 2116 (w), 2069 (s), 2046 (m), 2035 (vs) 2028 (sh), 2014 (m), 2004 (w), 1986 (vw), 1978 (m), 1951 (vw), 1927 (w) cm^{-1}; ^1H NMR (C_6D_6) δ 0.95 (d, J_{P-H} = 10.2 Hz); ^{13}C NMR (CO region; $CHFCl_2/CD_2Cl_2$; –115 °C) δ 211.9, 202.0 (J_{P-C} = 8.6 Hz), 192.5, 171.9 (ax-CO's) 192.2, 176.9, 174.7, 171.9, 171.0, 166.4, (eq-CO's); MS(EI) m/z 1202 (M^+ – CO). Anal. Calcd for $C_{17}H_9O_{14}POs_4$: C, 16.61; H, 0.74. Found: C, 16.84; H, 0.67.

Method 2. A solution of $Os_3(CO)_{10}(MeCN)_2$ (30 mg, 0.032 mmol) and $Os(CO)_4(PMe_3)$ (150 mg, 0.40 mmol) in toluene (10 mL) was stirred overnight. The solvent was then removed on the vacuum line and the $Os(CO)_4(PMe_3)$ removed from the remaining solid by sublimation at 40 °C (<0.02 mm) to a water-cooled probe.

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(1) Taken in part from: Martin, L. R. Ph.D. Thesis, Simon Fraser University, 1986.

(2) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Elmsford, NY, 1982; Chapter 40.

(3) Chini, P. *J. Organomet. Chem.* **1980**, *200*, 37.

(4) Shapley, J. R.; Pearson, G. A.; Tachikawa, M.; Schmidt, G. E.; Churchill, M. R.; Hollander, F. J. *J. Am. Chem. Soc.* **1977**, *99*, 8064.

(5) (a) Ditzel, E. J.; Holden, H. D.; Johnson, B. F. G.; Lewis, J.; Saunders, A.; Taylor, M. J. *J. Chem. Soc., Chem. Commun.* **1982**, 1373. (b) Johnson, B. F. G.; Khattar, R.; Lewis, J.; McPartlin, M.; Morris, J.; Powell, G. L. *J. Chem. Soc., Chem. Commun.* **1986**, 507. (c) Goudsmit, R. J.; Jeffrey, J. G.; Johnson, B. F. G.; Lewis, J.; McQueen, R. C. S.; Sanders, A. J.; Liu, J.-C. *J. Chem. Soc., Chem. Commun.* **1986**, 24.

(6) Ditzel, E. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Taylor, M. J. *J. Chem. Soc., Dalton Trans.* **1985**, 555.

(7) Couture, C.; Farrar, D. H. *J. Chem. Soc.*, Dalton *Trans.* **1986**, 1395.

(8) Beringhelli, T.; Ciani, G.; D'Alfonso, G.; De Maldê, V.; Sironi, A.; Freni, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1051.

(9) Hsu, L.-Y.; Hsu, W.-L.; Jan, D.-Y.; Shore, S. G. *Organometallics* **1986**, *5*, 1041, and references therein.

(10) Farrugia, L. J.; Howard, J. A. K.; Mitrprachachon, P.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1981**, 171.

(11) Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *Inorg. Chem.* **1984**, *23*, 4476.

(12) (a) Elliott, G. P.; Howard, J. A. K.; Nunn, M. C.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1986**, 431. (b) Delgado, E.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1986**, 2105, and references therein.

(13) Adams, R. D.; Babin, J. E.; Mathab, R.; Wang, S. *Inorg. Chem.* **1986**, *25*, 1623, and references therein.

(14) Colbran, S. B.; Johnson, B. F. G.; Lewis, J.; Sorrell, R. M. *J. Chem. Soc., Chem. Commun.* **1986**, 525.

(15) Einstein, F. W. B.; Jones, T.; Pomeroy, R. K.; Rushman, P. *J. Am. Chem. Soc.* **1984**, *106*, 2707.

(16) Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *Organometallics* **1985**, *3*, 250.

(17) Einstein, F. W. B.; Martin, L. R.; Pomeroy, R. K.; Rushman, P. *J. Chem. Soc., Chem. Commun.* **1985**, 345.

(18) Martin, L. R.; Einstein, F. W. B.; Pomeroy, R. K. *J. Am. Chem. Soc.* **1986**, *108*, 338.

(19) Martin, L. R.; Einstein, F. W. B.; Pomeroy, R. K. *Inorg. Chem.* **1985**, *24*, 2777.

(20) Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3942.

(21) Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Chem. Soc., Dalton Trans.* **1981**, 407.

The crude product was purified as in method 1; the yield was similar to method 1.

Preparation of $Os_4(CO)_{13}(PMe_3)$ (3). Method 1. A Carius tube fitted with a Teflon valve was charged with hexane (20 mL) and $Os_4(CO)_{14}(PMe_3)$ (85 mg, 0.071 mmol). The vessel and its contents were cooled to −196 °C and the tube was evacuated; the solution was degassed with two freeze–pump–thaw cycles. The solution was then stirred at 90 °C for approximately 24 h. During this time the tube was frequently reevacuated and the solution degassed. The progress of the reaction was followed by infrared spectroscopy (carbonyl region). After the 24-h period it appeared that no further changes were taking place in the relative intensities of the CO stretching bands in the spectrum. At this stage the cooled solution was chromatographed on a silica gel column (30 × 2.5 cm) with hexane–CH_2Cl_2 (9:1) as the eluant. The first, pale-yellow band was identified as $Os_3(CO)_{11}(PMe_3)$ by infrared spectroscopy. The second, brown-purple band was the desired product, $Os_4(CO)_{13}PMe_3$. The third band was the starting material; it partially overlapped the second band. Two further bands, pale orange and purple, were not identified. The second band was collected and the solvent removed on the vacuum line to leave the crude product $Os_4(CO)_{13}(PMe_3)$ (29 mg, 34%). The analytical sample was obtained by recrystallization from hexane: mp 183 °C; IR (hexane) ν(CO), 2091 (m), 2048 (vs), 2016 (s), 1992 (m) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.02 (d, J_{P-H} = 10.6 Hz); ^{13}C NMR (CO region; $CHFCl_2/CD_2Cl_2$; −30 °C) δ 181.0; MS(EI) m/z 1202 (M$^+$). Anal. Calcd for $C_{16}H_9O_{13}POs_4$: C, 16.00; H, 0.76. Found: C, 16.11; H, 0.79.

Method 2. A Pyrex tube with **2** (98 mg, 0.080 mmol) in hexane (50 mL) was subjected to UV irradiation for 2.5 h (200-W source, approximately 3 cm between the water-jacketed source and the edge of the reaction solution). Throughout the irradiation the solution was stirred and purged with N_2. After the irradiation the solution was purged for a further 5 min to ensure the complete removal of CO. The solution was then concentrated on the vacuum line and stored at −15 °C overnight. The supernatant hexane was then removed from the crystals of $Os_4(CO)_{13}(PMe_3)$ (82 mg, 86%) which were dried on the vacuum line. The compound was pure as determined by infrared spectroscopy.

X-ray Structure Determinations. The following procedure was employed for each of the three structure determinations. Additional details relating to an individual determination are given after the general procedure.

A crystal of suitable size (Table I) was mounted on an Enraf-Nonius CAD4F diffractometer. Examination of the systematic absences and Laue symmetry allowed the monoclinic space groups to be determined unambiguously. The triclinic space group was confirmed by the structure refinement. Diffraction data were collected at 20 ± 1 °C with the use of graphite-monochromated Mo Kα_1 radiation (λ = 0.7930 Å). Background measurements were made by extending the scan range by 25% on each side of the scan. Two standard reflections were monitored at least every 2 h during data collection and intensity data were scaled appropriately. Lorentz, polarization, and absorption corrections were applied. Accurate cell dimensions were assigned on the basis of 25 (24 for **1**) carefully centered high angle (2θ > 21°) reflections widely scattered in reciprocal space. ψ scans were obtained for a number of reflections (typically six) throughout the 2θ range of data collection and having χ near 90°. Crystal faces were measured with an independently mounted, modified optical telescope fitted with a filar eyepiece.

The osmium atoms were located by conventional methods; the other nonhydrogen atoms were located from Fourier difference maps alternated with least-squares refinement. Extinction was added as a refinable parameter for **1** and **3** (Table I).[22] For **2** those four reflections suffering most noticeably from extinction were removed from the refinement process.[23] Unit weights were used during the initial stages of refinement for all three determinations. After anisotropic refinement, the weight, ω, for each reflection was set to be $\omega = [\sigma^2(F) + KF^2]^{-1}$ and the value of K adjusted to remove trends in the average $\omega\Delta^2/\lambda$ in the error analysis. In each case the largest peaks in the final Fourier difference map were in the vicinity of the osmium atoms. Crystallographic data and details of each data collection are given in Table I. Neutral atom scattering factors with anomalous dispersion corrections were used.[24] The computer programs[25] used were from "The Vax 750/780 Crystal Structure System" except the atomic thermal ellipsoid diagrams of the molecules which were made with the SNOOPI program.

Table I. Summary of Crystal Data and Details of Intensity Collection for $Os_4(CO)_n(PMe_3)$ (n = 15, 14, 13)

	$Os_4(CO)_{15}$-(PMe_3) (1)	$Os_4(CO)_{14}$-(PMe_3) (2)	$Os_4(CO)_{13}$-(PMe_3) (3)
fw	1258	1230	1202
color	orange	deep red	burgundy
space group	$P\bar{1}$	$P2_1/a$	$P2_1/c$
cryst syst	triclinic	monoclinic	monoclinic
a, Å	12.473 (2)	13.525 (5)	15.470 (2)
b, Å	13.325 (2)	12.969 (6)	10.193 (1)
c, Å	17.547 (2)	14.825 (5)	16.527 (2)
α, deg	109.05 (1)		
β, deg	90.44 (1)	99.14 (3)	113.45 (1)
γ, deg	94.60 (1)		
V, Å^3	2745	2567	2390
Z	4	4	4
d_{calcd}, g/cm^3	3.036	3.185	3.337
μ(Mo Kα), cm^{-1}	186	199[a]	213
crystal size, mm	0.11 × 0.29 × 0.28	0.34 × 0.16 × 0.11	0.24 × 0.19 × 0.08
scan method	ω–2θ	ω–2θ	ω–2θ
scan range (2θ), deg	0.0–45.0	0.0–45.0	0.0–45.0
scan width (2θ), deg	1.3	1.3	1.3
scan rate (2θ), deg/min	1.4–6.6	1.4–6.6	1.4–6.6
colln range	$\pm h,+k,+l$	$\pm h,+k,+l$	$\pm h,+k,+l$
transmission coeff range	0.120–1.00	0.0555–0.146	0.0249–0.422
o. of unique reflcns	7167	3331	3104
no. of observed reflcns $I > 2.3\sigma I$	5172	2424	2060
no. of variables	386	325	163
R_1[b]	0.0367	0.0385	0.0470
R_2[c]	0.0407	0.0479	0.0601
K factor in wt scheme	0.0004	0.0008	0.0006
GOF	1.35	1.31	1.64
largest shift[d]	0.03	0.00	0.02
map σ, e/Å^3[e]	0.25	0.27	0.39
largest peak e/Å^3[f]	1.55	1.59	2.18
extinction parameter (×10^{-8})[g]	22 (1)		23 (3)

[a] An experimentally based absorption correction was applied, see the Experimental Section. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_2 = |\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2|^{1/2}$. [d] Largest shift/error in the final cycle of refinement. [e] Standard deviation of the final Fourier difference map. [f] Largest peak in the final Fourier difference map. [g] Parameter is g in the formula $F_c' = k|F_c|(1 + g|F_c|^2\mathrm{Lp}_2/p_1)^{-1/2}$ where F_c' is the corrected, calculated structure factor, k is a scale factor, Lp is the Lorentz polarization factor, and $P_n = 1 + \cos^{2n} 2\theta$.

$Os_4(CO)_{15}(PMe_3)$. An analytical absorption correction was applied.[26] Initial positions of a hydrogen atom on each of five of the methyl carbons of the two molecules in the asymmetric unit were located in a Fourier difference map that used only the inner data. These positions were used to calculate the positions of the second and third hydrogen atoms of the methyl groups. The positions of the hydrogen atoms on the sixth methyl group could not be located. At this point the phosphorus and methyl carbon atoms were allowed to vary anisotropically in the refinement and the weighting scheme was adjusted (R_1 = 0.037). Finally the positions of the hydrogen atoms were recalculated and

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(22) Larson, A. C. in *Crystallographic Computing*; Ahmed, F. R., Hall, S. R., Huber, C. P., Eds.; Munksgaard: Copenhagen, 1970.

(23) These four reflections were: 2,0,0, kF_0 = 710, F_c = 987; −1,1,1, kF_0 = 702, F_c = 757; −2,0,2 kF_0 = 818, F_c = 835; −4,0,2 kF_0 = 867, F_c = 1015.

(24) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

(25) (a) Gabe, E. *The Crystal Structure System*; Chemistry Division, National Research Council; Ottawa, 1983. (b) Davies, E. K. *CHEMGRAF Program Suite*; Chemical Crystallography Laboratory: University of Oxford, Oxford, 1982.

(26) North, A. C. T.; Phillips, D. C.; Mathews, F. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

Table II. Fractional Coordinates for $Os_4(CO)_{15}(PMe_3)$

atom	x	y	z	atom	x	y	z
				Molecule 1			
Os(11)	0.28363 (5)	0.95360 (6)	0.11918 (4)	C(115)	0.1827 (14)	1.1508 (16)	−0.0120 (11)
Os(12)	0.27094 (5)	1.18189 (6)	0.20523 (4)	C(116)	0.1755 (17)	1.3764 (19)	0.0385 (14)
Os(13)	0.24664 (6)	1.40409 (6)	0.24823 (4)	C(117)	0.3513 (16)	1.2846 (19)	0.0636 (13)
Os(14)	0.20324 (5)	1.27036 (6)	0.08238 (4)	C(118)	0.0571 (14)	1.2478 (16)	0.1087 (12)
P(1)	0.2743 (3)	0.7686 (4)	0.0516 (3)	O(14)	0.3865 (10)	1.0141 (11)	−0.0197 (8)
C(11)	0.1433 (15)	0.7001 (15)	0.0572 (13)	O(15)	0.2024 (11)	0.9256 (12)	0.2767 (9)
C(12)	0.2939 (15)	0.7320 (16)	−0.0548 (12)	O(16)	0.5126 (10)	0.9853 (12)	0.1930 (8)
C(13)	0.3712 (15)	0.6975 (16)	0.0888 (13)	O(17)	0.0560 (9)	0.9634 (10)	0.0577 (8)
C(14)	0.3459 (13)	0.9913 (15)	0.0316 (11)	O(18)	0.0351 (11)	1.1262 (12)	0.2355 (9)
C(15)	0.2309 (13)	0.9367 (15)	0.2169 (11)	O(19)	0.5100 (11)	1.2016 (13)	0.1711 (9)
C(16)	0.4266 (13)	0.9688 (15)	0.1648 (10)	O(110)	0.3378 (11)	1.1869 (13)	0.3704 (9)
C(17)	0.1412 (12)	0.9574 (14)	0.0796 (10)	O(111)	0.0114 (11)	1.3645 (13)	0.2857 (9)
C(18)	0.1233 (13)	1.1504 (15)	0.2239 (10)	O(112)	0.3004 (13)	1.4580 (14)	0.4263 (10)
C(19)	0.4172 (14)	1.1952 (16)	0.1804 (12)	O(113)	0.4845 (12)	1.4352 (13)	0.2115 (10)
C(110)	0.3111 (13)	1.1818 (15)	0.3048 (11)	O(114)	0.2055 (11)	1.6207 (13)	0.2382 (9)
C(111)	0.0978 (14)	1.3757 (16)	0.2698 (12)	O(115)	0.1722 (11)	1.0781 (12)	−0.0687 (9)
C(112)	0.2815 (15)	1.4373 (17)	0.3570 (12)	O(116)	0.1635 (14)	1.4396 (16)	0.0071 (11)
C(113)	0.3951 (15)	1.4207 (18)	0.2224 (12)	O(117)	0.4385 (13)	1.2901 (15)	0.0442 (11)
C(114)	0.2219 (16)	1.5342 (18)	0.2395 (13)	O(118)	−0.0333 (11)	1.2290 (12)	0.1170 (9)
				Molecule 2			
Os(21)	0.77334 (5)	0.03464 (5)	0.37813 (4)	C(215)	0.5986 (13)	−0.1955 (14)	0.4531 (10)
Os(22)	0.81459 (5)	−0.18932 (5)	0.30054 (4)	C(216)	0.7814 (12)	−0.2872 (14)	0.4589 (10)
Os(23)	0.80617 (5)	−0.41600 (6)	0.25594 (4)	C(217)	0.5625 (13)	−0.3083 (15)	0.2990 (11)
Os(24)	0.66744 (5)	−0.30249 (6)	0.38046 (4)	C(218)	0.6005 (14)	−0.4240 (16)	0.3979 (11)
P(2)	0.7459 (4)	0.2145 (4)	0.4453 (3)	O(24)	0.7657 (10)	0.0755 (11)	0.2159 (8)
C(21)	0.8585 (16)	0.3065 (16)	0.4408 (14)	O(25)	0.7891 (9)	−0.0126 (10)	0.5375 (8)
C(22)	0.6284 (16)	0.2564 (16)	0.4089 (13)	O(26)	1.0214 (9)	0.0687 (10)	0.3826 (7)
C(23)	0.7250 (16)	0.2469 (14)	0.5530 (12)	O(27)	0.5330 (9)	−0.0430 (10)	0.3527 (7)
C(24)	0.7665 (13)	0.0554 (15)	0.2738 (10)	O(28)	0.6469 (9)	−0.1910 (11)	0.1716 (8)
C(25)	0.7813 (12)	0.0013 (14)	0.4769 (10)	O(29)	0.9958 (9)	−0.1491 (10)	0.4290 (8)
C(26)	0.9282 (13)	0.0545 (15)	0.3819 (10)	O(210)	0.9814 (11)	−0.1600 (12)	0.1863 (9)
C(27)	0.6212 (12)	−0.0130 (14)	0.3627 (10)	O(211)	0.9921 (11)	−0.3910 (13)	0.3781 (9)
C(28)	0.7083 (13)	−0.1934 (14)	0.2187 (10)	O(212)	0.9733 (11)	−0.4719 (13)	0.1283 (9)
C(29)	0.9227 (12)	−0.1695 (13)	0.3825 (10)	O(213)	0.6366 (10)	−0.4324 (11)	0.1242 (8)
C(210)	0.9167 (14)	−0.1682 (16)	0.2320 (11)	O(214)	0.7368 (11)	−0.6369 (12)	0.2622 (9)
C(211)	0.9182 (14)	−0.3966 (17)	0.3358 (12)	O(215)	0.5510 (10)	−0.1268 (11)	0.4954 (8)
C(212)	0.9092 (14)	−0.4482 (16)	0.1789 (12)	O(216)	0.8455 (10)	−0.2780 (11)	0.5101 (8)
C(213)	0.7013 (14)	−0.4227 (16)	0.1737 (11)	O(217)	0.4940 (10)	−0.3062 (11)	0.2566 (8)
C(214)	0.7612 (14)	−0.5534 (16)	0.2602 (11)	O(218)	0.5552 (11)	−0.4990 (13)	0.4082 (9)

the structure was refined to completion by block diagonal methods. Final coordinates for the non-hydrogen atoms of 1 are given in Table II and bond length and angle data in Table III.

$Os_4(CO)_{14}(PMe_3)$. An experimentally determined absorption correction which had a μ value of 100 cm^{-1} was applied. All non-hydrogen atoms were allowed to vary anisotropically and then the weighting scheme was adjusted ($R_1 = 0.039$). Hydrogen atoms were included at calculated positions with a single isotropic temperature factor ($R_1 = 0.039$). The data were then refined to completion by full-matrix least-squares methods. Final coordinates for the non-hydrogen atoms of 2 are given in Table IV and bond lengths and angles for the molecule in Table V.

$Os_4(CO)_{13}(PMe_3)$. Initial phasing difficulties were overcome by application of analytical absorption correction.[26] Initial positions of one hydrogen atom on each methyl carbon atom were located from difference Fourier maps, the positions of the other hydrogen atoms were calculated. Investigation of the weighting scheme led to the assignment of a K value of 0.0006. The hydrogen atom positions were recalculated and the structure refined to completion by full-matrix least-squares methods. One large peak (2.2 e Å^{-3}, 5.6σ) in the final Fourier difference map was located inside the tetrahedron of osmium atoms at a distance of 1.319 (1) Å from Os(4) but there was no evidence to suggest it had any chemical significance. Final positional parameters for the non-hydrogen atoms of 3 are given in Table VI; bond lengths and selected angles for 3 are given in Table VII.

Results and Discussion

$Os_4(CO)_{15}(PMe_3)$. Reaction of $Os_3(CO)_{11}(CH_3CN)$ with $Os(CO)_4(PMe_3)$ in hexane at 60 °C afforded $Os_3(CO)_{11}[Os(CO)_4(PMe_3)]$ (1) in ~40% yield after 2 h (eq 1a). The product precipitated from solution which prevented decomposition (see below). Curiously, the same product was formed in the reaction of $Os_3(\mu\text{-}H)_2(CO)_{10}$ and $Os(CO)_4(PMe_3)$ in hexane at room temperature (eq 1b). The latter

$$Os_3(CO)_{11}(CH_3CN) + Os(CO)_4(PMe_3) \rightarrow \underset{\textbf{1}}{Os_3(CO)_{11}[Os(CO)_4(PMe_3)]} \quad (1a)$$

$$Os_3(\mu\text{-}H)_2(CO)_{10} + Os(CO)_4(PMe_3) \rightarrow \textbf{1} \quad (1b)$$

reaction is the preferred method of synthesis since the reaction time is shorter (1 h) and the yield higher (57%). The mechanism of this reaction is unknown; note it involves the loss of H_2 and a gain of a CO group in the product. Lewis and co-workers have recently reported a cluster build-up reaction carried out under mild conditions in which there is also a gain of a CO in the product.[27] The effect of CO pressure on the reaction shown as eq 1b was not investigated. However, it is known that $Os_3(\mu\text{-}H)_2(CO)_{10}$ reacts with CO to initially give $HOs_3(\mu\text{-}H)(CO)_{11}$ and then $Os_3(CO)_{12}$.[28] The latter cluster is inert to substitution at room temperature. Furthermore, 1 reacts with CO to give $Os_3(CO)_{12}$ and $Os(CO)_4(PMe_3)$.

Cluster 1 is a bright orange, air-stable solid that is insoluble in hexane but soluble in CH_2Cl_2, a solvent in which it slowly decomposes at room temperature. The solution

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[27] Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Morris, J.; Powell, G. L.; Raithby, P. R.; Vargas, M. D. *J. Chem. Soc., Chem. Commun.* **1986**, 429.

[28] (a) Shapley, J. R.; Keister, J. B.; Churchill, M. R.; DeBoer, B. G. *J. Am. Chem. Soc.* **1975**, *97*, 4145. (b) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1976**, *114*, 313.

Table III. Selected Molecular Dimensions for $Os_4(CO)_{15}(PMe_3)$

Bond Lengths (Å), Molecule 1			
Os(11)–Os(12)	2.939 (1)	Os(14)–C(118)	1.91 (2)
Os(11)–P(1)	2.354 (5)	P(1)–C(11)	1.83 (2)
Os(11)–C(14)	1.92 (2)	P(1)–C(12)	1.79 (2)
Os(11)–C(15)	1.92 (2)	P(1)–C(13)	1.83 (2)
Os(11)–C(16)	1.92 (2)	C(14)–O(14)	1.15 (2)
Os(11)–C(17)	1.91 (2)	C(15)–O(15)	1.16 (2)
Os(12)–Os(13)	2.849 (1)	C(16)–O(16)	1.15 (2)
Os(12)–Os(14)	2.923 (1)	C(17)–O(17)	1.15 (2)
Os(12)–C(18)	1.91 (2)	C(18)–O(18)	1.16 (2)
Os(12)–C(19)	1.89 (2)	C(19)–O(19)	1.17 (2)
Os(12)–C(110)	1.81 (2)	C(110)–O(110)	1.18 (2)
Os(13)–Os(14)	2.894 (1)	C(111)–O(111)	1.13 (2)
Os(13)–C(111)	1.93 (2)	C(112)–O(112)	1.17 (3)
Os(13)–C(112)	1.85 (2)	C(113)–O(113)	1.15 (2)
Os(13)–C(113)	1.92 (2)	C(114)–O(114)	1.19 (3)
Os(13)–C(114)	1.84 (2)	C(115)–O(115)	1.14 (2)
Os(14)–C(115)	1.89 (2)	C(116)–O(116)	1.16 (3)
Os(14)–C(116)	1.87 (2)	C(117)–O(117)	1.15 (3)
Os(14)–C(117)	1.88 (2)	C(118)–O(118)	1.16 (2)
Bond Angles (deg), Molecule 1			
Os(11)–Os(12)–Os(13)	165.32 (3)	Os(14)–Os(12)–C(110)	157.3 (6)
Os(13)–Os(12)–Os(14)	60.17 (3)	C(18)–Os(12)–C(19)	173.1 (8)
Os(12)–Os(13)–Os(14)	61.19 (3)	Os(14)–Os(13)–C(112)	157.4 (7)
Os(12)–Os(14)–Os(13)	58.64 (3)	Os(14)–Os(13)–C(114)	99.7 (7)
Os(12)–Os(11)–P(1)	174.0 (1)	C(111)–Os(13)–C(113)	175.6 (9)
Os(12)–Os(11)–C(14)	88.3 (6)	Os(13)–Os(14)–C(115)	162.5 (6)
Os(12)–Os(11)–C(15)	84.1 (6)	Os(12)–Os(14)–C(118)	89.2 (6)
Os(12)–Os(11)–C(16)	88.0 (5)	C(116)–Os(14)–C(117)	91.8 (9)
Os(12)–Os(11)–C(17)	84.9 (5)	Os(11)–P(1)–C(11)	113.4 (7)
C(14)–Os(11)–C(15)	171.3 (8)	Os(11)–P(1)–C(12)	114.3 (7)
C(26)–Os(11)–C(17)	172.8 (8)	Os(11)–P(1)–C(13)	114.9 (7)
Bond Lengths (Å), Molecule 2			
Os(21)–Os(22)	2.937 (1)	Os(24)–C(218)	1.88 (2)
Os(21)–P(2)	2.355 (5)	P(2)–C(21)	1.81 (2)
Os(21)–C(24)	1.94 (2)	P(2)–C(22)	1.79 (2)
Os(21)–C(25)	1.93 (2)	P(2)–C(23)	1.82 (2)
Os(21)–C(26)	1.93 (2)	C(24)–O(24)	1.13 (2)
Os(21)–C(27)	1.94 (2)	C(25)–O(25)	1.14 (2)
Os(22)–Os(23)	2.855 (1)	C(26)–O(26)	1.16 (2)
Os(22)–Os(24)	2.930 (1)	C(27)–O(27)	1.13 (2)
Os(22)–C(28)	1.93 (2)	C(28)–O(28)	1.13 (2)
Os(22)–C(29)	1.90 (2)	C(29)–O(29)	1.17 (2)
Os(22)–C(210)	1.83 (2)	C(210)–O(210)	1.17 (2)
Os(23)–Os(24)	2.894 (1)	C(211)–O(211)	1.16 (2)
Os(23)–C(211)	1.91 (2)	C(212)–O(212)	1.18 (2)
Os(23)–C(212)	1.84 (2)	C(213)–O(213)	1.15 (2)
Os(23)–C(213)	1.92 (2)	C(214)–O(214)	1.14 (2)
Os(23)–C(214)	1.90 (2)	C(215)–O(215)	1.18 (2)
Os(24)–C(215)	1.85 (2)	C(216)–O(216)	1.17 (2)
Os(24)–C(216)	1.92 (2)	C(217)–O(217)	1.14 (2)
Os(24)–C(217)	1.91 (2)	C(218)–O(218)	1.17 (2)
Bond Angles (deg), Molecule 2			
Os(21)–Os(22)–Os(23)	163.05 (3)	Os(24)–Os(22)–C(210)	159.3 (6)
Os(23)–Os(22)–Os(24)	60.02 (2)	C(28)–Os(22)–C(29)	173.8 (7)
Os(22)–Os(23)–Os(24)	61.28 (3)	Os(24)–Os(23)–C(212)	163.2 (6)
Os(22)–Os(24)–Os(23)	58.70 (2)	Os(22)–Os(23)–C(214)	156.9 (6)
Os(22)–Os(21)–P(2)	177.3 (1)	C(211)–Os(23)–C(213)	173.9 (8)
Os(22)–Os(21)–C(24)	90.6 (5)	Os(23)–Os(24)–C(215)	162.8 (6)
Os(22)–Os(21)–C(25)	84.5 (5)	Os(22)–Os(24)–C(218)	154.6 (6)
Os(22)–Os(21)–C(26)	82.21 (6)	C(216)–Os(24)–C(217)	174.5 (8)
Os(22)–Os(21)–C(27)	87.0 (5)	Os(21)–P(2)–C(21)	113.6 (7)
C(24)–Os(21)–C(25)	175.1 (7)	Os(21)–P(2)–C(22)	113.4 (7)
C(26)–Os(21)–C(27)	169.2 (7)	Os(21)–P(2)–C(23)	114.4 (6)

infrared spectrum of 1 shows only terminal CO stretches consistent with the absence of any bridging CO ligands in the compound as found in the solid-state structure.

Structure of 1. Bond lengths and angles for 1 are given in Table III. A view of one of the two independent molecules in the unit cell of 1 is shown in Figure 1. As can be seen the 18-electron complex $Os(CO)_4(PMe_3)$ acts as a two-electron donor ligand to the $Os_3(CO)_{11}$ unit via an unbridged, osmium–osmium dative bond. The presence of dative metal–metal bonds has been proposed before for some osmium clusters, but in these cases the bond was supported by other metal–metal bonds in the cluster.[29] An unsupported Ru–Ru dative bond has recently been observed in a pentanuclear ruthenium cluster.[30]

Table IV. Fractional Coordinates for $Os_4(CO)_{14}(PMe_3)$

atom	*x*	*y*	*z*
Os(1)	0.30601 (5)	0.46157 (6)	0.31561 (5)
Os(2)	0.24561 (6)	0.64841 (6)	0.23286 (5)
Os(3)	0.20186 (5)	0.45139 (7)	0.12628 (5)
Os(4)	0.28547 (6)	0.26800 (6)	0.23360 (6)
P(1)	0.2911 (4)	0.7534 (4)	0.3594 (4)
C(1)	0.217 (2)	0.738 (2)	0.448 (2)
C(2)	0.416 (2)	0.740 (2)	0.420 (1)
C(3)	0.285 (2)	0.889 (2)	0.334 (2)
C(11)	0.437 (2)	0.475 (2)	0.282 (1)
C(12)	0.188 (1)	0.459 (2)	0.368 (1)
C(13)	0.368 (2)	0.465 (2)	0.437 (1)
C(21)	0.380 (2)	0.661 (2)	0.202 (1)
C(22)	0.114 (2)	0.630 (2)	0.264 (1)
C(23)	0.196 (2)	0.755 (2)	0.150 (2)
C(31)	0.083 (2)	0.432 (2)	0.181 (1)
C(32)	0.334 (2)	0.480 (2)	0.085 (1)
C(33)	0.141 (2)	0.557 (2)	0.050 (1)
C(34)	0.167 (2)	0.342 (2)	0.044 (2)
C(41)	0.405 (2)	0.293 (2)	0.176 (2)
C(42)	0.172 (2)	0.256 (2)	0.297 (1)
C(43)	0.362 (2)	0.201 (2)	0.328 (2)
C(44)	0.248 (2)	0.147 (2)	0.161 (2)
O(11)	0.519 (1)	0.482 (1)	0.277 (1)
O(12)	0.123 (1)	0.458 (1)	0.411 (1)
O(13)	0.402 (1)	0.463 (2)	0.514 (1)
O(21)	0.460 (1)	0.676 (1)	0.189 (1)
O(22)	0.035 (1)	0.629 (1)	0.279 (1)
O(23)	0.169 (1)	0.823 (2)	0.102 (1)
O(31)	0.009 (1)	0.420 (1)	0.207 (1)
O(32)	0.403 (1)	0.496 (1)	0.058 (1)
O(33)	0.093 (1)	0.612 (2)	0.001 (1)
O(34)	0.142 (1)	0.278 (2)	−0.011 (1)
O(41)	0.474 (1)	0.300 (1)	0.142 (1)
O(42)	0.104 (1)	0.243 (1)	0.333 (1)
O(43)	0.408 (1)	0.155 (1)	0.391 (1)
O(44)	0.224 (2)	0.076 (2)	0.121 (2)

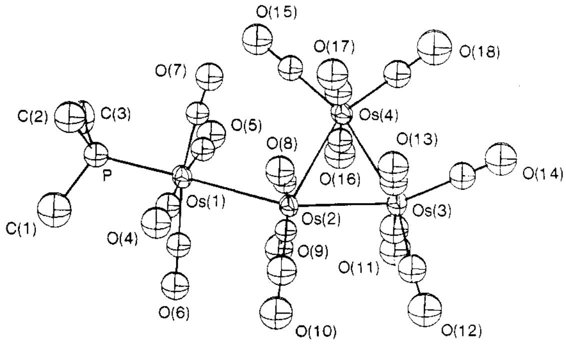
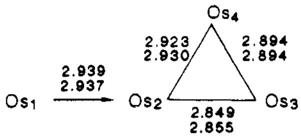


Figure 1. Molecular structure of molecule 2 of $Os_4(CO)_{15}(PMe_3)$ (1).

The Os–Os bond lengths (Å) within each of the two independent molecules of 1 are shown below (the standard deviation in each length is 0.001 Å). The donor–acceptor



Os–Os bond is long compared to most Os–Os bonds in trinuclear osmium clusters which are usually within 0.04 Å of 2.877 Å, the Os–Os distance in the parent $Os_3(CO)_{12}$.[31] This may indicate the Os–Os dative bond is weak which

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(29) John, G. R.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1979**, *181*, 143.

(30) Bruce, M. I.; Williams, M. L. *J. Organomet. Chem.* **1985**, *282*, C11.

(31) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

Table V. Selected Molecular Dimensions for $Os_4(CO)_{14}(PMe_3)$

Bond Lengths (Å)			
Os(1)–Os(2)	2.779 (2)	Os(4)–C(44)	1.93 (2)
Os(1)–Os(3)	2.935 (2)	P(1)–C(1)	1.79 (2)
Os(1)–Os(4)	2.784 (2)	P(1)–C(2)	1.78 (2)
Os(2)–Os(3)	3.013 (2)	P(1)–C(3)	1.80 (3)
Os(3)–Os(4)	2.982 (2)	C(11)–O(11)	1.13 (3)
Os(2)–P(1)	2.320 (6)	C(12)–O(12)	1.16 (3)
Os(1)–C(11)	1.92 (2)	C(13)–O(13)	1.16 (2)
Os(1)–C(12)	1.88 (2)	C(21)–O(21)	1.14 (2)
Os(1)–C(13)	1.86 (2)	C(22)–O(22)	1.12 (3)
Os(2)–C(21)	1.95 (2)	C(23)–O(23)	1.16 (3)
Os(2)–C(22)	1.92 (2)	C(31)–O(31)	1.13 (3)
Os(2)–C(23)	1.89 (2)	C(32)–O(32)	1.08 (3)
Os(3)–C(31)	1.93 (2)	C(33)–O(33)	1.14 (3)
Os(3)–C(32)	2.02 (2)	C(34)–O(34)	1.18 (3)
Os(3)–C(33)	1.88 (2)	C(41)–O(41)	1.13 (3)
Os(3)–C(34)	1.87 (2)	C(42)–O(42)	1.14 (3)
Os(4)–C(41)	1.97 (3)	C(43)–O(43)	1.19 (3)
Os(4)–C(42)	1.93 (3)	C(44)–O(44)	1.12 (3)
Os(4)–C(43)	1.82 (3)		
Bond Angles (deg)			
Os(2)–Os(1)–Os(3)	63.57 (3)	Os(1)–Os(2)–P(1)	97.7 (2)
Os(2)–Os(1)–Os(4)	126.28 (5)	Os(1)–Os(2)–C(23)	165.7 (7)
Os(3)–Os(1)–Os(4)	62.79 (3)	Os(2)–Os(3)–C(33)	74.1 (8)
Os(1)–Os(2)–Os(3)	60.74 (5)	Os(2)–Os(3)–C(34)	170.9 (8)
Os(2)–Os(3)–Os(1)	55.69 (3)	Os(3)–Os(4)–C(43)	155.5 (7)
Os(2)–Os(3)–Os(4)	111.76 (5)	Os(1)–Os(4)–C(44)	168.0 (8)
Os(1)–Os(3)–Os(4)	56.12 (3)	Os(4)–Os(1)–C(13)	116.0 (7)
Os(3)–Os(4)–Os(1)	61.09 (4)	Os(2)–Os(1)–C(13)	117.7 (7)
C(11)–Os(1)–C(12)	170.0 (8)	Os(2)–P(1)–C(1)	114.8 (9)
C(21)–Os(2)–C(22)	177.8 (8)	Os(2)–P(1)–C(2)	117.0 (7)
C(31)–Os(3)–C(32)	172.4 (8)	Os(2)–P(1)–C(3)	114.0 (8)
C(41)–Os(4)–C(42)	174.2 (9)		

Table VI. Fractional Coordinates for $Os_4(CO)_{13}(PMe_3)$

atom	x	y	z
Os(1)	0.72624 (6)	0.06807 (9)	0.16526 (7)
Os(2)	0.81211 (7)	0.08846 (10)	0.35340 (7)
Os(3)	0.84245 (7)	0.28599 (10)	0.24489 (7)
Os(4)	0.66698 (7)	0.26834 (10)	0.25142 (8)
P	0.7071 (4)	–0.1526 (6)	0.1181 (5)
C(1)	0.726 (2)	–0.272 (2)	0.197 (2)
C(2)	0.591 (2)	–0.187 (3)	0.032 (3)
C(3)	0.783 (2)	–0.207 (3)	0.062 (2)
C(11)	0.851 (2)	0.051 (2)	0.169 (2)
O(11)	0.921 (1)	0.019 (2)	0.162 (1)
C(12)	0.605 (2)	0.040 (2)	0.167 (2)
O(12)	0.534 (1)	–0.003 (2)	0.164 (1)
C(13)	0.676 (1)	0.141 (2)	0.052 (2)
O(13)	0.642 (1)	0.193 (2)	–0.019 (1)
C(21)	0.849 (2)	0.188 (3)	0.459 (2)
O(21)	0.875 (1)	0.254 (2)	0.522 (2)
C(22)	0.697 (2)	0.049 (3)	0.361 (3)
O(22)	0.637 (2)	–0.006 (3)	0.374 (2)
C(23)	0.857 (2)	–0.083 (3)	0.400 (2)
O(23)	0.885 (2)	–0.183 (3)	0.425 (2)
C(24)	0.936 (2)	0.104 (3)	0.351 (2)
O(24)	1.014 (1)	0.079 (2)	0.365 (2)
C(31)	0.958 (2)	0.282 (2)	0.232 (2)
O(31)	1.026 (1)	0.276 (2)	0.219 (1)
C(32)	0.792 (2)	0.398 (2)	0.150 (2)
O(32)	0.757 (1)	0.462 (2)	0.086 (2)
C(33)	0.879 (2)	0.425 (3)	0.328 (2)
O(33)	0.905 (2)	0.508 (2)	0.377 (2)
C(41)	0.690 (2)	0.411 (3)	0.332 (2)
O(41)	0.707 (1)	0.500 (2)	0.369 (2)
C(42)	0.556 (2)	0.233 (3)	0.268 (2)
O(42)	0.487 (2)	0.207 (2)	0.278 (2)
C(43)	0.606 (2)	0.370 (3)	0.148 (2)
O(43)	0.561 (2)	0.441 (2)	0.093 (2)

Table VII. Selected Molecular Dimensions for $Os_4(CO)_{13}(PMe_3)$

Bond Lengths (Å)			
Os(1)–Os(2)	2.861 (2)	Os(4)–C(42)	1.88 (3)
Os(1)–Os(3)	2.831 (1)	Os(4)–C(43)	1.89 (3)
Os(1)–Os(4)	2.842 (1)	P(1)–C(1)	1.73 (3)
Os(2)–Os(3)	2.857 (2)	P(1)–C(2)	1.83 (3)
Os(2)–Os(4)	2.869 (1)	P(1)–C(3)	1.85 (3)
Os(3)–Os(4)	2.765 (1)	C(11)–O(11)	1.18 (3)
Os(1)–P(1)	2.361 (6)	C(12)–O(12)	1.15 (3)
Os(1)–C(11)	1.91 (2)	C(13)–O(13)	1.20 (3)
Os(1)–C(12)	1.92 (3)	C(21)–O(21)	1.17 (4)
Os(1)–C(13)	1.87 (2)	C(22)–O(22)	1.17 (5)
Os(2)–C(21)	1.90 3)	C(23)–O(23)	1.13 (4)
Os(2)–C(22)	1.87 (4)	C(24)–O(24)	1.17 (4)
Os(2)–C(23)	1.92 (3)	C(31)–O(31)	1.15 (3)
Os(2)–C(24)	1.94 (3)	C(32)–O(32)	1.17 (4)
Os(3)–C(31)	1.89 (3)	C(33)–O(33)	1.12 (4)
Os(3)–C(32)	1.85 (3)	C(41)–O(41)	1.07 (4)
Os(3)–C(33)	1.90 (3)	C(42)–O(42)	1.18 (4)
Os(4)–C(41)	1.90 (3)	C(43)–O(43)	1.16 (4)
Weak Interactions (Å)			
Os(3)···C(11)	2.73 (2)	Os(4)···C(12)	2.68 (2)
Os(3)···C(24)	2.57 (3)	Os(4)···C(22)	2.80 (4)
Bond Angles (deg)			
Os(2)–Os(1)–Os(3)	60.24 (4)	Os(4)–Os(2)–C(21)	94.4 (8)
Os(2)–Os(1)–Os(4)	60.41 (4)	Os(4)–Os(2)–C(22)	69 (1)
Os(3)–Os(1)–Os(4)	58.34 (3)	Os(3)–Os(2)–C(24)	61.2 (9)
Os(1)–Os(2)–Os(3)	59.35 (4)	Os(1)–Os(2)–C(23)	108 (1)
Os(1)–Os(2)–Os(4)	59.45 (4)	Os(4)–Os(1)–C(12)	65.3 (7)
Os(3)–Os(2)–Os(4)	57.75 (4)	Os(2)–Os(3)–C(32)	148.3 (8)
Os(1)–Os(3)–Os(2)	60.41 (4)	Os(4)–Os(3)–C(33)	92.1 (9)
Os(1)–Os(3)–Os(4)	61.02 (3)	Os(1)–Os(3)–C(31)	112.5 (8)
Os(2)–Os(3)–Os(4)	61.35 (4)	Os(2)–Os(4)–C(43)	150 (1)
Os(1)–Os(4)–Os(2)	60.14 (4)	Os(3)–Os(4)–C(41)	93.7 (9)
Os(1)–Os(4)–Os(3)	60.64 (3)	Os(1)–Os(4)–C(42)	115 (1)
Os(2)–Os(4)–Os(3)	60.90 (4)	Os(1)–P(1)–C(1)	117 (1)
Os(2)–Os(1)–P(1)	111.8 (2)	Os(1)–P(1)–C(2)	113 (1)
Os(3)–Os(1)–C(11)	66.9 (7)	Os(1)–P(1)–C(3)	115 (1)
Os(2)–Os(1)–C(13)	152.4 (7)		

would be consistent with the low thermal stability of 1 in solution. The shortening of the Os–Os bond trans to the dative metal–metal bond is also consistent with the view that $Os(CO)_4(PMe_3)$ is a weak donor ligand.[32] This shortening may lead to the lengthening of the Os–Os bond cis to $Os(CO)_4(PMe_3)$. This type of reciprocal relationship between bond lengths within an Os_3 triangle was observed in $Os_3(\mu_3\text{-}S)_2(CO)_8(PMe_2Ph)$.[32] It is doubtful that the lengthening of the Os(2)–Os(4) bond can be attributed to the steric interaction between $Os(CO)_4(PMe_3)$ and the cis equatorial carbonyl on osmium(4). In $Os_3(CO)_{11}L'$ (L′ = $[(C_5H_5)Mo(CO)_2]_2(\mu\text{-}t\text{-BuCP})$) there is a severe interaction between the phosphorus donor ligand L′ and the cis equatorial CO ligand on the adjacent osmium atom, yet the Os–Os length cis to L′ (i.e., equivalent to Os(2)–Os(4)) is normal at 2.892 (1) Å.[33]

Compound 1 is a 64-electron cluster and its spiked triangular geometry with four metal–metal bonds is in agreement with current bonding theories of cluster compounds.[34] The clusters it most closely resembles are $Os_3(CO)_{10}(MeCN)(\mu\text{-H})Re(CO)_5$[35] and $Os_3(\mu\text{-H})(CO)_{10}(MeCN)Os(CO)_4(H)$[6] although, as stated, 1 is unique in having an unsupported dative metal–metal bond. The geometries found for the skeletons of other tetranuclear

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(32) Adams, R. D.; Horvath, I. T.; Segmüller, B. E.; Yang, L.-W. *Organometallics* **1983**, *2*, 144.

(33) Bartsch, R.; Hitchcock, P. B.; Meidine, M. F.; Nixon, J. F. *J. Organomet. Chem.* **1984**, *266*, C41.

(34) (a) Wade, K. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: Chichester, England, 1980; p 193. (b) Johnson, B. F. G.; Benfield, R. E. *Top. Stereochem.* **1981**, *12*, 253. (c) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311. (d) Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305. (e) Stone, A. J. *Inorg. Chem.* **1981**, *20*, 563. (f) Teo, B. K. *Inorg. Chem.* **1984**, *23*, 1251.

(35) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1981**, *20*, 4124.

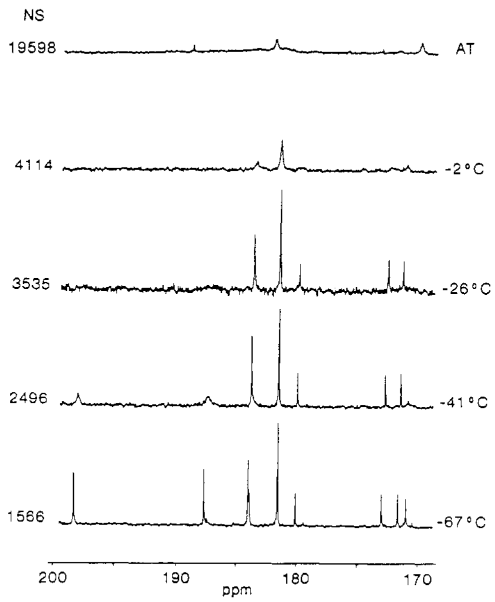


Figure 2. Variable-temperature, 100.6-MHz ^{13}C NMR spectra of 1 (^{13}CO enriched; CH_2Cl_2/CD_2Cl_2 solution; NS = number of scans). The three signals in the spectrum at ambient temperature (AT) are due to decomposition products of 1.

group 8 metal clusters with 64 electrons are the square with a ligand bridging all four metal atoms,[36] the planar rhomboid,[36,37] and the butterfly arrangement.[38,39] All these geometries are associated with clusters with bridging ligands and the requirements of these ligands may, in part, be responsible for the geometries observed.

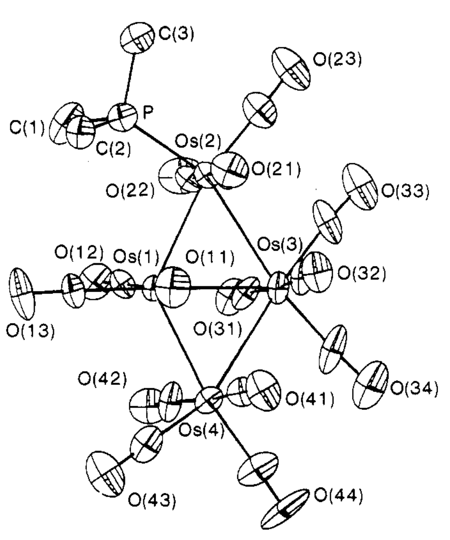
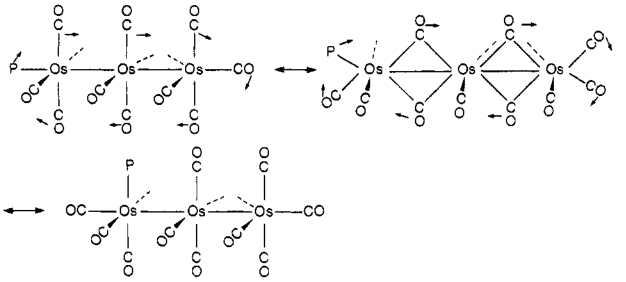


Figure 3. Molecular structure of $Os_4(CO)_{14}(PMe_3)$ (2).

Scheme I



Nonrigidity of 1. The ^{13}C NMR spectrum of a ^{13}CO-enriched sample of 1 in CH_2Cl_2/CD_2Cl_2 (4:1) at −67 °C was consistent with the solid-state structure: resonances at δ 198.4, 187.7, 184.0 (intensity 2, axial CO); 183.9, 180.1, 173.0, 171.6, 171.0 (intensity 1, equatorial CO); 181.6 (intensity 4, J_{P-C} = 4.0 Hz, $Os(CO)_4(PMe_3)$). When the solution was warmed, sets of signals collapsed to the base line at different rates (Figure 2) such that at ambient temperature no resonances could be detected, except for very weak signals due to $Os(CO)_4(PMe_3)$ and $Os_3(CO)_{12}$. These compounds resulted from partial decomposition of 1 during the long acquisition time of the spectrum at ambient temperature. Apart from the decomposition, the collapse process was reversible. (Higher temperatures were not investigated because of the extensive decomposition of 1 above room temperature). The mode of the collapse of the signals due to the $Os_3(CO)_{11}$ unit is typical of $Os_3(CO)_{11}(L)$ (L = PEt_3,[40] $P(OMe)_3$[41]) derivatives. A mechanism which involves an intermediate with two carbonyls bridging the Os–Os bond cis to the ligand L was proposed to account for the observed changes in the spectrum of $Os_3(CO)_{11}(PEt_3)$.[40] Of special interest is that at higher temperatures the carbonyls on the $Os(CO)_4(PMe_3)$ unit also undergo exchange with other carbonyls in the molecule. This exchange may occur via an intermediate with the dative Os–Os bond bridged by two carbonyls, in a manner previously proposed for $(Me_3P)(OC)_4OsW(CO)_5$[15] and $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$.[16] In 1, this would probably require simultaneous bridging of carbonyls along the appropriate edge of the Os_3 triangle as shown in Scheme I. The final product from such a rearrangement is an isomer of 1. There were weak signals in the ^{13}C NMR spectrum of 1 at −67 °C that may have been due to this second isomer.[42] When 1 was prepared from $Os_3(CO)_{11}(CH_3CN)$ and ^{13}CO-enriched $Os(CO)_4(PMe_3)$,[15] the ^{13}C NMR spectrum revealed that the ^{13}C label was equally distributed over all the carbonyl sites within the molecule. This result is consistent with the bridge–terminal exchanges proposed for 1.

$Os_4(CO)_{14}(PMe_3)$. As mentioned above, when 1 is heated in solution it fragments rather than produce a more condensed tetranuclear cluster. However, this transformation may be achieved chemically: dropwise addition of a solution of Me_3NO to one of $Os_4(CO)_{15}(PMe_3)$ results in formation of $Os_4(CO)_{14}(PMe_3)$ (2) (eq 2a). The cluster may also be formed by the addition of $Os(CO)_4(PMe_3)$ to $Os_3(CO)_{10}(CH_3CN)_2$ in toluene solution (eq 2b). It is a dark red, air-stable crystalline solid. Dilute solutions of 2 (for example, in hexane) are red whereas more concentrated solutions in CH_2Cl_2 are green. (For an explanation of this phenomenon see ref 43.) Dichroism is also exhibited by the formally unsaturated cluster $Re_4(\mu\text{-}H)_4(CO)_{12}$.[44]

$$Os_4(CO)_{15}(PMe_3) + Me_3NO \rightarrow \underset{\mathbf{2}}{Os_4(CO)_{14}(PMe_3)} \qquad (2a)$$

$$Os(CO)_{10}(CH_3CN)_2 + Os(CO)_4(PMe_3) \rightarrow \mathbf{2} \qquad (2b)$$

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[36] (a) Vahrenkamp, H.; Wolters, D. *Organometallics* **1982**, *1*, 874. (b) Gervasio, G.; Rossetti, R.; Stanghellini, P. L. *J. Chem. Soc., Chem. Commun.* **1977**, 387.

[37] Churchill, M. R.; Bueno, C.; Young, D. A. *J. Organomet. Chem.* **1981**, *213*, 139.

[38] Carty, A. J.; MacLaughlin, S. A.; Van Wagner, J.; Taylor, N. J. *Organometallics* **1982**, *1*, 1013.

[39] (a) Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J. *J. Chem. Soc., Chem. Commun.* **1981**, 476. (b) Broadhurst, P. V.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1982**, 1641. (c) Adams, R. D.; Yang, L.-W. *J. Am. Chem. Soc.* **1983**, *105*, 235. (d) Adams, R. D.; Horváth, I. T. *Inorg. Chem.* **1984**, *23*, 4718.

[40] Johnson, B. F. G.; Lewis, J.; Reichert, B. E.; Schorpp, K. T. *J. Chem. Soc., Dalton Trans.* **1976**, 1403.

[41] Alex, R. F.; Pomeroy, R. K. *Organometallics* **1987**, *6*, 2437.

[42] For $(Me_3P)(OC)_4OsW(CO)_5$, the amount of the second isomer was estimated to be 14% in CH_2Cl_2.[15]

[43] Cartwright, H. *J. Chem. Educ.* **1986**, *63*, 984.

[44] Johnson, J. R.; Kaesz, H. D. *Inorg. Synth.* **1978**, *18*, 60.

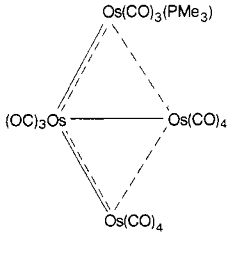
Table VIII. Analysis of the ^{13}C NMR Spectrum (Carbonyl Region) of 2

peak no.[a]	assignment[b]	chemical shift at −115 °C[c]	chemical shift at −26 °C[c]	calculated A value	calculated A signals averaged	calculated B values	calculated B signals averaged
1	C(11), C(12)	211.85					
2	C(21), C(22)	202.02	201.57	202.02	2	202.02	2
3	C(41), C(42)	192.54	191.57	192.54	3	192.54	3
4	C(13)	192.19	~190	191.90	1, 8	191.90	1, 8
5	C(23)	176.88	183.56	183.43	4, 6	184.54	4, 5
6	C(34)	174.66	173.05	173.95	5, 9	173.69	6, 7
7	C(43)	172.71					
8	C(31), C(32)	171.94	168.98	169.54	7, 10	168.69	9, 10
9	C(33)	171.01					
10	C(44)	166.36					

[a] Spectrum at −115 °C. [b] See text. [c] In $CHFCl_2/CD_2Cl_2$.

Structure of 2. The structure of 2 (Figure 3) consists of an almost planar Os_4 skeleton (the dihedral angle between the planes Os(1)–Os(2)–Os(3) and Os(1)–Os(3)–Os(4) is 177.10 (3)°). The periphery of the metal framework consists of two adjacent short Os–Os bonds (Os(1)–Os(2) = 2.779 (2) Å; Os(1)–Os(4) = 2.784 (2) Å) and two long Os–Os bonds (Os(2)–Os(3) = 3.013 (2) Å; Os(3)–Os(4) = 2.982 (2) Å). The short diagonal Os–Os vector is more typical of a normal Os–Os single bond (Os(1)–Os(3) = 2.935 (2) Å). (The average Os–Os bond length in $Os_3(CO)_{12}$, as previously mentioned, is 2.877 (3) Å.[31]) The structure found for 2 is very unusual for a 62-electron tetranuclear cluster. Most clusters of this type adopt the butterfly geometry,[11,38,45] the structure most compatible with polyhedral skeletal electron pair (PSEP) theory. We have found that $Os_4(\mu\text{-}H)_2(CO)_{13}(PMe_3)$, a cluster closely related to 1, also adopts the butterfly configuration.[46] On the other hand, $[Re_4(CO)_{16}]^{2-}$[47] and $HOs_3Re(CO)_{15}$[48] which like 2 contain no bridging ligands adopt a regular planar rhomboidal (flat butterfly) structure. In $Os_4(CO)_{13}(\mu\text{-}S)$[49] and $Os_3SnCl_2(CO)_{11}(\mu\text{-}CH_2)$[50] the metal skeletons are also essentially planar.

Long and short Os–Os bonds have often been observed in osmium clusters[49,51] but no explanation has been provided. We believe the Os–Os lengths in 2 are best rationalized in terms of three-center–two-electron metal–metal bonds (or two four-center–two-electron bonds) as shown. This leads to Os–Os bond orders of 1.5 and 0.5 and achieves an 18-electron configuration for each osmium atom. Similar arguments may possibly be used to rationalize the bonding in other metal clusters where unusual bond lengths occur. These unusual bonds, however, often occur[49,51] in nonadjacent positions in clusters where the three-center bonding described here is not possible. The cluster $[Pt_2Au_2(PPh_3)_4(CNC_6H_3Me_2)_4][PF_6]_2$ has adjacent, long Pt–Au bonds that have been rationalized in terms of partial three-center–two-electron bonds.[52]



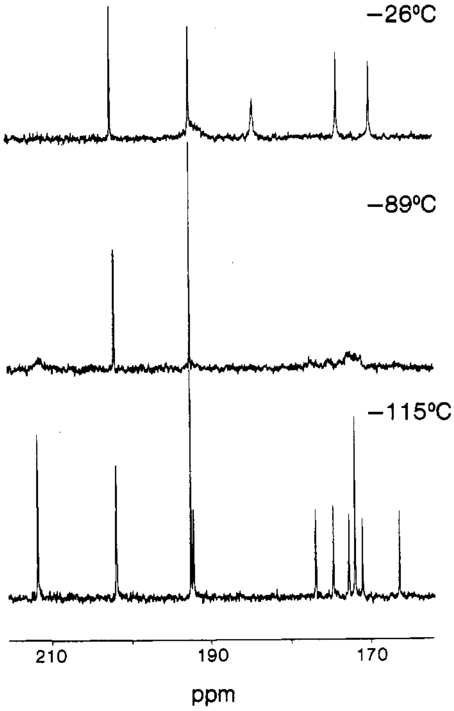


Figure 4. Variable-temperature 100.6-MHz ^{13}C NMR spectra of 2 (^{13}CO enriched; $CHFCl_2/CD_2Cl_2$ solution).

Nonrigidity of 2. A ^{13}CO-enriched sample of 2 in $CHFCl_2/CD_2Cl_2$ solution at −115 °C exhibited a ^{13}C NMR spectrum in the carbonyl region consistent with the structure found in the solid state: four resonances of relative intensity two (at δ 211.9, 202.0 (J_{P-C} = 8.6 Hz), 192.5, and 171.9) assigned to axial carbonyls, and six resonances of relative intensity one (at δ 192.2, 176.9, 174.7, 172.7, 171.0, and 166.4) assigned to equatorial carbonyls (Figure 4). From our studies[53] on an analogue of 2, $Os_4(CO)_{13}(PMe_3)[P(OMe)_3]$, it is probable that the signals at 211.9 and 171.9 ppm can be assigned to the axial car-

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(45) Some recent examples: (a) Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Puga, J.; Henrick, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1983** 1203. (b) Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Puga, J.; Raithby, P. R.; Whitmire, K. H. *Ibid.* **1983**, 1339. (c) Horwitz, C. P.; Holt, E. M.; Shriver, D. F. *J. Am. Chem. Soc.* **1985**, *107*, 281. See also: Bruce, M. I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 9, p 1395.

(46) Einstein, F. W. B.; Martin, L. R.; Pomeroy, R. K., to be submitted for publication.

(47) Churchill, M. R.; Bau, R. *Inorg. Chem.* **1968**, *7*, 2606.

(48) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1977**, *16*, 2493.

(49) Adams, R. D.; Horvåth, I. T.; Segmüller, B. E.; Yang, L.-W. *Organometallics* **1983**, *2*, 1301.

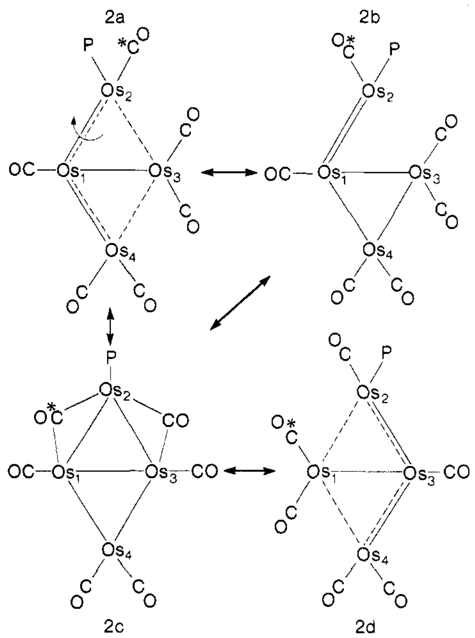
(50) Viswanathan, N.; Morrison, E. D.; Geoffroy, G. L.; Geib, S. J.; Rheingold, A. L. *Inorg. Chem.* **1986**, *25*, 3100.

(51) For example: (a) Mason, R.; Thomas, K. M.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1973**, *95*, 3802. (b) Adams, R. D.; Horvåth, I. T. *Ibid.* **1984**, *106*, 1869. (c) Adams, R. D.; Foust, D. F.; Mathur, P. *Organometallics* **1983**, *2*, 990.

(52) Briant, C. E.; Gilmour, D. I.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1986**, 835.

(53) Einstein, F. W. B.; Johnston, V. J.; Pomeroy, R. K., unpublished work.

Scheme II

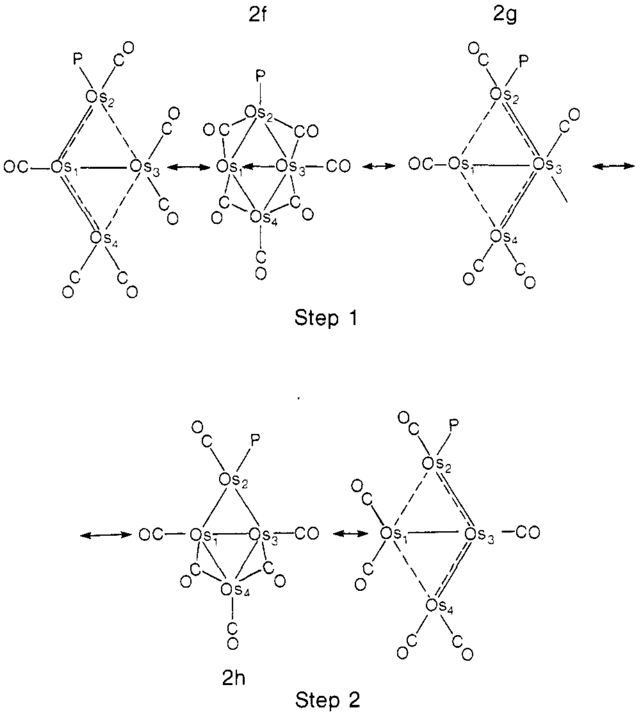


bonyls on Os(1) and Os(3), respectively. These are unusual positions for resonances of axial carbonyls in osmium clusters[40,41,54] (compare the ^{13}C NMR spectra of **1** and **2**) and may be a reflection of the unusual bonding in **2**, i.e., that Os(1) is electron deficient (deshielded) and Os(3) has an electron excess (shielded).[55] By analogy with the low field shift of the axial carbonyl resonances on Os(1), the signal at 192.2 ppm is assigned to the equatorial carbonyl on this atom.

When the solution of **2** was warmed to −89 °C, eight of the signals in the ^{13}C NMR spectrum broadened and collapsed to the base line (Figure 4). The two remaining signals were due to axial carbonyls, one of which could be assigned to the axial carbonyls on Os(2) by virtue of the phosphorus coupling; the other was probably due to the axial carbonyls on Os(4) as previously discussed. On further warming of the solution, four signals appeared at the average values of the original signals taken in pairs. From Table VIII it can be seen that the averaging can be interpreted in two ways with the data available. The first set of assignments is preferred since the averaged signals at 169.0 and 173.1 ppm appeared to sharpen at approximately the same rate which suggested that the chemical shift differences between the original signals undergoing coalescence were approximately the same. Furthermore, the first assignment gives the resonance at 176.9 as due to C(23). It has been observed before that substitution by a phosphorus ligand for an equatorial CO ligand in an Os(CO)$_4$ unit of a cluster causes a downfield shift of the remaining carbonyls.[40,41,56] Note that the argument on the mechanism presented below is not affected by which assignment is correct.

The observed pairwise collapse of the signals in the variable-temperature ^{13}C NMR spectra of **2** is not consistent with any of the various mechanisms previously proposed to account for fluxionality in osmium clusters.[57]

Scheme III



For example, the 3-fold twist and bridge–terminal carbonyl exchange mechanisms cause axial and equatorial signals to average; a merry-go-round rearrangement produces a different isomer of **2**. Furthermore, the process must involve bridging carbonyls in order to allow the equatorial carbonyl on Os(2) to exchange. The mechanism shown in Scheme II correctly accounts for the observed changes in the spectra (the axial carbonyls have been omitted in the scheme). The conversion of **2a** to **2c** could occur in one step or in two, via the intermediate **2b**. In either case the Os(2)–Os(3) bond would be broken which would be consistent with the X-ray results that indicate this bond is weak.

Fluxional processes that involve rearrangement of the metal framework of a cluster have rarely been proposed before. However, Johnson has recently suggested that when these rearrangements involve a single edge cleavage (as proposed here fore **2**) they may have low activation barriers.[58] Adams and co-workers have also reported a case of cluster rearrangement that occurs with a low energy barrier.[59]

The mechanism proposed for the rearrangement of **2** predicts the exchanges C(13) ↔ C(34), C(23) ↔ C(33), C(43) ↔ C(44), C(11,12) ↔ C(31,32); the axial carbonyls on Os(2) and Os(4) remain unaffected by the process. This mechanism leads to the assignment of the ^{13}C NMR signals given in Table VIII.[60] If a coalescence temperature of −89

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[54] (a) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic: New York, 1981; p 176. (b) Aime, S.; Osella, D.; Milone, L.; Rosenberg, E. *J. Organomet. Chem.* **1981**, *213*, 207.

[55] We have observed low values for the chemical shifts of some of the axial carbonyls in the formally unsaturated cluster, Os$_3$(μ-H)$_3$(CO)$_9$(SiPh$_3$): Willis, A. C.; Einstein, F. W. B.; Ramadan, R. M.; Pomeroy, R. K. *Organometallics* **1983**, *2*, 935.

[56] Alex, R. F.; Pomeroy, R. K. *J. Organomet. Chem.* **1985**, *284*, 379.

[57] (a) Johnson, B. F. G.; Benfield, R. E. In *Transition Metal Clusters*; Johnson, B. F. G. Ed.; Wiley: Chichester, England, 1980; p 471. (b) Mann, B. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 3, p 89. (c) Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

[58] Johnson, B. F. G. *J. Chem. Soc., Chem. Commun.* **1986**, 27.

[59] Adams, R. D.; Horváth, I. T.; Wang, S. *Inorg. Chem.* **1986**, *25*, 1617.

[60] It could be argued that since the axial carbonyls on Os(3) show abnormal field shifts, so should the equatorial carbons attached to this atom i.e., the resonances at highest field (171.0 and 166.4 ppm) should be assigned to C(33) and C(34) (or vice versa). However, the signals due to the analogous carbon atoms in Os$_4$(CO)$_{13}$(PMe$_3$)[P(OMe)$_3$] come to lower field than the signals due to the axial carbonyls on the osmium atom equivalent to Os(3).[53]

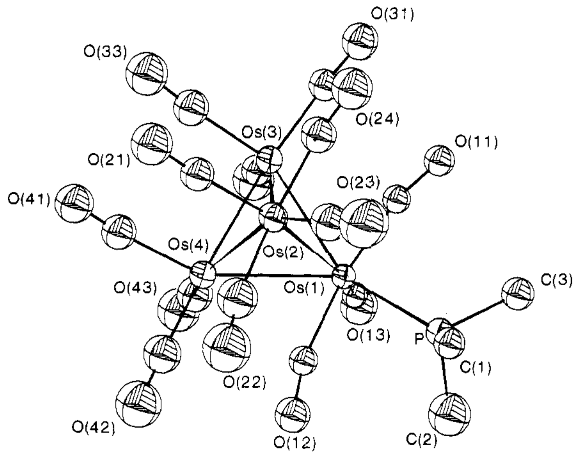


Figure 5. Molecular structure of $Os_4(CO)_{13}(PMe_3)$ (**3**).

°C is assumed for the signals at 171.0 and 176.9 ppm (in the spectrum at -115 °C) then an approximate $\Delta G^{\ddagger}$ value (at -89 °C) of 8.0 kcal mol^{-1} may be obtained.[61]

A referee has suggested the mechanism shown in Scheme III for the rearrangement (steps I and II may be reversed). It predicts the following exchanges: C(13) $\leftrightarrow$ C(23), C(33) $\leftrightarrow$ C(43), C(34) $\leftrightarrow$ C(44), C(11,12) $\leftrightarrow$ C(31,32), with the axial carbonyls on Os(2) and Os(4) again remaining unaffected. We have considered this mechanism[1] and originally rejected it as very unlikely. This is because it requires two different CO-bridging mechanisms to occur over the same osmium framework with approximately the same, very low, activation energy (no signals attributable to an intermediate such as **2e** were observed). Although CO exchanges[40,41,57] in trinuclear osmium clusters usually have higher activation energies than those observed in **2**, we have recently discovered a CO exchange in $WOs_2(CO)_{11}(PMe_3)_2$ which occurs with a low activation energy by what is believed to be an all-equatorial merry-go-round CO exchange across long W-Os bonds.[62] Therefore, although we still favor the mechanism shown in Scheme II, the alternative mechanism in Scheme III is now included here; it does have the advantage that no Os-Os bonds are broken. Studies on analogues of **2** are planned in an attempt to further elucidate the fluxional process in the cluster.

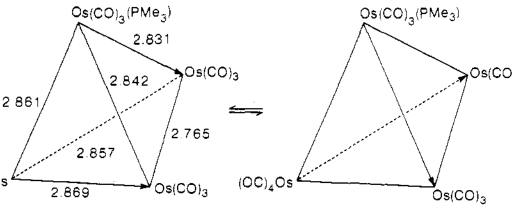
We point out here that the mechanisms in Schemes II and III are different from what we originally proposed.[18] In the original mechanism the axial carbonyls on Os(1) remain unaffected. However, from the discussion previously presented it is probable that it is the axial carbonyls on Os(4), along with those on Os(2), that are unaffected by the rearrangement.

$Os_4(CO)_{13}(PMe_3)$. The cluster $Os_4(CO)_{13}(PMe_3)$ (**3**) was isolated by heating **2** in hexane at 90 °C in a sealed tube for 24 h with frequent removal of the CO produced in the reaction (eq 3). The product was isolated in 34% yield

$$\mathrm{Os_4(CO)_{14}(PMe_3)} \xrightarrow[\text{or } h\nu]{90\ ^\circ\mathrm{C}} \underset{\mathbf{3}}{\mathrm{Os_4(CO)_{13}(PMe_3)}} + \mathrm{CO} \quad (3)$$

after chromatography. The yield was only moderate because decomposition took place during the reaction and because the reverse reaction (addition of CO to **3** to give **2**) takes place readily. It was subsequently found that **3** may be prepared in better yield by the ultraviolet irradiation of **2** in hexane.

Scheme IV



Structure of 3. A view of the molecule is shown in Figure 5. As can be seen the cluster adopts a tetrahedral arrangement of the metal atoms in agreement with PSEP theory for a 60-electron cluster. The cluster contains $Os(CO)_4$ and $Os(CO)_3(PMe_3)$ units and appears to be the first example of a tetrahedral cluster that has two metal atoms with four terminal ligands. It had been predicted that such a cluster would be unstable.[63]

The structure of **3** may also be rationalized by the application of the 18-electron rule to each osmium atom. This leads to partial dative bonds from the metals with four ligands to those with three ligands and is shown in Scheme IV.

The Os-Os bonds that are presumed partly dative are significantly longer than the covalent bond linking the $Os(CO)_3$ units (Scheme IV) which is consistent with the discussion presented earlier on the relative strengths of these bonds. However, the second covalent bond between the $Os(CO)_4$ and $Os(CO)_3(PMe_3)$ groupings is comparable in length to the partly dative bonds. This may indicate that this covalent bond is lengthened due to steric interaction between the $Os(CO)_4$ and $Os(CO)_3(PMe_3)$ fragments. Overall the Os-Os bonds are somewhat shorter than those in $Os_3(CO)_{12}$ as is generally the case for tetranuclear osmium clusters.[64]

In agreement with the calculations of Evans and Mingos the OsL_4 fragments maintain nearly C_{2v} symmetry.[63] There are weak semibridging interactions between four of the carbon atoms bonded to Os(1) and Os(2) and neighboring osmium atoms: Os(3)···C(11) = 2.73 (2), Os(3)···C(24) = 2.57 (3), Os(4)···C(12) = 2.68 (2), and Os(4)···C(22) = 2.80 (4) Å. (It should be noted that the solution infrared spectrum of **3** contains no absorptions that can be reasonably attributed to CO stretches of bridging carbonyl ligands.) These interactions are across the metal bonds that are considered to be partly dative; they probably relieve the charge buildup expected in such bonds.[65] As previously noted,[63] similar interactions are present in $Os_5(CO)_{16}$,[66] $Ru_4(\mu\text{-}H)_2(CO)_{13}$[67] and $FeRu_4(\mu\text{-}H)_2(CO)_{13}$.[68] In $FeOs_3(\mu\text{-}H)_2(CO)_{13}$[69] and $[Os_4(\mu\text{-}H)(CO)_{13}]^-$,[70] completely bridging CO ligands occur and there are no $M(CO)_4$ vertices.

Nonrigidity of 3. The ^{13}C NMR spectrum of **3** in $CHFCl_2/CD_2Cl_2$ at 0 °C consisted of a sharp singlet in the carbonyl region. The signal remained a singlet, although considerably broadened, even when the spectrum was determined with the sample at -125 °C (Figure 6).[71] This

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(61) Sandström, J. *Dynamic NMR Spectroscopy*; Academic: New York, 1982; p 96.

(62) Davis, H. B.; Pomeroy, R. K., unpublished results.

(63) Evans, D. G.; Mingos, D. M. P. *Organometallics* **1983**, *2*, 435.

(64) For example: Churchill, M. R.; Bueno, C.; Kennedy, S.; Bricker, J. C.; Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1982**, *21*, 627.

(65) Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1.

(66) Eady, C. R.; Johnson, B. F. G.; Lewis, J.; Reichert, B. E.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1976**, 271.

(67) Yawney, D. B. W.; Doedens, R. J. *Inorg. Chem.* **1972**, *11*, 838.

(68) Gilmore, C. J.; Woodward, P. *J. Chem. Soc. A* **1971**, 3453.

(69) Plotkin, J. S.; Alway, D. G.; Weisenberger, C. R.; Shore, S. G. *J. Am. Chem. Soc.* **1980**, *102*, 6156.

(70) Dawson, P. A.; Johnson, B. F. G.; Lewis, J.; Kaner, D. A.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 961.

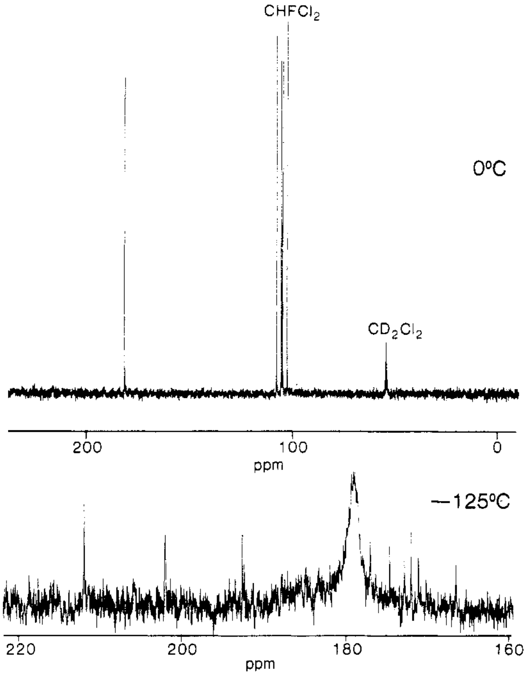
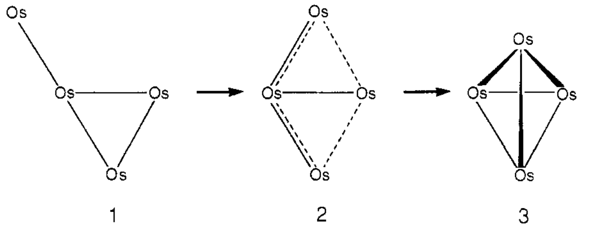


Figure 6. 100.6-MHz ^{13}C NMR spectra of **3** at 0 and −125 °C (^{13}CO enriched; $CHFCl_2/CD_2Cl_2$ solution). Note the expanded scale of the latter spectrum; the weak peaks in this spectrum are due to traces of **2**.

Scheme V



is, of course, indicative of fluxional behavior. The presence of semibridging carbonyl interactions in the solid-state structure of **3** suggests that the mechanism of the rearrangement involves bridge–terminal carbonyl exchange. Since only the spectrum of **3** undergoing fast exchange could be obtained, little more can be said concerning the mechanism of the fluxionality.

It is of interest that the barrier to carbonyl nonrigidity decreases going from **1** to **2** to **3**. This may be a reflection of the presumed increase in the electron density at the metal atoms going from **1** to **3**. It has been found that the barrier to carbonyl exchange in $Os_3(CO)_{11}(PR_3)$ (R = Et,[40] OMe[41]) is much lower than in $Os_3(CO)_{12}$ and this may also reflect the increased electron density at the osmium atoms in the clusters substituted with a phosphorus donor ligand.

Conclusion

The series $Os_4(CO)_n(PMe_3)$ (n = 15, 14, 13) is believed to be the first whereby a 64-electron cluster has been successively converted to a 62- and then to a 60-electron cluster (Scheme V).[72] The number of metal–metal interactions that accompany these conversions (i.e., four to five to six) is as expected from PSEP theory. However, the variations in the lengths within each cluster are difficult to rationalize by the theory in its present state, especially the variations in **2**. Application of the 18-electron rule to the individual osmium atoms in each cluster provides an adequate explanation of the variation in the bond lengths. For **2** it leads to Os–Os bonds of orders 1.5 and 0.5. Furthermore, the unusual nonrigidity exhibited by **2** may be rationalized in terms of a mechanism that involves the cleavage of one of the weak Os–Os bonds.

We are actively pursuing the synthesis and study of analogues of **2** and have found that $Os_4(CO)_{13}(PMe_3)[P(OMe)_3]$[53] and $Os_4(CO)_{15}$[73] have similar Os_4 skeletons as **2**. This indicates that the unusual Os–Os bond lengths in **2** are not due to packing forces or to the trans influences of the ligands.

The sequence of skeletal changes that accompanies the transformation of **1** to **2** and then **2** to **3** is of general interest to cluster synthesis. Although the conversion of **1** to **2** could not be brought about thermally, it should be noted that the mass spectra of all three clusters had $[Os_4(CO)_{13}(PMe_3)]^+$ as the ion of highest mass. The reverse reactions, the conversion of **3** to **2**, and **2** to **1**, and indeed of **1** to $Os_3(CO)_{12}$, readily occur when the clusters are treated with carbon monoxide. Pentacarbonylosmium (or $Os(CO)_4(PPh_3)$) has previously been observed as a product when osmium clusters of high nuclearity fragment under CO pressure.[74] The present study suggests that this fragmentation process may occur via a cluster with $Os(CO)_5$ (or $Os(CO)_4(PPh_3)$) as a ligand rather than by the release of an unsaturated fragment such as $Os(CO)_4$ from the main body of the cluster.

Acknowledgment. We thank Simon Fraser University for financial support. We also thank the Natural Sciences and Engineering Council of Canada for financial support in the form of operating grants (to F.W.B.E. and R.K.P.) and a postgraduate scholarship (to L.R.M.). We thank Dr. P. Rushman for some preliminary studies on **1** and Mr. V. J. Johnston for the preparation of **3** by method 2.

Registry No. **1**, 97252-63-6; **2**, 99706-91-9; **3**, 111290-90-5; $Os_3(\mu\text{-}H)_2(CO)_{10}$, 41766-80-7; $Os(CO)_4(PMe_3)$, 89579-59-9; $Os_3(CO)_{11}(MeCN)$, 65702-94-5; $Os_3(CO)_{11}(PMe_3)$, 51832-24-7.

Supplementary Material Available: Tables of hydrogen atom coordinates and anisotropic thermal parameters for **1**, **2**, and **3** (7 pages); listings of observed and calculated structures factors for **1**, **2**, and **3** (67 pages). Ordering information is given on any current masthead page.

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[71] The low-temperature spectrum shown in Figure 5 indicates the sample contained traces of **2**. This arose from the difficulty in following the chromatographic separation of **2** and **3** by infrared spectroscopy when samples enriched with ^{13}CO were used. However, that the peaks due to **2** are sharp in the spectrum indicates that the broadening of the signal due to **3** is genuine and not due to viscosity effects.

[72] The synthesis and interconversion of $Os_7(\mu\text{-}H)_2(CO)_n$ (n = 20, 21, 22) has recently been described.[27]

[73] Johnston, V. J.; Einstein, F. W. B.; Pomeroy, R. K. *J. Am. Chem. Soc.*, in press.

[74] (a) Nicholls, J. N.; Farrar, D. H.; Jackson, P. F.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1982**, 1395. (b) Farrar, D. H.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Rosales, M. J. *Ibid.* **1982**, 2051. See also: (a) Jeffrey, J. G.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Welch, D. A. *J. Chem. Commun.* **1986**, 318. (b) Adams, R. D.; Babin, J. E.; Mahtab, R.; Wang, S. *Inorg. Chem.* **1986**, *25*, 5.