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Photochemical Synthesis of Trinuclear Cluster Compounds of Osmium and a Group 6 Metal Atom. Structures of $(OC)_5M[Os(CO)_3(PMe_3)]_2$ (M = Cr, W), $(OC)_5Mo\{Os(CO)_3[P(OMe)_3]\}_2/[(MeO)_3P](OC)_4OsMo(CO)_5$ (1/1), and $(OC)_4W[(\mu\text{-}H)Os(CO)_3(PMe_3)]_2$

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Clusters of the type $(OC)_5M[Os(CO)_3(PR_3)]_2$ (M = Cr, Mo, W; R = Me, OMe; $R_3 = (OCH_2)_3CMe$) have been obtained (30–40% yield) by ultraviolet irradiation of $(R_3P)(OC)_4OsM(CO)_5$ complexes in C_6F_6. The crystal structures of $(OC)_5Cr[Os(CO)_3(PMe_3)]_2$ (**1**), $(OC)_5Mo\{Os(CO)_3[P(OMe)_3]\}_2$ (**2**) cocrystallized in a 1:1 ratio with $[(MeO)_3P](OC)_4OsMo(CO)_5$, and $(OC)_5W[Os(CO)_3(PMe_3)]_2$ (**3**) have been determined by X-ray crystallography. Compound **1** crystallizes in the space group $P\bar{1}$, with $a = 9.331$ (1) Å, $b = 12.013$ (1) Å, $c = 12.357$ (1) Å, $\alpha = 87.35$ (1)°, $\beta = 85.94$ (1)°, $\gamma = 68.81$ (1)°, and $Z = 2$, $R = 0.039$ for 3660 reflections ($I \geq 2.5\sigma(I)$). Compounds **2** and $[(MeO)_3P](OC)_4OsMo(CO)_5$ cocrystallize in the space group $P\bar{1}$ with $a = 8.788$ (1) Å, $b = 16.901$ (2) Å, $c = 18.456$ (2) Å, $\alpha = 68.88$ (1)°, $\beta = 81.75$ (1)°, $\gamma = 77.01$ (1)°, and $Z = 2$; $R = 0.037$ for 2886 reflections. Compound **3** crystallizes in the space group $P\bar{1}$ with $a = 9.540$ (2) Å, $b = 12.119$ (2) Å, $c = 12.278$ (2) Å, $\alpha = 86.69$ (1)°, $\beta = 88.74$ (1)°, $\gamma = 67.56$ (1)°, and $Z = 2$; $R = 0.028$ for 3437 reflections. Each cluster consists of a triangular MOs_2 unit with one phosphorus ligand trans to the Os–Os bond and the other cis to this bond; there are no bridging carbonyls. The radial carbonyls on the $M(CO)_5$ unit adopt a staggered arrangement with respect to the carbonyls on the osmium atoms. The ^{13}C NMR spectra of the $(OC)_5M[Os(CO)_3(PR_3)]_2$ clusters in solution at low temperature were consistent with the presence of two isomers, one with the structure found in the solid state, the other with both phosphorus ligands trans to the Os–Os bond. In all molecules the radial carbonyls of the $M(CO)_5$ group were chemically equivalent, but not equivalent to the axial carbonyl. This behavior is interpreted in terms of free rotation of the $M(CO)_5$ group about an axis that passes through M and the midpoint of the Os–Os vector. The phosphite derivative $[ax\text{-}(MeO)_3P](OC)_4W[Os(CO)_3(PMe_3)]_2$, (**4**) was prepared by heating **3** with $P(OMe)_3$ in hexane at 50 °C. The ^{13}C NMR spectrum of **4** indicated that, once again, the radial carbonyls on the W atom in each isomer were equivalent. The hydrido cluster $(OC)_4W[\mu\text{-}H)Os(CO)_3(PMe_3)]_2$ (**5**) was synthesized from **3** and hydrogen at 50 °C; its structure was determined by X-ray crystallography. Compound **5** crystallizes in the space group *Pbca* with $a = 15.339$ (4) Å, $b = 16.785$ (3) Å, $c = 20.633$ (6) Å, and $Z = 8$; $R = 0.055$ for 1591 observed reflections. The structure consists of a triangular array of metal atoms (Os–W = 3.154 (2) and 3.156 (3) Å, Os–Os = 2.964 (3) Å) with each PMe_3 ligand trans to the Os–Os bond. The spectroscopic evidence is consistent with a hydride ligand bridging each OsW vector. The ^{13}C NMR spectrum indicates that in solution **5** has the same structure as found in the solid state and the molecule is stereochemically rigid.

Introduction

We have recently reported the synthesis and characterization of complexes of the type $(R_3P)(OC)_4OsM(CO)_5$ (M = Cr, Mo, W; R = Me, OMe, Ph, etc.).[1] These complexes are of interest because they contain unbridged, dative metal–metal bonds. In the preparations of the tungsten and some of the molybdenum derivatives, intensely colored byproducts were observed, but in insufficient amounts for characterization. In one preparation of $[(MeO)_3P](OC)_4OsMo(CO)_5$, three deep red crystals were obtained in the crude product. An X-ray crystallographic study of one of these crystals revealed it to contain $[(MeO)_3P](OC)_4OsMo(CO)_5$ cocrystallized in a 1:1 ratio with $(OC)_5Mo\{Os(CO)_3[P(OMe)_3]\}_2$.[2] The latter compound was the first trinuclear cluster that contained both a group 6 and group 8 metal atom to be structurally characterized. This prompted an investigation into the rational synthesis of these clusters.

Herein we report the details of that study, namely, the preparation of $(OC)_5M[Os(CO)_3(PR_3)]_2$ clusters. The crystal structures of two more of these clusters are described along with the details of the structure mentioned above. The synthesis of $[(MeO)_3P](OC)_4W[Os(CO)_3(PMe_3)]_2$ and $(OC)_4W[(\mu\text{-}H)Os(CO)_3(PMe_3)]_2$ from $(OC)_5W[Os(CO)_3(PMe_3)]_2$ is also described. Aspects of this study have appeared in preliminary communications.[2,3]

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. The solvents hexane, CH_2Cl_2, C_6H_6, and C_6F_6 were scrupulously dried before use. The precursory compounds, $(L)(OC)_4OsM(CO)_5$ (M = Cr, Mo, W; L = PMe_3, $P(OMe)_3$, $P(OCH_2)_3CMe$), were synthesized according to the literature method.[1] An external, medium-pressure mercury discharge lamp (200 W, Hanovia Model 654 A36) contained in a water-cooled quartz jacket was employed in the irradiations; there was ~5 cm between the source and the edge of the reaction vessel.

Infrared spectra were obtained 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); for each compound, the pattern of the ions at highest mass corresponded to either $[P]^+$ or $[P]^+ - CO$, as con-

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Table I. Analytical, Yield, and Infrared Spectral Data for New Compounds

compound	% calcd C	% calcd H	% found C	% found H	yield, %	ν(CO), cm^{-1} [a]
$(OC)_5Cr[Os(CO)_3(PMe_3)]_2$ (**1**)	22.87	2.03	23.09	2.04	32	2073 (w), 2003 (s), 1991 (s), 1980 (w, sh), 1956 (w), 1940 (m), 1920 (w), 1886 (w, br)
$(OC)_5Cr\{Os(CO)_3[P(OMe)_3]\}_2$	20.65	1.84	20.78	1.89	22	2084 (w), 2026 (m), 2005 (vs), 1983 (m, sh), 1942 (m), 1921 (m)
$(OC)_5Mo[Os(CO)_3(PMe_3)]_2$	21.80	1.94	22.03	1.90	32	2074 (w), 2018 (s), 2004 (m), 1988 (vs), 1951 (m), 1947 (m), 1941 (w, sh), 1937 (w), 1908 (w)
$(OC)_5Mo\{Os(CO)_3[P(OMe)_3]\}_2$ (**2**)	19.77	1.76	19.86	1.89	22	2084 (w), 2027 (s), 2015 (m), 2000 (s), 1982 (w), 1974 (w), 1969 (w), 1951 (m), 1936 (w)
$(OC)_5W[Os(CO)_3(PMe_3)]_2$ (**3**)	19.93	1.77	20.27	1.71	39	2075 (w), 2014 (s), 2007 (m), 1989 (vs), 1944 (m), 1925 (w), 1904 (w)
$(OC)_5W\{Os(CO)_3[P(OMe)_3]\}_2$	18.22	1.62	18.25	1.62	30	2085 (w), 2027 (s), 2018 (m, sh), 2002 (vs), 1982 (w), 1947 (m), 1929 (m)
$(OC)_5W\{Os(CO)_3[P(OCH_2)_3CMe]\}_2$	21.58	1.55	21.54	1.59	53	2090 (w), 2027 (s), 2008 (s), 1918 (m, br)[b]
$[(MeO)_3P](OC)_4W[Os(CO)_3(PMe_3)]_2$ (**4**)	20.36	2.40	20.40	2.44	60	2060 (w), 1999 (m), 1980 (s), 1961 (w), 1944 (w), 1930 (w), 1916 (w, sh), 1887 (m), 1866 (w)
$(OC)_4Mo\{(\mu\text{-}H)Os(CO)_3[P(OMe)_3]\}_2$	19.09	2.00	19.26	2.16	*c*	2103 (w), 2051 (w, sh), 2022 (vs), 1986 (m, sh), 1971 (m, sh), 1956 (w, sh), 1902 (m, br), 1849 (m, br)[b]
$(OC)_4W[(\mu\text{-}H)Os(CO)_3(PMe_3)]_2$ (**5**)	19.24	2.00	19.45	1.82	63	2092 (m), 2040 (m), 2004 (vs), 1950 (m), 1880 (m), 1839 (m)[b]

[a] Hexane solution. [b] CH_2Cl_2 solution. [c] Small-scale reaction; yield not measured.

Table II. ^1H and $^{31}P\{^1H\}$ NMR Data for New Compounds[a]

compound	isomer	^1H, δ	$^{31}P\{^1H\}$, δ	ca. a/b ratio
$(OC)_5Cr[Os(CO)_3(PMe_3)]_2$	a		−40.4[b]	1.4
	b		−37.9	
$(OC)_5Cr\{Os(CO)_3[P(OMe)_3]\}_2$	a		100.6[b,c]	6
	b		104.5	
$(OC)_5Mo[Os(CO)_3(PMe_3)]_2$	a		−41.0	3
	b		−38.2	
$(OC)_5Mo\{Os(CO)_3[P(OMe)_3]\}_2$	a		103.5[b,c]	5.5
	b		107.5	
$(OC)_5W[Os(CO)_3(PMe_3)]_2$	a	1.9 (12)[f,g]	−42.3[d,e]	2.6
	b		−37.9	
$(OC)_5W\{Os(CO)_3[P(OMe)_3]\}_2$	a		100.6	5.3
	b		105.0	
$(OC)_5W\{Os(CO)_3[P(OCH_2)_3CMe]\}_2$	a		95.1, 92.8[b]	9
	b		96.8	
$[(MeO)_3P](OC)_4W[Os(CO)_3(PMe_3)]_2$	a	3.59 (11.9), 1.82 (9.9),[f] 1.72 (9.8)[b]	143.5, −45.0, −49.0[b]	1
	b	3.59 (11.9), 1.82 (9.9)[f]	142.1, −42.1	
$(OC)_4Mo\{(\mu\text{-}H)Os(CO)_3[P(OMe)_3]\}_2$		3.81 (12.3), −16.27 (17.9)		
$(OC)_4W[(\mu\text{-}H)Os(CO)_3(PMe_3)]_2$		1.12 (16), −16.25 (16.8)	−45.8	

[a] Unless otherwise stated, spectra were in $CDCl_3$ solution at 25 °C; figures in parentheses are J_{PH}; $^{31}P\{^1H\}$ NMR spectra are with reference to 85% H_3PO_4. [b] CD_2Cl_2 solution. [c] At −22 °C. [d] $CH_2Cl_2/CHFCl_2$ (~1:3 v/v) solution. [e] At −121 °C. [f] Signals due to different isomers not resolved. [g] Time-averaged spectrum due to rapid exchange of ligand position in isomer a at ambient temperature.

firmed by computer simulation. NMR spectra were recorded on a Bruker WM400 spectrometer (operating frequencies: 400 MHz for ^1H, 100.6 MHz for ^{13}C, and 162.0 MHz for ^{31}P). The ^{13}C NMR spectra were obtained on samples that were enriched with ^{13}CO (~30%). These were prepared either with ^{13}CO-enriched starting materials or by stirring the clusters in benzene at 50–80 °C under 1 atm of ^{13}CO (99% ^{13}C) for ~22 h; the enriched compounds were purified by column chromatography followed by recrystallization from CH_2Cl_2/hexane. Microanalyses were performed by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

Preparation of $(OC)_5M[Os(CO)_3(PR_3)]_2$ (M = Cr, Mo, W) Complexes. These complexes were prepared by the photolysis of a supersaturated solution of the appropriate $(R_3P)(OC)_4OsM(CO)_5$ compound in C_6F_6 (C_6H_6 may be used as the solvent in the preparation of $(OC)_5W[Os(CO)_3(PMe_3)]_2$). The solutions were thoroughly degassed by several freeze–pump–thaw cycles prior to photolysis. The pale yellow solutions turned deep red over the course of the photolysis; some solid decomposition products were also formed. Typical irradiation times ranged from ~2 h for M = W and R = Me, to 17 h for M = Mo and R = Me; the times also varied depending on the amount of starting material used. (The clusters, however, appeared stable to prolonged irradiation.) On completion of the photolysis the C_6F_6 was removed under vacuum (and recovered for further use). The remaining solid was dissolved in a minimum amount of CH_2Cl_2 and chromatographed on a column of neutral alumina with CH_2Cl_2/hexane (1/3 to 1/1, v/v) as the eluent. The deep red products were further purified by recrystallization either from CH_2Cl_2/hexane or C_6H_5Cl/CH_2Cl_2/hexane. Yields ranged from 30 to 40%. Yields and analytical and infrared spectral data are given in Table I; ^1H and $^{31}P\{^1H\}$ NMR data (where recorded) are given in Table II; ^{13}C NMR data for the complexes are given in Table III. Two

Table III. ^{13}C NMR Resonances for the Carbonyl Ligands of the New Compounds[a]

			$M(CO)_5$		$Os(CO)_3(PR_3)$	
compound	isomer	temp, °C	δ(*ax*-CO)	δ(*rad*-CO)	δ(*ax*-CO)	δ(*eq*-CO)
$(OC)_5Cr[Os(CO)_3(PMe_3)]_2$	a	−122	232.0	221.2	200.1, 201.8	180.7, 179.2
	b		232.0	223.3	199.7	177.4
$(OC)_5Cr\{Os(CO)_3[P(OMe)_3]\}_2$	a	−74	231.1	219.5	198.4 (11.1)[b] 196.4 (9.1)[b]	177.7
$(OC)_5W[Os(CO)_3(PMe_3)]_2$	a	−122	205.9	200.9 (117.6)[c]	200.0, 198.9	182.5, 180.9
	b		206.3	203.5 (119.1)[c]	190.7	178.7
$(OC)_5W\{Os(CO)_3[P(OMe)_3]\}_2$	a	−60	205.3	199.5 (117.0)[c]	196.7 (9.9)[b] 194.9	179.9, 177.5
	b		200.2			
$(OC)_5W\{Os(CO)_3[P(OCH_2)_3CMe]\}_2$	a	−30	205.1	199.1 (119)[c]	193.7 (12)[b] 192.2 (10)[b]	178.7, 176.9
$[(MeO)_3P](OC)_4W[Os(CO)_3(PMe)_3]_2$	a	+25		210.3 (12.6)[b]	188.0	183.6, 181.6
	b			210.2 (12.2)[b]	187.8	179.5
$(OC)_4W[(\mu\text{-}H)Os(CO)_3(PMe_3)]_2$		+25	204.7	202.2 (127)[c]	183.8	174.7

[a] In CD_2Cl_2/CH_2Cl_2 or $CD_2Cl_2/CHFCl_2$ solution; ^{13}CO-enriched samples. [b] J_{PC}. [c] J_{WC}.

variations of the preparation of the clusters are given in detail below.

Preparation of $(OC)_5W[Os(CO)_3(PMe)]_2$ (3). A supersaturated solution of $(Me_3P)(OC)_4OsW(CO)_5$ (100 mg, 0.14 mmol) in benzene (20 mL) was placed in a Pyrex Carius tube fitted with a Teflon valve. The tube was evacuated at −196 °C and the solution degassed by three freeze–pump–thaw cycles. The tube was sealed under vacuum and irradiated with UV light at room temperature for 37 min. The tube was then cooled to −196 °C and evacuated; the solution was degassed with two freeze–pump–thaw cycles. It was then irradiated for a further 90 min. During the irradiation the pale yellow solution turned red, and some solid decomposition product formed. An IR spectrum of the solution after a total 127-min irradiation indicated that no starting material remained. The C_6H_6 was removed on the vacuum line and the remaining solid dissolved in CH_2Cl_2 and chromatographed on a neutral alumina column (11 × 1 cm). A deep red band of $(OC)_5W[Os(CO)_3(PMe_3)]_2$ (3) was eluted with CH_2Cl_2/hexane (1/2, v/v). A bright yellow band of $(OC)_4W[(\mu\text{-}H)Os(CO)_3(PMe_3)]_2$ (5) was eluted with CH_2Cl_2/hexane (3/1, v/v). In this way 3 (28 mg, 39%) and 5 (16 mg, 23%) were obtained. Deep red crystals of 3, suitable for X-ray crystal structure determination, were grown at −20 °C from a mixture of C_6H_5Cl/CH_2Cl_2 with hexane layered on top of the solution. Bright yellow crystals of 5 were grown similarly from C_6H_6/hexane.

Cluster 3 was also prepared via a thermal route: A solution of $(Me_3P)(OC)_4)OsW(CO)_5$ (20 mg, 0.03 mmol) in benzene (20 mL) was placed in a Carius tube. The tube was evacuated at −196 °C and the solution degassed by two freeze–pump–thaw cycles. The stirred solution was heated at 70–80 °C for 42.2 h during which time the pale yellow solution turned red. The product was purified as above to yield 3 (5 mg, 33%).

Preparation of $(OC)_5Cr[Os(CO)_3(PMe_3)]_2$ (1). A solution of $(Me_3P)(OC)_4OsCr(CO)_5$ (100 mg, 0.18 mmol) in perfluorobenzene (10 mL) was sealed in a Pyrex Carius tube fitted with a Teflon valve. The tube was evacuated at −196 °C and the solution degassed by two freeze–pump–thaw cycles. The solution was irradiated for 11 h; the solution was degassed after 5 h and after 9.5 h. The solution turned from pale yellow to deep red during this time. When the reaction was judged complete, the C_6F_6 was removed on the vacuum line and recovered for further use. The remaining solid was dissolved in CH_2Cl_2 and placed on a neutral alumina column (12.5 × 1 cm). A deep red band of 1 was eluted with CH_2Cl_2/hexane (1/3, v/v); a pale amber band which contained small amounts of a compound, believed to be $(OC)_4Cr[(\mu\text{-}H)Os(CO)_3(PMe_3)]_2$ from its infrared spectrum, was eluted with CH_2Cl_2/hexane (1/1, v/v). Deep red crystals of 1 (33 mg, 37%) were obtained by recrystallization at −20 °C from C_6H_5Cl/CH_2Cl_2/hexane. One of these crystals was used for the X-ray structure determination.

Reaction of 3 with CO. A solution of 3 (~5 mg) in hexane (3 mL) was placed in a small, round-bottom flask fitted with a Teflon valve. The flask was evacuated at −196 °C and the solution degassed with several freeze–pump–thaw cycles. Carbon monoxide (1 atm) was added above the frozen solution. The solution was then stirred at 80 °C for 4 days. An IR spectrum (CO-stretching region) at this time indicated very little decomposition of 3 to $Os(CO)_4(PMe_3)$ and $W(CO)_6$ had occurred. The same procedure except that ^{13}CO (99%) replaced CO was used to prepare ^{13}CO-enriched 3.

Reaction of 3 with $P(OMe)_3$. A solution of 3 (47 mg, 0.05 mmol) and $P(OMe)_3$ (64 mg, 0.5 mmol) in hexane (20 mL) was placed in a 100-mL, round-bottom flask equipped with a Teflon valve. The vessel was evacuated at −196 °C and the solution degassed with one freeze–pump–thaw cycle. The reaction mixture was then heated at 50 °C for 31 h; the solution was degassed with a freeze–pump–thaw cycle after 11.8 h and 22 h. The vessel was cooled to room temperature, and the solvent and excess $P(OMe)_3$ were removed on the vacuum line. The remaining solid was dissolved in CH_2Cl_2 and subjected to chromatography (neutral alumina, 12 × 1 cm). Unreacted 3 was eluted from the column with CH_2Cl_2/hexane (1/3, v/v). This was followed by a purple band of a compound that was not identified. Elution with CH_2Cl_2/hexane (1/2, v/v) removed the major product as a deep orange band; the constituent of the final red band was also not identified. The orange band afforded a solid which was recrystallized from CH_2Cl_2/hexane at −20 °C to give $[(MeO)_3P](OC)_4W[Os(CO)_3(PMe_3)]_2$ (28 mg, 60%) as deep red crystals.

Reaction of 3 with H_2. A solution of 3 (21 mg, 0.021 mmol) in benzene (15 mL) was placed in a Carius tube fitted with a Teflon valve. The vessel was evacuated at −196 °C, and the solution was degassed with three freeze–pump–thaw cycles, after which the vessel was pressurized with H_2 (1 atm). The solution was stirred at 50 °C for 21.3 h during which time the deep red solution turned bright yellow and a small amount of dark solid formed. The solvent and excess H_2 were removed on the vacuum line and the crude product dissolved in CH_2Cl_2 and placed on a neutral alumina column. The major product was eluted from the column as a yellow band with CH_2Cl_2/hexane (2/1, v/v). In this way, $(OC)_4W[(\mu\text{-}H)Os(CO)_3(PMe_3)]_2$ (13 mg, 63%) was obtained as a bright yellow solid. The ^{13}CO-labeled product was obtained from ^{13}CO-labeled 3.

X-ray Structure Determinations. Crystals of $(OC)_5Cr[Os(CO)_3(PMe_3)]_2$ (1), $(OC)_5Mo\{Os(CO)_3[P(OMe)_3]\}_2/[(MeO)_3P](OC)_4OsMo(CO)_5$ (2′), $(OC)_5W[Os(CO)_3(PMe_3)]_2$ (3), and $(OC)_4W[(\mu\text{-}H)Os(CO)_3(PMe_3)]_2$ (5) were mounted on an Enraf-Nonius CAD-4F diffractometer and intensity data (Mo Kα graphite monochromator) collected at ambient temperature. Two intensity standards were measured every 2 h of acquisition time. These showed no significant variations during the course of data acquisition. The data were corrected analytically for absorption (checked versus measured Ψ-scan intensities).[4] Data reduction was performed, including intensity scaling and Lorentz and polarization corrections. The structures were solved by routine methods and were refined to a maximum|shift|/error ≤ 0.06. Methyl hydrogen atoms were included at calculated positions of 0.95 Å from their respective carbon atoms.

For 1, the final full-matrix least-squares refinement of 213 variables, for 3660 observations, included isotropic thermal parameters for all carbon atoms and anisotropic thermal parameters for the other non-hydrogen atoms. The largest peak in the final difference map was 2.2 (3) e $Å^{-3}$, at 1.05 Å from Os(1).

In the case of 2′ the trimetallic molecule displayed a "Star of David" disorder (10.5%). The orientation of the 10.5% molecule appeared to be related to that of the 89.5% molecule by a 180° rotation about a vector approximately parallel to the Os(1)–Mo bond and passing through the centroid of the Os_2Mo triangle, such that the P atoms for the 10.5% orientation coincided with those with the 89.5% orientation. The occupancy for P(1) and P(2) was therefore set to 1 while that for the remainder of the non-hydrogen atoms for this molecule was set to 0.895. The lighter atoms of the 10.5% orientation were omitted from the calculations. Final full-matrix, least-squares refinement of 332 parameters, for 2886 observations, included isotropic thermal parameters for the 89.5% occupied Os and Mo sites, the P atoms, and the O atoms bonded to P(1). More complex modeling of the disorder was not considered to be worthwhile. The largest peak in the final difference map (0.7 (2) e $Å^{-3}$) occurred 1.21 Å from O(31) and 1.49 Å from C(31). This and other peaks of similar magnitude undoubtedly reflect the unmodeled disorder.

For 3, final full-matrix least-squares refinement of 244 parameters, for 3437 observations, included isotropic thermal parameters for the carbonyl carbon atoms and anisotropic thermal parameters for the other non-hydrogen atoms. The largest peak in the final difference map (1.3 (2) e $Å^{-3}$) was found at 0.93 Å from Os(1).

The crystal used for the structure determination of 5 diffracted weakly; numerous attempts to obtain better crystals from differently recrystallized samples were unsuccessful. After refinement, including anisotropic thermal parameters for the Os, W, and P atoms ($R = 0.070$), an electron density difference Fourier map contained peaks of the order 3.0 e $Å^{-3}$ near the W and Os atoms. Analysis of the observed to calculated structure factor agreement indicated systematic errors which possibly arose from inadequately corrected absorption as suggested by poor agreement between observed Ψ-scan intensity variations and those calculated from the crystal face measurements. Use of an empirical absorption correction[5] based on the Ψ-scan measurements did not

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Table IV. Crystal Data for $(OC)_5Cr[Os(CO)_3(PMe_3)]_2$ (1), $[(MeO)_3P](OC)_4OsMo(CO)_5 \bullet (OC)_5Mo\{Os(CO)_3[P(OMe)_3]\}_2$ (2′), $(OC)_5W[Os(CO)_3(PMe_3)]_2$ (3), and $(OC)_4W[(\mu\text{-}H)Os(CO)_3(PMe_3)]_2$ (5)

	1	2′	3	5
cryst syst	triclinic	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	*Pbca*
a, Å	9.331 (1)	8.788 (1)	9.540 (2)	15.339 (4)
b, Å	12.013 (1)	16.901 (2)	12.119 (2)	16.785 (3)
c, Å	12.357 (1)	18.456 (2)	12.278 (2)	20.633 (6)
α, deg	87.35 (1)	68.88 (1)	86.69 (1)	
β, deg	85.94 (1)	81.75 (1)	88.74 (1)	
γ, deg	68.81 (1)	77.01 (1)	67.56 (1)	
V, Å^3	1287.9	2485.7	1309.9	5312.3
Z	2	2	2	8
fw	892.7	1694.9	1024.5	998.5
ρ_{calcd}, g cm^{-3}	2.302	2.265	2.598	2.497
μ(Mo Kα), cm^{-1}	104.3	83.1	143.3	141.3
cryst size, mm	0.14 × 0.20 × 0.28	0.10 × 0.14 × 0.20	0.07 × 0.16 × 0.21	0.08 × 0.12 × 0.14
λ, Å	0.710 69	0.710 69	0.710 69	0.710 69
transmission	0.07–0.18	0.34–0.57	0.17–0.45	0.23–1.00
min–max 2θ, deg	0–50	0–44	0–50	4–45
$R(F)^a$	0.039	0.037	0.028	0.055
$R_w(F)^b$	0.048^c	0.041^c	0.023^d	0.066^c

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for 3660, 2886, 3437, and 1591 observed data; $I \geq 2.5\sigma(I)$. [b] $R_w(F) = [\sum(w(|F_o| - |F_c|)^2)/\sum(wF_o^2)]^{1/2}$. [c] Unit weights. [d] $w = (\sigma^2(F_o) + 0.0003F_o^2)^{-1}$; GOF $= [\sum w(|F_o| - |F_c|)^2/\text{degrees of freedom}]^{1/2} = 1.208$.

Table V. Fractional Coordinates for $(OC)_5Cr[Os(CO)_3(PMe)_3]_2$ (1)

atom^a	x/a	y/b	z/c	$B_{iso}{}^b$
Os(1)	0.09406 (6)	0.11954 (4)	0.27151 (4)	2.82
Os(2)	0.05452 (6)	0.36526 (4)	0.25619 (4)	3.08
Cr(3)	0.36858 (22)	0.18731 (18)	0.19875 (17)	3.03
P(1)	0.1540 (5)	−0.0870 (3)	0.2544 (3)	3.69
P(2)	−0.2080 (4)	0.4742 (3)	0.2781 (4)	4.06
O(11)	0.2307 (15)	0.0768 (11)	0.4963 (9)	6.1
O(12)	−0.2287 (13)	0.1635 (11)	0.3652 (9)	5.6
O(13)	−0.0017 (13)	0.1348 (10)	0.0370 (8)	4.9
O(21)	0.0637 (14)	0.3448 (11)	0.5046 (9)	6.0
O(22)	0.1586 (16)	0.5770 (11)	0.2533 (14)	7.9
O(23)	0.0220 (16)	0.3708 (11)	0.0099 (10)	5.9
O(31)	0.4190 (14)	0.2851 (13)	0.4105 (11)	7.3
O(32)	0.5029 (14)	−0.0620 (11)	0.2963 (12)	7.0
O(33)	0.3332 (13)	0.1019 (12)	−0.0207 (10)	6.2
O(34)	0.3671 (16)	0.4075 (12)	0.0672 (12)	7.5
O(35)	0.7022 (11)	0.1192 (11)	0.1332 (10)	5.6
C(11)	0.1781 (17)	0.0970 (13)	0.4136 (12)	4.1 (3)
C(12)	−0.1032 (17)	0.1456 (13)	0.3298 (12)	4.0 (3)
C(13)	0.0358 (16)	0.1344 (12)	0.1221 (11)	3.4 (3)
C(21)	0.0623 (18)	0.3469 (14)	0.4112 (13)	4.3 (3)
C(22)	0.1112 (19)	0.5020 (15)	0.2516 (13)	4.7 (3)
C(23)	0.0367 (17)	0.3645 (13)	0.1014 (13)	4.1 (3)
C(31)	0.3952 (19)	0.2500 (14)	0.3313 (13)	4.7 (3)
C(32)	0.4389 (19)	0.0313 (15)	0.2623 (13)	4.5 (3)
C(33)	0.3391 (16)	0.1323 (13)	0.0656 (12)	3.8 (3)
C(34)	0.3547 (20)	0.3314 (15)	0.1186 (14)	5.0 (3)
C(35)	0.5742 (17)	0.1458 (13)	0.1593 (12)	3.9 (3)
C(1)	0.2830 (20)	−0.1587 (15)	0.1419 (14)	5.1 (3)
C(2)	−0.0182 (19)	−0.1227 (14)	0.2345 (13)	4.7 (3)
C(3)	0.2370 (22)	−0.1819 (17)	0.3700 (15)	6.0 (4)
C(4)	−0.3340 (23)	0.4370 (17)	0.1901 (16)	6.2 (4)
C(5)	−0.3004 (22)	0.4738 (16)	0.4113 (15)	5.9 (4)
C(6)	−0.2594 (22)	0.6322 (17)	0.2503 (16)	6.2 (4)

[a] The atom labels are different from those shown in ref 3 in order to make the labeling scheme consistent with that of 3. [b] B_{iso} (Å^2) is the mean of the principal axes of the thermal ellipsoid for the Os, Cr, P, and O atoms.

yield an improved agreement. As a last resort the observed data were "corrected" with the program DIFABS[6] (the correction was based on the model refined with only isotropic thermal parameters). Final full-matrix least-squares refinement of 140 parameters for 1591 observed data, including anisotropic thermal parameters for only the Os and W atoms, resulted in $R = 0.055$. The two hydride positions were computed with the program HYDEX.[7] The largest peak in the final difference map was 1.6 (4) e Å^{-3}.

Complex scattering factors for neutral atoms were used in the calculation of structure factors.[8] The programs used for data reduction, structure solution and refinement were from the NRC VAX Crystal Structure System and CRYSTALS.[9] Computations were carried out on a MicroVAX-II computer.

Crystallographic data are summarized in Table IV. The final positional and isotropic or equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Tables V–VIII. Additional experimental details, the hydrogen atom parameters, and anisotropic temperature factors are deposited as supplementary material.

Results and Discussion

Synthesis of $(OC)_5M[Os(CO)_3(PR_3)]_2$ (M = Cr, Mo, W) Clusters. The tungsten clusters and, to a lesser extent, the molybdenum analogues were observed in trace amounts in the synthesis of the corresponding $(R_3P)(OC)_4OsM(CO)_5$ complexes from $Os(CO)_4(PR_3)$ and $M(CO)_5(THF)$ (eq 1).[1] It was subsequently found that these

$$Os(CO)_4(PR_3) + M(CO)_5(THF) \xrightarrow{\leq 25\ ^\circ C} (R_3P)(OC)_4OsM(CO)_5 + \text{trace } (OC)_5M[Os(CO)_3(PR_3)]_2 \quad M = Mo, W \tag{1}$$

clusters could be prepared in 30–40% yield by the UV photolysis (through Pyrex) of the bimetallic complexes in C_6F_6 (eq 2). When benzene was used for the solvent no

$$(R_3P)(OC)_4OsM(CO)_5 \xrightarrow[C_6F_6]{h\nu} (OC)_5M[Os(CO)_3(PR_3)]_2 \quad M = Cr, Mo, W \tag{2}$$

cluster resulted. The exception was $(OC)_5W[Os(CO)_3(PMe_3)]_2$ (**3**) which could be prepared by the ultraviolet irradiation of $(Me_3P)(OC)_4OsW(CO)_5$ in benzene. A second product isolated, in 23% yield, from this reaction was $(OC)_4W[(\mu\text{-}H)Os(CO)_3(PMe_3)]_2$. This suggests in the other cases where benzene was used as the solvent that C–H activation of the solvent occurred to give unstable hydride complexes. It was also found that **3** was formed (~30% yield) when $(Me_3P)(OC)_4OsW(CO)_5$ was heated in benzene at 70–80 °C. Attempts to prepare **3** by the reaction of $W(CO)_4(CH_3CN)_2$ with $Os(CO)_4(PMe_3)$ gave only trace amounts of the cluster.

The reaction shown in eq 2 represents a rare example of the formation of a cluster compound by the photolysis of a dinuclear complex.[10] This can probably be attributed to the dative rather than nondative metal–metal bond in the $(R_3P)(OC)_4OsM(CO)_5$ complexes. The mechanism of formation of the clusters either by the route given in eq 1 or that in eq 2 is unclear. Irradiation of $(Me_3P)(OC)_4OsW(CO)_5$ in C_6F_6 with excess $Os(CO)_4(PMe_3)$ did not produce the heteronuclear cluster in increased yield, but rather $Os_3(CO)_9(PMe_3)_3$ was formed. Of relevance, is that we have isolated $(L_{PC})(OC)_4OsOs(CO)_3(L_{PC})W(CO)_5$

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(10) Adams, R. D. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1989; p 121.

Table VI. Fractional Coordinates for $[(MeO)_3P](OC)_4OsMo(CO)_5 \bullet (OC)_5Mo\{Os(CO)_3[P(OMe)_3]\}_2$ (2′)

atom[a]	x/a	y/b	z/c	B_{iso}[b]	atom[a]	x/a	y/b	z/c	B_{iso}[b]
Os(1)[c]	0.27360 (11)	0.22129 (6)	0.35890 (6)	4.19	O(121)	0.3297 (21)	1.0193 (12)	0.0491 (11)	8.8 (5)
Os(2)[c]	0.35425 (11)	0.34158 (6)	0.41588 (5)	4.03	O(122)	0.0098 (24)	0.6945 (14)	0.2252 (12)	10.6 (6)
Mo(3)[c]	0.55946 (23)	0.30469 (13)	0.28008 (12)	4.35	O(123)	−0.1187 (22)	0.9704 (12)	0.1813 (10)	8.8 (5)
Os(21)[d]	0.2453 (9)	0.2659 (5)	0.4181 (4)	3.86 (16)	O(124)	0.3210 (23)	0.8262 (13)	0.2924 (12)	10.0 (5)
Os(22)[d]	0.4196 (9)	0.2227 (5)	0.2912 (5)	4.20 (17)	O(125)	0.0286 (22)	0.8815 (12)	−0.0175 (12)	9.5 (5)
Mo(23)[d]	0.5291 (19)	0.3473 (10)	0.3444 (9)	3.7 (3)	C(11)[c]	0.180 (3)	0.3096 (15)	0.2685 (14)	5.1 (5)
Os(11)	0.46935 (10)	0.73632 (5)	0.09026 (5)	4.20	C(12)[c]	0.082 (3)	0.2100 (15)	0.4142 (14)	5.2 (5)
Mo(12)	0.17903 (22)	0.85322 (12)	0.13622 (11)	4.76	C(13)[c]	0.386 (3)	0.1386 (17)	0.4432 (15)	6.2 (6)
P(1)	0.2692 (9)	0.1144 (4)	0.3102 (4)	6.4	C(15)[c]	0.165 (4)	0.0025 (24)	0.4258 (23)	9.9 (10)
P(2)	0.1768 (8)	0.3185 (4)	0.5201 (4)	6.0	C(16)[c]	0.071 (4)	0.0922 (22)	0.2232 (19)	9.5 (9)
P(11)	0.6748 (7)	0.6396 (4)	0.0602 (4)	5.3	C(17)[c]	0.513 (5)	0.015 (3)	0.2671 (23)	11.3 (11)
O(11)[c]	0.1248 (19)	0.3582 (11)	0.2130 (10)	6.4 (4)	C(21)[c]	0.194 (3)	0.4212 (17)	0.3512 (15)	6.2 (6)
O(12)[c]	−0.0361 (22)	0.2018 (12)	0.4494 (11)	7.5 (5)	C(22)[c]	0.418 (3)	0.4318 (15)	0.4247 (13)	5.0 (5)
O(13)[c]	0.4545 (21)	0.0883 (12)	0.4981 (11)	7.4 (4)	C(23)[c]	0.518 (3)	0.2581 (16)	0.4783 (15)	5.7 (6)
O(15)[c]	0.245 (3)	0.0268 (13)	0.3688 (12)	12.1	C(25)[c]	−0.127 (5)	0.376 (3)	0.5414 (25)	13.0 (12)
O(16)[c]	0.130 (3)	0.1444 (11)	0.2549 (11)	9.3	C(26)[c]	0.103 (5)	0.181 (3)	0.634 (3)	13.7 (13)
O(17)[c]	0.407 (3)	0.0787 (14)	0.2639 (17)	14.9	C(27)[c]	0.297 (6)	0.352 (3)	0.618 (3)	14.0 (14)
O(21)[c]	0.0993 (20)	0.4695 (11)	0.3143 (10)	6.4 (4)	C(31)[c]	0.440 (3)	0.4263 (17)	0.2229 (14)	5.5 (6)
O(22)[c]	0.4613 (21)	0.4911 (12)	0.4281 (10)	7.6 (5)	C(32)[c]	0.492 (3)	0.2610 (16)	0.2036 (16)	6.1 (6)
O(23)[c]	0.6162 (20)	0.2147 (11)	0.5161 (10)	6.3 (4)	C(33)[c]	0.675 (3)	0.1834 (17)	0.3395 (15)	6.1 (6)
O(25)[c]	0.0044 (23)	0.3560 (12)	0.4985 (11)	7.8 (5)	C(34)[c]	0.680 (3)	0.3590 (18)	0.3294 (16)	6.9 (7)
O(26)[c]	0.1882 (24)	0.2227 (14)	0.5680 (12)	8.8 (5)	C(35)[c]	0.736 (3)	0.3167 (17)	0.2042 (17)	6.9 (7)
O(27)[c]	0.177 (3)	0.3634 (15)	0.5810 (14)	10.4 (6)	C(111)	0.583 (3)	0.7996 (16)	0.1212 (14)	6.9 (6)
O(31)[c]	0.3847 (20)	0.4887 (12)	0.1856 (10)	6.7 (4)	C(112)	0.4405 (25)	0.6703 (14)	0.1952 (13)	5.4 (5)
O(32)[c]	0.4696 (24)	0.2467 (13)	0.1518 (13)	9.2 (5)	C(113)	0.453 (3)	0.8264 (15)	−0.0110 (13)	5.4 (5)
O(33)[c]	0.7382 (22)	0.1147 (13)	0.3718 (11)	7.6 (5)	C(114)	0.315 (3)	0.6893 (14)	0.0640 (12)	5.4 (5)
O(34)[c]	0.7547 (23)	0.3961 (13)	0.3478 (11)	8.3 (5)	C(115)	0.722 (4)	0.5213 (25)	−0.0104 (21)	12.6 (11)
O(35)[c]	0.8348 (24)	0.3277 (13)	0.1530 (12)	8.8 (5)	C(116)	0.860 (5)	0.563 (3)	0.1699 (24)	13.9 (12)
O(111)	0.6600 (22)	0.8364 (12)	0.1419 (11)	8.9 (5)	C(117)	0.836 (4)	0.7423 (21)	−0.0496 (19)	10.0 (8)
O(112)	0.4189 (19)	0.6269 (11)	0.2608 (11)	8.0 (4)	C(121)	0.275 (3)	0.9560 (16)	0.0818 (14)	6.9 (6)
O(113)	0.4349 (19)	0.8835 (11)	−0.0682 (10)	7.4 (4)	C(122)	0.074 (3)	0.7523 (17)	0.1892 (15)	7.2 (6)
O(114)	0.2205 (19)	0.6619 (10)	0.0472 (9)	7.0 (4)	C(123)	−0.002 (3)	0.9251 (16)	0.1663 (14)	6.8 (6)
O(115)	0.6220 (21)	0.5866 (12)	0.0155 (11)	8.8 (5)	C(124)	0.269 (3)	0.8353 (16)	0.2345 (15)	7.0 (6)
O(116)	0.748 (3)	0.5612 (15)	0.1308 (14)	11.7 (6)	C(125)	0.080 (3)	0.8705 (16)	0.0406 (15)	6.9 (6)
O(117)	0.8244 (24)	0.6688 (14)	0.0147 (12)	10.5 (6)					

[a] The atom labels are different from those shown in ref 2 in order to make the labeling scheme of the trimetallic molecule consistent with those of 1 and 3. [b] B_{iso} (Å^2) is the mean of the principal axes of the thermal ellipsoid for Os(11)–Mo(13), Os(1)–P(1), O(115), O(116), and O(117). [c] Occupancy = 0.895. [d] Occupancy = 0.105.

(L_{PC} = $P(OCH_2)_3CMe$) in the reaction of $Os(CO)_4(L_{PC})$ with $W(CO)_5(THF)$.[11] This complex is believed to have two unbridged, dative metal–metal bonds in tandem (i.e., Os→Os→W). (The crystal structure of the closely related compound $(OC)_3(L_{PC})_2OsOs(CO)_4W(CO)_5$ confirms the presence of two unbridged, metal–metal bonds in a linear arrangement.[11]) The complex $(L_{PC})(OC)_4OsOs(CO)_3(L_{PC})W(CO)_5$ readily gave the cluster $(OC)_5W[Os(CO)_3(L_{PC})]_2$ on photolysis in C_6F_6. A tentative mechanism for the formation of the clusters that is consistent with these observations is shown in Scheme I (the eclipsed forms of the molecules with the PR_3 ligands cis to one another are drawn for convenience). The equilibria shown in sii and sv (for PR_3 = L_{PC}) have been established spectroscopically. Furthermore, the group 6 hexacarbonyl $M(CO)_6$ (step siii) always accompanied the formation of the clusters. Intermediates in steps si, siii, and siv other than those that we have proposed are possible. A more detailed study of this novel reaction, with particular emphasis on the primary photochemical step, is planned.

The $(OC)_5M[Os(CO)_3(PR_3)]_2$ compounds are deep red, air-stable crystalline solids. They are the first trinuclear clusters that contain both an osmium and a group 6 metal atom. Indeed, the chromium derivatives are, to our knowledge, the first cluster compounds containing osmium and chromium atoms.

Structure of $(OC)_5Cr[Os(CO)_3(PMe_3)]_2$ (1). The structures of three of the $(OC)_5M[Os(CO)_3(PR_3)]_2$ clusters were determined by X-ray crystallography, namely, $(OC)_5Cr[Os(CO)_3(PMe_3)]_2$ (1), $(OC)_5Mo\{Os(CO)_3[P(OMe)_3]\}_2$ (2), (cocrystallized in a 1:1 ratio with $[(MeO)_3P](OC)_4OsMo(CO)_5$), and $(OC)_5W[Os(CO)_3(PMe_3)]_2$ (3). The structures of 1 and 2 have been described (with figures) in preliminary communications.[2,3] The three clusters have the same MOs_2P_2 skeleton. For these reasons, only a figure of 3 is presented here (as Figure 1); figures of 1 and 2 are deposited in the supplementary material. The labeling scheme employed for the atoms is the same for each cluster, but is different to that used for 1 and 2 in the first reports of their structures. Bond length and angle data for the three molecules are given in Table IX.

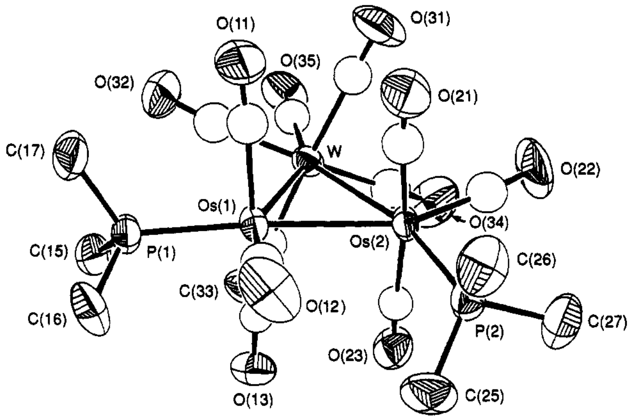

Figure 1. Molecular structure of $(OC)_5W[Os(CO)_3(PMe_3)]_2$ (3).

The metal atoms in 1, 2, and 3 are in a triangular array; there are no bridging ligands. Phosphorus-donor ligands

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[11] Batchelor, R. J.; Davis, H. B.; Einstein, F. W. B.; Pomeroy, R. K. *J. Am. Chem. Soc.* **1990**, *112*, 2036.

Table VII. Fractional Coordinates for $(OC)_5W[Os(CO)_3(PMe)_3]_2$ (3)

atom	*x/a*	*y/b*	*z/c*	B_{iso}[a]
Os(1)	−0.11876 (4)	−0.10663 (3)	−0.27557 (3)	2.991
Os(2)	−0.06682 (4)	−0.35510 (3)	−0.25981 (3)	3.194
W(3)	−0.38187 (4)	−0.17952 (3)	−0.20239 (3)	3.265
P(1)	−0.1788 (3)	0.09845 (21)	−0.25539 (21)	4.14
P(2)	0.1925 (3)	−0.46181 (23)	−0.27790 (24)	4.33
O(11)	−0.2804 (12)	−0.0518 (8)	−0.4980 (6)	7.5
O(12)	0.1885 (10)	−0.1511 (9)	−0.3711 (7)	7.6
O(13)	−0.0041 (8)	−0.1356 (7)	−0.0405 (5)	4.8
O(21)	−0.0965 (11)	−0.3188 (8)	−0.5087 (6)	7.2
O(22)	−0.1569 (12)	−0.5679 (8)	−0.2655 (9)	8.8
O(23)	−0.0215 (9)	−0.3709 (6)	−0.0110 (6)	5.6
O(31)	−0.4448 (10)	−0.2698 (9)	−0.4272 (7)	7.7
O(32)	−0.5395 (10)	0.0896 (7)	−0.2921 (8)	7.3
O(33)	−0.3251 (9)	−0.1050 (8)	0.0297 (6)	6.4
O(34)	−0.3636 (11)	−0.4179 (9)	−0.0714 (9)	8.5
O(35)	−0.7197 (8)	−0.1171 (8)	−0.1373 (7)	6.5
C(11)	−0.2187 (12)	−0.0757 (9)	−0.4158 (9)	4.59 (21)
C(12)	0.0690 (13)	−0.1319 (9)	−0.3324 (9)	4.62 (21)
C(13)	−0.0459 (10)	−0.1296 (8)	−0.1267 (7)	3.14 (16)
C(21)	−0.0878 (12)	−0.3278 (10)	−0.4155 (9)	4.70 (21)
C(22)	−0.1155 (13)	−0.4883 (10)	−0.2609 (9)	5.09 (23)
C(23)	−0.0400 (11)	−0.3620 (8)	−0.1027 (8)	3.67 (17)
C(31)	−0.4185 (12)	−0.2367 (9)	−0.3494 (9)	4.57 (21)
C(32)	−0.4702 (13)	−0.0073 (11)	−0.2604 (9)	5.09 (23)
C(33)	−0.3420 (11)	−0.1304 (9)	−0.0560 (8)	4.15 (19)
C(34)	−0.3616 (13)	−0.3341 (11)	−0.1231 (10)	5.32 (23)
C(35)	−0.5973 (12)	−0.1394 (9)	−0.1610 (8)	4.41 (20)
C(1)	−0.2916 (13)	0.1627 (9)	−0.1380 (9)	5.3
C(2)	−0.0102 (15)	0.1294 (10)	−0.2383 (11)	6.6
C(3)	−0.2794 (19)	0.2008 (10)	−0.3665 (10)	7.9
C(4)	0.2743 (14)	−0.4636 (12)	−0.4113 (11)	6.8
C(5)	0.3167 (13)	−0.4180 (13)	−0.1928 (12)	7.4
C(6)	0.2493 (15)	−0.6196 (10)	−0.2373 (12)	7.1

[a] B_{iso} ($Å^2$) is the mean of the principal axes of the thermal ellipsoid for the Os, W, P, and O atoms.

Table VIII. Fractional Coordinates (×10^4) for $(OC)_4W[(\mu\text{-}H)Os(CO)_3(PMe_3)]_2$ (5)

atom	*x/a*	*y/b*	*z/c*	U_{iso}[a]
Os(1)	8463 (1)	8283 (1)	9695.1 (9)	51
Os(2)	9134 (1)	9237 (1)	8593.5 (9)	49
W(3)	7297 (1)	8411 (1)	8440.7 (8)	48
P(1)	7859 (9)	7495 (8)	10502 (7)	67 (4)
P(2)	9417 (9)	9990 (8)	7669 (6)	68 (4)
O(11)	7334 (23)	9624 (20)	10241 (16)	90 (11)
O(12)	10052 (25)	8776 (22)	10507 (19)	103 (13)
O(13)	9447 (23)	6811 (22)	9110 (17)	96 (12)
O(21)	8176 (21)	10672 (21)	9184 (15)	78 (10)
O(22)	10834 (25)	9609 (20)	9247 (16)	88 (11)
O(23)	9897 (25)	7796 (23)	7933 (18)	101 (13)
O(31)	6306 (23)	9932 (23)	8926 (17)	89 (11)
O(32)	5522 (27)	7534 (26)	8637 (19)	115 (14)
O(33)	8082 (22)	6790 (24)	7908 (17)	94 (12)
O(34)	6694 (25)	8803 (22)	7034 (18)	98 (12)
C(11)	7781 (27)	9089 (25)	10008 (19)	50 (11)
C(12)	9462 (31)	8529 (28)	10201 (23)	70 (14)
C(13)	9068 (33)	7371 (31)	9332 (23)	74 (15)
C(21)	8512 (33)	10078 (32)	9002 (25)	74 (15)
C(22)	10198 (35)	9427 (31)	9047 (25)	79 (16)
C(23)	9612 (36)	8340 (37)	8232 (27)	95 (18)
C(31)	6685 (33)	9353 (31)	8748 (24)	77 (15)
C(32)	6205 (32)	7893 (29)	8561 (25)	72 (14)
C(33)	7805 (30)	7364 (30)	8110 (22)	66 (14)
C(34)	6933 (30)	8617 (27)	7618 (24)	71 (15)
C(1)	8163 (40)	6522 (39)	10510 (30)	117 (22)
C(2)	6692 (41)	7442 (40)	10503 (30)	114 (21)
C(3)	8103 (35)	7825 (34)	11299 (27)	98 (19)
C(4)	8657 (38)	10751 (37)	7462 (31)	112 (20)
C(5)	10388 (37)	10557 (33)	7687 (27)	99 (20)
C(6)	9485 (36)	9444 (33)	6954 (28)	97 (19)

[a] U_{iso} ($Å^2 \times 10^4$) is the cube root of the product of the principal axes of the thermal ellipsoid for the Os and W atoms.

Table IX. Selected Dimensions for $(OC)_5Cr[Os(CO)_3(PMe)_3]_2$ (1), $(OC)_5Mo\{Os(CO)_3[P(OMe)_3]\}_2$ (2), $(OC)_5W[Os(CO)_3(PMe_3)]_2$ (3), and $(OC)_4W[(\mu\text{-}H)Os(CO)_3(PMe_3)]_2$ (5)

	1	2	3	5
Bond Lengths, Å				
Os(1)–Os(2)	2.8384 (8)	2.854 (2)	2.8545 (7)	2.964 (3)
Os(1)–M	3.024 (2)	3.079 (3)	3.0642 (7)	3.154 (2)
Os(2)–M	2.996 (2)	3.041 (3)	3.0423 (8)	3.156 (3)
Os(1)–P(1)	2.355 (4)	2.299[a]	2.355 (3)	2.32 (1)
Os(1)–P(2)	2.326 (4)	2.270[a]	2.326 (3)	2.33 (1)
Bond Angles, deg				
Os(1)–M–Os(2)	56.25 (4)	55.59 (4)	55.74 (2)	56.04 (6)
Os(1)–Os(2)–M	62.37 (4)	62.88 (5)	62.52 (2)	61.93 (6)
Os(2)–Os(1)–M	61.38 (4)	61.53 (5)	61.74 (2)	62.03 (6)
M–Os(1)–P(1)	110.6 (2)	108.1[a]	111.40 (8)	113.6 (3)
Os(2)–Os(1)–P(1)	169.6 (1)	167.0[a]	169.39 (7)	175.5 (3)
M–Os(2)–P(2)	166.6 (2)	156.9[a]	166.42 (7)	108.9 (3)
Os(1)–Os(2)–P(2)	107.4 (1)	95.1[a]	107.72 (7)	170.3 (3)

[a] These values suffer systematic errors due to unmodeled disorder of the phosphorus atoms.

invariably occupy equatorial sites in triangular metal carbonyl clusters[12,13] and the clusters described here are no exception. As expected from the method of synthesis, the phosphorus ligands are on separate osmium atoms, with one trans to an Os–M bond and the other cis to the second Os–M bond. This arrangement of phosphorus ligands is in contrast to that in $M_3(CO)_{10}(PR_3)_2$ (M = Ru, Os) clusters[13] and $(OC)_4W[(\mu\text{-}H)Os(CO)_3(PMe_3)]_2$ (described below) where both phosphorus ligands are trans to the same metal–metal bond.

As previously mentioned, 1 is the first cluster compound that contains chromium and osmium atoms to be structurally characterized. The only other compounds structurally characterized with Os–Cr bonds are the precursor to 1 $(Me_3P)(OC)_4OsCr(CO)_5$ (Os–Cr = 2.9787 (14) Å)[1] and the related complexes $(OC)_4(Bu^tNC)OsCr(CO)_5$ (Os–Cr = 2.966 (2) Å) and $(OC)_3(Bu^tNC)_2OsCr(CO)_5$ (Os–Cr = 2.9693 (12) Å);[14] the Os–Cr bond in each of these three complexes is a dative metal–metal bond. The Os–Cr vectors in 1 are 2.966 (2) and 3.023 (2) Å. We have found that dative metal–metal bonds have comparable or slightly longer lengths than nondative metal–metal bonds between the same metal atoms.[1,15] The Os–Cr lengths in 1 must, therefore, be regarded as long for single Os–Cr covalent bonds. Support for this supposition is that both the Os–Cr lengths are considerably longer than the Os–Os bond in the molecule. The length of this bond is 2.8384 (8) Å, a length which may be compared to 2.877 (3) Å, the average Os–Os bond length in $Os_3(CO)_{12}$.[16]

The longer Os–Cr bond in 1 is cis to one of the PMe_3 ligands. The lengthening of this bond relative to the other Os–Cr bond in 1 may, therefore, be attributed to steric interactions between the methyl groups on the PMe_3 ligand

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(12) For example: (a) Dahm, D. J.; Jacobson, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 5106. (b) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 2397. (c) Benfield, R. E.; Johnson, B. F. G.; Raithby, P. R.; Sheldrick, G. M. *Acta Crystallogr., Sect. B.: Struct. Crystallogr. Cryst. Chem.* **1978**, *34*, 666. (d) Vênaläinen, T.; Pakkanen, T. *J. Organomet. Chem.* **1984**, *266*, 269. (e) Alex, R. F.; Einstein, F. W. B.; Jones, R. H.; Pomeroy, R. K. *Inorg. Chem.* **1987**, *26*, 3175. (f) Bruce, M. I.; Liddell, M. J.; Hughes, C. A.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1988**, *347*, 157.

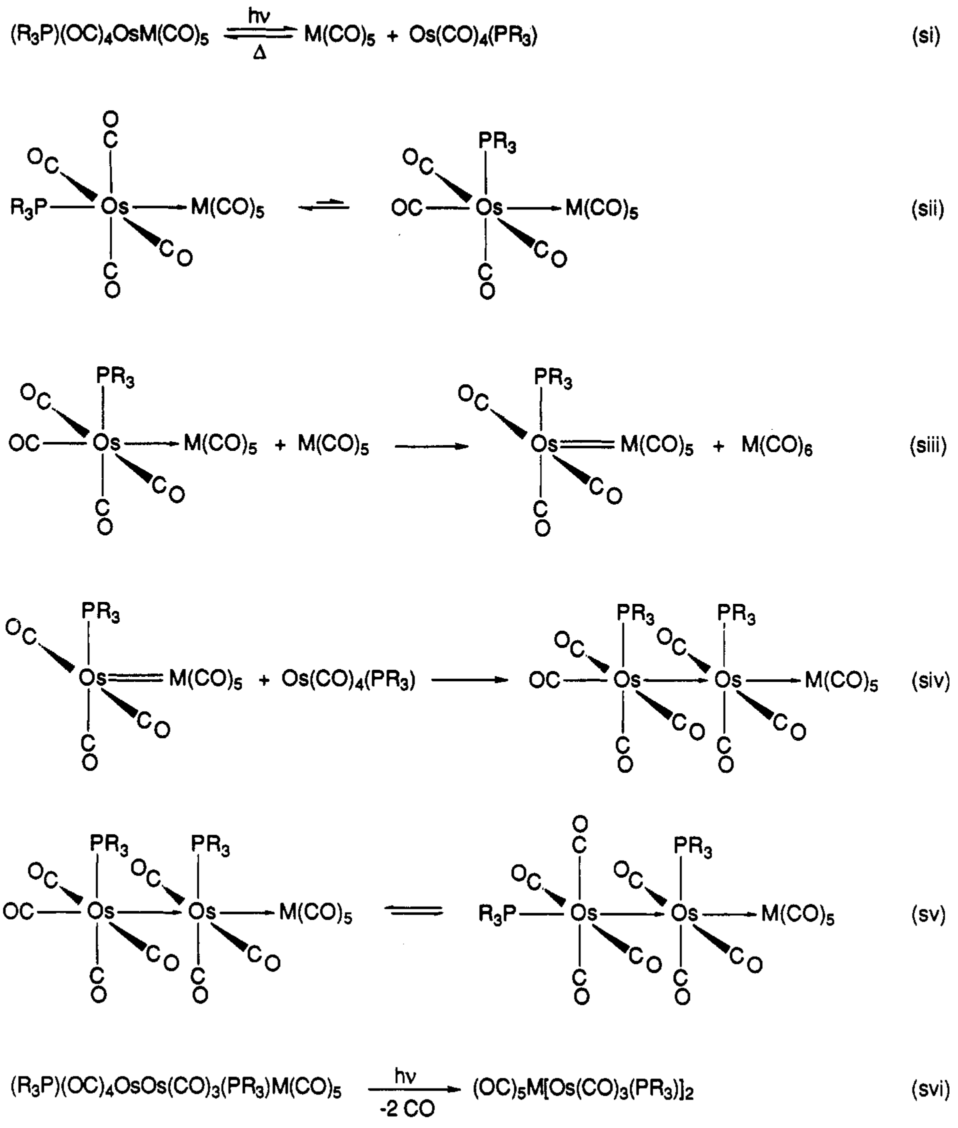
(13) (a) Bruce, M. I.; Matisons, J. G.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 2375. (b) Bruce, M. I.; Liddell, M. J.; Hughes, C. A.; Patrick, J. M.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1988**, *347*, 181.

(14) Shipley, J. A.; Batchelor, R. J.; Einstein, F. W. B.; Pomeroy, R. K. *Organometallics* **1991**, *10*, 3620.

(15) Einstein, F. W. B.; Jennings, M. C.; Krentz, R.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *Inorg. Chem.* **1987**, *26*, 1341.

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

Scheme I



and the radial carbonyls on the chromium atom.

In most trinuclear metal carbonyl clusters with no bridging carbonyls the axial carbonyls on one metal atom are eclipsed with respect to the axial carbonyls on a second metal atom.[12,13,16] This is also true for the equatorial carbonyls. In 1 (and 2 and 3), although the carbonyls on the osmium atoms are eclipsed with respect to one another those of the $Cr(CO)_5$ unit are staggered with respect to the carbonyls on the osmium atoms. This is illustrated for 3 in Figure 2. The dihedral angle between the Os(1)Os(2)Cr and C(32)CrC(34) planes in 1 is 26° (the corresponding dihedral angles in 2 and 3 are 19° and 23°, respectively). This staggered arrangement is more typical of bimetallic $(L)(OC)_4MM'(CO)_4(L')$ complexes where there is free rotation about the metal–metal single bond.[1,14,15,17] This point is relevant to the discussion on the bonding in the $(OC)_5M[Os(CO)_3(PR_3)]_2$ clusters given below.

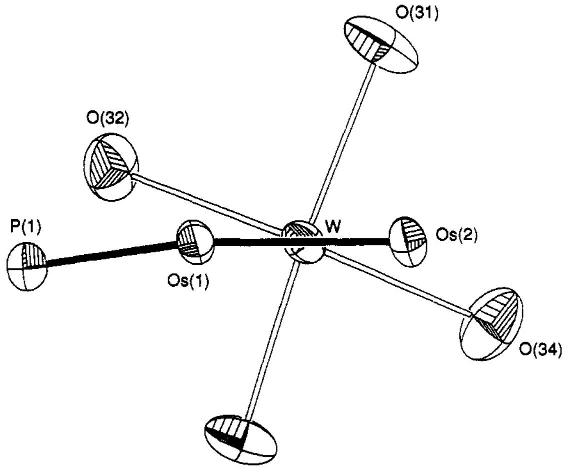


Figure 2. View of 3 that illustrates the orientation of the radial carbonyls on tungsten with respect to the WOs_2 plane.

That the dihedral angle between the Os(1)Os(2)Cr and C(32)CrC(34) planes is not closer to 45° probably reflects the different steric interactions between the radial carbonyls of the $Cr(CO)_5$ unit and carbonyl CO(22), and the $CH_3(15)$ and $CH_3(17)$ groups near the equatorial plane of the molecule. The radial carbonyls on the chromium atom that most closely approach the $CrOs_2$ plane are bent back from the osmium atoms (C(32)–Cr–C(34) = 164.3 (8)°). The other pair of radial carbonyls form a nearly linear

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(17) (a) Giordano, R.; Sappa, E.; Tiripicchoi, A.; Tiripicchio Camellini, M.; Mays, M. J.; Brown, M. P. *Polyhedron* **1989**, *8*, 1855. (b) Harris, G. W.; Boeyens, J. C. A.; Coville, N. J. *Organometallics* **1985**, *4*, 914. (c) Treichel, P. M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Elmsford, NY, 1982; Vol 4, p 11. (d) Boag, N. M.; Kaesz, H. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A.; Abel, E. W., Eds.; Pergamon: Elmsford, NY, 1982; Vol. 4, p 171.

arrangement at the chromium atom (C(31)–Cr–C(33) = 177.7 (7)°). It is remarkable that this molecule does not adopt a ground-state structure with three bridging carbonyls in the $CrOs_2$ plane, given that it contains a first-row transition-metal atom and two phosphine ligands. (Phosphine ligands in metal carbonyl clusters tend to stabilize structures with bridging carbonyls.[18]) As will be described in a future publication, in solution this isomer of **1** undergoes a low-energy carbonyl exchange process. A mechanism for the exchange that is consistent with the ^{13}C NMR data involves an intermediate with three bridging carbonyls in the metal–atom plane.

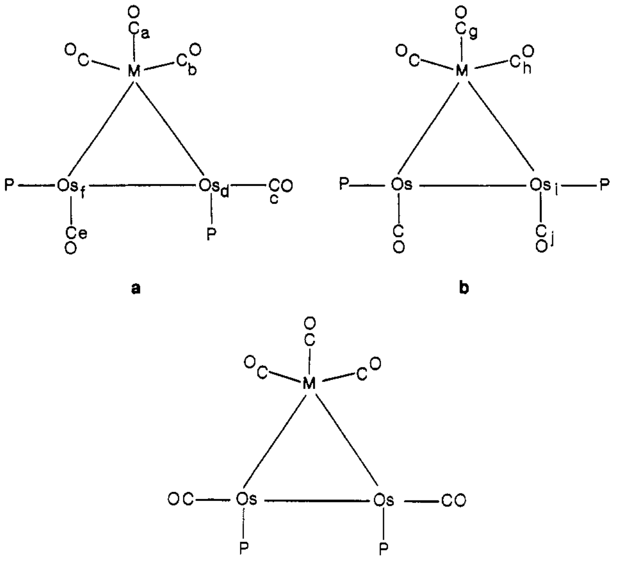
Structure of $(OC)_5Mo\{Os(CO)_3[P(OMe)_3]\}_2$/ $[(MeO)_3P](OC)_4OsMo(CO)_5$ (2′). As mentioned in the Introduction, the crystal used in this structure determination was isolated in the crude product of a preparation of $[(MeO)_3P](OC)_4OsMo(CO)_5$ by the method given in eq 1. The structure determination revealed an unusual example where two chemically different molecules had cocrystallized in the lattice in a 1:1 ratio. Only the structure of the trinuclear compound **2** will be discussed here. The structure of $[(MeO)_3P](OC)_4OsMo(CO)_5$ is similar to that found for $(Me_3P)(OC)_4OsM(CO)_5$ (M = Cr, W).[1] A view of $[(MeO)_3P](OC)_4OsMo(CO)_5$ is given in ref 2; bond length and angle data for the binuclear complex are deposited as supplementary material.

The Os–Mo bond lengths in **2** are 3.0407 (22) Å and 3.0788 (22) Å. These lengths are significantly longer than other unbridged Mo–Os distances reported in the literature: in $(\eta^5\text{-}C_5H_5)_2Mo_2Os_3(\mu\text{-}H)_2(CO)_{12}$ and $(\eta^5\text{-}C_5H_5)MoOs_3(\mu\text{-}H)_3(CO)_{11}$ the unbridged Mo–Os lengths range from 2.830 (1) to 2.952 (1) Å.[19] The Mo–Os lengths in **2** are, however, close to 3.075 (2) Å the length of the OsMo dative bond in $[(MeO)_3P](OC)_4OsMo(CO)_5$, the other molecule present in the structure.

As in **1**, the radial carbonyls of the $Mo(CO)_5$ unit are significantly rotated with respect to the carbonyls on the $Os(CO)_3[P(OMe)_3]$ groups; the radial carbonyls on the molybdenum atom that are closest to the $MoOs_2$ plane are also bent back (C(32)–Mo–C(34) = 161.9 (11)°) whereas the other pair of radial carbonyls form an almost linear arrangement at the Mo atom (C(31)–Mo–C(33) = 178.6 (10)°).

Structure of $(OC)_5W[Os(CO)_3(PMe_3)]_2$ (3). A view of the molecule is given in Figure 1; bond length and angle data are listed in Table IX. The Os-W bond lengths in **3** are 3.0427 (8) and 3.0646 (8) Å with the longer length corresponding to the bond that is cis to a PMe_3 ligand. These lengths are slightly shorter than 3.0756 (5) Å, the length of the dative Os-W bond in $(Me_3P)(OC)_4OsW(CO)_5$,[3] and 3.097 (1) Å, the length of the unsupported Os-W bond in $(\eta^5\text{-}C_5H_5)WOs_3(\mu\text{-}H)_2(\mu_3\text{-}CC_6H_4CH_3)(CO)_{12}$.[20] These lengths are, however, longer than unbridged Os-W bonds that occur in the metal skeletons of Os-W cluster compounds.[20,21] Once again, the radial carbonyls of the $M(CO)_5$ fragment are staggered with respect to the carbonyls of the $[Os(CO)_3(PR_3)]$ units, and the radial carbonyls on tungsten that are closest to the metal plane are bent back (C(32)–W–C(34) = 161.3 (5)°), while the C–W–C bond angle of the other pair of radial carbonyls is approximately linear (177.6 (5) Å).

Chart I



Spectroscopic Properties of the $(OC)_5M[Os(CO)_3(PR_3)]_2$ Clusters. The low-temperature ^{13}C NMR spectra and the ambient-temperature $^{31}P\{^1H\}$ NMR spectra of the $(OC)_5M[Os(CO)_3(PR_3)]_2$ clusters are similar (Tables II and III) and are consistent with the presence of two isomers in solution. The variable-temperature ^{13}C NMR spectra of the clusters are consistent with a number of carbonyl-exchange processes in the molecules; a detailed discussion of these exchange processes will form the subject of a future publication.

If the phosphorus ligands remain in equatorial sites on separate osmium atoms there are three possible isomers for the $(OC)_5M[Os(CO)_3(PR_3)]_2$ clusters. These have the phosphorus-donor ligands cis/trans (isomer a), trans/trans (isomer b), or cis/cis (isomer c) to the Os–Os bond (see Chart I, the axial carbonyls (f, d, and i) on the Os centers and two of the radial carbonyls on the W atom have been omitted for clarity). At low temperature the $^{31}P\{^1H\}$ NMR spectra of the clusters exhibit three signals consistent with the presence of isomer a plus either isomer b or c. (Isomer a is the structure adopted in the solid state by **1**–**3**, as previously discussed.) Isomers b and c cannot be distinguished by $^{31}P\{^1H\}$ or ^{13}C NMR spectroscopy. It is, however, believed that isomer b is the second isomer present in solution. This is the structure found in the solid state for clusters of the type $M_3(CO)_{10}(PR_3)_2$ (M = Ru, Os);[13] clusters of formula $Os_3(CO)_{10}(PR_3)_2$ also adopt two forms in solution that are believed to have structures similar to a and b.[22] Isomer b avoids the repulsive interactions between the substituents on the phosphorus atoms that are present in isomer c.[12f] Since the Os–Os distances in **1**, **2**, and **3** (2.8384 (8), 2.854 (2), and 2.8545 (7) Å, respectively) are shorter than in clusters of the type $Os_3(CO)_{10}(PR_3)_2$ (range 2.869 (1) to 2.910 (1) Å)[13b] it is ex-

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[18] For example: (a) Bruce, M. I.; Matisons, J. G.; Patrick, J. M.; White, A. H.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **1985**, 1223. (b) Albano, V.; Bellon, P. C.; Scatturin, V. *J. Chem. Soc., Chem. Commun.* **1967**, 730.

[19] Hsu, L.-Y.; Hsu, W.-L.; Jan, D.-Y.; Shore, S. G. *Organometallics* **1986**, *5*, 1041.

[20] Chi, Y.; Shapley, J. R.; Churchill, M. R.; Li, Y. *Inorg. Chem.* **1986**, *25*, 4165.

[21] Some examples: (a) Chi, Y.; Wu, C.-H.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1991**, *10*, 1676. (b) Chi, Y.; Shapley, J. R.; Ziller, J. W.; Churchill, M. R. *Organometallics* **1987**, *6*, 301. (c) Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *Inorg. Chem.* **1983**, *22*, 1579. (d) Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 6182. (e) Churchill, M. R.; Bueno, C.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 640. (f) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1979**, *18*, 843.

[22] (a) Deeming, A. J.; Donovan-Mtunzi, S.; Kabir, S. E.; Manning, P. *J. Chem. Soc., Dalton Trans.* **1985**, 1037. (b) Alex, R. F.; Pomeroy, R. K. *Organometallics* **1987**, *6*, 2437.

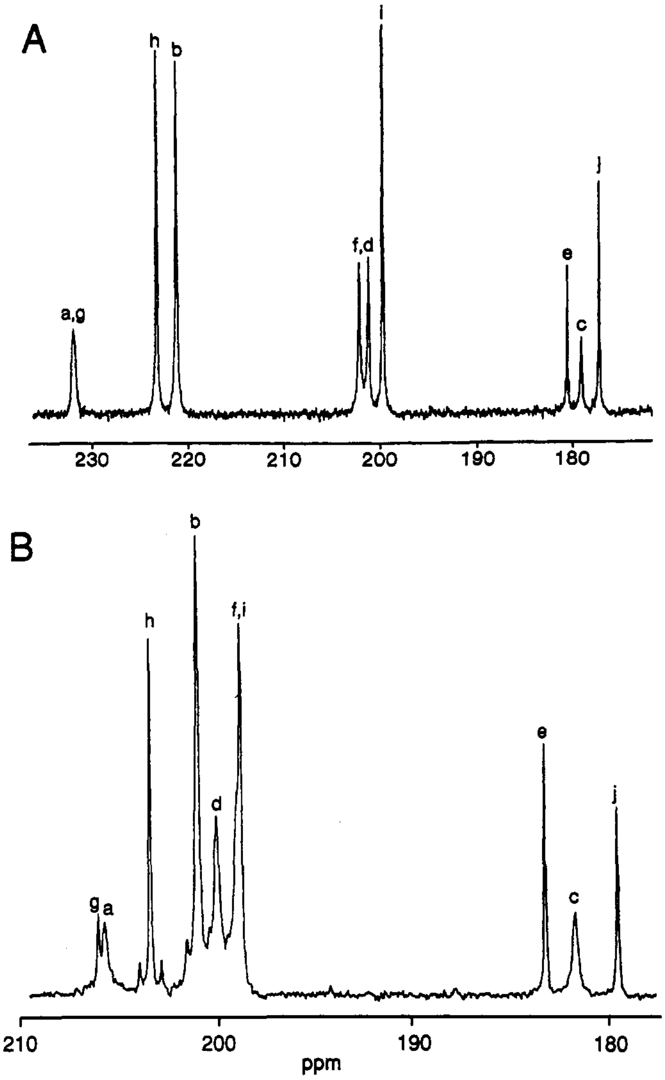

Figure 3. Part A shows the 100.6-MHz ^{13}C NMR spectrum of 1 (^{13}CO enriched) in $CHFCl_2/CD_2Cl_2$ solution at −122 °C and part B shows the corresponding spectrum of 3 under the same conditions. The assignment of the signals is as shown in Chart I except the signals labeled d, f, and i refer to the axial carbonyls on the osmium atoms labeled d, f, and i in Chart I.

pected that these interactions would be even greater in the heteronuclear clusters.

Low-temperature ^{13}C NMR spectra (carbonyl region) for 1 and 3 are shown in Figure 3. The assignment of the signals shown in the figure follows that given in Chart I (the axial carbonyls on the osmium atoms have been omitted along with two of the radial carbonyls of the $M(CO)_5$ unit). The assignment of the resonances, which we believe is unambiguous, is based on the following arguments: the intensity of the signals which are approximately proportional to the number of carbon atoms of that type in the molecule in question; the signals of the $M(CO)_5$ unit are downfield to ~200 ppm as previously observed for the derivatives of group 6 metal carbonyls;[1,14,23] the signals due to carbon atoms bound to tungsten show satellites due to ^{183}W–C coupling; the signals attributed to axial carbonyls on osmium are to low field compared to those due to equatorial carbonyls on these metal atoms;[22b,23,24] the mode of collapse of the signals at higher temperatures; and the proposed mechanism for the collapse. (Because of a low-energy carbonyl exchange process the signals due to isomer a of 3 except that at δ 182.5 are still somewhat broadened in the low-temperature spectrum.)

Remarkably, the spectra indicate that for each isomer of both molecules, the radial carbonyls of the $M(CO)_5$ unit are equivalent: a sharp singlet is observed for these carbonyls in each case. If the radial carbonyls on the group 6 atom adopted roughly axial and equatorial sites (similar to the carbonyls of the $Os(CO)_3(PMe_3)$ groups) three signals due to these carbonyls would be expected for isomer a and two for isomer b. Even if the radial carbonyls were perfectly staggered with respect to the MO_2 plane two signals would be expected for these carbonyls in isomer a.

This situation exists for all the $(OC)_5M[Os(CO)_3(PR_3)]_2$ clusters studied by low-temperature ^{13}C NMR spectroscopy, so possible accidental degeneracy of the resonances due to carbonyls in the various radial sites is most unlikely. We believe these results are best interpreted in terms of rapid rotation of the $M(CO)_5$ unit about an axis that passes through the group 6 metal atom, M, and the midpoint of the Os–Os bond. In this way the radial carbonyls are rendered equivalent on the NMR time scale, but not equivalent to the lone axial carbonyl of the $M(CO)_5$ unit. (Note there is an ambiguity in the description of the ligand positions in these clusters: the axial carbonyl of the $M(CO)_5$ unit lies in the MOs_2 plane, whereas the axial carbonyls of the $Os(CO)_3(PR_3)$ fragments are perpendicular to this plane.)

For two sites undergoing fast exchange, the rate constant required to observe broadening due to exchange is given by $\pi(\Delta\nu)^2/2(W - W_0)$, where $\Delta\nu$ is the chemical shift difference between the two signals when the molecule is rigid and $(W - W_0)$ is the line broadening.[25] In the rigid cluster $(OC)_4W[(\mu\text{-}H)Os(CO)_3(PMe_3)]_2$, described below, the chemical shift difference between the ^{13}C NMR signals due to the axial and equatorial carbonyls of the $W(CO)_4$ unit is ~2.5 ppm or ~250 Hz at an operating frequency of 100.6 MHz. If this is taken to be the chemical shift difference between the radial carbonyls when they are in the WOs_2 plane of 3 and when they are perpendicular to this plane, and if an observable line broadening of 4.0 Hz is assumed, then the $W(CO)_5$ unit in the cluster must be rotating at a rate $>2.5 \times 10^4\ s^{-1}$ at −122 °C.

Isomer a is found in the solid state for the $(OC)_5M[Os(CO)_3(PR_3)]_2$ clusters, and is the major form in solution (Table II). The behavior is solution is in contrast to that of $Os_3(CO)_{10}(PR_3)_2$ clusters where isomer b predominates.[22] Isomer a would be expected to be favored on steric grounds since in this isomer there are fewer repulsive interactions between the substituents on the bulky phosphorus ligands and the radial carbonyls on the group 6 atom. If this were the dominant factor in determining the isomer ratio one would expect more of isomer b upon substitution with a less bulky phosphorus ligand. This is not observed. For example, the a/b isomer ratio, on going from $(OC)_5W[Os(CO)_3(PMe_3)]_2$ to $(OC)_5W\{Os(CO)_3[P(OMe)_3]\}_2$ to $(OC)_5W\{Os(CO)_3[P(OCH_2)_3CMe]\}_2$, increases from ~2.6 to ~5.3 to ~9. This suggests that electronic factors are also important in determining the isomer ratio.

Metal–Metal Bonding in $(OC)_5M[Os(CO)_3(PR_3)]_2$. The NMR spectroscopic and X-ray structural evidence strongly indicate there is a low internal barrier to the rotation of the $M(CO)_5$ unit with respect to the [Os-

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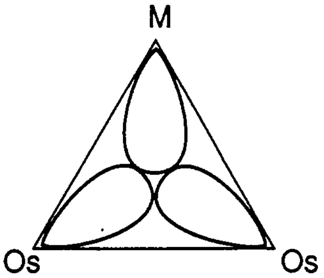
[23] Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic: New York, 1981.

[24] (a) Aime, S.; Osella, D.; Milone, L.; Rosenberg, E. *J. Organomet. Chem.* **1981**, *213*, 207. (b) Johnson, B. F. G.; Lewis, J.; Reichert, B. E.; Schorpp, K. T. *J. Chem. Soc., Dalton Trans.* **1976**, 1403.

[25] Sandström, J. *Dynamic NMR Spectroscopy*; Academic: New York, 1982; p 18.

Chart II



$(CO)_3(PMe_3)]_2$ half of these clusters. This behavior is similar to bimetallic molecules in which an $M(CO)_5$ moiety is bound through a single σ-bond to a second transition-metal fragment. For example, the ^{13}C NMR spectrum of $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$ in CD_2Cl_2 at −97 °C exhibits just a singlet for the radial carbonyls of the $W(CO)_5$ unit, consistent with free rotation of this unit with respect to the iridium moiety.[26] Furthermore, in this molecule and in the $(Me_3P)(OC)_4OsM(CO)_5$ (M = Cr, W) complexes, the crystal structures show that the radial carbonyls on the group 6 metal atom are staggered relative to the carbonyls on the iridium or osmium atom.

The metal–metal bonding in trinuclear metal carbonyl clusters with unbridged metal–metal bonds, such as $Os_3(CO)_{12}$, is often described in terms of two-center, two-electron metal–metal bonds.[27] If such were the case for the $(OC)_5M[Os(CO)_3(PR_3)]_2$ clusters, the $M(CO)_5$ unit would not be expected to rotate about its pseudo-4-fold axis. On the other hand, theoretical studies on trinuclear metal carbonyl clusters indicate that the metal–metal bonding should be described in terms of a molecular orbital in the center of the metal triangle plus edge-bridging molecular orbitals.[28] This suggests that the main bonding interaction in the metal skeleton of the present MOs_2 clusters is via a central molecular orbital as shown in Chart II.

It is well known that the square pyramidal $M(CO)_5$ fragment has only one low-energy acceptor orbital (which has a_1 symmetry).[29] The two electrons needed to fill the central molecular orbital are considered to come from the $[Os(CO)_3(PR_3)]_2$ grouping in order that the group 6 metal atom achieves an 18-electron configuration. In the pentanuclear cluster anions $[Ni_3M_2(CO)_{16}]^{2-}$ (M = Cr, Mo, W) each $M(CO)_5$ group is considered to be bonded to the three nickel atoms by only one delocalized electron-pair bond.[30]

The highest occupied molecular orbitals of the $M(CO)_5$ unit have b_1 and b_2 symmetry and are mainly the metal d_{xz} and d_{yz} orbitals, respectively.[29] There is, therefore, the possibility of π-back-bonding between one of these molecular orbitals and a suitable orbital on the $[Os(CO)_3(PR_3)]_2$ fragment. A recent EHMO calculation[31] for $[Os(CO)_4]_2$ indicates the LUMO is the $15b_1$ molecular orbital which is of the correct symmetry for overlap with the b_1 molecular orbital of the $M(CO)_5$ unit. Rotation of the $M(CO)_5$ unit would not alter the net bonding effect of this interaction. This is because the d_{xz} and d_{yz} orbitals have cylindrical symmetry about the pseudo-4-fold axis of the $M(CO)_5$ species. As the $M(CO)_5$ group is rotated it is possible to take linear combinations of the group 6 metal d_{xz} and d_{yz} orbitals so as to give the same overlap with the b_1 orbital on the $[Os(CO)_3(PR_3)]_2$ fragment. Any barrier to the rotation of the $M(CO)_5$ unit about the pseudo-4-fold axis would, therefore, arise from steric interactions, or repulsive interactions between filled molecular orbitals of the $M(CO)_5$ and $[Os(CO)_3(PR_3)]_2$ moieties. Evidently these interactions are small in these $(OC)_5M[Os(CO)_3(PR_3)]_2$ clusters.

Since the $Os(CO)_3(PR_3)$ fragment is isolobal with CH_2,[32] an alternative description of the bonding in $(OC)_5M[Os(CO)_3(PR_3)]_2$ is that it may be regarded as the interaction of the ethylene-like fragment $[Os(CO)_3(PR_3)]_2$ with the $M(CO)_5$ unit. There is formation of a σ-bond by the donation of electron density from the filled π-orbital on the diosmium fragment to the empty σ-orbital on $M(CO)_5$. Backbonding may occur via the filled d_{xz} orbital on M and the π^* MO on $[Os(CO)_3(PR_3)]_2$. As before, rotation of the $M(CO)_5$ unit relative to the diosmium moiety does not destroy this overlap since the filled d_{xz} and d_{yz} orbitals have cylindrical symmetry. As found in $M(CO)_5$(olefin) complexes,[33] it would be expected there would be a low barrier to the rotation of the olefin-like $[Os(CO)_3(PR_3)]_2$ about the $M(CO)_5$ unit. The short Os–Os bonds found in **1**–**3** are consistent with some residual double-bond character in these bonds. This view of the bonding of an $M(CO)_5$ fragment to two other metal atoms in a trinuclear cluster was first proposed by Stone and co-workers for $(OC)_5M[M'M''(\mu\text{-}CO)_2(\eta^5\text{-}C_5Me_5)_2]$ (M′ = M″ = Co, Rh; M′ = Co, M″ = Rh) clusters.[34]

$[(MeO)_3P](OC)_4W[Os(CO)_3(PMe_3)]_2$ (4). This deep red, air-stable cluster was prepared in 60% yield by the reaction of $P(OMe)_3$ and **3** in hexane at 50 °C (eq 3). The

$$(OC)_5W[Os(CO)_3(PMe_3)]_2 + P(OMe)_3 \rightarrow \underset{\mathbf{4}}{[(MeO)_3P](OC)_4W[Os(CO)_3(PMe_3)]_2} \quad (3)$$

ease of substitution of **3** may be compared to that of $Os_3(CO)_{12-x}(PR_3)_x$ clusters which typically requires temperatures well in excess of 100 °C to effect substitution of a carbonyl ligand by a phosphorus donor ligand in the absence of a catalyst.[35]

The $^{31}P\{^1H\}$ and ^{13}C NMR spectra of **4** (Tables II and III) indicated the presence of two isomers of the cluster in solution analogous to isomers a and b proposed for **3**, but with the axial carbonyl of the $W(CO)_5$ replaced by a $P(OMe)_3$ ligand. The a/b ratio for **4** was estimated to be 1/1 from the $^{31}P\{^1H\}$ NMR spectrum. Comparison of this ratio to that of **3** again suggests an electronic influence in determining the isomer ratio. The ^{13}C NMR spectrum of **4** recorded at room temperature was consistent with the free rotation of the $W(CO)_4[P(OMe)_3]$ unit with respect to the $[Os(CO)_3(PMe_3)]_2$ fragment in both isomers at this temperature.

$(OC)_4W[(\mu\text{-}H)Os(CO)_3(PMe_3)]_2$ (5). As mentioned above, this compound was isolated along with **3** from the

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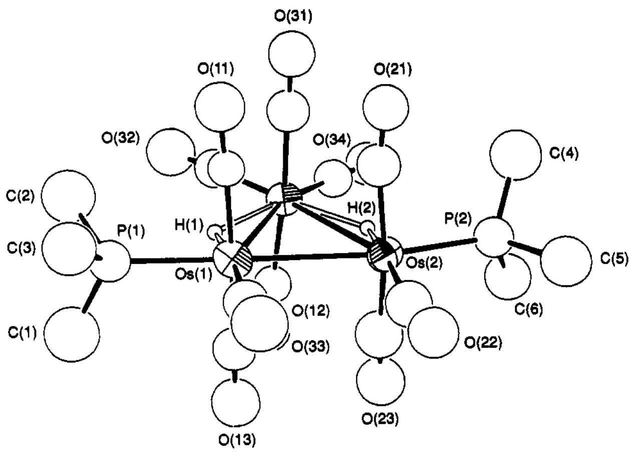

Figure 4. Molecular structure of $(OC)_4W[(\mu\text{-}H)Os(CO)_3(PMe_3)]_2$ (**5**).

ultraviolet irradiation of $(Me_3P)(OC)_4OsW(CO)_5$ in benzene. It was also isolated, in 63% yield, by the treatment of **3** in benzene with H_2 (1 atm) at 50 °C. Preliminary results indicate that the Cr and Mo analogues of **5** can also be prepared by the latter method. In contrast to the other clusters described here which are red, **5** is bright yellow.

The structure of **5** was determined by X-ray crystallography. A view of the molecule is shown in Figure 4; bond length and angle data are given in Table IX. There are several differences between the structure of **5** and that of **3**. In **5** the carbonyls of the $W(CO)_4$ grouping are typical of $M(CO)_4$ units in trinuclear metal carbonyl clusters in that the axial carbonyls are approximately perpendicular to the metal plane and the equatorial carbonyls lie approximately in the plane: the dihedral angle between the Os(1)Os(2)W and C(32)WC(34) planes is 6°. Furthermore, the phosphine ligands in **5** are both trans to the Os–Os bond rather than cis/trans as in **3**. As mentioned previously, in the structures of $Os_3(CO)_{10}(PR_3)_2$ clusters that have been determined by X-ray crystallography the phosphorus ligands are both trans to the same Os–Os bond in the solid state.[13b] Whereas the Os–Os bond length in **3** (2.8545 (7) Å) is somewhat shorter than the average Os–Os bond length in $Os_3(CO)_{12}$ (2.877 Å),[16] the Os–Os bond length in **5** is significantly longer (2.964 (3) Å) than this length.

The hydride ligands were not located in the X-ray study. The ^1H and ^{31}P NMR evidence indicates that each WOs vector is bridged symmetrically by a hydride ligand. Calculations with the HYDEX program[7] also placed the hydride ligands in these positions.

It is well known that when a single hydride ligand bridges a metal–metal bond the metal–metal vector is lengthened with respect to that of an unbridged metal–metal bond.[16,21f,36] The OsW vectors in **5** are equal within experimental error (3.154 (2) and 3.156 (3) Å) and, to our knowledge, they are the longest OsW lengths yet reported. The lengths may be compared to the corresponding lengths in **3** of 3.0423 (8) and 3.0642 (7) Å, and the WOs lengths of the W(μ-H)Os linkages in $WOs_3(\mu\text{-}H)_3(CO)_{11}(\eta^5\text{-}C_5H_5)$ of 3.073 (2) and 3.082 (3) Å.[21f]

As stated above, the spectroscopic data are consistent with **5** having the same structure in solution as found in the solid state. The ^1H NMR spectrum of the cluster in the hydride region exhibited a singlet with a small (16.7 Hz) coupling to phosphorus in agreement with a cis arrangement of a phosphine ligand with a given hydride ligand. The resonance also exhibited coupling to ^{183}W (~36 Hz). The $^{31}P\{^1H\}$ NMR spectrum of **5** was a singlet consistent with the presence of only one isomer in solution and in which the phosphorus atoms are chemically equivalent.

The ^{13}C NMR spectrum in the carbonyl region of **5** in $CDCl_3$ at room temperature had four signals in an approximate intensity ratio of 2:2:4:2 (the signal of intensity 4 was somewhat broadened probably due to unresolved coupling to the phosphorus atoms). The two signals to low field of 200 ppm at δ 202.2 (J_{WC} = 127.2 Hz) and δ 204.7 (J_{WC} = 164.0 Hz) were assigned to the axial and equatorial carbonyls, respectively, of the $W(CO)_4$ unit by analogy to the spectra of other tungsten carbonyl complexes (including **3** and **4**).[1,14,23] The resonances of intensity 4 at δ 183.8 and intensity 2 at δ 174.4 are assigned to axial and equatorial carbonyls, respectively, of the $[Os(CO)_3(PMe_3)]_2$ fragment. The ^{13}C NMR spectrum of **5** is therefore not only consistent with the structure found in the solid state for **5**, but also indicates that the metal framework and the carbonyls in the molecule are rigid in solution at room temperature. This is in marked contrast to the nonrigidity shown by **3**.

In a description of the skeletal bonding in **5**, it should be noted that $(Me_3P)(OC)_3(H)Os\text{–}Os(H)(CO)_3(PMe_3)$ is electron precise and each osmium atom has an 18-electron configuration (the $Os(H)(CO)_3(PR_3)$ unit is isolobal with CH_3). The triphenyl phosphine analogue of this compound has been reported.[37] The bonds of $(Me_3P)(OC)_3(H)Os\text{–}Os(H)(CO)_3(PMe_3)$ with the $W(CO)_5$ moiety are therefore believed to be three-center, two-electron Os(μ-H)W bonds. In this respect it is similar to the Re(μ-H)Re bond in $(OC)_5Re(\mu\text{-}H)Re_2(CO)_9$ reported many years ago by Kaesz and co-workers.[38]

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Supplementary Material Available: Figures of the molecular structures of **1**, **2**, and $[(MeO)_3P](OC)_4OsMo(CO)_5$, a table of bond lengths and angle data for $[(MeO)_3P](OC)_4OsMo(CO)_5$, a listing of supplementary crystallographic data for the structure determinations, and tables of fractional coordinates and isotropic temperature factors for the hydrogen atoms and anisotropic temperature factors for **1**, **2′**, **3**, and **5** (11 pages). Ordering information is given on any masthead page.

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