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Complexes with Unbridged Dative Bonds between Osmium and a Group 6 Element. Structures of $(Me_3P)(OC)_4OsM(CO)_5$ (M = Cr, W)

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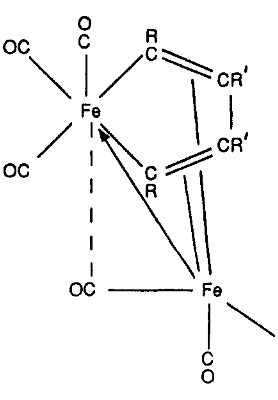
Complexes of the type $(R_3P)(OC)_4OsM(CO)_5$ (R = Me, OMe, Ph, etc.; M = Cr, Mo, W) have been prepared from the reaction of $Os(CO)_4(PR_3)$ and $M(CO)_5(THF)$ in hexane. The structures of $(Me_3P)(OC)_4OsCr(CO)_5$ (1) and $(Me_3P)(OC)_4OsW(CO)_5$ (2) have been determined by X-ray crystallography: Compound 1 crystallizes in the space group $P2_1/n$, with $a = 9.231$ (1) Å, $b = 18.153$ (1) Å, $c = 10.865$ (1) Å, $\beta = 91.08$ (1)°, and $Z = 4$; $R = 0.023$, $R_w = 0.028$ for 1748 observed reflections. Compound 2 crystallizes in the space group $P2_1/n$, with $a = 8.832$ (1) Å, $b = 16.241$ (2) Å, $c = 12.988$ (2) Å, $\beta = 101.99$ (1)°, and $Z = 4$; $R = 0.019$, $R_w = 0.023$ for 2189 observed reflections. In both 1 and 2 the $Os(CO)_4(PMe_3)$ molecule acts as a ligand to the $M(CO)_5$ fragment via an unbridged donor-acceptor metal-metal bond (Os-Cr = 2.9787 (14) Å; Os-W = 3.0756 (5) Å); the phosphine ligand is trans to the metal-metal bond. The major spectroscopic features of the $(R_3P)(OC)_4OsM(CO)_5$ complexes indicate these compounds adopt the same structure in solution. There are, however, weak signals in the ^{13}C (and ^1H and ^{31}P) NMR spectra that are consistent with small amounts of the isomer with the phosphorus ligand cis to the metal-metal bond. For 2, the isomers were shown to be in rapid equilibrium by the spin saturation transfer technique. The well-known mechanism that involves pairwise carbonyl exchange between metal atoms accounts for the observations regarding the isomerization. The homoleptic derivative $(OC)_5OsCr(CO)_5$ has also been prepared. Although unstable in solution at room temperature, the ^{13}C NMR spectrum in CD_2Cl_2 at −40 °C indicates it also has a structure with an unbridged, Os-Cr dative bond.

Introduction

It has been known for some time that the metal atom in some low-valent organometallic complexes can behave as a Lewis base and form a donor-acceptor bond with a non-transition-metal atom in a Lewis acid.[1] Two recent examples are $Fe(CO)_2(PMe_2Ph)_2[CS_2C_2(CO_2Me)_2](HgCl_2)$[2] and $(\eta^5\text{-}C_5H_5)Rh(PMe_3)_2(Al_2Me_2Cl_2)$.[3] However, the possibility that a neutral 18-electron organometallic compound can act as a two-electron donor ligand toward a second transition-metal atom appears not to have been widely explored. The bond between the two species in the resulting adduct would be a donor-acceptor (or dative) metal-metal bond. Bonds of this type have been proposed before in organometallic complexes in order that each metal attains an 18- or, in some cases, 16-electron configuration. The first such proposal appears to be that of Hock and Mills for compound I (R = OH, R′ = Me).[4]



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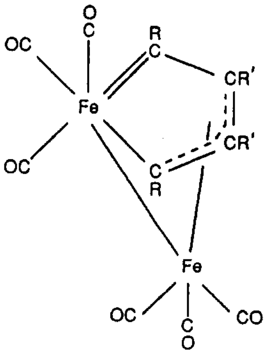

II

In most examples where a dative metal-metal bond is thought present, the bond is supported by bridging ligands[5] or nondative metal-metal bonds in a cluster framework.[6] For this reason alternative electron-counting schemes are usually possible in which the metal-metal bond can be regarded as a nondative, covalent bond. For example, an alternative representation for I is shown as II. Furthermore, MO calculations on complexes thought to contain dative metal-metal bonds bridged by carbonyls indicate there is little direct metal-metal interaction.[5]

A dative metal-metal bond has been proposed as present in $(OC)_4CoRh(CO)(PEt_3)_2$.[7] However, consideration of each half of the molecule shows that the $Co(CO)_4$ and $Rh(CO)(PEt_3)_2$ fragments each need one electron to yield 18- and 16-electron configurations, respectively. For this reason we believe the metal-metal bond in this compound should be regarded as a polar covalent bond even though it readily dissociates in CH_3CN to give $[Co(CO)_4]^-$ and $[Rh(CO)(PEt_3)_2(CH_3CN)]^+$.[7]

An ambiguity in electron counting exists in the anionic complexes $[(OC)_5M'M(CO)_5]^-$ (M′ = Mn, Re; M = Cr, Mo, W)[8] and $[(H)(OC)_4FeM(CO)_5]^-$ (M = Cr, W).[9] Location of the negative charge on the non group 6 metal atom results in a dative metal-metal bond description for the ions, whereas location of the charge on the group 6 metal leads to a covalent metal-metal bond formulation. For the latter complexes, evidence has been presented that the negative charge is located on the iron atom and, therefore, the dative bond formalism is correct.[9] On the other hand,

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Table I. Analytical and Mass and Infrared Spectral Data for New Compounds

	anal.					
	calcd		found			
	C	H	C	H	mass spectrum	ν(CO),[a] cm^{-1}
$(OC)_5OsCr(CO)_5$	32.74		32.74		M^+	2144.5 (m), 2049.5 (m), 1924 (m)
$(Me_3P)(OC)_4OsCr(CO)_5$	25.27	1.59	25.44	1.61	M^+	2092 (w), 2025 (m), 2009 (s), 1910 (s), 1885 (m)
$(PhMe_2P)(OC)_4OsCr(CO)_5$	32.29	1.76	32.06	1.63	M^+	2102.5 (w), 2025 (m), 2008.5 (s), 1909.5 (s), 1885 (m)
$(Ph_2MeP)(OC)_4OsCr(CO)_5$	38.05	1.89	38.60	1.89	[b]	2102.5 (w), 2025 (m), 2010.5 (s), 1911.5 (s), 1885 (m)
$(Ph_3P)(OC)_4OsCr(CO)_5$	42.86	2.00	42.61	2.03	[b]	2102 (w), 2025 (m), 2010 (s), 1913.5 (s), 1885 (m)
$[(MeO)_3P](OC)_4OsCr(CO)_5$	23.27	1.45	23.33	1.33	[b]	2093 (vw), 2021 (s), 1915 (s), 1895 (s)
$[MeC(CH_2O)_3P](OC)_4OsCr(CO)_5$	26.18	1.41	26.32	1.48	M^+	2107 (vw), 2029 (s), 1915 (s), 1887 (m, sh)
$(Me_3P)(OC)_4OsMo(CO)_5$	23.46	1.48	23.36	1.40	M^+	2090 (w), 2042 (m), 2003 (s), 1922 (s), 1883 (m)
$(Ph_3P)(OC)_4OsMo(CO)_5$	40.51	1.99	39.74	1.82	[b]	2098.5 (w), 2046 (m), 2005.5 (s), 1923.5 (s), 1881.5 (m)
$[(MeO)_3P](OC)_4OsMo(CO)_5$	21.76	1.36	21.96	1.32	[b]	2097 (vw), 2048 (m), 2013 (s), 1926.5 (s), 1886 (m)
$(Me_3P)(OC)_4OsW(CO)_5$	20.53	1.29	20.50	1.21	M^+	2092.5 (w), 2040 (m), 2009 (s), 1912.5 (s), 1877.5 (m)
$(PhMe_2P)(OC)_4OsW(CO)_5$	26.72	1.45	26.77	1.52	M^+	2103 (w), 2040.5 (m), 2010.5 (s), 1911.5 (s), 1876 (m)
$(Ph_2MeP)(OC)_4OsW(CO)_5$	32.00	1.59	31.95	1.35	[b]	2103 (w), 2042.5 (m), 2010 (s), 1912.5 (s), 1878.5 (m)
$(Ph_3P)(OC)_4OsW(CO)_5$	36.50	1.70	36.22	1.58	[b]	2104 (w), 2043.5 (m), 2011 (s), 1914 (s), 1879 (m)
$[(MeO)_3P](OC)_4OsW(CO)_5$	19.26	1.20	19.33	1.13	[b]	2101.5 (w), 2044 (m), 2019.5 (s), 1914.5 (s), 1882 (m)
$[MeC(CH_2O)_3P](OC)_4OsW(CO)_5$	21.72	1.17	21.74	1.20	M^+	2108 (w), 2044 (m), 2030 (s), 1915 (s), 1881 (m)

[a] CH_2Cl_2 solution. [b] A satisfactory EI mass spectrum could not be obtained.

we have shown that complexes with dative metal–metal bonds often isomerize irreversibly to a form with a covalent metal–metal bond.[10] This suggests that the description of these anions with covalent metal–metal bonds should also be considered. No doubt, the correct description probably lies between these two views; i.e., the charge is delocalized over both metal atoms. This would be in keeping with Pauling's electroneutrality principle.

In 1983 we reported the synthesis of $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$ from $Os(CO)_5$ and $GeCl_4$. The crystal structure of this complex revealed that the neutral 18-electron compound $Os(CO)_5$ acts as a donor ligand to the second osmium atom via an unbridged, donor–acceptor metal–metal bond.[11] This is believed to be the first case of a complex of this type. Since that initial report we have described several other complexes in which a neutral 18-electron compound acts as a ligand to a second metal center through an unbridged dative bond.[10,12–15] Complexes of this type, however, remain extremely rare; the only other examples we are aware of are $(\eta^5\text{-}C_5Me_5)[(PrO)_3P](OC)IrRh(CO)[P(OPr)_3](Cl)$[16] and $(\eta^5\text{-}C_5H_5)(OC)_2RhPt(CO)(C_6F_5)_2$.[17] On the other hand, complexes with apparent dative metal–metal bonds supported by bridging ligands[5,18] or as part of a metal cluster framework are becoming increasingly common.[15,19]

In this paper we report the preparation and characterization of complexes of the type $(R_3P)(OC)_4OsM(CO)_5$ (M = Cr, Mo, W). These complexes are examples of compounds that contain unbridged, dative bonds between transition metals from different groups. Some of these compounds exhibit dynamic isomerism which is unusual for dinuclear carbonyl derivatives in which each metal is six coordinate. We also report the synthesis of $(OC)_5OsCr(CO)_5$ the first neutral, homoleptic carbonyl compound with an unbridged, dative metal–metal bond. The synthesis, structure, and nonrigidity of $(Me_3P)(OC)_4OsW(CO)_5$ has been the subject of a preliminary communication.[12]

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. Hexane, tetrahydrofuran (THF), and dichloromethane were distilled under nitrogen from potassium, potassium benzophenone ketyl, and P_2O_5, respectively. The osmium compounds $Os(CO)_4(L)$ (L = CO, PMe_3, PPh_3, $P(OCH_2)_3CMe$) were prepared by literature methods.[20,21] The phosphite derivative $Os(CO)_4[P(OMe)_3]$ was synthesized from $Os(CO)_5$ and $P(OMe)_3$[21] (also, see below) and had spectroscopic properties as previously reported.[22] The carbonyls $M(CO)_6$ (M = Cr, Mo, W) were obtained commercially as were the phosphorus ligands with the exception of $P(OCH_2)_3CMe$ which was prepared by the literature method.[23] An external, medium-pressure mercury discharge lamp (200-W, Hanovia Model 654 A36) contained in a water-cooled quartz jacket was employed in the UV irradiations. There were ~5 cm between the source and the edge of the reaction vessel.

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 (Table I) were obtained with a Hewlett-Packard 5985 GC–MS instrument. NMR spectra (Tables II and III) 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, for the most part, on samples that were enriched with ^{13}CO

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

compound	isomer[c]	^{1}H δ	^{31}P{^{1}H}[b] δ	isomer ratio
$(Me_3P)(OC)_4OsCr(CO)_5$	**a**	2.03 (10.3)	−52.3	~6
	b	1.87 (10.2)	*d*	
$(PhMe_2P)(OC)_4OsCr(CO)_5$		2.30 (9.9)	−41.8	~50[e]
$(Ph_2MeP)(OC)_4OsCr(CO)_5$		2.54 (9.2)	−22.8	>50[e]
$(Ph_3P)(OC)_4OsCr(CO)_5$			−0.2	
$[(MeO)_3P](OC)_4OsCr(CO)_5$	**a**	3.68 (13.2)	100.6	~50
	b	3.74 (12.0)	*d*	
$[MeC(CH_2O)_3P](OC)_4OsCr(CO)_5$	**a**	4.37 (5.0), 0.85	84.2	10
	b	4.33 (5.0), 0.80	81.5	
$(Me_3P)(OC)_4OsMo(CO)_5$	**a**	2.01 (10.3)	−53.0	3.2
	b	1.91 (10.2)	−62.3	
$[(MeO)_3P](OC)_4OsMo(CO)_5$	**a**	3.71 (13.1)	102.9	13.3
	b	3.77 (12.0)	87.1	
$(Me_3P)(OC)_4OsW(CO)_5$	**a**	2.02 (10.3)	−53.2	3.3
	b	1.93 (10.2)	−62.3	
$(PhMe_2P)(OC)_4OsW(CO)_5$	**a**	2.29 (9.8)	−42.7	14.5
	b	2.21 (10.0)	*d*	
$(Ph_2MeP)(OC)_4OsW(CO)_5$		2.53 (9.2)	−23.9	>50[e]
$(Ph_3P)(OC)_4OsW(CO)_5$	**a**		−1.4	>50[e]
	b		−11.1	
$[(MeO)_3P](OC)_4OsW(CO)_5$	**a**	3.73 (13.0)	99.6	13.5
	b	3.78 (11.8)	83.4	
$[MeC(CH_2O)_3P](OC)_4OsW(CO)_5$	**a**	4.37 (5.0), 0.85	82.4	1.5
	b	4.33 (5.0), 0.81	80.4	

[a] $CDCl_3$ or CD_2Cl_2 solution; figures in parentheses are J_{P-H}. [b] Reference: external 85% H_3PO_4. [c] See text. [d] Not observed. [e] Weak signals (~2% intensity of major signals) were observed that may have been due to **b** (see text).

Table III. ^{13}C NMR Resonances for the Carbonyl Ligands and Methyl Groups of $(L)(OC)_4OsM(CO)_5$ Derivatives[a]

		$M(CO)_5$		$Os(CO)_4L$	
compound	isomer	δ(ax-CO)	δ(rad-CO)	δ(CO)	δ(Me)
$(OC)_5OsCr(CO)_5$[b]		227.8	220.3	179.4, 163.3	
$(Me_3P)(OC)_4OsCr(CO)_5$		230.7	223.3	189.4 (2.0)	23.3 (37.5)
$(PhMe_2P)(OC)_4OsCr(CO)_5$		230.5	223.1	189.1	22.3 (38.8)
$(Ph_2MeP)(OC)_4OsCr(CO)_5$		230.3	222.8	189.0	22.7 (38.0)
$(Ph_3P)(OC)_4OsCr(CO)_5$		230.1	222.5	188.9	
$[(MeO)_3P](OC)_4OsCr(CO)_5$		227.7	222.8	186.8 (5.2)	*c*
$[MeC(CH_2O)_3P](OC)_4OsCr(CO)_5$[b]	**a**	230.1	222.6	184.6	
	b	229.3	221.0	187.0 (19.0), 179.9 (120.9), 167.0 (10.5)[f]	
$(Me_3P)(OC)_4OsMo(CO)_5$[b]	**a**	217.1	210.7	188.6	24.3 (37.2)
	b	*c*	209.7	190.8 (13.6)[c]	22.0 (38.9)
$(Ph_3P)(OC)_4OsMo(CO)_5$		216.7	210.2	188.4	
$[(MeO)_3P](OC)_4OsMo(CO)_5$	**a**	216.7	210.3	186.4 (4.8)	*c*
	b		209.3		
$(Me_3P)(OC)_4OsW(CO)_5$	**a**	204.6 (2.2, 179.1[d])	202.8 (124.9)[d]	186.7 (3.0, 92[e])	23.2 (37.1)
	b	202.9	202.5 (125.2)[d]	188.3 (13.2), 176.0 (71.1), 170.3 (8.9)[f]	20.8 (37.7)
$(PhMe_2P)(OC)_4OsW(CO)_5$		204.6 (2.2)	202.7 (124.8)[d]	186.5	21.9 (37.5)
$(Ph_2MeP)(OC)_4OsW(CO)_5$		204.3	202.5 (125.0)[d]	186.3	22.5 (37.6)
$(Ph_3P)(OC)_4OsW(CO)_5$		204.1 (2.1)	202.4 (125.5)[d]	186.3 (1.7)	
$[(MeO)_3P](OC)_4OsW(CO)_5$	**a**	204.4	202.3 (124.6)[d]	184.1 (5.0)	54.0 (40.2)
	b	*c*	201.8	*c*	
$[MeC(CH_2O)_3P](OC)_4OsW(CO)_5$	**a**	204.1 (4.7, 178[d])	202.2 (124.5)[d]	182.3 (5.2, 91.5[e])	*c*
	b	203.3	201.7 (125)[d]	183.7 (19.0), 177.6 (122.0), 167.2 (11.3)[f]	

[a] CD_2Cl_2/CH_2Cl_2 (1/4, v/v) solution; ^{13}CO-enriched samples; figures in parentheses are J_{P-C} unless otherwise stated. [b] Spectrum at −30 or −40 °C. [c] Not observed. [d] J_{W-C}. [e] J_{Os-C}. [f] See text.

(~30%); the ^{13}C NMR resonances for the phosphorus ligand were either weak or (R = Ph) not observed. The microanalyses were obtained by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

Preparation of $Os(CO)_4(L)$ ($L = PMe_2Ph, PMePh_2$). The complexes were prepared in good yield from $Os(CO)_5$ (~0.12 g; ~0.36 mmol) and an equimolar amount of phosphine in hexane (20 mL) at 100 °C under CO (50 atm) for 16 h.[21] The $Os(CO)_4(PMe_2Ph)$ complex was purified by sublimation at 70 °C (<0.02 mm); the $Os(CO)_4(PMePh_2)$ complex was purified by precipitation from hexane. The latter compound was obtained as an oil; although a C/H microanalysis of it was not obtained, it appeared pure by infrared spectroscopy. $Os(CO)_4(PMe_2Ph)$: IR (hexane) ν(CO), 2061 (s), 1981 (m), 1939 (vs) cm^{-1}; ^{13}C{^{1}H} NMR δ(CO) 189.7 (d, J_{P-C} = 5.0 Hz); MS (EI) *m/z* $M^+ - n(CO)$ (n = 0–4). Anal. Calcd for $C_{12}H_{11}O_4POs$: C, 32.74; H, 2.52. Found: C, 32.57; H, 2.44. $Os(CO)_4(PMePh_2)$: IR (hexane) ν(CO), 2060.5 (s), 1981.5 (m), 1939 (vs) cm^{-1}; ^{13}C{^{1}H} NMR δ(CO) 189.6 (d, J_{P-C} = 5.2 Hz); MS (EI) *m/z* $M^+ - n(CO)$ (n = 0–4).

Preparation of $M(CO)_5(THF)$ (M = Cr, Mo, W). A quartz Carius tube (30 × 3 cm; fitted with a Teflon valve) with a magnetic stir bar was charged with $M(CO)_6$ (ca. 0.2 mmol) and THF (10 mL), cooled to −196 °C, and evacuated; the solution was degassed with two freeze–pump–thaw cycles. The stirred solution was subjected to UV irradiation at room temperature. The irradiation was for a period of 1–2 h; the exact time depended on the quantity and particular carbonyl used. The conversion of $M(CO)_6$ to $M(CO)_5(THF)$ was monitored by IR spectroscopy; it took longer for $Cr(CO)_6$ than for either $Mo(CO)_6$ or $W(CO)_6$. Complete conversion to $M(CO)_5(THF)$ was possible for M = Cr and W, but decomposition of the Mo derivative occurred before conversion was complete. After irradiation, the solvent was removed under reduced pressure and the tube containing the residual solid was immediately cooled to −196 °C to prevent decomposition.

Preparation of ^{13}CO-Enriched $M(CO)_5(THF)$. A solution of $M(CO)_5(THF)$ in THF was prepared as described above. The tube was then pressurized with ^{13}CO (99% ^{13}CO; ~1.5 atm) and the solution subjected to further UV irradiation for ~18 h. The tube was then frozen and evacuated; the solution was degassed with two freeze-pump-thaw cycles. The ^{13}CO-enriched $M(CO)_6$ was then converted to ^{13}CO-enriched $M(CO)_5(THF)$ as described above for $M(CO)_6$. The amount of ^{13}CO enrichment was estimated to be ~50%.

Preparation of $(R_3P)(OC)_4OsM(CO)_5$ (M = Cr, Mo, W) Derivatives. The derivatives were all prepared by the reaction of $Os(CO)_4(PR_3)$ with $M(CO)_5(THF)$ in hexane at or below room temperature. Details of three variations of the preparation are given below. The yields were 70–80%, 20–30%, and 50–60% for the chromium, molybdenum, and tungsten derivatives, respectively. The chromium compounds were bright yellow, the molybdenum compounds colorless to pale yellow, and the tungsten compounds pale yellow. All compounds could be handled in air for short periods with no apparent decomposition although prolonged exposure did eventually result in decomposition. Analytical and mass and infrared spectral data for new compounds are given in Table I, ^1H and $^{31}P\{^1H\}$ NMR data in Table II, and ^{13}C NMR data in Table III. Because of the small quantities isolated, ^1H and ^{31}P NMR data were not obtained for some compounds.

Preparation of $(Me_3P)(OC)_4OsCr(CO)_5$. A solution of $Cr(CO)_5(THF)$ in THF (20 mL) was prepared from $Cr(CO)_6$ (150 mg, 0.68 mmol), as described above. The solvent was removed on the vacuum line and the remaining orange solid cooled immediately to −196 °C. A solution of $Os(CO)_4(PMe_3)$ (200 mg, 0.53 mmol) in hexane (20 mL) was added to the frozen $Cr(CO)_5(THF)$. The resulting mixture was then allowed to warm, with stirring, to room temperature. The solution was stirred for a further 15 min. The solvent was removed, and the yellow precipitate was washed with hexane and dried on the vacuum line. The yellow solid was dissolved in CH_2Cl_2 (3 mL) and chromatographed on a short column of Florisil. Elution with CH_2Cl_2/hexane (2/1, v/v) gave a bright yellow band which was collected. Removal of the solvent gave pure $(Me_3P)(OC)_4OsCr(CO)_5$ (0.223 g, 74%). The analytical sample was obtained by recrystallization from CH_2Cl_2/hexane.

Preparation of $[(MeO)_3P](OC)_4OsMo(CO)_5$. A solution of $Mo(CO)_5(THF)$ was prepared from $Mo(CO)_6$ (300 mg, 1.14 mol). The solution of $Mo(CO)_5(THF)$ was evaporated to near dryness and cooled to −196 °C. A solution of $Os(CO)_4[P(OMe)_3]$ (185 mg, 0.43 mmol) in hexane (20 mL) was added to the frozen $Mo(CO)_5(THF)$. The resulting mixture was allowed to warm to −78 °C where it was stirred for 30 min with the exclusion of light, whereupon a yellow solid formed. The mixture was stirred for a further 20 min at room temperature, and the solvent was removed on the vacuum line. The remaining solid was chromatographed on a Florisil column (11 × 1 cm) with CH_2Cl_2/hexane as the eluant (1/5, v/v, followed by 1/1). A yellow band of the desired product separated. It was contaminated by traces of a deep red compound that has been subsequently identified as $(OC)_5Mo[Os(CO)_3(P(OMe)_3)]_2$.[26] The contaminated product was purified by two recrystallizations from CH_2Cl_2/hexane, followed by chromatography on a short silica gel column (5 × 1 cm), and finally by a third recrystallization from CH_2Cl_2/hexane. In this way $[(MeO)_3P](OC)_4OsMo(CO)_5$ (79 mg, 28%) was obtained as pale yellow crystals.

In the preparation of $(Ph_3P)(OC)_4OsMo(CO)_5$, the solution of $Mo(CO)_5(THF)$ was reduced in volume until approximately 5 mL of THF remained. (The THF helped increase the stability of $Mo(CO)_5(THF)$ in hexane and also increased the solubility of the $Os(CO)_4(PPh_3)$.)

Preparation of $[(MeO)_3P](OC)_4OsW(CO)_5$. A solution of $W(CO)_5(THF)$ was prepared from $W(CO)_6$ (300 mg, 0.85 mmol) as described previously. The solution was reduced in volume to approximately 5 mL and then added dropwise to a vigorously stirred solution of $Os(CO)_4[P(OMe)_3]$ (200 mg, 0.5 mmol) in hexane (40 mL). The $W(CO)_5(THF)$ was added until it appeared, by infrared spectroscopy, that reaction was complete. The crude product that had precipitated from the solution was purified by chromatography on Florisil (17 × 1 cm) with CH_2Cl_2/hexane (1/5, v/v) as the eluant. The compound thus obtained was contaminated by traces of a deep red compound believed to be $(OC)_5W\{Os(CO)_3[P(OMe)_3]\}_2$. This was removed by recrystallization from CH_2Cl_2/hexane to give the desired product $[(MeO)_3P](OC)_4OsW(CO)_5$ (192 mg, 51%) as pale yellow, air-stable crystals.

Table IV. Crystal Data, Data Collection, and Refinement of the Structures

	1	2
formula	$C_{12}H_9CrO_9OsP$	$C_{12}H_9O_9OsPW$
fw	570.37	702.22
color	yellow	pale yellow
space group	$P2_1/n^a$	$P2_1/n^a$
a, Å	9.231 (1)	8.832 (1)
b, Å	18.153 (1)	16.241 (2)
c, Å	10.865 (1)	12.988 (2)
β, deg	91.08 (1)	101.99 (1)
V, Å^3	1820.3	1822.3
Z	4	4
ρ_{calcd}, g cm^{-3}	2.081	2.560
μ, cm^{-1}	76.88	135.42
cryst dimens, mm	$0.2 \times 0.2 \times 0.2^b$	$0.07 \times 0.18 \times 0.19$
max variatn in trans coeff	0.926–1.000^c	0.557–0.139
ψ-scan width, deg	$0.65 + 0.36 \tan \theta$	$0.60 + 0.35 \tan \theta$
ψ-scan speed, deg min^{-1}	0.7–4.0	0.5–3.3
2θ range, deg	3–50	3–48
no. of unique reflcns	3188	2844
no. of obsd reflcns^d	1748	2189
no. of variables	217	245
final R_f	0.023	0.019
final $R_{wF}{}^f$	0.028	0.023

[a] Nonstandard setting for $P2_1/c$. [b] Dimensions approximate: shape of crystal irregular. [c] Empirical correction. [d] $I \geq 2.3\sigma(I)$. [e] $R_w = \sum||F_o| - |F_c||/\sum|F_o|$. [f] $R_{wF} = (\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2)^{1/2}$.

Preparation of $(OC)_5OsCr(CO)_5$. A hexane solution of $Os(CO)_5$ was added to an approximately equimolar quantity of solid $Cr(CO)_5(THF)$ maintained at −196 °C. The frozen mixture was then allowed to warm to room temperature, whereupon the product $(OC)_5OsCr(CO)_5$ (~80% yield) precipitated as a yellow microcrystalline solid. The compound was purified by dissolving it in cold CH_2Cl_2, quickly filtering the resulting solution through a short column of Florisil, and eluting the filtrate into cold hexane which immediately precipitated the product. The compound is unstable in CH_2Cl_2 at room temperature. The ^{13}C NMR spectrum was obtained on a sample prepared from ^{13}CO-enriched $Cr(CO)_5(THF)$; the sample solutions were prepared and stored at −40 °C.

X-ray Analysis of $(Me_3P)(OC)_4OsM(CO)_5$ (M = Cr, W). Crystals of each complex that were suitable for X-ray crystallography were grown from CH_2Cl_2/hexane. The structural analysis of $(Me_3P)(OC)_4OsW(CO)_5$ has been previously outlined;[12] the analysis of the chromium compound is described here in detail. Preliminary precession and Weisenberg photographs (Cu Kα, λ = 1.5418 Å) were used to determine the approximate cell dimensions and space group of the compound. A single crystal of $(Me_3P)(OC)_4OsCr(CO)_5$ was selected, sealed in a thin-walled glass capillary, and mounted on an Enraf-Nonius CAD4F diffractometer. Accurate cell dimensions were determined by least-squares refinement of the diffractometer angles of 25 reflections (with 17.4° < 2θ < 24.0°) chosen from a variety of points in reciprocal space and measured with Mo Kα radiation (λ = 0.71069 Å).

The intensities of a unique data set were measured at 20 °C, as outlined in Table IV. Background measurements were made by extending the scan range by 25% at each side of the scan. Measurement of two standard reflections every 60 min allowed monitoring of crystal decay and stability of the detection chain. (The decay of the crystal was negligible during data collection.) The data were corrected for Lorentz and polarization effects. Because the crystal had an irregular but approximately spherical shape, a spherical absorption correction was applied. The data were also corrected for extinction.

The structure was solved by Patterson methods, and all atoms were located from subsequent difference syntheses. Coordinates of the hydrogen atoms were refined with physically reasonable (fixed B_{iso}) temperature factors. Final cycles of refinement were by full-matrix least-squares analysis with anisotropic temperature factors for all non-hydrogen atoms, with hydrogen atoms included as fixed contributions (B_{iso}(hydrogen) = 7.9 Å^2) which gave final agreement factors of R = 0.023 and R_w = 0.028 (Table IV) for 218

Table V. Positional and Thermal Parameters $(Me_3P)(OC)_4OsCr(CO)_5$ (1) and $(Me_3P)(OC)_4OsW(CO)_5$ (2)

	x	y	z	B_{iso},[a] Å^2
		Compound 1		
Os	0.00289 (3)	0.25345 (2)	0.22718 (3)	3.61 (1)
Cr	0.0489 (1)	0.09108 (7)	0.2223 (1)	3.93 (6)
P	−0.0254 (2)	0.3819 (1)	0.2143 (2)	4.01 (11)
C(1)	0.0732 (10)	−0.0083 (5)	0.2175 (8)	5.1 (5)
C(2)	−0.0349 (10)	0.0839 (5)	0.3783 (9)	5.2 (5)
C(3)	−0.1363 (10)	0.0810 (5)	0.1441 (8)	5.0 (5)
C(4)	0.1366 (9)	0.1006 (5)	0.0693 (9)	5.2 (5)
C(5)	0.2312 (9)	0.1046 (4)	0.2982 (8)	4.7 (5)
C(6)	−0.0530 (9)	0.2362 (5)	0.0554 (9)	4.7 (5)
C(7)	0.0666 (8)	0.2482 (6)	0.3995 (8)	4.9 (4)
C(8)	−0.1923 (10)	0.2298 (5)	0.2779 (8)	5.1 (6)
C(9)	0.2029 (10)	0.2559 (5)	0.1797 (8)	4.9 (4)
C(10)	−0.2072 (9)	0.4129 (5)	0.1751 (8)	5.6 (5)
C(11)	0.0238 (10)	0.4340 (5)	0.3480 (9)	5.8 (5)
C(12)	0.0831 (9)	0.4222 (5)	0.0942 (9)	5.5 (5)
O(1)	0.0915 (8)	−0.0715 (4)	0.2128 (7)	7.0 (5)
O(2)	−0.0864 (8)	0.0764 (5)	0.4734 (7)	8.7 (5)
O(3)	−0.2468 (8)	0.0727 (4)	0.0997 (7)	7.8 (5)
O(4)	0.1958 (8)	0.1051 (5)	−0.0227 (7)	8.0 (6)
O(5)	0.3438 (7)	0.1091 (4)	0.3423 (7)	7.1 (5)
O(6)	−0.0858 (7)	0.2267 (4)	−0.0431 (6)	6.1 (4)
O(7)	0.1002 (7)	0.2447 (5)	0.4990 (6)	7.4 (5)
O(8)	−0.3058 (7)	0.2162 (5)	0.3082 (8)	8.5 (6)
O(9)	0.3219 (7)	0.2569 (4)	0.1511 (7)	7.4 (5)
		Compound 2		
Os	0.96215 (3)	0.32679 (2)	0.18428 (2)	2.96 (1)
W	1.17355 (3)	0.18782 (2)	0.13602 (2)	3.07 (1)
P	0.77827 (21)	0.43005 (11)	0.19518 (13)	3.40 (8)
C(1)	1.3096 (9)	0.0958 (5)	0.1172 (5)	4.4 (4)
C(2)	1.1099 (8)	0.1291 (4)	0.2575 (6)	3.7 (4)
C(3)	0.9983 (9)	0.1316 (5)	0.0320 (6)	4.0 (4)
C(4)	1.2341 (7)	0.2491 (5)	0.0142 (5)	3.7 (4)
C(5)	1.3543 (9)	0.2430 (5)	0.2335 (5)	4.4 (4)
C(6)	0.9206 (9)	0.3339 (5)	0.0311 (6)	4.4 (4)
C(7)	1.0368 (8)	0.3062 (5)	0.3345 (6)	4.1 (4)
C(8)	0.8166 (8)	0.2364 (4)	0.1771 (5)	3.9 (4)
C(9)	1.1390 (9)	0.3992 (5)	0.1888 (6)	4.8 (4)
C(10)	0.5911 (10)	0.4085 (6)	0.1097 (7)	4.8 (5)
C(11)	0.7354 (11)	0.4480 (6)	0.3224 (7)	5.2 (5)
C(12)	0.8263 (13)	0.5286 (6)	0.1501 (8)	6.0 (6)
O(1)	1.3869 (7)	0.0414 (4)	0.1058 (5)	7.1 (4)
O(2)	1.0721 (7)	0.0954 (3)	0.3259 (4)	5.6 (3)
O(3)	0.9047 (7)	0.0978 (4)	−0.0267 (5)	6.8 (4)
O(4)	1.2708 (7)	0.2828 (4)	−0.0527 (4)	6.5 (4)
O(5)	1.4600 (7)	0.2734 (4)	0.2838 (5)	6.4 (4)
O(6)	0.8982 (7)	0.3439 (4)	−0.0558 (4)	6.5 (4)
O(7)	1.0835 (7)	0.2948 (4)	0.4208 (4)	6.5 (4)
O(8)	0.7297 (7)	0.1835 (3)	0.1736 (5)	5.9 (4)
O(9)	1.2433 (8)	0.4401 (4)	0.1904 (6)	8.3 (5)

[a] $B_{iso} = 8\pi^2[(U_{11}{}^2 + U_{22}{}^2 + U_{33}{}^2)/3]^{1/2}$.

variables. The final difference map was featureless apart from a few peaks and troughs close to the Os atom (±0.7 (1) e Å^{-3}). Neutral-atom scattering factors with anomalous dispersion corrections were used.[24] Computer programs[25] were run on a VAX-11/750 computer.

Positional and thermal parameters and bond lengths and selected angles for 1 and 2 are given in Tables V and VI, respectively.

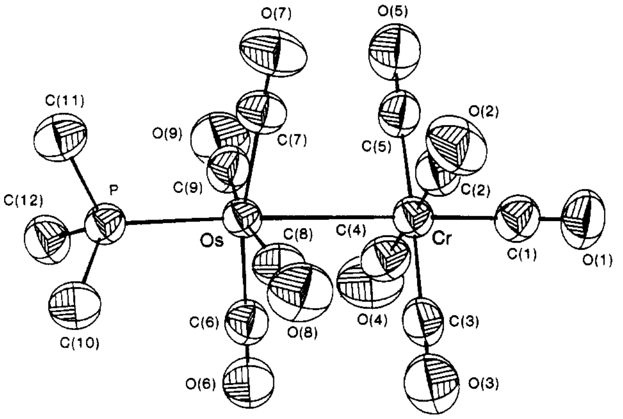

Figure 1. Molecular structure of $(Me_3P)(OC)_4OsCr(CO)_5$ (1).

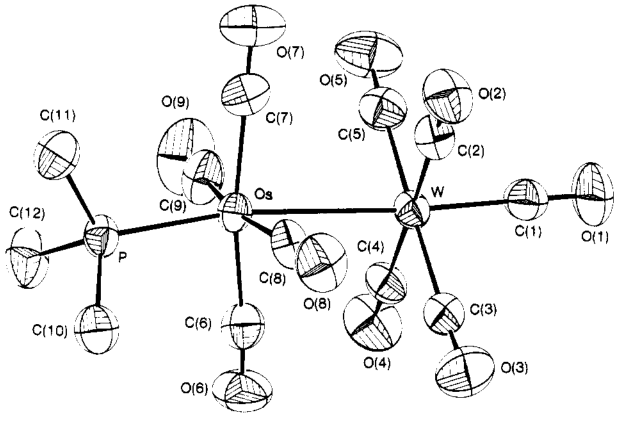

Figure 2. Molecular structure of $(Me_3P)(OC)_4OsW(CO)_5$ (2).

Results and Discussion

The complexes $(R_3P)(OC)_4OsM(CO)_5$ (R = Me, Ph, OMe, etc.; M = Cr, Mo, W) were prepared by the reaction of $Os(CO)_4(PR_3)$ with $M(CO)_5(THF)$ in hexane at or below room temperature (eq 1). The complexes were isolated

$$Os(CO)_4(PR_3) + M(CO)_5(THF) \rightarrow (Me_3P)(OC)_4OsM(CO)_5 \quad (1)$$

as yellow, air-stable, crystalline solids after chromatography. In the preparation of the molybdenum and tungsten derivatives trace amounts of an intensely colored product were also formed. These compounds have subsequently been shown to be the trinuclear clusters $(OC)_5M[Os(CO)_3(PR_3)]_2$ (M = Mo, W).[26] A rational synthesis of these clusters, including the chromium analogues, and a detailed study of their remarkable nonrigid properties will form the subject of a separate paper.[27,28]

The yields of the $(R_3P)(OC)_4OsM(CO)_5$ complexes were 70–80%, 20–30%, and 50–60% for the chromium, molybdenum, and tungsten derivatives, respectively. This variability in yield may be a reflection of the relative stabilities of the $M(CO)_5(THF)$ derivatives that in the solid state appeared to show an order of stability of Cr > W > Mo. On the other hand, it may be a reflection of the Lewis acidity of the $M(CO)_5$ fragment. The yields do not reflect the stability of the complexes in solution: the tungsten derivatives are more stable than the corresponding molybdenum compounds which in turn are more stable than the chromium analogues. (The decomposition is discussed in more detail below.) The $(R_3P)(OC)_4OsM(CO)_5$ complexes are insoluble in hexane but soluble in the more polar CH_2Cl_2. We have found that complexes with dative

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Table VI. Bond Lengths (Å) and Selected Angles (deg) for $(Me_3P)(OC)_4OsCr(CO)_5$ (1) and $(Me_3P)(OC)_4OsW(CO)_5$ (2)

1		2	
Os–Cr	2.9787 (14)	Os–W	3.0756 (5)
Os–P	2.351 (2)	Os–P	2.359 (2)
Cr–C(1)	1.819 (9)	W–C(1)	1.965 (8)
Cr–C(2)	1.881 (10)	W–C(2)	2.021 (7)
Cr–C(3)	1.904 (9)	W–C(3)	2.045 (8)
Cr–C(4)	1.871 (10)	W–C(4)	2.034 (7)
Cr–C(5)	1.876 (9)	W–C(5)	2.028 (8)
Os–C(6)	1.952 (9)	Os–C(6)	1.950 (8)
Os–C(7)	1.954 (9)	Os–C(7)	1.954 (8)
Os–C(8)	1.942 (9)	Os–C(8)	1.941 (7)
Os–C(9)	1.927 (9)	Os–C(9)	1.946 (8)
P–C(10)	1.812 (8)	P–C(10)	1.824 (9)
P–C(11)	1.785 (9)	P–C(11)	1.794 (8)
P–C(12)	1.813 (9)	P–C(12)	1.786 (9)
C(1)–O(1)	1.16 (1)	C(1)–O(1)	1.145 (10)
C(2)–O(2)	1.15 (1)	C(2)–O(2)	1.149 (9)
C(3)–C(3)	1.13 (1)	C(3)–O(3)	1.142 (10)
C(4)–O(4)	1.15 (1)	C(4)–O(4)	1.129 (9)
C(5)–O(5)	1.14 (1)	C(5)–O(5)	1.136 (10)
C(6)–O(6)	1.12 (1)	C(6)–O(6)	1.117 (10)
C(7)–O(7)	1.12 (1)	C(7)–O(7)	1.126 (10)
C(8)–O(8)	1.13 (1)	C(8)–O(8)	1.146 (9)
C(9)–O(9)	1.15 (1)	C(9)–O(9)	1.132 (10)
Cr–Os–P	175.18 (6)	W–Os–P	171.31 (4)
Cr–Os–C(6)	81.9 (2)	W–Os–C(6)	80.2 (2)
Cr–Os–C(7)	85.9 (3)	W–Os–C(8)	89.1 (2)
Cr–Os–C(8)	85.4 (3)	W–Os–C(8)	81.9 (2)
Cr–Os–C(9)	83.1 (3)	W–Os–C(9)	86.1 (2)
Os–Cr–C(1)	178.7 (3)	Os–W–C(1)	175.2 (2)
Os–Cr–C(2)	89.5 (3)	Os–W–C(2)	84.7 (2)
Os–Cr–C(3)	88.6 (3)	Os–W–C(3)	93.1 (2)
Os–Cr–C(4)	89.4 (3)	Os–W–C(4)	93.9 (2)
Os–Cr–C(5)	89.4 (3)	Os–W–C(5)	88.9 (2)
C(1)–Cr–C(2)	90.6 (4)	C(1)–W–C(2)	90.9 (3)
C(1)–Cr–C(3)	90.1 (4)	C(1)–W–C(3)	88.7 (3)
C(1)–Cr–C(4)	90.6 (4)	C(1)–W–C(4)	90.5 (3)
C(1)–Cr–C(5)	91.8 (4)	C(1)–W–C(5)	89.5 (3)
C(2)–Cr–C(3)	90.8 (4)	C(2)–W–C(3)	90.6 (3)
C(2)–Cr–C(4)	178.1 (4)	C(2)–W–C(4)	178.6 (3)
C(2)–Cr–C(5)	89.6 (4)	C(2)–W–C(5)	91.8 (3)
C(3)–Cr–C(4)	90.7 (4)	C(3)–W–C(4)	89.4 (3)
C(3)–Cr–C(5)	178.0 (4)	C(3)–W–C(5)	177.0 (3)
C(4)–Cr–C(5)	88.8 (4)	C(4)–W–C(5)	88.2 (3)
Cr–C(1)–O(1)	178.4 (9)	W–C(1)–O(1)	178.9 (7)
Cr–C(2)–O(2)	177.2 (9)	W–C(2)–O(2)	179.2 (6)
Cr–C(3)–O(3)	177.5 (8)	W–C(3)–O(3)	177.2 (7)
Cr–C(4)–O(4)	177.1 (8)	W–C(4)–O(4)	178.6 (6)
Cr–C(5)–O(5)	176.3 (7)	W–C(5)–O(5)	176.2 (6)
P–Os–C(6)	94.3 (2)	P–Os–C(6)	91.9 (2)
P–Os–C(7)	97.8 (3)	P–Os–C(7)	98.9 (2)
P–Os–C(8)	97.7 (3)	P–Os–C(8)	94.8 (2)
P–Os–C(9)	93.9 (3)	P–Os–C(9)	97.3 (2)
C(6)–Os–C(7)	167.8 (4)	C(6)–Os–C(7)	169.0 (3)
C(6)–Os–C(8)	90.3 (4)	C(6)–Os–C(8)	90.8 (3)
C(6)–Os–C(9)	89.1 (4)	C(6)–Os–C(9)	88.5 (3)
C(7)–Os–C(8)	89.0 (3)	C(7)–Os–C(8)	90.1 (3)
C(7)–Os–C(9)	89.2 (3)	C(7)–Os–C(9)	88.4 (3)
C(8)–Os–C(9)	168.5 (4)	C(8)–Os–C(9)	167.9 (3)
Os–C(6)–O(6)	179.6 (8)	Os–C(6)–O(6)	175.0 (7)
Os–C(7)–O(7)	178.5 (7)	Os–C(7)–O(7)	178.3 (6)
Os–C(8)–O(8)	179.6 (8)	Os–C(8)–O(8)	179.2 (6)
Os–C(9)–O(9)	179.6 (8)	Os–C(9)–O(9)	178.6 (7)
Os–P–C(10)	115.0 (3)	Os–P–C(10)	112.1 (3)
Os–P–C(11)	116.8 (3)	Os–P–C(11)	116.8 (3)
Os–P–C(12)	112.3 (3)	Os–P–C(12)	113.8 (4)
C(10)–P–C(11)	104.3 (4)	C(10)–P–C(11)	104.7 (4)
C(10)–P–C(12)	103.2 (4)	C(10)–P–C(12)	102.7 (5)
C(11)–P–C(12)	103.7 (5)	C(11)–P–C(12)	105.5 (5)

metal–metal bonds are much less soluble in hexane than closely related complexes with covalent metal–metal bonds.[10,14] The insolubility may reflect the polar nature of the dative bond.

Structures of $(Me_3P)(OC)_4OsM(CO)_5$ (M = Cr, W). Views of $(Me_3P)(OC)_4OsCr(CO)_5$ (1) and $(Me_3P)(OC)_4OsW(CO)_5$ (2) are shown in Figures 1 and 2, respectively; bond length and angle data for the molecules are given in Table VI. As can be seen from the figures, the geometry about each molecule is similar; the 18-electron compound $Os(CO)_4(PMe_3)$ acts as a two-electron donor ligand toward the metal atom of the $M(CO)_5$ moiety through an unsupported donor–acceptor metal–metal bond; the PMe_3 group is trans to this bond.

In each molecule both metal atoms have approximate octahedral coordination although the radial carbonyls on $Os(CO)_4(PMe_3)$ lean inward (those on $M(CO)_5$ do not). This is a general observation of complexes of this type.[14] The inward leaning may indicate a small bonding interaction between the filled d orbitals on M and the π^* orbitals of the radial carbonyls on osmium. A similar argument has been used to rationalize the inward leaning of the radial carbonyls on the terminal $Mn(CO)_5$ units in $[Mn_3(CO)_{14}]^-$.[29] These interactions cannot be considered as semibridging interactions by the carbonyls: in **1** the shortest contact of this type is 3.325 (8) Å (Cr···C(6)), whereas in **2** it is 3.349 (7) Å (W···C(6)) (the Os–C(6)–O(6) unit in each molecule is essentially linear). This may be compared to $(\eta^6\text{-}C_6H_6)(OC)Cr(\mu\text{-}CO)_2Rh(CO)(\eta^5\text{-}C_5H_5)$ where two carbonyls on the chromium atom semibridge the rhodium atom.[30] Surprisingly, EHMO calculations on this molecule indicate that there is net donation from the HOMO on the $(\eta^5\text{-}C_5H_5)Rh(CO)$ fragment to the LUMO of the $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ unit that is located on the bridging carbonyls and that there is little direct metal–metal overlap.[5]

The Cr–Os bond length in **1** is 2.9787 (14) Å. The only other Cr–Os vectors reported in literature are 2.996 (2) and 3.024 (2) Å found for $(OC)_5Cr[Os(CO)_3(PMe_3)]_2$ (which is prepared from **1**).[28] We have, however, argued that the bond between the chromium atom and the two osmium atoms in the trinuclear cluster is a single three-center, two-electron metal–metal bond so that direct comparison of the Cr–Os lengths in this compound with that in **1** may not be justified.

The Os–W bond length in **2** is 3.0756 (5) Å which is longer than the lengths for most unbridged Os–W bonds reported in the literature.[31] These lengths, however, refer to cluster compounds in which each metal atom is bonded to at least two others. In $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{12}(\mu_3\text{-}CC_6H_4CH_3)(\mu\text{-}H)_2$ the tungsten atom is linked to the rest of the cluster through a single metal–metal bond of length 3.097 (1) Å,[32] a length not significantly different (in a chemical sense) to that in **2**. For the isomers $(Me_3P)(OC)_4OsRe(CO)_4(Br)$ and $(Br)(Me_3P)(OC)_3OsRe(CO)_5$, with a dative and covalent metal–metal bond, respectively, the dative metal–metal bond is marginally longer than the covalent metal–metal bond.[14]

In both molecules, **1** and **2**, the M–C (M = Cr, W) bond length of the M–CO grouping trans to the osmium atom is significantly shorter than the M–C lengths to the radial

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[29] Bau, R.; Kirtley, S. W.; Sorrell, T. N.; Winarko, S. *J. Am. Chem. Soc.* **1974**, *96*, 988.

[30] Barr, R. D.; Green, M.; Marsden, K.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 507.

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

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

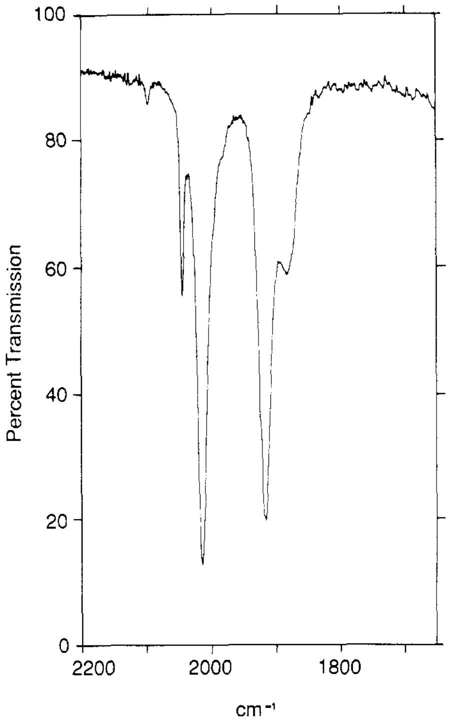

Figure 3. Carbonyl stretching region of the infrared spectrum of **2** in CH_2Cl_2 solution.

carbonyls (Table VI). A similar effect was observed in $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$ where it was argued that this indicated that the 18-electron complex was a weak donor ligand.[13] This is consistent with other evidence concerning the donor strength of the $Os(CO)_4(PR_3)$ ligands presented below. For complexes with an $Os(CO)_4(PMe_3)$ ligand that have been structurally characterized, it is found that the Os–P distance is insensitive to the acceptor half of the molecule.[14]

Spectroscopic Properties and Isomerization of $(R_3P)(OC)_4OsM(CO)_5$ Complexes. The solution infrared spectra of the $(R_3P)(OC)_4OsM(CO)_5$ complexes exhibit only terminal carbonyl stretches (see Figure 3) consistent with the structures found for **1** and **2** in the solid state. A detailed analysis of the spectra was not carried out, but it is probable from a comparison of the infrared spectra of these compounds with those of other $M(CO)_5(L')$ complexes[9,13,33] that the intense band between 1910 and 1930 cm^{-1} can be assigned to the E_1 mode that mainly involves the carbonyls of the $M(CO)_5$ unit. The frequency of this band may therefore be taken as an approximate indication of the donor–acceptor properties of L′. On this basis $Os(CO)_4(PMe_3)$ is a stronger donor than $Os(CO)_4[P(OMe)_3]$ (for L′ = $Os(CO)_4(PMe_3)$, ν(CO) = 1912 cm^{-1}; for L′ = $Os(CO)_4[P(OMe)_3]$, ν(CO) = 1925 cm^{-1}). This is as expected given the donor properties of PMe_3 and $P(OMe)_3$.[34] Similarly, $Os(CO)_4(PMe_3)$ may be ranked as a slightly better donor than THF (for $W(CO)_5(THF)$ we observe ν(CO) at 1929.5 cm^{-1} in THF, in agreement with the literature value[9]). Use of these arguments leads to the conclusion that $Os(CO)_4(PMe_3)$ has stronger donor–acceptor character than PPh_3 since the appropriate band for $W(CO)_5(PPh_3)$ occurs at 1941 cm^{-1} in hexane.[35] This is surprising since PPh_3 displaces $Os(CO)_4(PMe_3)$ from **2**.

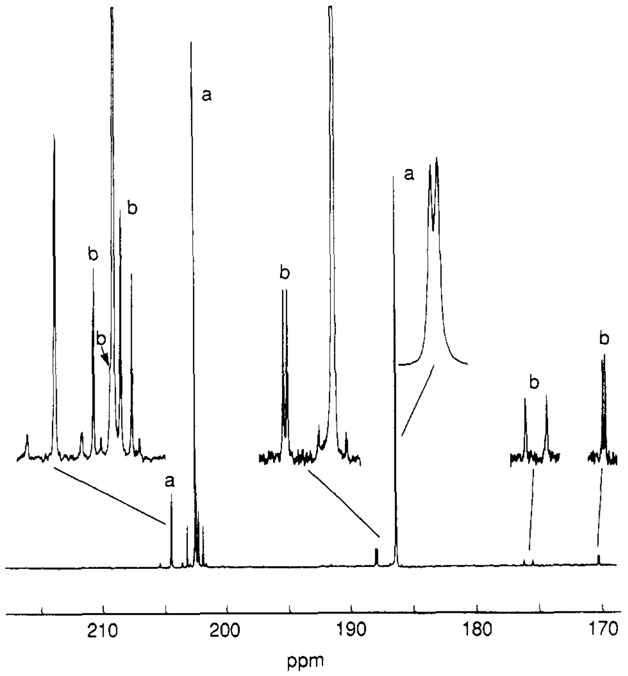

Figure 4. Carbonyl region of the ^{13}C NMR spectrum of **2** (^{13}CO-enriched sample; CH_2Cl_2/CD_2Cl_2 solution). See the text for an explanation of the assignment of signals.

This is discussed in more detail below.

The major signals in the carbonyl region of the ^{13}C NMR spectra of the $(R_3P)(OC)_4OsM(CO)_5$ complexes are also consistent with the solid-state structures. For example, the ^{13}C NMR spectrum of ^{13}CO-enriched **2** (Figure 4) exhibits a doublet (J_{P-C} = 3.0 Hz) at δ 186.7 of intensity 4 assigned to the radial carbonyls on osmium. This signal has weak satellites attributed to coupling to ^{187}Os (spin = $^1/_2$, 1.6% natural abundance); the value of the coupling (~92 Hz) is in agreement with other ^{187}Os–C couplings recently reported in the literature.[36] There are also two signals in the intensity ratio of 1:4 at δ 204.6 (J_{P-C} = 2.2 Hz) and 202.8 assigned to the axial and radial carbonyls of the $W(CO)_5$ unit, respectively. Each signal exhibits the expected coupling to ^{183}W (spin = $^1/_2$, 14.3% natural abundance).

Bodner and co-workers have argued that the chemical shift difference ($\Delta\delta$) between the chemical shift due to the radial carbonyls in $Cr(CO)_5(L')$ complexes compared to that due to $Cr(CO)_6$ can be taken as a measure of the donor-acceptor properties of L′.[37] For example, the $\Delta\delta$ values for the derivatives with L′ = PCl_3, PPh_3, and PBu_3 are 0.18, 5.25, and 6.08, respectively. A $\Delta\delta$ value 10.8 is obtained for **1** (we observe the ^{13}C NMR resonance of $Cr(CO)_6$ in CD_2Cl_2 at 212.5 ppm) which leads to the conclusion that $Os(CO)_4(PMe_3)$ has a stronger donor–acceptor ratio than common phosphorus-donor ligands. This is consistent with CO-stretching frequency data described above. The use of the Bodner method to compare the donor–acceptor properties of $Os(CO)_4(PR_3)$ ligands with those of more conventional ligands may not be justified since there may be factors that affect the chemical shift in the $(R_3P)(OC)_4OsCr(CO)_5$ derivatives that are not present in simple $Cr(CO)_5(L')$ compounds. The $\Delta\delta$ values for $(L)(OC)_4OsCr(CO)_5$ complexes are 10.8 for L = PMe_3, 10.0 for L = PPh_3, and 7.8 for L = CO (see below) which

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[33] Adams, D. M. *Metal-Ligand and Related Vibrations*, St. Martin's: New York, 1968; p 143.

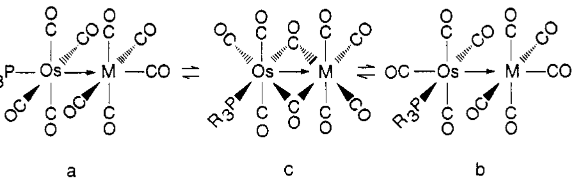
[34] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

[35] Reported ν(CO) vibrations for $W(CO)_5(PPh_3)$ are 2075 (m), 1980 (sh), and 1938 (vs) cm^{-1} in CCl_4: Magee, T. A.; Matthews, C. N.; Wang, T. S.; Wotiz, J. H. *J. Am. Chem. Soc.* **1961**, *83*, 3200.

[36] Gallop, M. A.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1987**, 1831.

[37] Bodner, G. M.; May, M. P.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951.

Scheme I



is consistent with the anticipated donor strength of the $Os(CO)_4(L)$ ligand given the accepted donor strength of L of $PMe_3 > PPh_3 > CO$.[34]

Bucher and Schenk[38] have proposed that the $J(^{183}W-^{13}C)$ coupling constant to the carbonyl trans to L′ in $W(CO)_5(L')$ compounds is a measure of the trans influence of L′. The range in the 23 coupling constants they measured was 102.5 Hz for L′ = CPh_2 (strongest trans influence) to 175.8 Hz for L′ = I^- (weakest trans influence).[38] Of the tungsten compounds studied here, only for **2** and $[MeC(CH_2O)_3P](OC)_4OsW(CO)_5$ were $J(^{183}W-^{13}C_{ax})$ couplings clearly observed (e.g. Figure 4). Their respective values of 179.1 and 178 Hz rank the $Os(CO)_4(L)$ (L = PMe_3, $P(OCH_2)_3CMe$) ligands as having the weakest trans influence of any ligand so far studied by this method.

The ^{13}C (and ^1H and ^{31}P) NMR spectra of most of the $(R_3P)(OC)_4OsM(CO)_5$ derivatives contained weak signals consistent with the presence of the isomer with the PR_3 ligand cis to the metal–metal bond (e.g., **b**, Scheme I). This was investigated in detail for **2**. The ^{13}C NMR spectrum shown in Figure 4 represents an overnight accumulation of transients carried out on a sample of **2** that had been enriched to ~30% in ^{13}CO. As can be seen, there are three signals in the Os–CO region in the intensity ratio of 2:1:1 at δ 188.3, 176.0, and 170.3 consistent with the presence of ~20% of **2b**. Two of the signals of intensity 2 and 1 show small (cis) phosphorus couplings (13.2 and 8.9 Hz, respectively), whereas the other signal shows a large (trans) coupling (71.1 Hz) as expected for structure **2b**. The resonance of the carbonyl trans to the dative metal–metal bond occurs at an unusually high field and appears to be characteristic of this grouping.[10,11] This shift is contrary to that expected from simple bonding arguments: donation of electron density from osmium to tungsten should result in deshielding at the carbon atom trans to the dative metal–metal bond, and consequently a shift to low field of the ^{13}C resonance associated with that carbon atom. Changes in chemical shifts opposite to that expected from simple theory is a common problem in the study of ^{13}C chemical shifts of metal carbonyl derivatives. These anomalous changes have usually been rationalized in terms of changes to the ΔE parameter in the paramagnetic contribution to the chemical shift.[37-39]

The two isomers of **2** were shown to be in rapid equilibrium by a spin saturation transfer experiment (Figure 5). (NMR line-broadening studies were not attempted due to the instability of the compound in solution at higher temperatures.) Saturation of the signal at 2.03 ppm assigned to **2a** in the ^1H NMR of **2** in CD_2Cl_2 caused transfer to the signal at 1.93 ppm (assigned to **2b**). A similar experiment was carried out with $Os(CO)_4(PMe_3)$ added to the solution. There was no transfer to the doublet due to the added component, nor was the transfer to the signal due to **2b** affected (Figure 5). This result indicates that dissociation of **2** into $Os(CO)_4(PMe_3)$ and $W(CO)_5$ as separate species into the bulk solvent was not involved in the isomerization (separation into these fragments followed by rearrangement within a solvent cage cannot, however, be ruled out). There was also no exchange with ^{13}CO when **2** was stirred in CH_2Cl_2 under 1 atm of this reagent, nor did **2** immediately react, in solution at room temperature, with PMe_2Ph. Also relevant, is that when **2** was prepared from ^{13}CO-enriched $Os(CO)_4(PMe_3)$, it was found that the ^{13}CO-labeled carbonyls had become scrambled over both metal atoms in the product. Similar behavior was observed when the $(R_3P)(OC)_4OsM(CO)_5$ derivatives were prepared from ^{13}CO-enriched $M(CO)_5(THF)$.

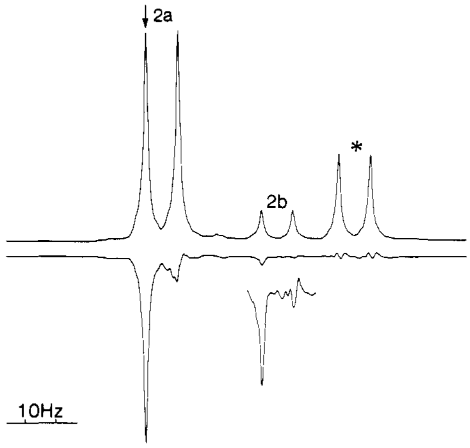


Figure 5. Spin saturation transfer experiment on **2**. Irradiation of the lowest field ^1H NMR resonance due to **2a** resulted in transfer to the corresponding signal of the second isomer **2b**. No transfer occurred to the signal due to added $Os(CO)_4(PMe_3)$ (*).

A mechanism that accounts for all these observations is the well-known[40] terminal–bridge carbonyl exchange that also results in isomerization; this is shown in Scheme I. We have proposed a similar mechanism for $(\eta^5-C_5Me_5)(OC)_2IrW(CO)_5$ (**3**) that also has an unbridged dative metal–metal bond.[13] This molecule is rigid in solution at −97 °C, but carbonyl exchange becomes rapid at room temperature such that an averaged signal is observed for the carbonyls in the ^{13}C NMR spectrum. The low barrier to carbonyl exchange in **2** and **3**, and presumably other $(R_3P)(OC)_4OsM(CO)_5$ derivatives, may be contrasted to the behavior of $(OC)_5MnRe(^{13}CO)_5$ (**4**) where in solution at 75 °C scrambling of carbonyls between the two metals took several hours to detect by infrared spectroscopy. (An intramolecular, pairwise carbonyl-exchange mechanism was also proposed for the rearrangement in **4**.[41]) The low activation barrier to carbonyl exchange in the complexes with dative metal–metal bonds is probably due to the bridged intermediate (i.e., **c**, Scheme I) lying close in energy to the unbridged form. There are several compounds in the literature that are similar to the present compounds, but the isomer with bridging or semibridging carbonyls is the observed form in the ground state.[5,30,42]

The isomer ratios for the $(R_3P)(OC)_4OsM(CO)_5$ complexes as determined by ^1H or ^{31}P NMR spectroscopy are given in Table II. (The ratios were found to be somewhat solvent dependent.) For the phosphine complexes the isomer ratio decreased as the size of the phosphine in-

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(38) Buchner, W.; Schenk, W. A. *Inorg. Chem.* **1984**, *23*, 132.

(39) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic: New York, 1981; p 6.

(40) (a) Adams, R. D.; Cotton, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 6589. (b) Cotton, F. A.; Hunter, D. L. *Inorg. Chim. Acta* **1974**, *11*, L9. (c) Band, E.; Muetterties, E. L. *Chem. Rev.* **1978**, *78*, 639. (d) Mann, B. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 3, p 89.

(41) Schmidt, S. P.; Basolo, F.; Jensen, C. M.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 1894.

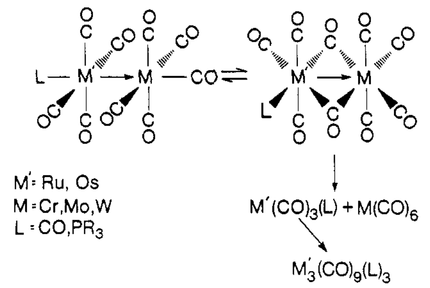
(42) For example, $(OC)_3Fe(\mu-CO)_2Rh(CO)(\eta^5-C_5Me_5)$: Aldridge, M. L.; Green, M.; Howard, J. A. K.; Pain, G. N.; Porter, S. J.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 1333.

creased so that for the (methyldiphenylphosphine)- and (triphenylphosphine)tungsten derivatives less than 2% existed as the radial isomer. A $^{31}P\{^1H\}$ NMR spectrum of $(Ph_3P)(OC)_4OsW(CO)_5$ with overnight accumulation of transients gave essentially one resonance, although a weak signal of ~2% the intensity of the major signal was observed at ~10 ppm to higher field, the region expected for the resonance of the minor isomer. The observed trend for the isomer ratios of the phosphine-substituted complexes can be explained by steric arguments. In these dinuclear compounds, a phosphine ligand in a radial position on the osmium atom makes close contact with two of the radial carbonyls on the group 6 atom. For this reason it is expected that the bulky phosphine ligand will preferentially occupy the axial site rather than carbon monoxide. As the size[34] of the phosphine ligand is increased by successive replacement of methyl groups with phenyl substituents, there will be a greater tendency to occupy the axial site, as observed.

Because the molybdenum and tungsten atoms have similar covalent radii, the complexes of the metals are expected to exhibit similar isomer ratios which was found for the cases studied. The covalent radius of the chromium atom is smaller than that of either molybdenum or tungsten (compare the metal–metal bond lengths in **1** and **2**). There would therefore be more repulsive interactions between the substituents on the phosphine ligand and the radial carbonyls on chromium in the chromium derivatives and consequently less tendency for the phosphine to occupy a site cis to the metal–metal bond. It is thus not surprising that for these derivatives the minor isomer was only clearly observable for $(L)(OC)_4OsCr(CO)_5$ when L = $P(OCH_2)_3CMe$ or PMe_3. Even then, the ratio of major to minor isomer was much larger for the chromium derivatives than for the corresponding tungsten compounds (Table II).

The $^{31}P\{^1H\}$ NMR spectrum of $[(MeO)_3P](OC)_4OsCr(CO)_5$ (**5**) in CH_2Cl_2/CD_2Cl_2 indicated only one isomer was present. The ^1H NMR spectrum of this complex did, however, have a weak doublet which may have indicated the presence of ~2% of the minor isomer. Because solutions of the chromium compounds slowly decomposed, it was difficult to distinguish weak signals in the NMR spectra arising from decomposition products from those that may have been due to the minor isomer. Certainly the minor isomer of **5** was present to a lesser extent than in **1**. This was also found for the corresponding tungsten compounds where the isomer ratio was found to be 13.5:1 for the $P(OMe)_3$ derivative and 3.3:1 for the PMe_3 analogue. The cone angle[34] of $P(OMe)_3$ (107°) is less than that of PMe_3 (118°). The cone angle of the phosphite is, however, calculated with the OMe arms folded back whereas the common conformation for this ligand has two of the OMe arms opened out.[43] In this conformation the OMe arms may well have greater steric interactions with the radial carbonyls on the group 6 atom than the methyl groups of a PMe_3 ligand in the same position. (This is indicated from models based on structures of **2** and $[(MeO)_3P](OC)_4OsMo(CO)_5$.[26]) This could therefore lead to smaller amounts of the isomer **b** for the $P(OMe)_3$ derivative compared to the PMe_3 analogue, as observed. If electronic factors were important in determining the **a**:**b** isomer ratio, it would be expected the $P(OMe)_3$ and $P(OCH_2)_3CMe$ derivatives would have similar ratios. However, the greatest amount of the minor isomer was found for $[MeC(CH_2O)_3P](OC)_4OsW(CO)_5$ (**6**), that is, with the phosphorus ligand with the smallest cone angle (the cone angle of $P(OCH_2)_3CMe$ is 101°).[34] That the isomer ratios for **2** and **6** are similar suggests that the ratio is not sensitive to changes in the electronic properties[34] of the phosphorus ligand.

Scheme II



Decomposition of Complexes. The $(R_3P)(OC)_4OsM(CO)_5$ complexes decomposed in solution at room temperature to yield $Os_3(CO)_9(PR_3)_3$[44] and $M(CO)_6$, as identified by infrared spectroscopy. For example, when a CH_2Cl_2 solution of **1** was exposed to air, a band in the infrared spectrum attributed to $Cr(CO)_6$ (at 1981 cm^{-1}) appeared that after about 20 min had an intensity equal to the most intense CO stretch of the starting material. By comparison, when a solution of **2** was exposed to air, the infrared absorption attributed to $W(CO)_6$ (at 1976 cm^{-1}) had not reached the same intensity even after 3 h. Degassed solutions stirred under vacuum were much more stable: a sample of **1** showed only slight decomposition, and a sample of **2** no decomposition, after 24 h under these conditions. Although not studied in detail, the molybdenum complexes appeared slightly more stable than the chromium analogues.

A mechanism that accounts for the observed decomposition products and that is also consistent with the mechanism proposed for the isomerization is shown in Scheme II.

The reaction of $Ru(CO)_4(PMe_3)$ with $M(CO)_5(THF)$ (M = Cr, W) visibly yielded an intermediate product at low temperature, but it rapidly decomposed at ambient temperature to give $M(CO)_6$ and $Ru_3(CO)_9(PMe_3)_3$.[45] There was no evidence for adduct formation in the reactions of $Fe(CO)_5$, $Fe(CO)_4(PMe_3)$, and $Fe(CO)_3(PMe_3)_2$ with $W(CO)_5(THF)$. Darensbourg and co-workers have reported the preparation, from $[Fe(CO)_4(H)]^-$ and $M(CO)_5(THF)$ (M = Cr, W), of $[(H)(OC)_4FeW(CO)_5]^-$ which, as mentioned in the Introduction, is believed to contain an unbridged FeW dative bond.[9] This appears to indicate that complexes with dative metal–metal bonds may be formed by first-row transition-metal compounds if the metal center is sufficiently basic as in $[Fe(CO)_4(H)]^-$. It is, however, pointed out that the CO stretching frequencies of $Fe(CO)_4(PMe_3)$ and $Os(CO)_4(PMe_3)$ are virtually identical[21] so that based on this criterion the electron density at each metal in these two compounds is similar.

Slow reaction of **2** with PPh_3 in solution at room temperature gave $Os(CO)_4(PMe_3)$ and $W(CO)_5(PPh_3)$[35] as identified by infrared spectroscopy (eq 2). This, of course,

$$(Me_3P)(OC)_4OsW(CO)_5 + PPh_3 \rightarrow W(CO)_5(PPh_3) + Os(CO)_4(PMe_3) \quad (2)$$

indicates $Os(CO)_4(PMe_3)$ is a weaker Lewis base toward

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[43] Cobbledick, R. E.; Einstein, F. W. B.; Pomeroy, R. K.; Spetch, E. R. *J. Organomet. Chem.* **1980**, *195*, 77.

[44] (a) Tripathi, S. C.; Srivastava, S. C.; Mani, R. P.; Shrimal, A. K. *Inorg. Chim. Acta* **1975**, *15*, 249. (b) Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1. (c) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1973**, 2727.

[45] Bruce, M. I.; Kehoe, D. C.; Matisons, J. G.; Nicholson, B. K.; Rieger, P. H.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* **1982**, 442.

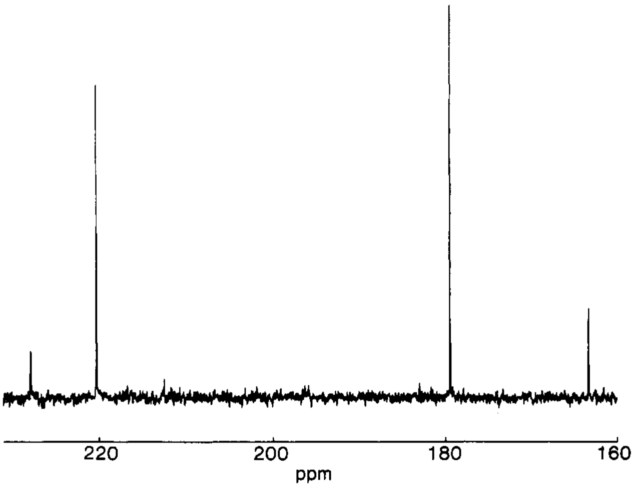

Figure 6. ^{13}C NMR spectrum at -40 °C of $(OC)_5OsCr(CO)_5$ (^{13}CO-enriched sample; CH_2Cl_2/CD_2Cl_2 solution).

$W(CO)_5$ than PPh_3. (Similar chemistry is exhibited by $[(H)(OC)_4FeW(CO)_5]^-$.[9]) As discussed above, infrared and ^{13}C NMR data indicate $Os(CO)_4(PMe_3)$ has stronger donor-acceptor properties than PPh_3. This may mean that $Os(CO)_4(PMe_3)$ acts as a π-donor toward the group 6 metal atom (i.e., the filled Os d orbitals interact with the corresponding orbitals on M). The nonsynergistic nature of this interaction could weaken the Os-M σ-bond. Steric interactions between the radial substituents on the metal atoms could also weaken the Os-M dative bond. In other words, the metal-ligand bond strength need not be related to the donor-acceptor properties of the ligand.

$(OC)_5OsCr(CO)_5$. Of special interest in this study was the isolation of the homoleptic complex $(OC)_5OsCr(CO)_5$ (7) from the reaction of $Os(CO)_5$ and $Cr(CO)_5(THF)$ in hexane. As the solid, 7 is a moderately air-stable, yellow crystalline solid. In CH_2Cl_2 solution, however, it decomposes to $Os_3(CO)_{12}$ and $Cr(CO)_6$ with a half life of only about 2 min. Unfortunately, crystals of 7 suitable for an X-ray diffraction study could not be obtained. The spectroscopic properties of the complex, however, leave no doubt as to its identity. In particular, the ^{13}C NMR spectrum of 7 (^{13}CO-enriched) in CD_2Cl_2 at -40 °C consists (Figure 6) of four resonances in the carbonyl region in a 1:4:4:1 intensity pattern in accord with a rigid structure with an unbridged, donor-acceptor metal-metal bond. The IR spectrum of a freshly prepared sample of 7 in CH_2Cl_2 contained only terminal carbonyl stretches consistent with the unbridged structure. Attempts to prepare the tungsten (or molybdenum) analogue of 7 have so far been unsuccessful. From a consideration of the stabilities of the $(Me_3P)(OC)_4OsM(CO)_5$ complexes, it would be expected that $(OC)_5OsM(CO)_5$ (M = Mo, W) should be more stable than 7 and that the failure to prepare these compounds is due to kinetic rather than thermodynamic reasons.

Conclusions

This is the first systematic study of the ability of neutral 18-electron compounds to act as ligands. For the acceptor half of the $(R_3P)(OC)_4OsM(CO)_5$ molecules, the order of stability appeared to be W > Mo > Cr even though the yields of the complexes were Cr > W > Mo. For the donor half, stable complexes could only be isolated when the third-row transition-metal compound $Os(CO)_4(PR_3)$ acted as the donor. Complexes of $Ru(CO)_4(PMe_3)$ apparently formed at low temperature but decomposed at ambient temperature. In other studies, we have prepared complexes in which $Ru(CO)_4(PMe_3)$ acts as a ligand but they are much less stable than their osmium counterparts.[10] In no case, in this or in other investigations, have we been able to isolate adducts in which $Fe(CO)_4(PMe_3)$ acts as a ligand. It therefore appears that the strength of dative metal-metal bonds increases on going to a metal lower in the periodic table in much the same way as covalent metal-metal bonds. A systematic investigation of the effect of the ancillary ligands on the formation of dative metal-metal bonds has not been carried out although, as expected, $Os(CO)_4(PR_3)$ is a much better donor ligand than $Os(CO)_5$.

Further investigations on the ability of neutral 18-electron compounds to act as ligands are in progress. For example, preliminary results indicate the surprising result that complexes with $Os(CO)_3(PMe_3)_2$ acting as a ligand are less stable than the $Os(CO)_4(PMe_3)$ analogues.[27] It is also hoped to carry out detailed kinetic studies on $(R_3P)(OC)_4OsM(CO)_5$ complexes in order to obtain a more quantitative estimate of the strengths of the metal-metal bonds in these compounds.

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Supplementary Material Available: Tables of hydrogen atom coordinates and anisotropic thermal parameters for 1 and 2 (4 pages); listings of observed and calculated structure factors for 1 and 2 (30 pages). Ordering information is given on any masthead page.