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Compounds with Unbridged Dative Metal−Metal Bonds of Formula $(R_3P)_2(OC)_3OsW(CO)_5$ and Related Complexes

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Complexes of formula $(R_3P)_2(OC)_3OsW(CO)_5$ and similar complexes have been prepared from $W(CO)_5(THF)$ and $Os(CO)_3(PR_3)_2$ in CH_2Cl_2/hexane at room temperature. The analogous Cr complexes could not be synthesized except for $[MeC(CH_2O)_3P]_2(OC)_3OsCr(CO)_5$ and $(Me_2PCH_2CH_2PMe_2)(OC)_3OsCr(CO)_5$, that is, with sterically undemanding P substituents. Tungsten compounds with P ligands with cone angles greater than ∼125° could also not be prepared. The crystal structures of $(Me_2PCH_2CH_2PMe_2)(OC)_3OsM(CO)_5$ (M = Cr, W), $[MeC(CH_2O)_3P]_2(OC)_3OsW(CO)_5$ (**2**), $(OC)_3(Me_3P)_2OsW(CO)_5$ (**3**), $[MeC(CH_2O)_3P](OC)_3(Me_3P)OsW(CO)_5$ (**4**), and $[(MeO)_3P](OC)_3(Me_3P)OsW(CO)_5$ (**5**) reveal that all have unbridged OsM bonds that are considerably longer than the corresponding OsM bond in $(Me_3P)(OC)_4OsM(CO)_5$. The P ligands have an axial, radial arrangement except in **3**, where the PMe_3 ligands have a trans, diradial orientation. In **4** and **5** the phosphite ligands are in the site trans to the OsW bond even though they have smaller cone angles than the PMe_3 ligand. Solution NMR data indicates that for **2** and **3** both the *ax,rad* and *dirad* isomers are present; for **4** both *ax,rad* forms are present, whereas for **5** only the solid state form is found. There was no evidence in solution for the *dirad* forms of **4** and **5**. (The ^{13}C NMR spectra of the compounds also indicated that $^2J_{PC}$ becomes zero for PMC angles of about 103°.) The unusual site preference of the P ligands in these molecules is interpreted in terms of steric effects and an electronic preference for a good π-acceptor ligand to adopt the position trans to the dative metal−metal bond. Complexes **2**, **3**, and **5** react with PPh_3 in CH_2Cl_2 at room temperature over 2 days to give $W(CO)_5(PPh_3)$ and $Os(CO)_3(PR_3)(PR'_3)$ in the order **3** > **5** > **2**.

Introduction

Over the past 15 years we have reported several investigations on complexes with unbridged donor−acceptor bonds between two transition metals.[1−9] In one study we reported the synthesis of complexes of the type $(R_3P)(OC)_4OsM(CO)_5$ (M = Cr, Mo, W; PR_3 = phosphine or phosphite) which were found to exist as two isomers in solution.[2] The predominate form has the structure found in the solid state with the P-ligand trans to the OsM bond; the minor isomer has this ligand cis to the metal−metal bond.

The bis-substituted compounds $Os(CO)_3(PR_3)_2$ (e.g., R = Me) might be expected to act as stronger donor ligands than the $Os(CO)_4(PR_3)$ analogues because there should be an increase in electron density at the Os atom when a carbonyl ligand is replaced with a better σ-donor PR_3 ligand. On the other hand, steric interactions between the PR_3 ligand that is necessarily cis to the metal−metal bond and the radial carbonyls on the $M(CO)_5$ acceptor fragment would disfavor metal−metal bond formation. An initial investigation of $(OC)_3(Me_3P)_2OsW(CO)_5$ showed that in the solid state both PMe_3 ligands are cis to the OsW bond and in solution this isomer was somewhat more preferred to the form with one PMe_3 group trans to the OsW bond. This unexpected result suggested that more subtle factors were important in determining the isomer ratios in $(R_3P)_2(OC)_3OsW(CO)_5$ complexes that warranted further study. Herein we report the details of this study, the results of which may be useful in the rationalization of the unusual distribution of isomers observed for $M'_2(CO)_{10-x}(PR_3)_x$ (M′ = Mn, Re; x = 2, 3) complexes.

Experimental Section

Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere with the use of standard Schlenk techniques. Hydrocarbon solvents were refluxed over potassium and distilled and stored over molecular sieves before use. Dichloromethane was dried in a similar manner except that P_2O_5 was employed as the

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drying agent. Pentacarbonylosmium, $Os(CO)_5$, and $Os(CO)_4(PMe_3)$ were prepared by literature procedures.[10,11] The precursory complexes $M(CO)_5(THF)$ (M = Cr, W) were prepared by a literature method;[2] representative preparations of the $Os(CO)_3(PR_3)_2$ compounds are described below. NMR spectra were recorded on a Bruker AMX400 spectrometer at the appropriate operating frequencies for ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra. Samples of the dinuclear complexes used for $^{13}C\{^1H\}$ NMR spectra were enriched to ~30% ^{13}CO from more highly ^{13}CO-enriched $M(CO)_5(THF)$;[2] it was found that the ^{13}CO was equally distributed over all CO sites in the products. Spectra that required long accumulation times often exhibited weak peaks due to the decomposition products $W(CO)_6$ and $Os(CO)_3(PR_3)_2$.

Preparation of $Os(CO)_3(PMe_2Ph)_2$. Method A. To a round-bottom flask (~100 mL; fitted with a Teflon valve) was added $Os(CO)_5$ (~225 mg; ~0.68 mmol) in hexane (50 mL) and PMe_2Ph (220 mg; 1.59 mmol). The flask was cooled to −196 °C, the solution degassed with three freeze−pump−thaw cycles, and the flask sealed under vacuum. The vessel and contents were heated with stirring at 90 °C for 28 h (after 5 h the vessel was evacuated and the solution degassed as previously described). After this period the evacuation and degassing of the solution was repeated, and the vessel and contents were heated at 140 °C for a further 12 h to give a yellow solution. The flask was cooled and the solution transferred to a Schlenk flask and the solvent removed on the vacuum line; most of the excess PMe_2Ph was removed by vacuum distillation to a probe cooled to −78 °C. The remaining waxy solid was recrystallized from hexane at −20 °C to yield the desired product, $Os(CO)_3(PMe_2Ph)_2$ (170 mg; 46%), as an orange oil.

Preparation of $Os(CO)_3(PMe_3)[P(OCH_2)_3CMe]$. Method B. A round-bottom flask (as previously described) was charged with $Os(CO)_4(PMe_3)$ (205 mg; 0.54 mmol), $P(OCH_2)_3CMe$ (80 mg, 0.55 mmol), and hexane (45 mL). The flask was evacuated and the solution degassed in the normal manner. The flask and contents were heated at 140 °C for 28 h (the solution was stirred during this time). The flask was evacuated and the solution degassed once during the 28 h period. On cooling the flask to room temperature, a pale yellow precipitate formed; an IR spectrum of the reaction solution at this stage showed only bands due to the product. The mother solution was removed from the solid which was recrystallized from CH_2Cl_2/hexane to afford $Os(CO)_3(PMe_3)[P(OCH_2)_3CMe]$ (184 mg); a further 48 mg of product was obtained when the mother solution was concentrated and stored at −20 °C for a total yield of 86%.

Preparation of $Os(CO)_3(Me_2PCH_2CH_2PMe_2)$. Method C. A rocking autoclave (480 mL; Parr Instrument Co.) was charged under a nitrogen flush with $Os_3(CO)_{12}$ (0.52 g; 0.57 mmol), $Me_2PCH_2CH_2PMe_2$ (0.53 g; 3.5 mmol), and hexane (120 mL); the autoclave was quickly sealed, flushed three times with CO, and then pressurized with CO (~90 atm). The autoclave was then rocked at 290−300 °C for 24 h. The autoclave was cooled to room temperature and the pale yellow solution transferred to a Schlenk flask (a small quantity of an as yet unidentified red solid remained in the autoclave). The desired product of $Os(CO)_3(Me_2PCH_2CH_2PMe_2)$ (0.35; 61%) was obtained upon storing the solution at −35 °C. Repeating the preparation but with a CO pressure of 200 atm resulted in a lower yield (21%) of the product. Similarly, use of method A to prepare $Os(CO)_3(Me_2PCH_2CH_2PMe_2)$ resulted in a lower yield (32%).

The phosphite derivative $Os(CO)_3[P(OCH_2)_3CMe]_2$ is a white crystalline solid that showed no apparent decomposition after several days in air; on the other hand, $Os(CO)_3(Me_2PCH_2CH_2PMe_2)$ is a pale yellow solid that is extremely sensitive to air. The following derivatives were fully characterized. The other derivatives were characterized by IR and mass spectroscopy; all gave a parent ion by EIMS except $Os(CO)_3[P(OCH_2)_2CMe]_2$. $Os(CO)_3(PMe_3)_2$: IR (hexanes) ν(CO) 1866 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.80 (t, apparent J_{PH} = 4.1 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −48.75; $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 1:4) δ 200.9 (t, apparent J_{PC} = 12.2 Hz), 24.9 (t, apparent J_{PC} = 19.4 Hz); triplets observed at δ 180.7 and 14.8 are attributed to $Os(CO)_2(PMe_3)_2(Cl)_2$, which results from slow reaction of $Os(CO)_3(PMe_3)_2$ with the solvent;[12] MS (EI) *m/z* 428 (M^+). Calcd for $C_9H_{18}O_3OsP_2$: C, 25.35; H, 4.25. Found: C, 25.46; H, 4.26. $Os(CO)_3[P(OCH_2)_2CMe]_2$: IR ($CH_2Cl_2$) ν(CO) 2012 (vw), 1930 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 0.78 (s); 4.29 (t, apparent J_{PH} = 2.4 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 96.7; $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 1:4) δ 192.7 (t, J_{PC} = 17.5 Hz), 77.9 (t, apparent J_{PC} = 2.3 Hz), 34.1 (t, apparent J_{PC} = 17.9 Hz), 17.4 (d, J_{PC} = 1.5 Hz). Calcd for $C_{13}H_{18}O_9OsP_2{\cdot}CH_2Cl_2$: C, 25.65; H, 3.08. Found: C, 25.73; H, 3.03 (the presence of CH_2Cl_2 was confirmed by ^1H NMR spectroscopy). $Os(CO)_3(PMe_3)[P(OCH_2)_2CMe]$: IR ($CH_2Cl_2$) ν(CO) 2018 (vw), 1988 (vw), 1902 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 0.77 (s); 1.81 (dd, $^2J_{PH}$ = 10.2 Hz, $^4J_{PH}$ = 2.9 Hz), 4.26 (d, J_{PC} = 4.9 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −49.4 (d, $^2J_{PP}$ = 267 Hz), 97.2 (d); $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 1:4) δ 196.7 (dd, J_{PC} = 15.6, 13.0 Hz), 77.7 (d, J_{PC} = 6.9 Hz), 33.9 (d, J_{PC} = 35.5 Hz), 24.2 (dd, J_{PC} = 37.7, 3.4 Hz), 17.5 (s); MS (EI) *m/z* 500 (M^+). Calcd for $C_{11}H_{18}O_6OsP_2$: C, 26.51; H, 3.64. Found: C, 26.60; H, 3.58. Method of synthesis and IR data for all the bis-substituted mononuclear compounds are deposited as Supporting Information.

Preparation of $(Me_2PCH_2CH_2PMe_2)(OC)_3OsCr(CO)_5$ (1Cr). A quartz Carius tube was charged with $Cr(CO)_6$ (150 mg, 0.68 mmol) and THF (25 mL) and cooled to −196 °C, and the solution was degassed with three freeze−pump−thaw cycles. The solution, with stirring, was then irradiated with UV light (200 W Hanovia lamp) for approximately 2 h. The volume of the solution of $Cr(CO)_5(THF)$ was reduced to about 1 mL and cooled to −196 °C. A solution of $Os(CO)_3(Me_2PCH_2CH_2PMe_2)$ (90 mg, 0.21 mmol) in CH_2Cl_2 (4.0 mL) and hexane (15 mL) was added to the frozen mixture. The tube and contents were allowed to warm to room temperature, and the solution was stirred for 2 h. The solvent was removed on the vacuum line and the remaining solid stirred with hexane (40 mL) to remove most of the unreacted $Cr(CO)_6$. The hexane was decanted from the solid that was dissolved in a minimum of CH_2Cl_2 and chromatographed on silica gel (12 × 1.0 cm) with CH_2Cl_2 as the eluant. The yellow fraction was collected and concentrated in volume; hexane was added until a precipitate just began to form, whereupon the solution was stored at −15 °C for 3 days. The yellow crystals of **1Cr** (49 mg, 36%) were washed with hexane and dried on the vacuum line. IR (CH_2Cl_2) ν(CO): 2055 (m), 1999 (m), 1979 (m), 1959 (vs), 1901 (vs), 1894 (sh), 1868 (m) cm^{-1}. Calcd for $C_{14}H_{16}CrO_8OsP_2$: C, 27.27; H, 2.60. Found: C, 27.28; H, 2.66. Complexes of the formula $(R_3P)_2(OC)_3OsM(CO)_5$ (M = Cr, W) and $[(RO)_3P](Me_3P)(OC)_3OsW(CO)_5$ along with the tungsten analogue of **1Cr** (**1W**) were prepared in a manner similar to the method described above; yields ranged from a low of 28% for **1W** to 50−64% for most of the $(R_3P)_2(OC)_3OsM(CO)_5$ and $[(RO)_3P](Me_3P)(OC)_3OsW(CO)_5$ products. The complexes are stable in air for short periods and range in color from pale yellow for $[MeC(CH_2O)_3P]_2(OC)_3OsW(CO)_5$ to deep yellow for **1Cr**. Selected IR data (CH_2Cl_2; ν(CO)): **2**, 2082 (m), 2036 (s), 2019 (sh), 1998 (s), 1911 (vs), 1864 (s); **3**, 2060 (m), 2054 (w), 2012 (w), 2001 (m),1977 (sh), 1958 (vs), 1906 (vs), 1873 (sh); **4**, 2070 (m), 2026 (m), 1998 (m), 1979 (vs), 1906 (vs), 1863 (m) cm^{-1}. Complete analytical and IR spectroscopic data for the new compounds have been deposited as Supporting Information. NMR data are given in Tables1 and 2.

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Table 1. ^1H and $^{31}P\{^1H\}$ NMR Data for $(R_3P)_2(OC)_3Os\ M(CO)_5$ (M = Cr, W) Complexes[a]

$(PR_3)_2/M$		^1H NMR[b] δ	$^{31}P\{^1H\}$ NMR[c] δ	isomer ratio[d]
$[P(OCH_2)_3CMe]_2/Cr$	*ax, rad*	4.32 (5.0), 4.28 (5.2), 0.83, 0.78	88.7 (32.0), 87.5	5.1
	dirad	4.27 (3.0), 0.78	83.4	
$Me_2PCH_2CH_2PMe_2/Cr$ (**1Cr**)	*ax, rad*	1.99 (10.2), 1.88 (m), 1.74 (9.8)	6.3 (0), 8.0	
$[P(OCH_2)_3CMe]_2/W$	*ax, rad* (**2**)	4.32 (5.0), 4.27 (5.0), 0.84, 0.79; 3.44 (5.3), 3.43 (5.3), −0.29, −0.35[e]	87.6 (32.9), 85.2; ~97.5, ~88[e]	1.7 0.2[e,f]
	dirad	4.28 (t, 2.6), 0.78 3.34 (t, 2.6), −0.39[e]	82.4 82.4[e]	
$[P(OMe)_3]_2/W$	*ax, rad*	3.69 (7.0), 3.67 (8.2)	106.3 (34.3), 90.8	3.9
	dirad	3.70 (t, 5.9)	89.7	
$(PMe_3)_2/W$	*ax, rad*	1.88 (9.3), 1.79 (10.3)	−57.8 (17.5), −62.9	0.9
	dirad (**3**)	1.86 (4.0)	−64.1	
$(PMe_2Ph)_2/W$	*ax, rad*	7.38−7.02 (m), 1.86 (9.4), 1.71 (9.2)	−44.0 (18.3), −53.2	24
	dirad	2.12 (br t, 4.0)	−52.7	
$Me_2PCH_2CH_2PMe_2/W$ (**1W**)	*ax, rad*	1.97 (10.1), 1.89−1.85 (m), 1.78 (9.9)	5.5 (0), −8.0	
$(Ph_2PCH_2CH_2PPh_2)/W$	*ax, rad*	7.51, 7.49, 2.66, 2.62	32.5 (0), 18.1	
$(PMe_3)/[P(OCH_2)_2CMe]/W$	*ax, rad*[g] (**4**)	4.27 (5.0), 1.89(10.4), 0.80	89.7 (22.4), −53.6 (21.4)	(0.7)
	ax, rad[h,i]	4.33 (5.0), 1.80 (10.0), 0.85	85.4 (28.5), −60.5 (28.5)	
$(PMe_3)/[P(OMe)_3]/W$ (**5**)	ax, rad[g]	3.68 (12.5), 1.76 (10.1)	105.7 (31.6), 59.1 (31.6)	*i*
$(PMe_3)/[P(O\text{-}o\text{-}C_6H_4Me)_3]/W$	*ax, rad*[g]	7.28−7.07 (m), 2.33, 1.82 (10.0)	87.7 (26.5), −61.0 (26.5)	*i*

[a] CD_2Cl_2 solution, ambient temperature. [b] J_{PH} or apparent J_{PH} in parentheses. [c] J_{PP} in parentheses. [d] *ax,rad*/*dirad* (*2,3*/*3,2*) except for **4** (see text). [e] Toluene-d_8 solution. [f] Determined from the ^1H NMR spectrum. [g] *Axial*-phosphite. [h] *Axial*-PMe_3, see text. [i] Diradial isomer (*3,2*) not detected.

X-ray Analyses of $(Me_2PCH_2CH_2PMe_2)(OC)_3OsM(CO)_5$ (M = Cr, 1Cr; M = W, 1W), $[MeC(CH_2O)_3P]_2(OC)_3OsW(CO)_5$ ($2\cdot CH_2Cl_2$; $2\cdot C_7H_8$), $(OC)_3(Me_3P)_2OsW(CO)_5$ (3), $[MeC(CH_2O)_3P](OC)_3](Me_3P)OsW(CO)_5$ (4), and $[(MeO)_3P](OC)_3](Me_3P)OsW(CO)_5$ (5). The crystals were grown from CH_2Cl_2/hexane except those of $\mathbf{2\cdot C_7H_8}$, which were grown from toluene/hexane. The structures were determined at St. Mary's University. The diffraction data were collected by using a Siemens SMART/CCD diffractometer equipped with an LT-II low-temperature device. The data were collected at −90 °C except those for $\mathbf{2\cdot C_7H_8}$, where the temperature was −50 °C. Diffraction data were corrected for absorption with the SADABS program. The program SHELXTL was used for the solutions of the structures and their refinements, which were based on F^2.[13] Crystal structure data can be found in Tables 3 and 4; selected bond lengths and angles are given in Tables 5 and 6.

Results and Discussion

Most of the precursory $Os(CO)_3(PR_3)_2$ compounds used in syntheses of the $(R_3P)_2(OC)_3OsW(CO)_5$ complexes have not been previously reported. These compounds were synthesized by three different reactions, examples of which are summarized in eqs 1−3. They are air-sensitive white or pale yellow solids, except $Os(CO)_3(PMe_2Ph)_2$, which was isolated as an orange oil. The derivative with the chelate bisphosphine, $Os(CO)_3(dmpe)$ (dmpe = $Me_2PCH_2CH_2PMe_2$), was particularly air-sensitive and was not characterized fully, although the $M(CO)_5$ (M = Cr, W) derivatives reported below were well-behaved solids. In unpublished work, we have found that in solution or in the solid-state $Os(CO)_3(PMe_3)_2$ reacts with oxygen to give the carbonate compound $Os(CO)_2(CO_3)(PMe_3)_2$; it also reacts slowly with CH_2Cl_2 at room temperature to yield $Os(CO)_2(PMe_3)_2(Cl)_2$.[12] The spectroscopic properties of the derivatives with monodentate P ligands are consistent with trigonal bipyramidal coordination for the Os atom and a diaxial arrangement of the noncarbonyl ligands.

$$\text{Method A:}\ Os(CO)_5 + PMe_2Ph \xrightarrow{140\ °C} Os(CO)_3(PMe_2Ph)_2 \quad (1)$$

$$\text{Method B:}\ Os(CO)_4(PMe_3) + P(OCH_2)_3CMe \xrightarrow{140\ °C} Os(CO)_3(PMe_3)[P(OCH_2)_3CMe)] \quad (2)$$

$$\text{Method C:}\ Os_3(CO)_{12} + Me_2P(CH_2)_2PMe_2 \xrightarrow[\text{CO, 90 atm}]{\sim 300\ °C} Os(CO)_3[Me_2P(CH_2)_2PMe_2)] \quad (3)$$

The $(R_3P)_2(OC)_3OsW(CO)_5$ (e.g., R = Me, R = OMe) complexes were isolated (in moderate to good yield) from the reaction of $W(CO)_5(THF)$ and $Os(CO)_3(PR_3)_2$ (in a 1:1 molar ratio) in hexane/CH_2Cl_2 at room temperature (eq 4). Some mixed derivatives of the type $(Me_3P)[(RO)_3P]((OC)_3OsW(CO)_5$ were prepared in a similar manner.

$$Os(CO)_3(PR_3)_2 + W(CO)_5(THF) \xrightarrow{25\ °C} (R_3P)_2(OC)_3OsW(CO)_5 \quad (4)$$

The binuclear complexes could only be prepared when the PR_3 ligand had a cone angle (θ) of less than ~125°. Thus, $(Me_3P)_2(OC)_3OsW(CO)_5$ and $(PhMe_2P)_2(OC)_3OsW(CO)_5$ could be isolated, but the corresponding PEt_3, $PMePh_2$, and PPh_3 compounds could not be synthesized, nor could $(Ph_3P)(Me_3P)(OC)_3OsW(CO)_5$. The cone angles of PMe_3, PMe_2Ph, $PMePh_2$, PEt_3, and PPh_3 are 118°, 122°, 132°, 136°, and 145°, respectively.[14]

The only derivatives in which the acceptor moiety was $Cr(CO)_5$ (i.e., $(R_3P)_2(OC)_3OsCr(CO)_5$) that could be prepared were with sterically undemanding P ligands, namely, $(dmpe)(OC)_3OsCr(CO)_5$ (eq 5) and $[MeC(OCH_2)_3P]_2(OC)_3OsCr(CO)_5$ (θ for $P(OCH_2)_3CMe$ =

$$Os(CO)_3[Me_2P(CH_2)_2PMe_2] + M(CO)_5(THF) \xrightarrow{25\ °C} [Me_2P(CH_2)_2PMe_2](OC)_3OsM(CO)_5 \quad (5)$$

$$M = Cr,\ \mathbf{1Cr};\ M = W,\ \mathbf{1W}$$

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Table 2. $^{13}C\{^1H\}$ NMR Data for Selected $(R_3P)_2(OC)_3Os\,M(CO)_5$ (M = Cr, W) Complexes[a]

$(PR_3)_2$/M		δ (CO)[b]		δ (PR_3)[b]
		$M(CO)_5$	$Os(CO)_3$	
$Me_2PCH_2CH_2PMe_2$/Cr (**1Cr**)	*ax, rad*	233.8 (1C,1.6), 227.4 (4C)	199.4 (2C,13.7), 187.6 (1C, 67.5, 4.8)	22.8 (30.5), 16.5 (34.5)
$[P(OMe)_3]_2$/W	*ax, rad*	207.6 (1C,5.3), 205.2 (4C, 124[c])	194.7 (2C, 19.1), 184.3 (1C, 113.7, 7.6)	54.6 (4.7)
	dirad	206.5 (1C), 204.2 (4C, 127,[c] 1.5)	195.8 (t, 2C, 16.0), 175.6 (t,1C,13.7)	
$(PMe_3)_2$/W	*ax, rad*	207.4 (1C, 178,[c] 3.0), 206.6 (4C, 125,[c] 2.3)	196.7 (2C, 13.0), 187.7 (1C, 70.2, 4.6)	24.8 (34.3), 23.0 (35.8, 3.8)
	dirad (**3**)	206.3 (4C, 125,[c] 2.7), 205.4 (1C, 167[c])	198.7 (t,4C, 9.2), 179.1 (t, 1C, 10.3)	23.8 (t, 19.5)
$Me_2PCH_2CH_2PMe_2$, W (**1W**)	*ax, rad*	207.6 (1C, 4.0), 206.4 (4C, 125,[c] 2.4)	196.6 (2C, 12.8), 186.0 (1C, 69.9, 4.8)	35.3 (36.2, 15.3), 32.2 (34.1, 8.8), 22.7 (34.5), 17.4 (35.3)
$(PMe_3)/[P(OCH_2)_2CMe]$/W	*ax, rad*[d]	207.7 (1C, 3.0), 205.6 (4C, 125.3,[c] 1.5)	193.0 (2C, 119.3), 188.8 (1C, 119.9, 4.2),	78.1 (6.5), 34.4 (35.9), 24.1 (36.4), 17.2
	ax, rad[e] (**4**)	206.9 (1C, 5.7), 205.9 (4C, 125.3[c])	193.6 (2C, 14.1), 182.3 (1C, 68.1, 7.4)	77.9 (7.0), 34.4 (36.6), 22.2 (37.8, 5.0), 17.2
$(PMe_3)/[P(OCH_3)_3]$/W (**5**)	*ax, rad*[e]	206.7 (1C, 5.3), 205.9 (4C, 125[c])	196.0 (2C, 13.7), 183.4.0 (2C, 67.5, 7.2)	22.0 (38.2, 4.6)[f]
$(PMe_3)/[P(O\text{-}o\text{-}C_6H_4Me)_3]$/W	*ax, rad*[e]	204.9 (1C), 203.7 (4C,126.8[c])	191.8 (2C, 14.1), 186.6 (1C, 67.4, 6.0)	

[a] CH_2Cl_2/CD_2Cl_2 (4:1) solution, ambient temperature. [b] J_{PC} in parentheses unless otherwise stated. [c] J_{WC}. [d] *ax*-PMe_3. [e] *rad*-PMe_3 (see Figures 5 and 7). [f] Resonance due to OMe assumed obscured by solvent signals; vw doublet observed at δ 24.2 (36.6).

101°).[14] No attempt was made to synthesize the molybdenumanalogues since it had been previously found that yields of the similar $(R_3P)(OC)_4OsMo(CO)_5$ complexes were significantly lower than those of either of the Cr or W congeners.[2,3]

Undoubtedly, the necessity of having a bulky PR_3 ligand cis to the metal−metal bond causes steric interactions with the radial (equatorial) carbonyls on the group 6 atom such that for bulky phosphines the $(R_3P)_2(OC)_3OsW(CO)_5$ derivatives are too unstable to isolate. Similarly, the failure to prepare the Cr analogues with still smaller P ligands can be attributed to increased steric interactions between the PR_3 and the radial Cr carbonyls because of the shorter OsCr bond. It may be that even in the absence of steric effects that the OsCr bond is weaker than the OsW bond and also contributes to the instability of the Cr compounds. Molecular orbital calculations indicate that the OsCr bond in $(OC)_5OsCr(CO)_5$ is weaker than the OsW bond in $(OC)_5OsW(CO)_5$.[15]

All the binuclear compounds described here are moderately air-stable, crystalline solids that range in color from pale yellow to bright yellow. The colors appear to correlate with the expected strength of the dative metal−metal bond as would be predicted if the electronic transition giving rise to the visible absorption is due to the σ-to-σ^* transition associated with the metal−metal bond.[16,17] For example, the OsW bond in $[MeC(CH_2O)_3P]_2(OC)_3OsW(CO)_5$ is thought to be among the strongest of these complexes (see below), and the complex is a much paler yellow than the corresponding PMe_3 and PMe_2Ph derivatives. The chromium compounds are deep yellow.

Structural Studies. The compounds $(Me_2PCH_2CH_2PMe_2)(OC)_3OsM(CO)_5$ (M = Cr, **1Cr**; M = W; **1W**) are isostructural; a view of **1Cr** is shown in Figure 1 with selected bond length and angle data for **1Cr** and **1W** given in Table 5. In each case the 18-electron compound $Os(CO)_3$(dmpe) acts as two-electron donor ligand toward the 16-electron $M(CO)_5$ moiety via an unbridged dative metal−metal bond.

The OsCr bond length in **1Cr** (3.0287(4) Å) is significantly longer than the OsCr dative bonds in $(Me_3P)(OC)_4OsCr(CO)_5$ (2.979(1) Å),[2] $(OC)_4(Bu^tNC)OsCr(CO)_5$ (2.966(2) Å), and $(OC)_3(Bu^tNC)_2OsCr(CO)_5$ (2.969(1) Å).[3] (In the last two compounds the noncarbonyl ligands are cis to the OsCr bond.) It is tempting to attribute the lengthening in **1Cr** to the repulsive interactions between the radial carbonyls of the $Cr(CO)_5$ moiety and the methyl substituents on the P atom that are cis to the OsCr bond. But as can be seen from Figure 1, the small bite angle of the bidentate phosphine (P(1)OsP(2) = 83.02(3)°) pulls these methyl groups away from the Cr atom. As discussed below, there may be an electronic component that contributes to the weakening of the OsCr bond.

The OsW bond length in **1W** (3.0984(5) Å) is also longer than the corresponding bond in $(Me_3P)(OC)_4OsW(CO)_5$ (3.0756(5) Å),[2] but the difference is not as large

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Table 3. Crystal Structure Data for $(Me_2PCH_2CH_2PMe_2)(OC)_3OsM(CO)_5$ (M = Cr, 1Cr; M = W, 1W), $[MeC(OCH_2)_3P]_2(OC)_3OsW(CO)_5{\cdot}C_6H_5Me$ ($2{\cdot}C_7H_8$), and $2{\cdot}CH_2Cl_2$

	1Cr	**1W**	**$2{\cdot}C_7H_8$**	**$2{\cdot}CH_2Cl_2$**
empirical formula	$C_{14}H_{16}CrO_8OsP_2$	$C_{14}H_{16}O_8OsP_2W$	$C_{25}H_{26}O_{14}OsP_2W$	$C_{19}H_{20}Cl_2O_{14}OsP_2W$
fw	616.41	748.26	986.45	979.24
color	yellow	yellow	pale yellow	pale yellow
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	14.8500(7)	14.9516(7)	11.9236(6)	9.4407(5)
b (Å)	8.4469(4)	8.5143(4)	18.1638(9)	11.3968(6)
c (Å)	16.6956(8)	16.8825(8)	15.3294(8)	14.6652(8)
α (deg)				86.851(1)
β (deg)	102.066(1)	102.689(1)	110.8430(10)	78.524(1)
γ (deg)				66.128(1)
V ($Å^3$), Z	2048.0(2), 4	2096.7(2), 4	3102.7(3), 4	1413.5(2), 2
D(calcd) ($Mg{\cdot}m^{-3}$)	1.999	2.370	2.112	2.301
abs coeff (mm^{-1})	6.920	11.723	7.964	8.923
indpdt reflns	4766 [R(int) = 0.0295]	4863 [R(int) = 0.0925]	5469 [R(int) = 0.0538]	4885 [R(int) = 0.0345]
R_F[a]	0.0216	0.0671	0.0324	0.0566
R_{wF}[b]	0.0566	0.1555	0.0556	0.1533

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

Table 4. Crystal Structure Data for $(OC)_3(Me_3P)_2OsW(CO)_5$ (3), $[MeC(CH_2O)_3P](OC)_3(Me_3P)OsW(CO)_5$ (4) and $[(MeO)_3P](OC)_3(Me_3P)OsW(CO)_5$ (5)

	3	**4**	**5**
empirical formula	$C_{14}H_{20}O_8OsP_2W$	$C_{16}H_{18}C_{l0.2}O_{11}OsP_2W$	$C_{14}H_{18}O_{11}OsP_2W$
fw	752.29	829.38	798.27
color	yellow	yellow	yellow
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$C2/c$	$P2_12_12_1$	$P2_1/n$
a (Å)	14.3551(9)	11.4419(6)	10.1342(5)
b (Å)	13.2658(8)	12.5953(7)	19.0605(9)
c (Å)	11.1820(7)	16.2012(9)	12.1613(6)
β (deg)	100.852(1)		103.1020(10)
V ($Å^3$), Z	2091.3(2), 4	2334.8(2), 4	2288.0(2), 4
D(calcd) ($Mg{\cdot}m^{-3}$)	2.389	2.359	2.317
abs coeff (mm^{-1})	11.754	10.572	10.761
indpdt reflns	2309 [R(int) = 0.0290]	5459 [R(int) = 0.0499]	5335 [R(int) = 0.0407]
R_F[a]	0.0253	0.0366	0.0296
R_{wF}[b]	0.0656	0.0871	0.0637

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

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $(Me_2PCH_2CH_2PMe_2)(OC)_3OsM(CO)_5$ (M = Cr, 1Cr; M = W, 1W)

	1Cr	**1W**
	Bond Lengths	
Os−M	3.0287(4)	3.0984(5)
Os−P(1)	2.3360(7)	2.338(3)
Os−P(2)	2.3959(7)	2.395(3)
M−C(1)	1.819(3)	1.95(1)
M−C_{rad} (range)	1.881(3)−1.897(3)	2.01(2)−2.05(1)
Os−C (range)	1.918(3)−1.943(3)	
	Bond Angles	
M-Os−P(1)	175.90(2)	176.56(8)
M-Os−P(2)	99.70(2)	99.07(7)
P(1)−Os−P(2)	83.02(3)	83.05(10)
P(1)−Os−C(7)	97.37(9)	98.4(3)
P(1)−Os−C(8)	103.64(9)	104.7(3)
C(7)−O−C(8)	158.6(1)	156.7(5)
	Nonbonding Contacts	
C(7)···M	3.289	3.318
C(8)···M	3.286	3.299

as that in the Cr compounds. Nondative osmium−tungsten bond lengths in cluster compounds are usually in the range 2.65−3.03 Å and consequently significantly shorter than the OsW bond in **1W**.[18−20] In (η-C_5H_5)WOs_3(μ-H)$_3$(μ_3-CC_6H_4Me)$(CO)_{12}$ there is, however, an OsW bond of length 3.097(1) Å that is unsupported by other metal−metal bonds in the cluster unit or bridged by a ligand.[19] This distance is within a standard deviation of the OsW distance in **1W**.

As can be seen from Figure 1, there is a significant leaning of the radial carbonyls on the donor Os atom toward the acceptor Cr (or W) atom. This is observed in all the structures described here. The distances from the C atom of these carbonyls to the group 6 metal atom in each case (Tables 4 and 5) are greater than 3.25 Å and are therefore essentially nonbonding. We have proposed that the closer the C(7)OsC(8) angle is to octahedral geometry (i.e., 180°), the stronger the donor−acceptor interaction.[9] (Consider the precursory $Os(CO)_3(PR_3)_2$ compound going from the trigonal bipyramidal

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[18] Some recent examples: (a) Shiu, C.-W.; Chi, Y.; Carty, A. J.; Peng, S.-M.; Lee, G.-H.; *Organometallics* **1997**, *16*, 5368. (b) Chi, Y.; Chung, C.; Chou, Y.-C.; Su, P.-C.; Chiang, S.-J.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1997**, *16*, 1702. (c) Su, C.-J.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *J. Cluster Sci.* **1996**, *7*, 85. (d) Park, J. T.; Chung, J.-H.; Song, H.; Lee, K.; Lee, J.-H.; Park, J.-R.; Suh, I.-H. *J. Organomet. Chem.* **1996**, *526*, 215. (e) Huang, T.-K.; Chi, Y.; Peng, S.-M.; Lee, G.-H.; Wang, S.-L.; Liao, F.-L. *Organometallics* **1995**, *14*, 2164. (f) Su, P.-C.; Chiang, S.-J.; Chang, L.-L.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1995**, *14*, 4844. (g) Gong, J.-H.; Hwang, D.-K.; Tsay, C.-W.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1994**, *13*, 1720. (h) Gong, J.-H.; Chen, C. C.; Chi, Y.; Wang, S.-L.; Liao, F.-L. *J. Chem. Soc., Dalton Trans.* **1993**, 1829.

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Table 6. Selected Bond Lengths (Å) and Angles (deg) for $[MeC(CH_2O)_3P]_2(OC)_3OsW(CO)_5 \cdot C_6H_5Me$ ($2 \cdot C_7H_8$), $2 \cdot CH_2Cl_2$, $(OC)_3(Me_3P)_2OsW(CO)_5$ (3), $[MeC(CH_2O)_3P](OC)_3(Me_3P)OsW(CO)_5$ (4), and $[(MeO)_3P](OC)_3(Me_3P)OsW(CO)_5$ (5)

	$2 \cdot C_7H_8$	$2 \cdot CH_2Cl_2$	3[a]	4	5
			Bond Lengths		
Os−W	3.0831(4)	3.0818(7)	3.1397(4)	3.0956(5)	3.1136(3)
Os−P(1)	2.272(2)	2.276(3)	2.397(1)	2.268(2)	2.295(1)
Os−P(2)	2.315(2)	2.312(3)		2.419(2)	2.422(1)
W−C(1)	1.953(8)	1.97(1)	1.938(8)	1.92(1)	1.960(5)
$W-C_{rad}$ (range)	2.009(7)−2.036(8)	2.03(2)−2.05(2)	2.028(5)−2.029(5)	2.01(1)−2.02(1)	2.012(6)−2.032(7)
Os−C (range)	1.945(7)−1.954(8)	1.93(1)−1.96(1)	1.906(7)[b]−1.942(4)c	1.92(1)−1.94(1)	1.925(6)−1.938(7)
			Bond Angles		
W−Os−P(1)	171.73(4)	173.02(8)	92.85(3)	166.45(6)	168.65(3)
W−Os−P(2)	94.03(4)	91.70(8)		100.98(6)	99.83(3)
P(1)−Os−P(2)	93.95(6)	95.10(11)	174.30(6)	92.44(7)	91.52(4)
P(1)−Os−C(7)	98.2(2)	99.8(4)	102.3(1)	97.9(3)	101.4(2)
P(1)−Os−C(8)	102.3(2)	99.5(4)		101.3(3)	100.7(1)
C(7)−Os−C(8)	159.2(3)	160.6(6)	155.3(3)[e]	160.3(4)	157.2(2)
			Nonbonding Contacts		
C(7)···W	3.343	3.308	3.321[f]	3.382	3.359
C(8)···W	3.362	3.418		3.399	3.361

[a] Molecule has a 2-fold axis. [b] Os−C(5). [c] Os−C(4). [d] C(4)−Os−C(5). [e] C(4)−Os−C(4′). [f] C(4)···W

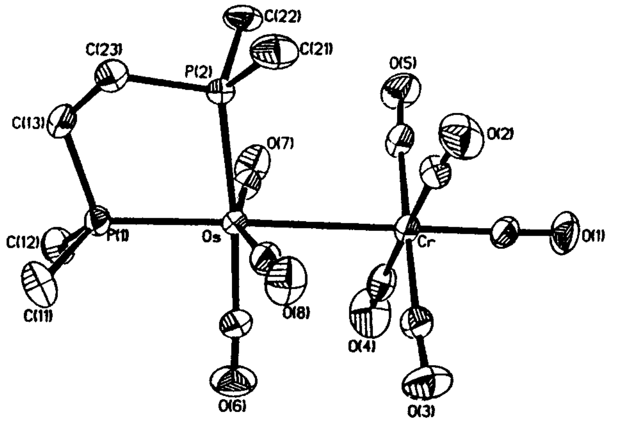

Figure 1. Molecular structure of $(dmpe)(OC)_3OsCr(CO)_5$ (**1Cr**). Compound **1W**, $(dmpe)(OC)_3OsW(CO)_5$, is isostructural with **1Cr**.

geometry it has in the uncomplexed state to the geometry it has in $(R_3P)_2(OC)_3OsM(CO)_5$.) The C(7)OsC(8) angles in **1Cr** and **1W** are 158.6(1)° and 156.7(5)°, respectively. The corresponding angles in $(Me_3P)(OC)_4OsCr(CO)_5$ and $(Me_3P)(OC)_4OsW(CO)_5$ are 167.8(4)° and 168.5(4)°, and 167.9(3)° and 169.0(3)°, respectively.[2] These observations are therefore also consistent with the view that the donor−acceptor metal−metal bond is weaker in **1Cr** and **1W** than in the corresponding $(Me_3P)(OC)_4OsM(CO)_5$ compounds. As mentioned in the Introduction, it might have been expected that the presence of two strong donor ligands on the donor Os atom would increase the strength of the donor−acceptor metal−metal bond.

For reasons discussed in the spectroscopic section, two structures of $[MeC(CH_2O)_3P]_2(OC)_3OsW(CO)_5$ were determined, one of a sample crystallized from CH_2Cl_2 (**$2 \cdot CH_2Cl_2$**) and the other obtained from toluene (**$2 \cdot C_7H_8$**). Each structure revealed the same isomer, but each had a molecule of solvation in the lattice. The bond lengths and angles in each structure of **2** are not significantly different (Table 6). The *R* factor for the structure of **$2 \cdot C_7H_8$** (hereafter, **2**) is smaller than that for **$2 \cdot CH_2Cl_2$**, and therefore discussion is restricted to the former structure. A view of the molecule is shown in Figure 2. Compound **2** has the expected configuration, with one phosphite ligand cis to the OsW bond (i.e., a radial site) and the other trans to this bond (the axial site). We refer to this isomer as the *ax,rad* isomer. The OsW bond length 3.0831(4) Å is marginally shorter than the corresponding distance in **1W**; the C(7)−Os−C(8) angle is 159.2(3)°.

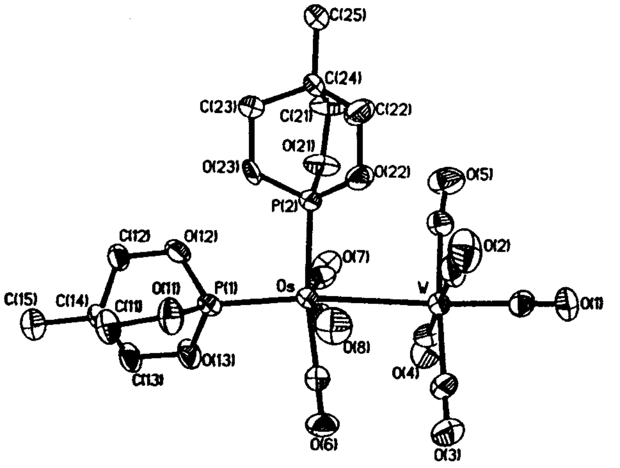

Figure 2. Molecular structure of *OC-6-2,3*-$[MeC(CH_2O)_3P]_2(OC)_3OsW(CO)_5$ (**2**).

The molecule $(OC)_3(Me_3P)_2OsW(CO)_5$ (**3**) crystallizes with a crystallographic 2-fold axis that passes through C(5)OsWC(1). Unexpectedly, this compound has both phosphorus ligands in mutually trans sites that are cis to the OsW bond (Figure 3); that is, the solid state form of **3** is the trans diradial (*dirad*) isomer. Discussion of the possible reasons for the isomer distributions in these complexes is postponed to a subsequent section of this paper. The OsW bond in **3** at 3.1397(4) Å (Table 6) is exceptionally long and may be compared to the other OsW lengths reported in this study (range 3.0831(4)−3.1136(3) Å) and that in $(Me_3P)(OC)_4OsW(CO)_5$ (3.0756(5) Å).[2] The OsW distance may also be compared to the OsW vectors, of 3.154(2) and 3.156(3) Å, in $(OC)_4W[(\mu\text{-}H)Os(CO)_3(PMe_3)]_2$, thought to be the longest OsW vectors reported (it is well known that the presence of a single bridging hydride ligand significantly lengthens a metal−metal bond over the unbridged distance).[20]

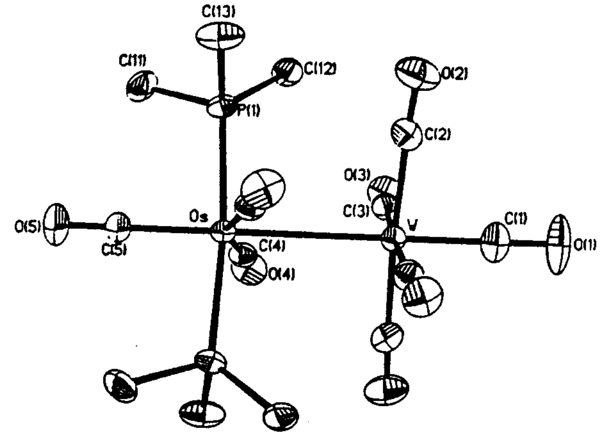

Figure 3. Molecular structure of *OC-6-3,2*-$(OC)_3(Me_3P)_2$-$OsW(CO)_5$ (**3**).

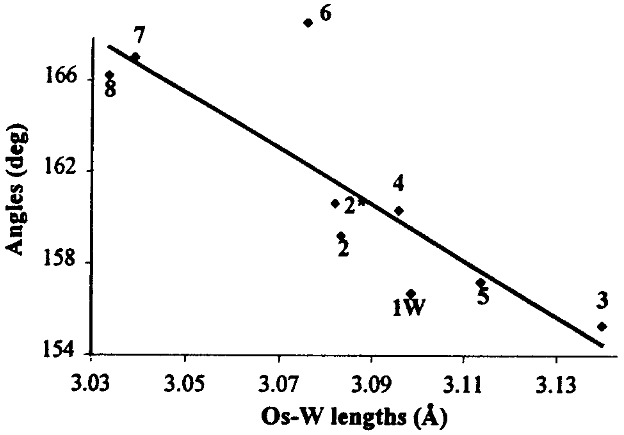

Figure 4. Plot of the radial C−Os−C angle versus the Os−W bond length in complexes that contain unbridged OsW dative bonds. **6** = $(Me_3P)(OC)_4OsW(CO)_5$; **7** = $(OC)_3$-$[MeC(OCH_2)_3P]_2OsOs(CO)_4W(CO)_5$; **8** = $(OC)_4(Bu^tNC_2Os$−$Os(CO)_3(CNBu^t)W(CO)_5$.[2,4]

The length of the dative OsW bond in **3** indicates that it is exceptionally weak. Also consistent with this view is that the C(4)OsC(4′) angle is 155.3(3)°. This is some 35° from the corresponding angle in the precursory trigonal bipyramidal $Os(CO)_3(PMe_3)_2$ compound and 25° from that for ideal octahedral coordination about the Os atom. Figure 4 shows a plot of the radial C−Os−C angle versus the OsW bond length in the structures with unbridged OsW dative bonds. As can be seen from the figure, there is a reasonably good correlation between the two parameters given the expected variation in bond angles due to packing forces. It has been estimated by Martin and Orpen that packing effects can contribute differences of 1−2° to the valence angles at a metal and in some cases over 3°.[21] (In the two forms of **2** the radial C−Os−C angles differ by 1.6°.)

The increase in the OsW length in **3** may be readily interpreted in terms of the large steric interactions between the PMe_3 ligands and the radial carbonyls on the tungsten atom that weaken the OsW bond in **3**. There may, however, be an electronic component to the weakening of the Os−W bond (see below).

A view of $[MeC(CH_2O)_3P](OC)_3(Me_3P)OsW(CO)_5$ (**4**) is shown in Figure 5; the structure of $[(MeO)_3P](OC)_3$-$(Me_3P)OsW(CO)_5$ (**5**) is similar to that of **4**, that is, with the phosphite ligand trans to the OsW bond. The structural parameters (Table 6) of **4** and **5** are as might be expected from those obtained for compounds **2** and **3**. The OsW lengths are 3.0956(4) Å in **4** and 3.1136(3) Å in **5**. The difference in these two lengths can probably be attributed to fewer steric interactions between the phosphite and PMe_3 ligands in **4**, which in turn reduces the steric interactions between the latter ligand and the radial carbonyls on the tungsten atom. The W−Os−P(PMe_3) angle in **4** (100.98(5)°) is slightly larger than that in **5** (99.83(3)°) despite the shorter OsW bond in **4**. The C(7)−Os−C(8) angles are 160.3(4)° in **4** and 157.2(2)° in **5**.

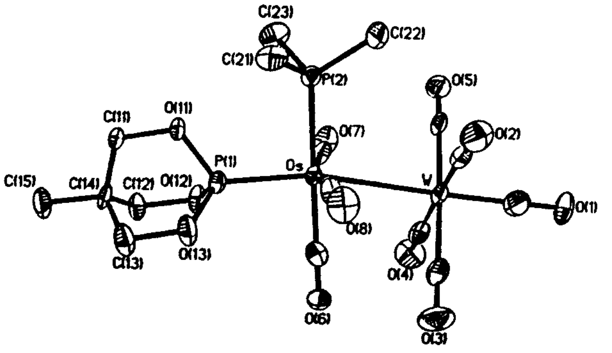

Figure 5. Molecular structure of $[MeC(CH_2O)_3P](OC)_3$-$(Me_3P)OsW(CO)_5$ (**4**). The structure of $[(MeO)_3P](OC)_3$-$(Me_3P)OsW(CO)_5$ (**5**) is similar to **4**.

The OsP Distances. The OsP distances in the structures are collected in Tables 5 and 6. The OsP lengths of the phosphite ligands are significantly shorter than those that involve phosphine substituents. This shortening is typical and ascribed to increased back-donation to the phosphite ligand.[22,23]

The OsP distances (*rad*-OsP) to a PMe_3 or dmpe ligand that is cis to the OsW (or OsCr) bond are exceptionally long. In **1Cr** and **1W** the *rad*-Os−P distances are 2.3959(7) and 2.395(3) Å, respectively; in **3** the OsP distances are crystallographically equivalent at 2.397(1) Å; in **4** and **5** the Os−P(PMe_3) distances are 2.419(2) and 2.422(1) Å, respectively. We have determined the structures of nine cluster compounds containing an Os−PMe_3 unit; with one exception the OsP distances are in the range 2.318(4)−2.363(2).[8,20,24,25] The exception is $Os_5(CO)_{15}$(*eq*-PMe_3) (OsP = 2.396(4) Å), in which the phosphine occupies a sterically crowded site in the cluster.[25] In $(Me_3P)(OC)_4OsW(CO)_5$ the OsP distance (that is trans to the OsW bond) is 2.359(2) Å.[2] The OsP lengths may also be compared to 2.345(2) and 2.478(1) Å, the OsP lengths in $Os_3(CO)_{11}(PEt_3)$ and Os_3-$(CO)_{11}(PBu^t_3)$, respectively.[23,26] The lengthening of the *cis*-Os−P(phosphine) distances in **1W**, **3**, **4**, and **5** can therefore be attributed mainly to excessive steric interactions between the methyl substituents and the radial

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[26] Hansen, V. M.; Ma, A. K.; Biradha, K.; Pomeroy, R. K.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 5267.

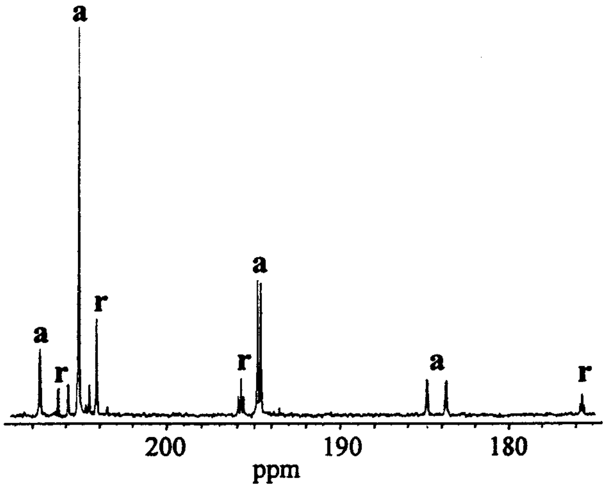


Figure 6. $^{13}C\{^1H\}$ NMR spectrum (carbonyl region) of $[(MeO)_3P]_2(OC)_3OsW(CO)_5$ (**9**) in CD_2Cl_2/CH_2Cl_2. Peaks marked with an **a** and **r** are due to the axial and radial/diradial isomers, respectively.

carbonyls on the W atom, although there may also be an electronic component to the lengthening (see below).

In the structures where both P substituents are identical, but are cis and trans to the OsM bond (i.e.,**1Cr**, **1W** and **2**), there is a significant difference in the length of the Os−P bonds. The Os−P(1) (i.e., trans to the W atom) distance in **2** is 2.272(2) Å, whereas the corresponding Os−P(2) (i.e., trans to a carbonyl) distance is 2.315(2) Å. It may be that the difference in the OsP lengths in **2** is not entirely due to different steric interactions given the small size of the $P(OCH_2)_3CMe$ (as mentioned above, θ for $P(OCH_2)_3CMe = 101°$). We have found a similar difference in the RuSi lengths in compounds of the type $(Dnr)Ru(CO)_3(SiCl_3)_2$ (Dnr = 18e organometallic ligand such as $Os(CO)_4(PMe_3)$).[9] The difference was rationalized in terms of π-bonding properties of the ligands involved. The metal grouping is considered to be a π-donor ligand and is therefore expected to increase the π back-bonding to the ligand trans to it and thereby shorten the metal−ligand bond. On the other hand, a carbonyl ligand will reduce the back-bonding to the ligand trans to it and hence lengthen the appropriate metal−ligand bond. Obviously, the same arguments could account for part of the difference in the OsP distances in **2**. Likewise, the different trans influences of the CO and $W(CO)_5$ units could contribute to the differences of the OsP lengths in **1Cr** and **1W**.

NMR Studies. The NMR spectra for **1Cr** and **1W** are consistent with the solid state structure as the only structure in solution (Tables 1 and 2). The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of many of the other new compounds indicate the presence of two, and only two, isomers in solution. The solution $^{13}C\{^1H\}$ NMR spectrum in the carbonyl region of $[(MeO)_3P]_2(OC)_3OsW(CO)_5$ (**9**) in CH_2Cl_2/CD_2Cl_2 is shown in Figure 6. This spectrum was chosen for display because the PC couplings in the phosphite derivatives are larger than the couplings in the phosphine complexes, as is typical, and the isomer distribution in **9** is such as to make the assignment of the resonances simple.

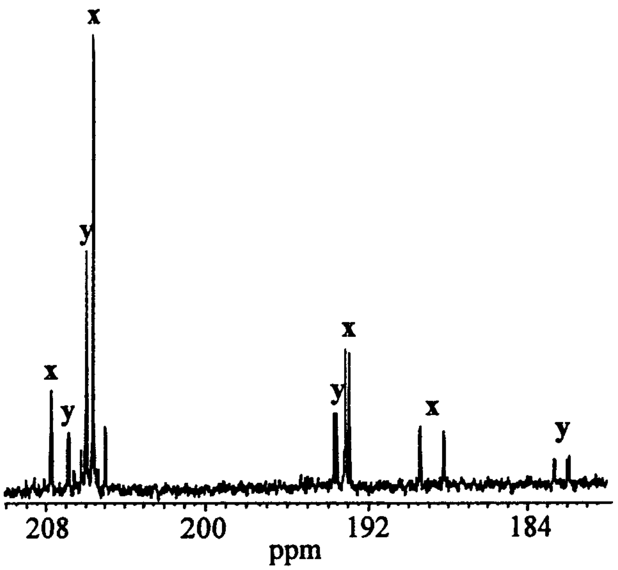
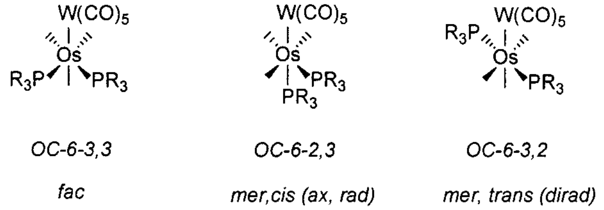


Figure 7. $^{13}C\{^1H\}$ NMR spectrum (carbonyl region) of $[MeC(CH_2O)_3P](Me_3P)_2(OC)_3OsW(CO)_5$ (**5**) in CD_2Cl_2/CH_2Cl_2. Peaks marked with an **x** and **y** are due to the *ax*-PMe_3/*rad*-$P(OCH_2)_3CMe$ isomer and *ax*-$P(OCH_2)_3CMe$/*rad*-PMe_3 isomers, respectively.

Chart 1



If the PR_3 ligands remain attached to the Os atoms, there are three possible geometric isomers for $(R_3P)_2(OC)_3OsW(CO)_5$. The fac isomer of $Os(CO)_3(PR_3)_2[W(CO)_5]$ is designated according to IUPAC convention as the *OC-6-3,3* form; the mer,cis (*ax*,*rad*) isomer as *OC-6-2,3*; and the mer,trans (*dirad*) form as *OC-6-3,2*.[27] Here the isomers will be designated *3,3*, *2,3*, and *3,2*, respectively, as shown in Chart 1. The isomers may readily be distinguished by NMR spectroscopy (Tables 1 and 2). Isomer *3,3* (i.e., the facial isomer) with the two noncarbonyl ligands in radial sites that are mutually cis was not observed, presumably due to the excessive steric interactions present in this form. This isomer, however, is the thermodynamically preferred form for $(OC)_3(Bu^tNC)_2OsW(CO)_5$ complexes.[3]

For the mixed derivatives (e.g., **4** and **5**) there are two possible *ax,rad* isomers depending on which P ligand is trans to the OsW bond. For complex **4**, NMR evidence indicates that both isomers with an axial P ligand are present in solution (Tables 1 and 2; Figure 7). A detailed analysis of the NMR spectra of **4** leads to the conclusion that the most prevalent form in solution has the PMe_3 ligand trans to the $W(CO)_5$ grouping (i.e., (*ax*-Me_3P)$(OC)_3$[*rad*-$MeC(CH_2O)_3P$]$Os[W(CO)_5]$). The preferred isomer in solution is therefore not the form found in the solid state. For compound **5**, the only isomer that was observed in solution was the solid state form, namely, that with the phosphite ligand trans to the tungsten

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[27] (a) Block, B. P.; Powell, W. H.; Fernelius, W. C. *Inorganic Nomenclature: Principles and Practice*; American Chemical Society: Washington, DC, 1990. (b) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; HarperCollins: New York, 1993; p A-71.

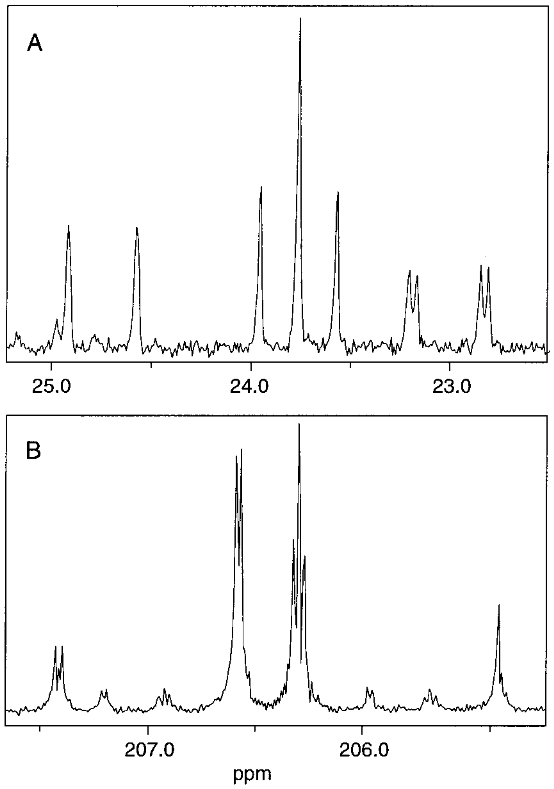
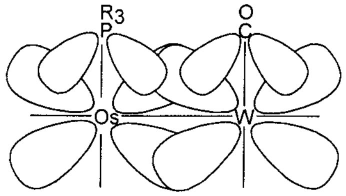


Figure 8. $^{13}C\{^1H\}$ NMR spectrum of **3** (CD_2Cl_2/CH_2Cl_2 solution) in the methyl region (A) and the W−CO region (B).

atom. In both cases, only very weak peaks were present in the various NMR spectra, which might indicate the presence of a *dirad* isomer. The only form of $[(o\text{-}MeC_6H_4O)_3P](OC)_3(Me_3P)OsW(CO)_5$ detected in solution was also the *ax*-phosphite/*rad*-phosphine isomer.

The NMR spectra of these complexes show additional interesting features that will be illustrated here with a detailed discussion of the spectra of **3**. The ^1H NMR spectrum exhibits a triplet typical of a virtually coupled system of a *trans*-$(Me_3P)M(PMe_3)$ grouping.[28,29] This resonance is therefore assigned to *3,2*-**3**, the structure found in the solid state. The remaining resonances in the spectrum consist of two doublets and are assigned to the *2,3* isomer with one PMe_3 grouping trans to the OsW bond. Interestingly, the methyl region of the $^{13}C\{^1H\}$ NMR spectrum of **3** exhibits a similar pattern except that the high-field doublet shows a further small ($^3J_{PC} = 3.8$ Hz) three-bond phosphorus coupling (Figure 8A). The resonance that shows the extra coupling is probably due to the PMe_3 ligand that is trans to the OsW bond. The chemical shift of this signal (δ 23.0) is identical to that of the major (axial) isomer of $(Me_3P)(OC)_4OsW(CO)_5$ (δ 23.0).[2] On the other hand, the chemical shift of the other doublet is to low field of δ 23.0, the region where the resonances of the corresponding methyl groups of *3,3*-**3** and *2,2*-**4** occur (Table 2). The structures described above indicate that a PMe_3 group cis to the OsW bond is more weakly bound to the Os atom than a PMe_3 bound at the axial site. This would result in changes to the OsP bonding (e.g., the amount of s character in the bond) so that perhaps three-bond PC coupling is observed to the methyl groups of the more strongly bound axial PMe_3, but not to the radial PMe_3 ligand in *2,3*-**3**.

Chart 2



The $^{31}P\{^1H\}$ NMR spectrum consists of a singlet at δ −64.2 assigned to *3,2*-**3** and two doublets at δ −57.8 and −62.9 assigned to *2,3*-**3**. The resonance at δ −62.9 is attributed to the P atom cis to the tungsten atom on the basis that it should have a chemical shift that is similar to that of *3,2*-**3** and to the resonance of the minor, radial isomer of $(Me_3P)(OC)_4OsW(CO)_5$; the latter signal occurs at δ −62.3, whereas the resonance of the other (major) isomer of this compound appears at δ −53.2.[2]

In the $^{13}C\{^1H\}$ NMR spectrum of ^{13}CO-enriched **3** (CO region), the resonances to low field of 200 ppm are readily assigned to CO ligands attached to tungsten by analogy with the spectra of similar derivatives and because the peaks exhibit coupling to ^{183}W (Figure 8B; cf. Figure 6).[2,3,30,31] The W−CO signals to higher field at δ 206.3 and 205.4 in a 4:1 ratio are assigned to the carbonyls of the $W(CO)_5$ moiety of *2,3*-**3**; the more intense signal is a triplet, but the weaker signal is a singlet. That the chemical shift of the signal due to the axial carbonyl is to high field of the resonance due to the radial carbonyls is unusual. In all other complexes reported here, and of the type $(L)_x(OC)_{5-x}OsM(CO)_5$ (M = Cr, Mo, W; L = PR_3, $x = 1$; L = $CNBu^t$, $x = 1$, 2) and $W(CO)_5(PR_3)$, this resonance appears to low field of that due to the radial carbonyls.[2−4,30,31] The observation of an apparent three-bond, cis, cis coupling (∼2.7 Hz) from P to C is also unprecedented in our studies on these and similar complexes (Figure 8B). Two-bond, PC cis couplings are normally small (e.g., Table 2), and three-bond, cis, cis couplings might therefore be expected to be so small as to be unobservable. It is proposed that this coupling is through-space coupling where the π-acceptor orbitals on the PMe_3 and adjacent carbonyls are linked via the filled d orbitals on the metal atoms, as shown in Chart 2.

The other two resonances in the W−CO region, due to the axial and radial carbonyls of *2,3*-**3**, occur at δ 207.4 and 206.6, respectively, and are doublets. The small coupling (3.0 Hz) to the signal due to the axial carbonyl is assigned to a conventional three-bond, trans, trans coupling to the P atom in the radial site on the Os atom. We have occasionally observed similar couplings in $(R_3P)(OC)_4OsM(CO)_5$ compounds; it is also seen in the spectrum of **1Cr**, **1W**, and **9** (Table 2; Figure 6).

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[30] Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic: New York, 1981; p 159.

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The coupling (∼2.3 Hz) to the signal due to the radial carbonyls of *2,2*-**3** is also attributed to through-space PC coupling. If this interpretation is correct, then these through-space couplings in **3** would also be consistent with severe steric interactions between the radial PMe_3 groups and the radial carbonyls on tungsten. Similar through-space PC coupling has been recently reported for $W(CO)_5(\eta^1\text{-}PPh_2CH_2PPh_2)$.[32]

Buchner and Schenk have measured the W couplings to the ^{13}C NMR resonances of the carbonyls in 23 complexes of the type $W(CO)_5(L)$.[31] The coupling to the resonance due to the radial carbonyls varied over the narrow range 124.0−131.6 Hz, whereas the couplings to the resonance due to the carbonyl trans to L ranged from 149 Hz for $[W(CO)_5(H)]^-$ to 175.8 Hz for $[W(CO)_5(I)]^-$. In **3** the coupling to the signals attributed to the radial carbonyls of each isomer are ∼125 Hz. The trans WC coupling in *2,2*-**3** is 178 Hz, and in *3,3*-**3** it is 167 Hz. The trans coupling is 179.1 Hz in $(Me_3P)(OC)_4OsW(CO)_5$. That these trans WC couplings are, with the exception of that in *3,2*-**3**, outside the previous known range illustrates the unusual character of these 18e ligands.

The resonances between δ 175 and 200 are attributed to carbonyls bound to the osmium atom (e.g., Figure 6). The triplet (of intensity 1) to highest field (at δ 179.1) is assigned to the carbonyl trans to the dative OsW bond of *3,2*-**3**. It has been observed previously that the resonances of carbonyl ligands trans to dative metal−metal bonds occur at unusually high fields.[2,3,9] The triplet of intensity 2 at δ 198.7 is attributed to the equatorial Os−CO ligands of *3,2*-**3**. The doublet of doublets centered at δ 187.7 is readily assigned to the Os−CO of *2,3*-**3** that is both cis and trans to a PMe_3 ligand on the basis of the large (70.2 Hz) and small (4.6 Hz) couplings to the signal and its intensity of 1.

The remaining peak at δ 196.7 of intensity 2 is therefore assigned to the two radial carbonyls on the Os atom of *2,3*-**3** that are chemically equivalent. The resonance of these carbonyls in all the complexes studied here (Table 2; Figures 6 and 7) is a doublet rather than the expected doublet of doublets due to coupling to two chemically different P atoms. In other words, one of the two-bond PC couplings is unobservable even though both phosphorus atoms are nominally in cis positions in the axial, radial isomer. But as is found in the crystal structures of these complexes, the carbonyls in question lean toward the W atom and the P(1)−Os−C(radial) angle opens to between 97.9(3)° and 104.7(3)° (Tables 5 and 6) and evidently causes the coupling to drop to zero. This type of angular dependence of two bond PC coupling has been observed previously.[26,33-35] For example, in clusters of formula $Os_3(CO)_{11}(PR_3)$ (the PR_3 ligand is in an equatorial site of the triangular Os_3 skeleton) the (cis) PC coupling to the axial carbonyls of the $Os(CO)_3(PR_3)$ unit is in the range 5.9−13.7 Hz. On the other hand, the coupling to the equatorial carbonyl is not detectable.[26,34,35] The P−Os−CO(*eq*) angle in these clusters is normally in the range 95−102°. This is because the opposing OsOsOs angle is close to 60°, required by the triangular geometry of the metal nucleus.[23,26,36]

Of the three mechanisms by which nuclear spin coupling occurs, the mechanism that involves Fermi contact interaction between nuclear moments and electron spins in s orbitals is believed to be the most important.[29,37] The theoretical estimation of the size of the Fermi contact term involves mixing in contributions from excited electronic triplet states with the ground singlet state. For $^2J_{PP}$ couplings, it is assumed that an excitation from an orbital to another of the same symmetry makes a negative contribution to the coupling, whereas a transition involving orbitals of opposite symmetry produces a positive contribution. In this way, it has been possible to rationalize why cis $^2J_{PP}$ couplings in metal complexes are usually negative whereas the corresponding trans couplings are usually positive.[29,37] As originally suggested by Carty and co-workers, it is therefore probable that the cis $^2J_{PC}$ parameters in organometallic molecules are also negative whereas the trans couplings are positive.[33] (Note there is a phase change of the lobe of the π MO of the metal atom that links the C and P atoms when the configuration is changed from cis to trans.) If this is the case, there must be an angle between 90° and 180° where the negative and positive contributions to the coupling exactly cancel. If this is assumed and that the coupling constant $^2J_{PC}$ follows a simple linear relationship with the P−Os−C angle, then by using the values of the cis and trans coupling constants in these complexes, a value of ∼103° for the P−Os−C angles is obtained where the coupling constant should be zero. These values are in agreement with the angles found in the X-ray structures for these compounds (Tables 5 and 6). The results indicate that the distorted octahedral geometry observed for the Os atom in the solid state structures of the $(R_3P)_2(OC)_3OsM(CO)_5$ complexes is also maintained in solution.

Of related interest is that the (cis) $^2J_{PP}$ coupling constants in **1Cr** and **1W** are also unobservable, whereas in the derivatives with nonchelate P ligands this coupling is in the range 17.5−34.3 Hz. Because of the small bite angle of the dmpe ligand, the P−Os−P angles in **1Cr** and **1W** are ∼83°, whereas in the compounds with monodentate P ligands in axial and radial sites this angle ranges from 91.52(4)° to 95.1(1)°.

Carbonyl Exchange in the $(R_3P)_2(OC)_3OsW(CO)_5$ Complexes. The ^{13}CO-enriched samples used to obtain the ^{13}C NMR spectra were prepared by the addition of the appropriate unenriched $Os(CO)_3(PR_3)_2$ compound to ^{13}CO-enriched $W(CO)_5(THF)$. It is apparent from Figures 6 and 7 that the C-13 label is equally distributed over all carbonyl sites, which indicates that CO exchange occurs in **9** and **5** on the synthetic time scale. This behavior was observed for all complexes studied by ^{13}C NMR spectroscopy (Table 2). Isomerization and

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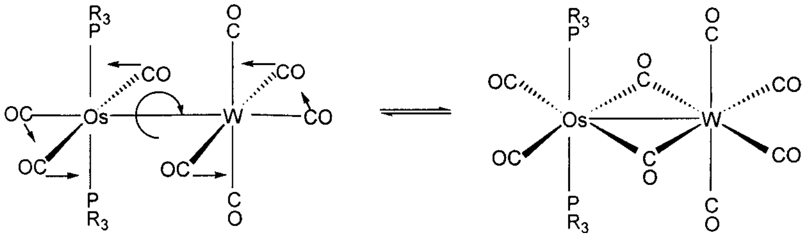
Scheme 1



carbonyl scrambling are common properties of complexes with dative metal–metal bonds.[2,3] In $(\eta^5\text{-}C_5R_5)(OC)_2IrW(CO)_5$ (R = H, Me) carbonyl exchange is so rapid at, or just below, room temperature that it can be detected by NMR line-broadening techniques.[38]

For CO exchange to occur between the two metals, bridging carbonyls must of course be involved. The well-known merry-go-round CO-exchange mechanism along with free rotation about the Os–W bond in *3,2*-$(R_3P)_2(OC)_3OsW(CO)_5$ exchanges all carbonyls as shown in Scheme 1. The polar nature of the dative metal–metal bond probably facilitates the formation of the bridged intermediate as originally proposed by Cotton for $(\eta\text{-}C_5H_5)(OC)_2V(\mu\text{-}CO)_2V(CO)(\eta\text{-}C_5H_5)$.[39] Of interest is that the preparation of **1Cr** and **1W** from $Os(CO)_3(dmpe)$ and ^{13}CO-enriched $M(CO)_5(THF)$ also yielded products with the C-13 label equally scrambled over all carbonyl sites. For the above mechanism to exchange the carbonyls that are cis to both P ligands requires the intermediacy of the *3,3*-isomer (i.e., the cis-diradial form; Chart 1) in the exchange. Exchange of these carbonyls with the unique Os–CO can, however, be brought about by a localized twist mechanism at the osmium atom, which is proposed below to account for the isomerization in these compounds.

For $(OC)_5MnRe(^{13}CO)_5$ carbonyl exchange occurs at a detectable rate (4.7×10^{-5} s) at 65 °C ($\Delta G^{\ddagger}_{338} = 26.5$ kcal mol^{-1}).[40] This is considerably slower than in the $(R_3P)_2(OC)_3OsM(CO)_5$ complexes, but this may be due to the presence of the P ligands in the latter derivatives. It is known that CO exchange is considerably more facile in $Os_3(CO)_{11}(PR_3)$ clusters than in the parent carbonyl $Os_3(CO)_{12}$.[34,35]

Isomerization in $(R_3P)_2(OC)_3OsW(CO)_5$ Complexes. As previously discussed, the NMR results are consistent with the presence of two isomers in solution for most of the $(R_3P)_2(OC)_3OsM(CO)_5$ complexes studied, whereas the X-ray studies show there is only one form in the solid state. This suggested that the isomers are in dynamic equilibrium in solution at ambient temperatures. Experiments were therefore carried out to determine an approximate rate for the isomerization.

A solution of **3** in CD_2Cl_2 with added PPh_3 was prepared at −40 °C and a $^{31}P\{^1H\}$ NMR spectrum recorded at −40 °C as soon as possible after the preparation of the sample. The spectrum of **3** showed only the singlet due to the *3,2*-form, that is, the form found in the solid state. The sample was allowed to stand at −10 °C for ~3.5 h and then at 0 °C for a further 2 h. During this period $^{31}P\{^1H\}$ NMR spectra were recorded periodically of the reaction solution, which showed isomerization to the equilibrium mixture. From the NMR spectra in the initial stages of the reaction a rate of approximately 4×10^{-5} s^{-1} was estimated for the isomerization at −10 °C ($\Delta G^{\ddagger}_{263} = {\sim}21$ kcal mol^{-1}). A similar experiment was carried out with compound **2** except that a temperature of 0 °C was maintained throughout the experiment. In this case, the initial spectrum exhibited only the two doublets of *2,3*-**2** (along with the singlet due to the added PPh_3); the equilibration was judged to be complete after approximately 1 h, that is, somewhat faster than the equilibration of **3** (allowing for the difference in temperature of the two experiments). As expected from the reactions of **2** and **3** with PPh_3 described below, there was no signal due to $W(CO)_5(PPh_3)$ observed during the isomerizations. This indicates that the isomerization does not occur by complete dissociation into $W(CO)_5$ and $Os(CO)_3(PR_3)_2$ fragments.

Variable-temperature ^1H NMR spectra of **2** in *o*-xylene-d_{10} showed the onset of coalescence of the signals due to the two isomers above 100 °C. The coalescence of the CH_2 resonances due to *2,3*-**2** was judged to occur at just above 125 °C (the highest temperature investigated), from which a $\Delta G^{\ddagger}$ of ~22 kcal mol^{-1} at 127 °C for the isomerization was estimated. The ^1H NMR spectrum above 100 °C indicated extensive decomposition of **2** to $Os(CO)_3[P(OCH_2)_3CMe]_2$, as expected from the experiments described below.

The merry-go-round carbonyl exchange can also account for the isomerization in $(R_3P)(OC)_4OsM(CO)_5$ complexes, but it cannot bring about conversion of the two isomers observed for $(R_3P)_2(OC)_3OsW(CO)_5$ complexes. This is because the movement of one of the P ligands in the diradial isomer to the axial site requires the second PR_3 to bridge the two metals (Scheme 2). Ligands of the type PR_3 very rarely bridge two metal atoms, and there is no evidence for any $W-PR_3$ species in these reactions.

A mechanism that brings about isomerization of the *2,3* and *3,2* isomers is a 3-fold twist mechanism at the Os atom, as shown in Scheme 3. Such a mechanism has been implicated in the isomerization of a number of metal carbonyl derivatives.[41] We have also recently described the nondissociative rearrangement *mer,cis*-

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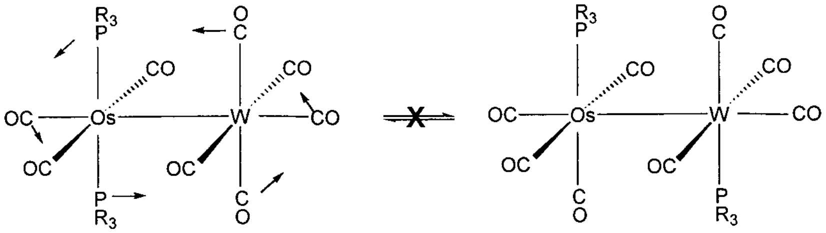
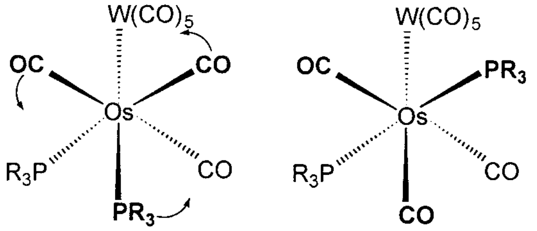
Scheme 2



Scheme 3



$Os(CO)_3(PMe_3)(Cl)_2$ to the *fac* form.[42] The geometry of the Os atom in these complexes approximates an edge-bridged trigonal bipyramid. The mechanism of isomerization might therefore be better described as intermediate between a trigonal twist mechanism typical of an octahedral molecule and the turnstile rotation mechanism postulated to take place in some trigonal bipyramidal complexes.[43]

Conversion of one $M'_2(CO)_{10-n}(PR_3)_n$ ($M' = Mn, Re$; $n = 1-3$) isomer to a second form has been occasionally observed. The *diax* and *ax,rad* forms of $Re_2(CO)_8(PMe_2Ph)_2$ are in equilibrium in solution at 80 °C.[44] Nubel and Brown found that 1,2-*rad,rad*-$Re_2(CO)_8(L)_2$ (L = PMe_3, $P(OMe)_3$, or $P(OPh)_3$) were stable in solution at 25 °C for at least a day, whereas 1,2-*ax,rad*-$Re_2(CO)_8(L)_2$ (L = $PBu^n{}_3$, PPh_3) isomerized to the diaxial isomer under the same conditions.[45] These observations indicate that the barriers to isomerism in the group 7 derivatives are also much higher than for the $(R_3P)_2(OC)_3OsW(CO)_5$ complexes.

Isomer Ratios for $(R_3P)_2(OC)_3OsW(CO)_5$ Complexes. The approximate *2,3*/*3,2* isomer ratios for the $(R_3P)_2(OC)_3OsW(CO)_5$ complexes in CD_2Cl_2 as determined by $^{31}P\{^1H\}$ NMR spectroscopy are given in Table 1. The effect of solvent on the isomer distribution was not investigated in detail. It was, however, observed that the *2,3*/*3,2* ratio for **2** in CD_2Cl_2 was 1.7, whereas in the less polar toluene-d_8 the ratio had decreased to 0.2 (i.e., more of *3,2*-**2** is present in toluene). For this reason, the crystal structure of **2** that had been recrystallized from toluene was determined. The only crystals that were suitable for X-ray crystallography revealed they were also the *2,3* isomer.

Of the complexes studied, only for **3** is the *3,2* (i.e., *dirad*) isomer more prevalent in CD_2Cl_2 solution, and **3** was the only derivative found by X-ray crystallography to be the *3,2* form in the solid state. The stability of this form was unexpected given that axial/radial ratio for $(Me_3P)(OC)_4OsW(CO)_5$ in CH_2Cl_2 is 3.3.[2] For a rationalization of the isomer distribution in **3** and other $(R_3P)_2(OC)_3OsW(CO)_5$ complexes account must be taken of all the various steric and electronic interactions in each isomer. Only the $W(CO)_5/PR_3$ (S(WP)) and the PR_3/PR_3 (S(PP)) steric interactions are, however, considered important. A particular bonding interaction will depend on the ligand trans to the bond.[46] The electronic preferences in each isomer can therefore be expressed in three terms of the type T(X,Y) where X and Y are the atoms trans to each other. The important energy terms (*E*) of each form are therefore

$$E(2,3) = S(WP) + S(PP) - [T(WP) + T(PC) + T(CC)]$$

$$E(3,2) = 2S(WP) - [T(WC) + T(PP) + T(CC)]$$

$$E(3,3) = 2S(WP) + S(PP) - [T(WC) + 2T(PC)]$$

The *3,3* compound is the least preferred from steric considerations and is not observed for the $(R_3P)_2(OC)_3OsW(CO)_5$ complexes. The *3,3* form is however the predominant form in solution for $(OC)_3(Bu^tNC)_2OsW(CO)_5$, and the *2,3* isomer is not observed.[3]

The difference in these terms for the *3,2* (*dirad*) and *2,3* (*ax,rad*) configurations is

$$[S(WP) - S(PP)] - [T(WC) + T(PP) - T(WP) - T(PC)]$$

The preference for the *3,3* form of **3** may be because S(WP) is smaller than S(PP). A steric argument cannot however be used to rationalize why **4** has the sterically undemanding $P(OCH_2)_3CMe$ in the axial site (Figure 5). The electronic terms would be dominant in molecules where steric interactions are small (as in $(OC)_3(Bu^tNC)_2OsW(CO)_5$) or where S(WP) is approximately equal to S(PP).

In terms of both σ- and π-bonding considerations, T(PC) (i.e., a P donor ligand trans to a carbonyl) is expected to be more preferred (more negative) than T(PP). This leads to the conclusion that, in the absence of steric effects, in order for the *3,2* isomer to be preferred, T(WC) must be greater (in a negative sense) than T(WP). It might have been expected from σ-bonding arguments that there would be a preference for the strong σ-donor P-ligand to be trans to the dative OsW bond, but this appears not to be the case in these compounds. That T(WC) is apparently more negative than T(WP) can, however, be rationalized with π bonding arguments. There is expected to be repulsive dπ–

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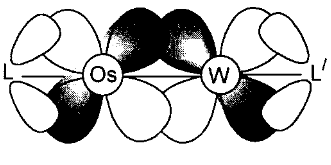
Chart 3



dπ interactions across the OsW bond that would be minimized by having strong π acceptor ligands in both sites trans to the bond (as shown in Chart 3).[2,3,9] This should also increase the back-bonding to the two ligands trans to the OsW bond. Consistent with this view is that the OsC distance trans to the OsW bond in **3** is considerably shorter than the other Os−CO distances (1.906(7) vs 1.942(4)(1) Å). Furthermore, in all the structures the WC bond to the carbonyl trans to osmium is significantly shorter than the other WC bonds (Tables 5 and 6).

That *3,2*-$(OC)_3(Me_3P)_2OsW(CO)_5$ is slightly thermodynamically preferred over the *2,3* form could in part be attributed to an electronic preference to have a carbonyl ligand (i.e., a strong π-acceptor ligand) trans to the dative OsW bond. Likewise, this argument can explain why the better π-acceptor phosphite ligands have some preference for the axial site over PMe_3.

Trimethylphosphine is a strong donor ligand, and in **3** these ligands would be expected to expand the Os 5d orbitals and thereby increase the OsW dπ−dπ repulsive interactions. Because of the increased dπ−dπ interactions, $Os(CO)_3(PMe_3)_2$ (or $Os(CO)_3[Me_2P(CH_2)_2PMe_2]$) might be a weaker donor ligand than $Os(CO)_4(PMe_3)$ even if steric effects were neglected.

The arguments presented here might be useful in the rationalization of the unusual isomer distribution in compounds of formula $M'_2(CO)_{10-n}(L)_n$ ($L = PR_3$, $n = 1-3$: L = CNR, $n = 1-4$).[44,45,47,48] In many of these complexes, however, it has not been established that the isomer observed is the thermodynamically preferred form. Furthermore, the M′M′ bond lengths in $M'_2(CO)_{10-n}(L)_n$ ($n = 0, 1, 2$) complexes are insensitive to the nature of L.[44,48]

Reaction of 2, 3, and 5 with PPh_3. Solutions of **2**, **3**, and **5** in CH_2Cl_2 each with an excess of PPh_3 were stirred at room temperature; the solutions were monitored periodically by IR spectroscopy over 44 h. After this period, in all cases there were intense bands due to $W(CO)_5(PPh_3)$ (at 2072 (m), 1975 (m), 1938 (s) cm^{-1}).[2,17,49] For the reactions that involved **3** and **5** the strong peak due to the mononuclear Os complex (i.e., $Os(CO)_3(PR_3)(PR'_3)$) was also clearly visible, consistent with the simple displacement of the Os ligand by PPh_3 (eq 6).

$$(R_3P)_2(OC)_3OsW(CO)_5 + PPh_3 \xrightarrow{25\ ^\circ C} Os(CO)_3(PR_3)_2 + W(CO)_5(PPh_3) \quad (6)$$

For **2**, this peak (at 1930 cm^{-1}) would have been obscured by those of **2** and $W(CO)_5(PPh_3)$, but strong absorptions at 1919 and 1891 cm^{-1} suggested the formation of $Os(CO)_3(PPh_3)[P(OCH_2)_3CMe]$ in this reaction. In the reaction of **3** there were also medium−weak bands at 2034 and 2017 cm^{-1} attributed to $Os(CO)_2(PMe_3)_2(Cl)_2$ and $Os(CO)_2(CO_3)(PMe_3)_2$, respectively, due to reaction of $Os(CO)_3(PMe_3)_2$ with CH_2Cl_2 and with oxygen, respectively, that has been mentioned above.[12] The cleavage of **5** by PPh_3 was a relatively clean reaction, the IR spectra of which showed reasonable isosbestic points after 68 h (Supporting Information).

For the reaction that involved **2**, the solution after 44 h had IR bands due to the starting material that were equally as strong as those of $W(CO)_5(PPh_3)$; for **3** there were no CO stretches due to the starting material, whereas for the experiment with **5** there were only very weak IR peaks arising from the binuclear precursor. These observations are consistent with the view that the OsW bond strengths decrease in the order **2** > **5** > **3,** and this is the order one might have predicted on the basis of steric arguments and the OsW bond lengths in these complexes.

The $(Me_3P)(OC)_4OsW(CO)_5$ complex also undergoes cleavage with PPh_3 in solution to give $W(CO)_5(PPh_3)$. (The reaction is complete in 30 min if the reaction is irradiated with blue light.)[17] The thermal reaction is, however, much slower than that of **3**, with IR bands due to the starting complex still visible after 9 days.[17] It should be pointed out, however, that the latter experiment was carried out in benzene rather than dichloromethane and in the dark with rigorous exclusion of oxygen. We have some evidence that complexes with dative osmium−metal bonds are somewhat less stable in the presence of trace oxygen, but this has not been thoroughly investigated.

Conclusions

Complexes of formula $(R_3P)_2(OC)_3OsM(CO)_5$ (M = Cr, W) appear less stable than the $(R_3P)(OC)_4OsM(CO)_5$ analogues, especially for the Cr derivatives, where only the $Os(CO)_3[P(OCH_2)_3CMe]_2$ and $Os(CO)_3(dmpe)$ derivatives could be prepared. On the basis of the bonding properties of the PR_3 and CO ligands, $Os(CO)_3(PR_3)_2$ might have been expected to be a better donor ligand than $Os(CO)_4(PR_3)$. There are, however, other subtle electronic factors that may work to nullify the increased basicity of the bis-substituted molecule. The presence of the second PMe_3 would increase the electron density on the Os atom, which would result in expansion of the valence orbitals of osmium. This in turn would increase the dπ−dπ repulsive interactions between the metal atoms and weaken the metal−metal bond (Chart 3). Reorganizational energy is needed to go from the uncomplexed five-coordinate state to the complexed six-coordinate geometry of the donor moiety, and this might be greater for $Os(CO)_3(PR_3)_2$ than for the monosubstituted compound.[9,15] There is also the requirement in the $(R_3P)_2(OC)_3OsM(CO)_5$ complexes that one bulky PR_3 ligand be cis to the OsM bond, and this will increase

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the steric interactions in the $(R_3P)_2(OC)_3OsM(CO)_5$ complexes compared to those in the $(R_3P)(OC)_4OsM(CO)_5$ compounds. Increased steric repulsions may be the major cause of decreased stability of the bis-substituted products, but such interactions cannot explain the isomer distribution in $(R_3P)_2(OC)_3OsM(CO)_5$ compounds.

In solution the $(R_3P)_2(OC)_3OsW(CO)_5$ derivatives undergo intramolecular CO exchange and isomerism on the synthetic time scale. Such behavior is also observed for the $(R_3P)(OC)_4OsW(CO)_5$ analogues.[2] Carbonyl exchange in binuclear metal carbonyl compounds is common, but it is of interest that such exchange in $MnRe(CO)_{10}$ only occurs at a measurable rate at 65 °C.[40]

The isomer distribution found for the $(R_3P)_2(OC)_3OsM(CO)_5$ complexes in solution was unexpected. For example, in CH_2Cl_2 solution the *dirad* isomer of $(Me_3P)_2(OC)_3OsW(CO)_5$ was slightly more favored over the *ax*,*rad* form; the *dirad* form is also the structure adopted in the solid state. It is proposed that if the steric repulsions in the various isomers are roughly comparable, then the best π-acceptor ligand will adopt the site trans to the dative metal−metal bond since it reduces the $d\pi - d\pi$ repulsions between the metal atoms. This also explains why for the $(phosphite)(OC)_3(Me_3P)OsW(CO)_5$ complexes there is a preference for the phosphite ligand to occupy the least sterically hindered site (i.e., trans to the OsW bond) even when the phosphite has a smaller cone angle than the trimethylphosphine ligand.

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Supporting Information Available: Figures showing structures of **1W** and **5** and IR spectra of the reaction of **5** with PPh_3; tables of crystal structure and refinement data, atomic coordinates, thermal parameters, bond lengths and angles for compounds **1Cr**, **1W**, **2**, **3**, **4**, **5**, synthetic and IR data for $Os(CO)_3(PR_3)(PR'_3)$ complexes, and analytical and IR data for $(R_3P)_2(OC)_3OsM(CO)_5$ (M = Cr, W) complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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