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Synthesis and Reactivity Studies of the Stable Bimetallic Formyl Complexes $[(CO)_4W(\mu\text{-}PPh_2)_2Os(CHO)(CO)_2(PR_3)]^-$. Crystal and Molecular Structure of a Methylation Product $(CO)_4\overline{W(\mu\text{-}PPh_2)(\eta^2(P,C)\text{-}\mu\text{-}PPh_2CHOMe)Os}(CO)_2(PMePh_2)$ Which Derives by Coupling of Phosphido and Carbene Ligands

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Abstract: The binuclear complex $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Os}(CO)_3$ has been prepared by the reaction of $Li_2[W(CO)_4(PPh_2)_2]$ with $Os(CO)_4Br_2$. It reacts with L = PMe_3 and $PMePh_2$ to give the adduct complexes $(CO)_4W(\mu\text{-}PPh_2)_2Os(CO)_3L$. These in turn react with $[BHEt_3]^-$ to give the binuclear formyl complexes $[(CO)_4W(\mu\text{-}PPh_2)_2Os(CHO)(CO)_2L]^-$. These are stable at elevated temperatures with the PMe_3 derivative decomposing at 78 °C with $t_{1/2}$ = 4.3 h by loss of CO to give the hydride complex $[(CO)_4W(\mu\text{-}PPh_2)_2OsH(CO)_2(PMe_3)]^-$. The $PMePh_2$ derivative decomposes at 110 °C via competing CO and $PMePh_2$ loss to yield a mixture of $[(CO)_4W(\mu\text{-}PPh_2)_2OsH(CO)_2L]^-$ with L = CO and $PMePh_2$. Protonation of the formyl complexes leads to conversion of one μ-PPh_2 ligand into a PPh_2H ligand and migration of hydride to Os to give complexes of the type $(CO)_5\underline{W(\mu\text{-}PPh_2)Os}H(CO)_2(PR_3)(PPh_2H)$. Reaction of the formyl complexes with $[(CH_3)_3O]BF_4$ gives the derivatives $(CO)_4\overline{W(\mu\text{-}PPh_2)(\eta^2(P,C)\text{-}\mu\text{-}PPh_2CHOMe)Os}(CO)_2(PR_3)$ in which the μ-PPh_2CHOMe ligand derives by coupling of carbene and phosphido ligands. The $PMePh_2$ derivative has been characterized by a complete single-crystal X-ray diffraction study. It crystallizes in the space group $P2_1/n$ with a = 13.907 (3) Å, b = 13.367 (2) Å, c = 24.344 (5) Å, β = 90.60 (2)°, V = 4525 (3) Å^3, and Z = 4. The structure has been refined for the 4967 reflections with $I > 2.5\sigma(I)$ to R_1 = 0.037 and R_2 = 0.042. The W and Os atoms are joined by a direct single metal–metal bond (3.022 (1) Å) and bridged by μ-PPh_2 and $\eta^2(P,C)$-μ-PPh_2CHOMe ligands. The W is further coordinated by four CO's and the Os by two CO's and a $PMePh_2$ ligand. Complexes similar to the methylation products with $\eta^2(P,C)$-μ-$PPh_2CHOC(O)Me$ ligands derive from treatment of the formyl complexes with acetyl chloride.

Binuclear and polynuclear formyl complexes[1] are of interest because the possibility exists that the reactive formyl ligand may be stabilized by simultaneous coordination to two or more metals[2] and their chemistry may differ significantly from that of mononuclear formyl complexes. For example, in our initial studies in this area[3] we demonstrated that the formyl ligand in $[Os_3(CO)_{11}(CHO)]^-$ is readily converted into a μ-CH_2 ligand in $Os_3(CO)_{11}(\mu\text{-}CH_2)$.[3] Similar reactions with mononuclear formyl complexes do not lead to methylene-containing products.

We are in the process of preparing further examples of binuclear and polynuclear formyl compounds and examining their reactivity characteristics.[4,5] Osmium seems an excellent choice for one or all the metals in such compounds since both mononuclear and polynuclear Os formyl complexes have been demonstrated to be sufficiently stable for further study.[3,5,6] Herein we describe the synthesis, stability, and reactivity properties of one class of binuclear phosphido-bridged WOs formyl complexes, $[(CO)_4W(\mu\text{-}PPh_2)_2Os(CHO)(CO)_2(PR_3)]^-$. One of the unique aspects of this chemistry involves methylation and acylation of the formyl ligand leading to products in which the resultant carbene ligands couple with bridging phosphido ligands.[7]

Experimental Section

$W(CO)_4(PPh_2H)_2$ was prepared by the literature method,[4,8] and $Os(CO)_4Br_2$ was synthesized by a modification of the procedure of Calderazzo,[9] using 1700 psi 3:1 CO/H_2 pressure and heating at 165 °C for 48 h. $PMePh_2$, PMe_3 (Strem), MeLi, $[(CH_3)_3O]BF_4$, $CH_3C(O)Cl$, $Li[BEt_3H]$, and $Li[BEt_3D]$ (Aldrich) were used as received without further purification. Unless otherwise specified, all operations were performed under a prepurified N_2 atmosphere using rigorously dried and deoxygenated solvents and standard Schlenk techniques. The spectroscopic instruments employed in this research have been previously described.[4] Field desorption (FD) mass spectra were recorded by Robert Hale at the Tennessee Eastman Co., Kingsport, Tenn. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Synthesis of $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Os}(CO)_3$, 1. MeLi (2.85 mL of a 1.2 M solution in tetrahydrofuran (THF)) was added to a solution of $W(CO)_4(PPh_2H)_2$ (1.114 g, 1.71 mmol) in 70 mL of THF in a 100-mL Schlenk flask and stirred for 5 min to generate $Li_2[W(CO)_4(PPh_2)_2]$ in situ. The resultant orange solution was added via cannula to a solution of $Os(CO)_4Br_2$ (1.607 g, 1.71 mmol) in 130 mL of THF in a 500-mL Schlenk flask. This red solution was heated at reflux for 1 h, cooled, and rotary evaporated in air leaving a red oil. The oil was dissolved in a minimum of CH_2Cl_2 and adsorbed onto 2 g of SiO_2 by rotary evaporation. This silica was loaded midway down a glass chromatography column. Elution with hexane afforded a yellow fraction containing mostly $W(CO)_5(PPh_2H)$, followed by an orange fraction of **1**. Complex **1** was isolated as an orange, air-stable microcrystalline solid in 65% yield (1.045 g, 1.11 mmol) by solvent evaporation from this fraction: MS, m/e (EI) 940 (M^+), 912 ($M^+ - CO$), 884 ($M^+ - 2CO$), 856 ($M^+ - 3CO$), 828 ($M^+ - 4CO$), 800 ($M^+ - 5CO$), 772 ($M^+ - 6CO$), 744 ($M^+ - 7CO$); IR (CH_2Cl_2) ν_{CO} 2040 (s), 2010 (s), 1950 (sbr), 1930 (s), (hexane 2039 (s), 2010 (s), 1962 (msh), 1954 (vs), 1937 (m). Anal. Calcd for $C_{31}H_{20}O_7OsP_2W$: C, 39.57; H, 2.13. Found: C, 39.55; H, 2.35.

Synthesis of $(CO)_4W(\mu\text{-}PPh_2)_2Os(CO)_3(PMePh_2)$, 2. Compound **1** (900 mg, 0.958 mmol) was dissolved in 25 mL of acetone in air in a

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400-mL beaker. This was placed in the back of a fume hood, and $PMePh_2$ (266 μL, 1.437 mmol) was added. After evaporation of the acetone, the residue was suspended in 25 mL of acetone and again allowed to evaporate in the fume hood. This procedure was repeated four times, and then the yellow residue was collected on a medium porosity frit and washed with 2 × 20 mL of benzene, 2 × 10 mL of hexane, and 1 × 2 mL of CH_2Cl_2, and dried in vacuo for 12 h. This afforded **2** as a yellow powder in 95% yield (1.038 g, 0.910 mmol). Recrystallization from acetone/hexane afforded an analytically pure sample: MS, *m/e* (FD) 1112 (M^+ – CO); IR (CH_2Cl_2) ν_{CO} 2105 (w), 2030 (s), 2020 (msh), 1998 (s), 1885 (sh), 1875 (s), 1840 (s) cm^{-1}. Anal. Calcd for $C_{44}H_{33}O_7OsP_3W$: C, 46.32; H, 2.89. Found: C, 46.24; H, 2.84.

Synthesis of $(CO)_4W(\mu\text{-}PPh_2)_2Os(CO)_3PMe_3$, 3. Compound **1** (200 mg, 0.213 mmol) was dissolved in a minimum of benzene and diluted with 70 mL of hexane in a 100-mL Schlenk flask to which was added PMe_3 (43 μL, 0.43 mmol). Irradiation, while stirring, with a Hanovia 450-W Hg arc lamp produced a yellow precipitate within minutes. After 20 min the solution was filtered under N_2 and the filtrate returned to the Schlenk flask and irradiated. This procedure was repeated six times. The air-stable yellow precipitate was collected on a medium porosity frit and washed with 2 × 10 mL of hexane and 1 × 2 mL of benzene and then dried in vacuo for 12 h to give **3** in 92% yield (217 mg, 0.196 mmol). Recrystallization from CH_2Cl_2/hexane afforded an analytically pure sample: MS, *m/e* (FD) 1016 (M^+); IR (CH_2Cl_2) ν_{CO} 2105 (w), 2030 (s), 2020 (msh), 1998 (s), 1887 (ssh), 1875 (s), 1844 (s) cm^{-1}. Anal. Calcd for $C_{34}H_{29}O_7OsP_3W$: C, 40.15; H, 2.85. Found: C, 39.99; H, 2.99.

Synthesis of $[Li(THF)_{1.5}][(CO)_4W(\mu\text{-}PPh_2)_2Os(CO)_2(CHO)(PMePh_2)]$, 4. Li[$BEt_3H$] (720 μL of a 1 M solution in THF) was added to a stirred suspension of **2** (500 mg, 0.357 mmol) in 5 mL of THF at 22 °C. All the solid dissolved within 5 min to give a clear orange solution. Ten milliliters of hexane was layered on top of the THF, and this mixture was placed in a freezer overnight. The yellow crystals that deposited were collected on a Schlenk frit under N_2, washed with 2 × 5 mL of hexane, and dried in vacuo for 1 h. This afforded **4** in 90% yield (404 mg, 0.321 mmol): IR (THF) ν_{CO} 1983 (s), 1963 (s), 1870 (sbr), 1830 (m), ν_{CHO} 1525 (w) cm^{-1}. Anal. Calcd for $C_{40}H_{46}LiO_{8.5}OsP_3W$: C, 47.77; H, 3.66. Found: C, 47.49; H, 4.29.

Synthesis of $[Li(THF)_x][(CO)_4W(\mu\text{-}PPh_2)_2Os(CO)_2(CHO)(PMe_3)]$, 5. Using a procedure identical with that to prepare **4**, complex **5** was prepared in 85% yield (189 mg, 0.167 mmol) from **3** (200 m, 0.197 mmol) and Li[BEt_3H] (300 μL of a 1 M solution in THF). This compound was isolated as a solid following the procedure for **4**, but satisfactory C, H analyses were not obtained because of apparent variable quantities of THF solvate present in the solid: IR (THF) ν_{CO} 1988 (s), 1958 (s), 1865 (sbr), 1825 (s); ν_{CHO} 1525 (w) cm^{-1}.

Thermal Decomposition of 4 and 5. Compound **4** (30 mg, 0.024 mmol) was dissolved in 1 mL of $(CD_3)_2SO$ in a 5-mm NMR tube. This was heated at 100 °C for 11 h, and the ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded. The products as identified by their NMR spectra were $PMePh_2$, $Li[(CO)_4W(\mu\text{-}PPh_2)_2Os(H)(CO)_3]$, **6** (~75% yield by NMR integration), and $Li[(CO)_4W(\mu\text{-}PPh_2)_2Os(H)(CO)_2(PMePh_2)]$, **7** (~25% yield). The thermal decomposition of **5** was also monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Both showed the formation of $Li[(CO)_4W(\mu\text{-}PPh_2)_2Os(H)(CO)_2(PMe_3)]$, **8**.

Synthesis $(CO)_4W(\mu\text{-}PPh_2)(\eta^2(P,C)\text{-}\mu\text{-}PPh_2CHOMe)Os(CO)_2PMePh_2$, 9. A solution of **4** in 30 mL of THF, generated from **2** (200 mg, 0.175 mmol) and Li[BEt_3H] (180 μL of a 1 M solution in THF), was reduced in vacuo to a yellow oil and redissolved in 10 mL of CH_3NO_2. This yellow suspension was transferred via cannula into a 100-mL Schlenk flask containing $[(CH_3)_3O]BF_4$ (26 mg, 0.176 mmol). The solution turned red immediately and was stirred for 10 min during which time a red solid precipitated. The CH_3NO_2 was removed in vacuo and the red residue recrystallized from CH_2Cl_2/pentane to yield air-stable red crystals of the $1.5CH_2Cl_2$ adduct of **9** (167 mg, 0.145 mmol) in 83% yield: MS, *m/e* (FD) 1156 (M^+); IR (CH_2Cl_2) ν_{CO} 2030 (s), 2000 (s), 1953 (s), 1905 (s) cm^{-1}. Anal. Calcd for $C_{46.5}H_{39}Cl_3O_7OsP_3W$: C, 43.47; H, 3.04. Found: C, 43.16; H, 3.25.

Synthesis of $(CO)_4W(\mu\text{-}PPh_2)(\eta^2(P,C)\text{-}\mu\text{-}PPh_2CHOMe)Os(CO)_2PMe_3$, 10. Complex **10** was synthesized from **3** (200 mg, 0.197 mmol) in a manner analogous to **9**. The removal of solvent in vacuo gave a red oil containing a mixture of isomers **10a** and **10b**. This was dissolved in THF and stirred for 12 days at 22 °C or for 12 h at reflux to give a yellow-orange solution. Chromatography on SiO_2 in the manner described for complex **1** with a 20% CH_2Cl_2/pentane eluant afforded a yellow fraction containing **10b** followed by a yellow band of an unidentified compound. Removal of solvent from the first fraction afforded **10b** as an air-stable yellow powder in 77% yield (156 mg, 0.151 mmol). Recrystallization from acetone/pentane afforded an analytically pure sample: MS *m/e* (FD) 1032 (M^+); IR (CH_2Cl_2) ν_{CO} 2026 (s), 1998 (vs), 1948 (s), 1906 (s) cm^{-1}. Anal. Calcd for $C_{35}H_{33}O_7P_3W$: C, 40.70; H, 3.20. Found: C, 40.36; H, 3.20.

Synthesis of $(CO)_4W(\mu\text{-}PPh_2)(\eta^2(P,C)\text{-}\mu\text{-}PPh_2CHOC(O)Me)Os(CO)_2PMePh_2$, 11. To a solution of **4** in 30 mL of THF, generated from **2** (250 mg, 0.219 mmol) and Li[BEt_3H] (225 μL of a 1 M solution in THF), was added CH_3COCl (15 μL, 0.222 mmol). The solution was stirred for 1 h after which time a red color persisted. Removal of solvent in vacuo followed by SiO_2 chromatography, in the manner described for **1**, using a 30% CH_2Cl_2/pentane eluant afforded a light yellow band of **1** followed by small red and yellow bands of unidentified compounds and then a red band of complex **11**. Removal of solvent gave **11** as a pink air stable powder (139 mg, 0.120 mmol) in 55% yield. Washing a sample of **11** with CH_2Cl_2, benzene, and then pentane afforded an analytically pure sample as a $0.5CH_2Cl_2$ solvate: IR (CH_2Cl_2) ν_{CO} 2030 (s), 2003, 1995 (sh), 1960 (s), 1900 (ssh), 1871 (sbr), and ν_{COCH_3} 1595 (w) cm^{-1}. Anal. Calcd for $C_{46.5}H_{38}ClO_8OsP_3W$: C, 45.64; H, 3.11. Found: C, 45.50; H, 3.10.

Synthesis of $(CO)_4W(\mu\text{-}PPh_2)(\eta^2(P,C)\text{-}\mu\text{-}PPh_2CHOC(O)Me)Os(CO)_2PMe_3$, 12. To a solution of **5** in 30 mL of THF, generated from **3** (220 mg, 0.216 mmol) and Li[BEt_3H] (220 μL of a 1 M solution in THF), was added CH_3COCl (15 μL, 0.222 mmol). This solution was stirred for 1 h after which time an orange color persisted. Removal of solvent in vacuo gave an orange oil of a mixture of isomers **12a** and **12b**. This was dissolved in THF and stirred for 8 days at 22 °C or 24 h at reflux to yield **12b** as the only detectable product. Subsequent removal of solvent by rotary evaporation gave an orange oil that was extracted with toluene (20 mL). The orange toluene extract was filtered and rotary evaporated to dryness. The orange residue was dried in vacuo for 12 h to give **12b** as an air stable orange powder (192 mg, 0.186 mmol) in 86% yield. Recrystallization from acetone/pentane afforded a pure sample. MS, *m/e* (FD) 1060 (M^+); IR (CH_2Cl_2) ν_{CO} 2027 (s), 2002 (s), 1958 (s), 1900 (ssh), 1875 (sbr), and ν_{COCH_3} 1599 (w) cm^{-1}. Anal. Calcd for $C_{36}H_{33}O_8OsP_3W$: C, 40.75; H, 3.11. Found: C, 40.64; H, 3.24.

Synthesis of $(CO)_5W(\mu\text{-}PPh_2)OsH(CO)_2(PPh_2H)(PMePh_2)$, 13. To a solution of **4** in 20 mL of THF, generated in situ from **2** (1.038 g, 0.910 mmol) and Li[BEt_3H] (2 mL of a 1 M solution in THF), was added 2 mL of glacial CH_3COOH. After the solution was stirred for 5 min, solvent was removed from the orange solution by rotary evaporation. The resultant orange oil was allowed to stand in air for 12 h and then extracted with toluene until the extracts were colorless. The combined toluene extracts were dried over $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation. The resultant orange microcrystals were dried in vacuo for 12 h to give $(CO)_5W(\mu\text{-}PPh_2)Os(H)(CO)_2(PPh_2H)(PMePh_2)$, **13**, in 87% yield (904 mg, 0.792 mmol). Recrystallization from CH_2Cl_2/hexane afforded analytically pure material: MS, *m/e* (FD) 1142 (M^+); IR (CH_2Cl_2) ν_{CO} 2060 (w), 2030 (w), 1997 (m), 1975 (w), 1920 (s), 1886 (m) cm^{-1}. Anal. Calcd for $C_{44}H_{35}O_7OsP_3W$: C, 46.23; H, 3.06. Found: C, 46.38; H, 3.29.

Synthesis of $(CO)_5W(\mu\text{-}PPh_2)OsH(CO)(PPh_2H)(PMe_3)$, 14. Using a procedure identical with that used to prepare **13**, reaction of **5** with glacial CH_3COOH led to the isolation of $(CO)_5W(\mu\text{-}PPh_2)Os(H)(CO)_2(PPh_2H)(PMe_3)$, **14**, in 85% yield as yellow microcrystals: IR (CH_2Cl_2) ν_{CO} 2060 (m), 2035 (w), 2000 (w), 1970 (w), 1915 (s), 1895 (ssh) cm^{-1}. Anal. Calcd for $C_{34}H_{31}O_7OsP_3W$: C, 40.07; H, 3.05. Found: C, 39.66; H, 2.97.

X-ray Diffraction Study of 9. Red crystals of **9** were grown by slow evaporation of a saturated CH_2Cl_2 solution of the complex. A crystal measuring 0.33 × 0.33 × 0.42 mm was mounted in an arbitrary orientation on a glass fiber that was then fixed into an aluminum pin and mounted onto a eucentric goniometer. Diffraction data were collected on an Enraf-Nonius four-circle CAD4 automated diffractometer controlled by a PDP 8a computer. The Enraf-Nonius program SEARCH was employed to obtain an orientation matrix for data collection and to provide cell dimensions.[10] Details of the data collection and reduction procedures have been previously described.[11] Pertinent crystal and intensity data are listed in Table I.

The W, Os, and P atoms were located by Patterson heavy-atom techniques. The coordinates of the remaining non-hydrogen atoms were determined by successive least-squares refinements and difference Fourier maps. Phenyl and methyl hydrogens were fixed at idealized positions best matching those found in a difference electron density synthesis (C–H bond length of 0.97 Å) with fixed isotropic temperature factors of *B* =

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(10) All programs used in this study are part of the "Enraf-Nonius Structure Determination Package (SDP plus, version 1)"; Enraf-Nonius: Delft, Holland, 1982.

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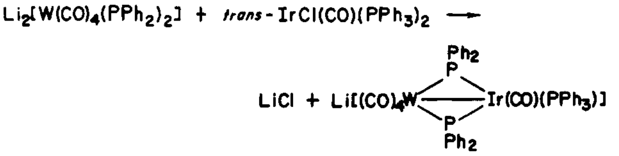
Table I. Crystallographic Summary for $(CO)_4W(\mu\text{-}PPh_2)(\eta^2(P,C)\text{-}\mu\text{-}PPh_2CHOMe)Os(CO)_2(PMePh_2)$, **9**

Crystal Data	
mol formula	$C_{45}H_{37}O_7OsP_3W$
crystal	monoclinic
space group	$P2_1/n$
a, Å	13.907 (3)
b, Å	13.367 (2)
c, Å	24.344 (5)
β, deg	90.60 (2)
V, Å^3	4525 (3)
Z	4
ρ(calcd), g cm^{-3}	1.799
abs coeff μ, cm^{-1}	56.73
T, °C	22
Measurement of Intensity Data	
diffractometer	Enraf-Nonius CAD4
radiation	Mo Kα (λ 0.71073 Å)
monochromator	graphite crystal
scan type	θ–2θ
scan speed, deg min^{-1}	variable 1–4
takeoff angle, deg	2.8
scan width, deg	(0.70 + 0.347 tan θ)
std reflctns	3 every 1 h
data limits, deg	$3.2 < 2\theta < 44.4$
reflctns measd	6258
unique data	5683
obsd data ($I > 2.5\sigma(I)$)	4967
anisotropic drift correction	0.943–1.076
R_1	0.037
R_2	0.042
esd	5.107
max shift/error	0.030

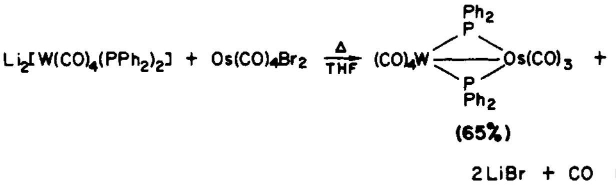
5.0 Å^2. In the final cycle, least-squares convergence was achieved upon refinement of the positional and anisotropic thermal parameters of all non-hydrogen atoms. The structure converged to $R_1 = 0.037$ and $R_2 = 0.042$ using unit weights. The residuals are defined as $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $R_2 = [\sum(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$. Final positional parameters are listed in Table II, and relevant bond distances and angles are summarized in Table III. Tables of thermal parameters, calculated hydrogen atom positions, complete bond lengths and angles, and structure factors are given in the supplementary material.

Results

Preparation and Characterization of $(CO)_4W(\mu\text{-}PPh_2)_2Os(CO)_3$, 1, and $(CO)_4W(\mu\text{-}PPh_2)_2Os(CO)_3L$ (2, L = $PMePh_2$; 3, L = PMe_3). We have previously demonstrated the preparation of phosphido-bridged binuclear complexes by the reaction of (diphenyl phosphido)carbonylmetalates with metal chlorides, e.g., eq 1.[4,12] This synthetic chemistry is easily extended to WOs complexes by reaction of $Li_2[W(CO)_4(PPh_2)_2]$, generated in situ by deprotonation of $W(CO)_4(PPh_2H)_2$, with $Os(CO)_4Br_2$ which gives the expected binuclear complex **1** in good yield (eq 2).



(1)



(2)

Table II. Atomic Positional Parameters for $(CO)_4W(\mu\text{-}PPh_2)(\eta^2(P,C)\text{-}\mu\text{-}PPh_2CHOMe)Os(CO)_2(PMePh_2)$, **9**

atom	x	y	z
CS	−0.01996 (3)	0.41221 (3)	0.13039 (2)
H	0.01154 (3)	0.19282 (3)	0.15433 (2)
P(1)	0.1094 (2)	0.3020 (2)	0.2177 (1)
P(2)	−0.1342 (2)	0.3035 (2)	0.1697 (1)
P(3)	−0.0951 (2)	0.5657 (2)	0.1400 (1)
O(1M)	0.1040 (5)	0.5115 (6)	0.2206 (3)
O(1)	−0.1167 (7)	0.0724 (8)	0.0694 (4)
O(2)	0.1214 (6)	0.2552 (7)	0.0461 (3)
O(3)	−0.0658 (7)	0.0672 (7)	0.2556 (4)
O(4)	0.1754 (7)	0.0308 (8)	0.1508 (4)
O(5)	−0.0887 (8)	0.3764 (8)	0.0118 (4)
O(6)	0.1674 (6)	0.4900 (7)	0.0832 (3)
C(2M)	−0.1204 (9)	0.6016 (9)	0.2108 (4)
C(1B)	0.0483 (7)	0.4244 (8)	0.2134 (4)
C(1M)	0.1146 (9)	0.5464 (10)	0.2752 (5)
C(1)	−0.0705 (9)	0.1155 (8)	0.1011 (5)
C(2)	0.0809 (8)	0.2432 (9)	0.0854 (5)
C(3)	−0.0411 (8)	0.1126 (9)	0.2188 (5)
C(4)	0.1156 (9)	0.091 (1)	0.1515 (5)
C(5)	−0.0685 (8)	0.3902 (9)	0.0564 (5)
C(6)	0.0973 (8)	0.4618 (9)	0.1017 (4)
C(10)	0.2369 (7)	0.3242 (8)	0.2026 (4)
C(11)	0.2783 (8)	0.298 (1)	0.1528 (5)
C(12)	0.375 (1)	0.312 (1)	0.1442 (6)
C(13)	0.4329 (9)	0.348 (1)	0.1852 (7)
C(14)	0.394 (1)	0.374 (1)	0.2342 (6)
C(15)	0.2963 (9)	0.363 (1)	0.2432 (5)
C(20)	0.1228 (8)	0.2524 (9)	0.2879 (4)
C(21)	0.0940 (9)	0.301 (1)	0.3353 (5)
C(22)	0.107 (1)	0.251 (1)	0.3863 (5)
C(23)	0.145 (1)	0.158 (1)	0.3891 (5)
C(24)	0.175 (1)	0.110 (1)	0.3430 (6)
C(25)	0.1619 (8)	0.1564 (9)	0.2927 (5)
C(30)	−0.1838 (7)	0.3258 (8)	0.2378 (4)
C(31)	−0.2734 (8)	0.368 (1)	0.2436 (5)
C(32)	−0.3098 (9)	0.390 (1)	0.2948 (6)
C(33)	−0.253 (1)	0.373 (1)	0.3407 (6)
C(34)	−0.165 (1)	0.329 (1)	0.3369 (5)
C(35)	−0.1303 (8)	0.3042 (9)	0.2851 (5)
C(40)	−0.2422 (7)	0.2598 (9)	0.1334 (5)
C(41)	−0.2842 (9)	0.310 (1)	0.0895 (5)
C(42)	−0.366 (1)	0.273 (1)	0.0630 (7)
C(43)	−0.403 (1)	0.185 (1)	0.0806 (7)
C(44)	−0.365 (1)	0.133 (1)	0.1249 (7)
C(45)	−0.2834 (9)	0.171 (1)	0.1509 (6)
C(50)	−0.0322 (8)	0.6770 (8)	0.1150 (4)
C(51)	−0.0746 (9)	0.7472 (9)	0.0812 (5)
C(52)	−0.024 (1)	0.8307 (9)	0.0644 (6)
C(53)	0.070 (1)	0.845 (1)	0.0811 (6)
C(54)	0.113 (1)	0.775 (1)	0.1150 (6)
C(55)	0.064 (1)	0.693 (1)	0.1321 (5)
C(60)	−0.2120 (8)	0.5713 (8)	0.1053 (4)
C(61)	−0.2188 (8)	0.570 (1)	0.0425 (5)
C(62)	−0.306 (1)	0.571 (1)	0.0214 (5)
C(63)	−0.391 (1)	0.570 (1)	0.0516 (6)
C(64)	−0.3848 (9)	0.570 (1)	0.1084 (6)
C(65)	−0.2977 (9)	0.570 (1)	0.1356 (5)
C	0.218 (2)	0.549 (2)	0.489 (1)
CL(1)	0.1596 (6)	0.6612 (7)	0.5094 (3)
CL(2)	0.1327 (9)	0.500 (1)	0.4407 (5)

Complex **1** has been spectroscopically characterized. NMR data (^{31}P, ^1H) for it and all the new compounds described herein are summarized in Table IV. The mass spectrum of **1** shows a parent ion m/e (EI) 940 with fragment ions corresponding to the stepwise loss of seven carbonyl ligands. The $^{31}P\{^1H\}$ NMR spectrum of **1** shows a single resonance at δ 148.2 assigned to equivalent μ-PPh_2 ligands. The downfield position of this resonance implies the presence of a W–Os bond in **1**, consistent with the structure drawn in eq 2. It is now well established that when μ-PPh_2 ligands bridge two metals joined by a metal–metal bond their resonances appear downfield (δ 300–50) whereas when no metal–metal bond is present, upfield resonances (δ 50 to −300) are found.[13] However, there are exceptions to this correlation

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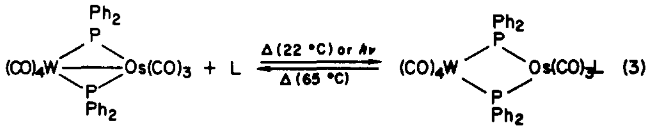
(12) (a) Breen, M. J.; Duttera, M. R.; Geoffroy, G. L.; Novotnak, G. C.; Roberts, D. A.; Shulman, P. M.; Steinmetz, G. R. *Organometallics* **1982**, *1*, 1008. (b) Breen, M. J.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1069.

Table III. Selected Bond Lengths (Å) and Angles (deg) in **9**

		Bond Lengths			
W–Os	3.022 (1)	W–C(3)	2.04 (1)	Os–C(5)	1.94 (1)
W–P(1)	2.521 (3)	W–C(4)	1.99 (1)	Os–C(6)	1.90 (1)
W–P(2)	2.538 (3)	Os–P(2)	2.357 (7)	P(1)–C(1B)	1.85 (1)
W–C(1)	2.01 (1)	Os–P(3)	2.314 (3)	O(1M)–C(1B)	1.14 (1)
W–C(2)	2.05 (1)	Os–C(1B)	2.24 (1)	O(1M)–C(1M)	1.42 (1)
		Bond Angles			
Os–W–P(1)	68.53 (7)	P(2)–W–C(1)	86.7 (3)	P(2)–Os–C(5)	92.8 (4)
Os–W–P(2)	49.22 (7)	P(2)–W–C(2)	107.8 (3)	P(2)–Os–C(6)	161.2 (4)
Os–W–C(1)	107.0 (3)	P(2)–W–C(3)	84.6 (3)	P(3)–Os–C(5)	94.1 (4)
Os–W–C(2)	65.9 (3)	P(2)–W–C(4)	170.4 (4)	P(3)–Os–C(6)	96.7 (4)
Os–W–C(3)	127.4 (3)	W–Os–P(2)	54.64 (7)	C(1B)–Os–P(3)	92.0 (3)
Os–W–C(4)	139.7 (4)	W–Os–P(3)	154.97 (7)	C(1B)–Os–C(5)	173.5 (4)
P(1)–W–P(2)	90.17 (9)	W–Os–C(1B)	80.5 (3)	C(1B)–Os–C(6)	86.8 (4)
P(1)–W–C(1)	175.6 (4)	W–Os–C(5)	94.7 (4)	W–P(1)–C(1B)	103.3 (3)
P(1)–W–C(2)	93.2 (4)	W–Os–C(6)	106.6 (4)	W–P(2)–Os	76.14 (8)
P(1)–W–C(3)	91.6 (4)	P(2)–Os–C(1B)	87.9 (3)	C(1B)–O(1M)–C(1M)	116.4 (8)
P(1)–W–C(4)	91.4 (4)	P(2)–Os–P(3)	101.6 (1)	P(1)–C(1B)–O(1M)	118.2 (7)
				Os–C(1B)–O(1M)	113.9 (6)

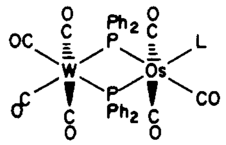
so caution must be exercised in its use.[14] A metal–metal bond in complex **1** is also necessary to give a satisfactory 18-electron count at each metal.

Compound **1** reacts with PMePh$_2$ and PMe$_3$ to afford derivatives in which the metal–metal bond is displaced and phosphine has added to the osmium center (eq 3). These phosphine derivatives were isolated in high yield and have been spectroscopically characterized. Resonances assigned to the μ-PPh$_2$ and PR$_3$ ligands are seen in the ^{31}P{^{1}H} NMR spectrum of each (Table IV) with coupling and ^{183}W satellite patterns consistent with their formulations. The upfield chemical shifts for the μ-PPh$_2$ ligands argue for the absence of metal–metal bonds in **2** and **3**,[13] as required for PR$_3$ addition without ligand loss. The absence of ^{183}W satellites on the PR$_3$ resonances in **2** and **3** also imply that these ligands are located on Os and not W. Also, the magnitude of the ^{31}P–^{31}P coupling constants imply that the added PR$_3$ ligand is trans to one μ-PPh$_2$ ligand and cis to the other in **2** and **3**; the structure drawn below is indicated.



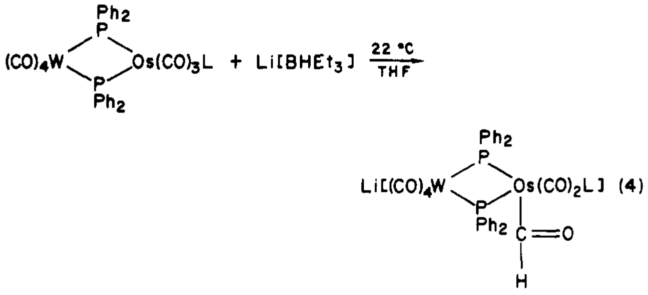
1

2, L = PMePh$_2$ (95%)
3, L = PMe$_3$ (92%)



Although both the ligand addition reactions of eq 1 occur under either thermal or photochemical conditions, we have found it most convenient to prepare **2** by a thermal procedure using excess phosphine and **3** via a photochemical route, as outlined in the Experimental Section. Interestingly, the ligand addition reactions of eq 3 are reversible. When complex **2** was heated in THF, complete dissociation of the PMePh$_2$ ligand occurred before the THF reached reflux, and **1** was quantitatively formed. Dissociation of PMe$_3$ from **3** is slower, requiring several hours at refluxing THF temperature for significant dissociation to take place.

Formyl Derivatives of 2 and 3. Complex **1** reacts with Li[BHEt$_3$] at –90 °C to give a very unstable formyl derivative, as evidenced by the appearance of an IR band at 1550 cm^{-1}. However, this species rapidly decomposes upon warming above –20 °C, and a complex mixture of unidentified products results. In contrast, the PR$_3$ derivatives **2** and **3** react cleanly with Li[BHEt$_3$] at 22 °C to afford formyl complexes **4** and **5** in high yield (eq 4). Complex **4** was isolated as a solid containing 1.5THF molecules per formula unit, but complex **5** was not isolated in pure form. Both **4** and **5** show formyl vibrations at 1525 cm^{-1}, and they have formyl ^{1}H NMR resonances at δ 15.1 (dd, $J_{^1\text{H}-^{31}\text{P}}$ = 24.1, 4.6 Hz) and δ 15.1 (t, $J_{^1\text{H}-^{31}\text{P}}$ = 9.4 Hz), respectively. The ^{31}P{^{1}H} NMR data (Table IV) are also consistent with the indicated formulations, each showing upfield resonances for the two nonequivalent μ-PPh$_2$ ligands and a third resonance assigned to the PR$_3$ ligand on Os. The available spectral data do not indicate to which metal, W or Os, the formyl ligand is bound. However, the reactivity data discussed below indicate its location on Os, as illustrated in eq 4.



4, L = PMePh$_2$ (90%)
5, L = PMe$_3$ (85%)

We have also observed that occasionally additional formyl ^{1}H NMR resonances at δ 15.4 (dd, J = 9.6, 10.8 Hz) and δ 15.2 (br m) are respectively seen upon reaction of **2** and **3** with [BHEt$_3$]$^-$, and we attribute these to isomers of **4** and **5**. The intensity of these minor formyl resonances are generally less than 5% the intensity of the major formyl resonances, although in one preparation of **4** the δ 15.4 (dd) resonance was ~65% the intensity of the δ 15.1 (dd) resonance. Low-intensity resonances are also apparent in the ^{31}P{^{1}H} NMR spectra of **4** and **5** that are similar in position and coupling patterns to the main resonances. These minor resonances are also present in the analytically pure sample of **4**. Although the data is not conclusive, we believe that the less abundant formyl complexes are geometrical isomers of the major complexes. In support of this suggestion, protonation of the solutions containing the isomers of **4** always gave complex **13** (see below, eq 10) in 80–87% yield, regardless of the relative ratios of the two isomers. In Table IV, the predominant isomers are denoted **4a** and **5a** with the less abundant isomers labeled **4b** and **5b**.

Thermal Decomposition of the Formyl Complexes 4 and 5. These formyl complexes are surprisingly stable. The ^{1}H NMR

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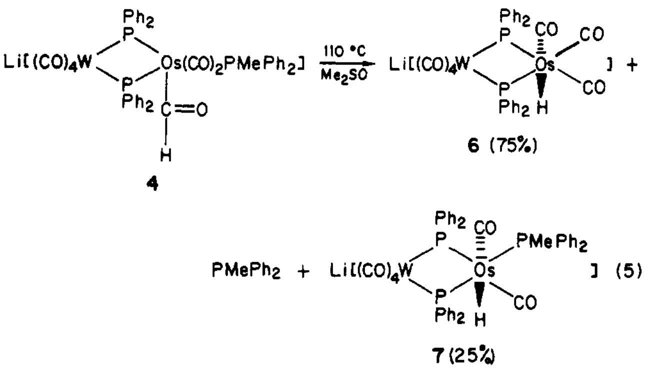
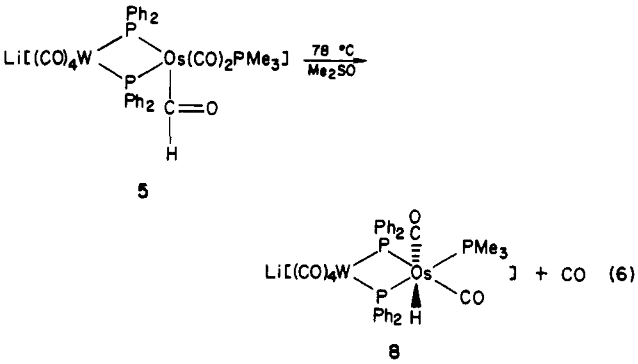
[13] (a) Petersen, J. L.; Stewart, R. P., Jr. *Inorg. Chem.* **1980**, *19*, 186. (b) Carty, A. J.; Machaughlin, S. A.; Taylor, N. J. *J. Organomet. Chem.* **1981**, *204*, C27. (c) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (d) Johannsen, G.; Stetzer, O. *Chem. Ber.* **1977**, *110*, 3438. (e) Carty, A. J. *Adv. Chem. Ser.* **1982**, *196*, 163.

[14] Jones, R. A.; Wright, T. C.; Atwood, J. C.; Hunter, W. E. *Organometallics* **1983**, *2*, 470.

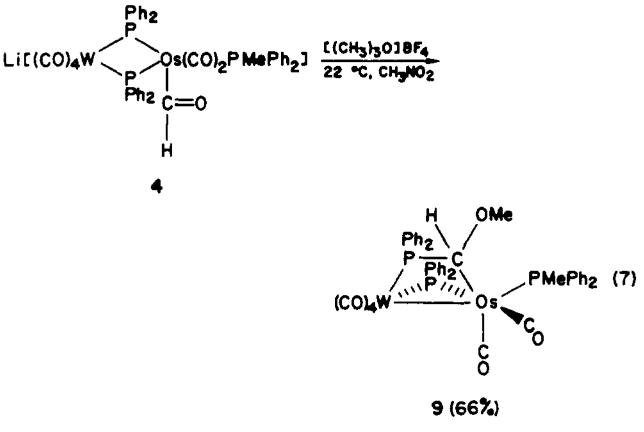
spectrum of a sample of **4** that had been heated to 65 °C for 1 h showed no decomposition. However, when heated at 110 °C for 11 h, a mixture of the hydride complexes **6** and **7** resulted along with free $PMePh_2$ (eq 5). Complexes **6** and **7** could not be separated but were characterized by their ^1H and $^{31}P\{^1H\}$ NMR spectra (Table IV). Both show hydride ^1H NMR resonances without ^{183}W satellites and the expected ^{31}P NMR pattern for the formulations given in eq 5. Complex **6** derives from **4** by $PMePh_2$ loss followed by hydride migration to Os, whereas **7** arises via CO dissociation.



The formyl complex **5** decays only by CO loss to give the hydride complex **8** as the sole detectable product (eq 6). At 78 °C this reaction proceeds with $t_{1/2}$ = 4.3 h. Spectroscopic data for **8** (Table IV) are consistent with the given formulation. In particular, the absence of ^{183}W satellites on the ^1H NMR hydride resonance of **8**, as well as the coupling of this ligand to all three phosphorus nuclei, imply its location on Os. The formation of *osmium hydride* products **6**, **7**, and **8** upon decomposition of the formyl complexes **4** and **5** is consistent with the formyl ligands in the latter complexes being located on Os.



Reaction of 4 and 5 with $[(CH_3)_3O]BF_4$. Treatment of formyl complex **4** with $[(CH_3)_3O]BF_4$ in CH_3NO_2 at 22 °C results in formation of complex **9** (eq 7). Complex **9** possesses a bridging $\eta^2(P,C)$-μ-PPh_2CHOMe ligand formed by coupling of a phosphido ligand with a methoxymethylene ligand, the latter generated by methylation of the formyl ligand. An ORTEP drawing of **9** is shown in Figure 1, and its spectroscopic data (Table IV) are consistent with the determined structure.



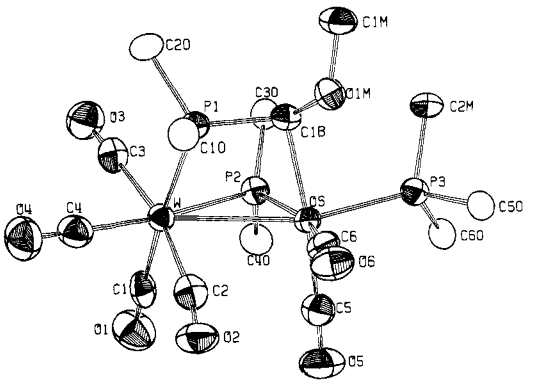
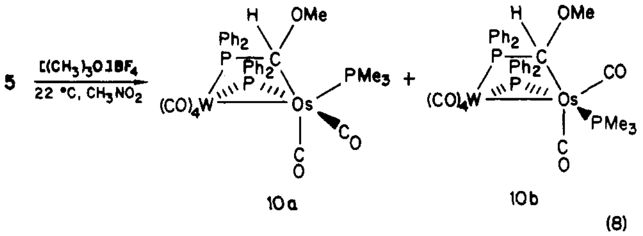
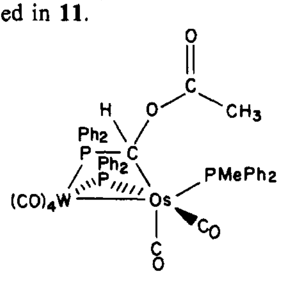


Figure 1. A view of the inner core of $(CO)_4W(\mu\text{-}PPh_2)(\eta^2\text{-}(P,C)\text{-}\mu\text{-}PPh_2CHOMe)Os(CO)_2(PMePh_2)$. The bridgehead carbons of the phosphorus phenyl rings are shown as open circles. Thermal ellipsoids are drawn at the 50% probability level. A drawing showing the complete atom-numbering scheme is given in the supplementary material.

Methylation of formyl complex **5** gives similar results except that two isomers of the product are formed (eq 8). Careful ^{31}P NMR monitoring showed that **10a** forms first and that it slowly converts to **10b** over a period of several days. The $^{31}P\{^1H\}$ NMR spectra of **10a** and **10b** (Table IV) are consistent with their formulations, but the magnitudes of the coupling constants indicate different stereochemistries at Os. Isomer **10a** gives a spectrum with coupling constants similar to **9**, implying a similar stereochemistry, with the PMe_3 ligand cis to both bridging ligands. In contrast, isomer **10b** shows a large (J = 139.7 Hz) ^{31}P–^{31}P coupling to the μ-PPh_2 phosphorus and a small (J = 6.2 Hz) coupling to the μ-PPh_2CHOMe phosphorus which implies that the PMe_3 ligand is trans to the former and cis to the latter phosphorus, as indicated in eq 8.



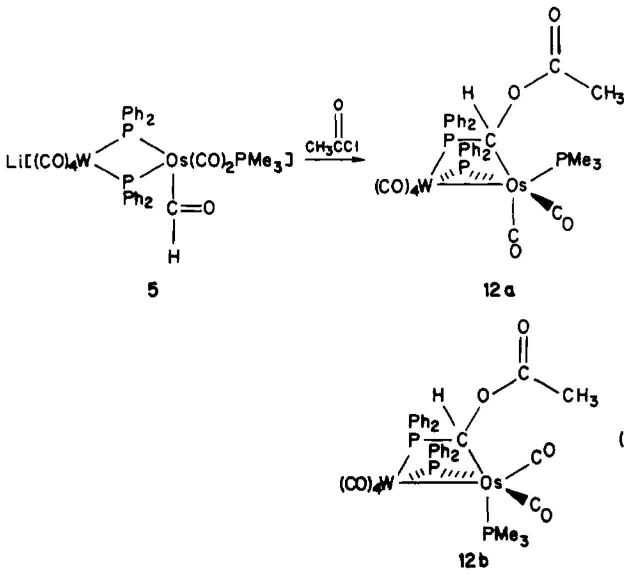
Reaction of 4 and 5 with Acetyl Chloride. When a THF solution of formyl complex **4** was treated with acetyl chloride at 22 °C, a red compound **11** was obtained. The low solubility of this material has precluded complete NMR characterization but its C, H analysis and ^1H NMR data are consistent with the formulation $(CO)_4W(\mu\text{-}PPh_2)(\eta^2(P,C)\text{-}\mu\text{-}PPh_2CHOC(O)CH_3)Os(CO)_2PMePh_2$. By analogy to the product from the reaction of formyl complex **5** with acetyl chloride we presume that it has the structure indicated in **11**.



11

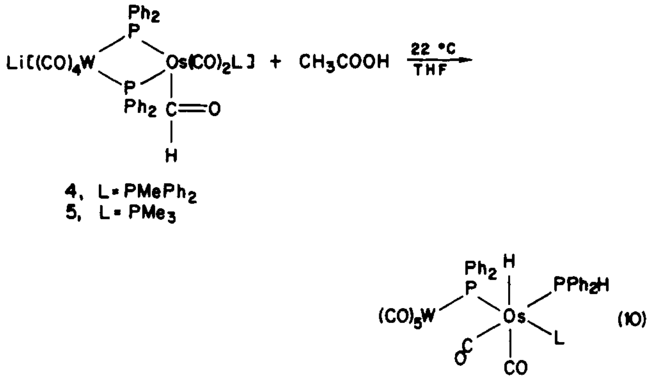
When formyl complex **5** was treated with acetyl chloride, a product was obtained which shows an IR spectrum identical with that of **11**. However, this material is quite soluble and has been characterized spectroscopically. The data indicate formation of two geometrical isomers **12a** and **12b** containing $\eta^2(P,C)$-μ-

$PPh_2CHOC(O)CH_3$ ligands (eq 9). Careful monitoring of the reaction by ^{31}P NMR spectroscopy showed that **12a** forms first and that it slowly converts to **12b** over 8 days at 22 °C. The kinetic isomer **12a** has never been obtained free of the thermodynamic isomer **12b**. However, following heating the **12a**/**12b** mixture at 65 °C for 24 h, isomer **12b** is quantitatively produced and can be isolated pure by recrystallization. The $^{31}P\{^1H\}$ NMR data for **12a** and **12b** are consistent with the structures drawn in eq 9.



5 **12a** **12b** (9)

Protonation of 4 and 5. Treatment of the formyl complexes **4** and **5** with glacial acetic acid led to isolation of the products shown in eq 10. Although the yields of **13** and **14** were high, the overall reaction which occurs is quite complicated. It involves protonation of one phosphido ligand to give an Os-bound PPh_2H, hydride migration to Os, and CO migration to W. When complex **4**, which was labeled with deuterium at the formyl position, was allowed to react with CH_3COOH, complex **13** was obtained with the deuterium at the hydride position. The PPh_2H hydrogen must then derive from the added acid, but we have no further information to offer on the course of this reaction. Spectral data for **13** and **14** are consistent with the indicated formulations. Furthermore, complex **13** has been fully characterized by a single-crystal X-ray diffraction study, details of which will be reported separately.



4, L = $PMePh_2$
5, L = PMe_3

13, L = $PMePh_2$ (87%)
14, L = PMe_3 (85%) (10)

X-ray Diffraction Study of $(CO)_4W(\mu\text{-}PPh_2)(\eta^2(P,C)\text{-}\mu\text{-}PPh_2CHOMe)Os(CO)_2(PMePh_2)$, 9. An ORTEP drawing of the inner core of complex **9** is shown in Figure 1. The W and Os atoms are bridged by μ-PPh_2 and $\eta^2(P,C)$-μ-PPh_2CHOMe ligands with W further coordinated by four CO's and the Os by two CO's and a terminal $PMePh_2$ ligand. The W–Os distance of 3.022 (1) Å is consistent with the presence of a metal–metal bond between these metals. This distance compares well with WOs distances found in other compounds (e.g., $WOs_3H_3(CO)_{11}Cp$,[15] W–Os = 3.073 (2), 3.082 (3), 2.880 (3) Å; $WOs_3H(CO)_{12}Cp$,[15] W–Os = 2.914 (3), 2.935 (3), 2.908 (3) Å; $WOs_3(\mu\text{-}CC_6H_4Me)(CO)_{11}Cp$,[16] W–Os = 2.915 (1), 2.867 (1) Å. As Figure 1 illustrates, the core of the molecule is bent with a dihedral angle of 76.6° between the W-P(2)-Os and W-P(1)-C(1B)-Os planes. All distances and angles within the $\eta^2(P,C)$-μ-PPh_2CHOMe ligand appear normal.

Discussion

The primary objective of this study was to prepare binuclear WOs formyl complexes and evaluate their bonding characteristics, stability, and derivative chemistry. Formyl complexes do result from treatment of complexes **1**, **2**, and **3** with $Li[BHEt_3]$ but that derived from the metal–metal bonded complex $(CO)_4W(\mu\text{-}PPh_2)_2Os(CO)_3$, **1**, is extremely unstable and decomposes above –20 °C. This is presumably because the formyl complex has access to an open coordination site that can easily form via metal–metal bond cleavage; thus, hydride migration to Os readily occurs at the expense of the Os–W bond. In contrast, complexes **2** and **3** have no metal–metal bonds, and the formyl complexes that derive from them are quite stable, decomposing slowly at temperatures in excess of 70–80 C. Indeed, complexes **4** and **5** are among the most stable formyl complexes yet reported.[4,17,18]

These are the first isolable heterobinuclear formyl complexes and also the first phosphido-bridged formyl complexes. While several phosphido-bridged binuclear complexes have been shown to react with alkylating agents RLi to yield binuclear acyl derivatives,[12b,19] these same complexes do not yield stable formyl derivatives upon treatment with borohydride reagents.[12b,20] For example, Collman et al.[19] demonstrated that $(CO)_3Fe(\mu\text{-}PPh_2)_2Fe(CO)_3$ yields a stable acetyl derivative $[(CO)_3Fe(\mu\text{-}PPh_2)_2Fe(CO)_2(C(O)CH_3)]^-$ upon treatment with MeLi. In contrast, Wojcicki and co-workers[20] recently reported that reaction of $(CO)_3Fe(\mu\text{-}PPh_2)_2Fe(CO)_3$ with $Li[BHEt_3]$ did not give a corresponding formyl complex. The success in preparing WOs formyl complexes **4** and **5** is apparently due to two factors: (1) the absence of metal–metal bonds in the precursor carbonyl complexes that denies easy access to an open coordination site for deinsertion and (2) the presence of two third-row metals that have slow ligand dissociation rates.

The chemistry of binuclear and polynuclear formyl complexes has been relatively unexplored and is an area which needs further study. In earlier work we had shown that both protonation and methylation of the formyl cluster $[Os_3(CO)_{11}(CHO)]^-$ led to formation of the methylene-bridged cluster $Os_3(CO)_{11}(\mu\text{-}CH_2)$.[3] We wondered whether similar transformations would occur with the binuclear formyl complexes **4** and **5**. As detailed above, μ-CH_2 complexes do not result from protonation or methylation of the formyl complexes. Protonation instead leads to the complex bridge-elimination reaction shown in eq 10 in which a μ-PPh_2 ligand is converted into a terminal PPh_2H ligand. Data to be published elsewhere imply that this reaction proceeds through initial protonation at either W or one of the μ-PPh_2 ligands rather than at the formyl oxygen.[22] Methylation gives the unusual

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(19) Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Moore, E. J.; Rose-Munch, F. *Inorg. Chem.* **1982**, *21*, 146.

(20) Yu, Y.; Gallucci, J.; Wojcicki, A. *J. Am. Chem. Soc.* **1983**, *105*, 4826.

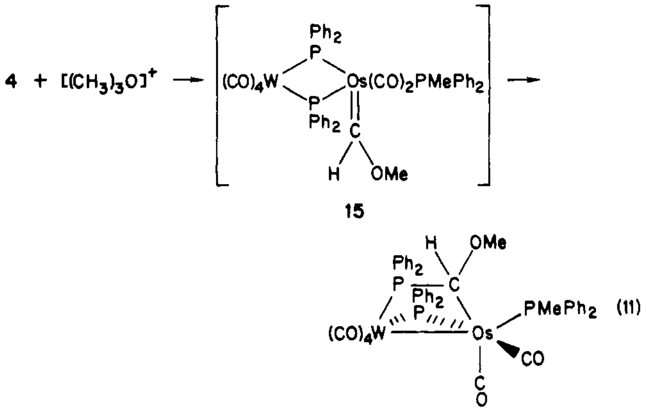
(21) See, for example: (a) Braunstein, P.; Matt, D.; Fischer, J.; Ricard, L.; Mitchler, A. *Nouv J. Chim.* **1980**, *4*, 493. (b) Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J.; Mitschler, A.; Ricard, L. *J. Am. Chem. Soc.* **1981**, *103*, 5115. (c) Klein, H.; Wenninger, J.; Schubert, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 1391. (d) Lindner, E.; Bouachir, F.; Hiller, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 1146. (e) Schore, N. E.; Hope, H. *J. Am. Chem. Soc.* **1980**, *102*, 4251.

Table IV. ^{31}P and ^{1}H NMR Data[a,b]

compd	$\delta(P_\mu)$	$\delta(P_{Os})$	$\delta(P_W)$	$J_{^{31}P_\mu-^{31}P_\mu}$	$J_{^{31}P_\mu-^{31}P_M}$	$J_{^{31}P_M-^{31}P_M}$	$J_{^{31}P-^{183}W}$	δ(H)	$J_{^1H-^1H}$	$J_{^1H-^{31}P}$
1	148.2 s						150.6			
2	−122.9 dd	−25.0 dd		39.8	91.2		201.8			
	−130.6 dd				4.3		191.7			
3	−136.1 dd	−60.0 dd		39.7	88.6		199.3			
	−143.8 dd				3.8		190.8			
4a	−107.4 dd	−11.7 dd		42.5	137.0		191.0	15.4 dd		9.6, 10.8
	−121.4 dd				13.2		173.2			
4b	−110.5 dd	−20.0 dd		95.5	108.3		c	15.1 dd		4.6, 24.1
	−134.6 dd				11.9					
5a	−115.3 dd	−39.6 dd		51.4	138.6		179.7	15.1 t		9.4
	−131.2 dd				15.8		169.2			
5b	−125.0 dd	−43.5 dd		44.5	143.7		*c*	15.2[c]		
	−131.0 dd				15.8					
6	−137.8 s						177.4	−4.1 t		13.6
7	−119.4 dd	−3.5 dd		45.5	142.2		173.2	−3.7 ddd		22.5, 17.6, 11.5
	−128.7 dd				15.0		165.4			
8	−127.5 dd	−44.8 dd		46.5	141.3		171.4	−4.2 ddd		22.6, 16.1, 11.5
	−135.3 dd				14.7		162.5			
9	79.1 d	−7.0 d	−1.9 dd		14.6 (P_W)		194.1 (P_W)	2.8 s (OMe)		8.0, 5.8, 3.6
					9.4 (P_{Os})		140.4 (P_μ)	4.4 ddd (C*H*OMe)		
10a	81.6 dd	−32.2 dd	−4.0 dd		12.8 (P_W)	8.8	193.0 (P_W)	2.9 s (OMe)		
					3.9 (P_{Os})		142.6 (P_μ)	4.4 ddd (C*H*OMe)		8.7, 6.7, 3.3
10b	84.7 dd	−47.5 dd	20.7 dd		8.8 (P_W)	6.6	209.7 (P_W)	2.84 s (OMe)		
					140.7 (P_{Os})		166.9 (P_μ)	5.0 ddd (C*H*OMe)		9.0, 7.3, 5.3
11[d]								4.2 s (OC(O)Me)		
								4.3 dd (C*H*OAc)		5.7, 3.0
12a	78.2 dd	−41.8 dd	−6.0 dd		29.2 (P_W)	15.9	*c*	4.2 s (OC(O)Me)		
					11.5 (P_{Os})			*c* (C*H*OAc)		
12b	88.0 dd	−37.5 dd	3.0 dd		53.0 (P_W)	169.4	197.5 (P_W)	3.9 s (OC(O)Me)		
					29.6 (P_{Os})		149.2 (P_μ)	*c* (CHOAc)		
13	−64.9 dd	−11.2 dd			9.6	22.9	205.2 (P_μ)	6.6 dddd (PPh_2H)	3.6	396, 12.4, 10.8
		−20.5 dd			122.0			−3.6 dddd (OsH)	3.6	31.3, 16.2, 12.5
14	−67.8 dd	−16.0 dd			14.0	16.8	199.5 (P_μ)	6.7 dddd (PPh_2H)	2.6	403, 16.6, 11.6
		−50.2 dd			123.2			−6.4 dddd (OsH)	2.6	29.6, 18.7, 10.9

[a] Solvents used: C_6D_6 (**1**, **10a**, **10b**, **13**, **14**), CD_2Cl_2 (**2**, **3**, **9**), $(CD_3)_2SO$ (**4a**, **4b**, **5a**, **5b**, **6**, **7**, **8**), and $(CD_3)_2CO$ (**12a**, **12b**). *J* values in hertz. [b] P_μ = μ-*P*Ph$_2$; P_w = μ-*P*Ph$_2$CHOR; P_{Os} = PMe$_3$, PMePh$_2$. [c] Not resolved. [d] Low solubility precluded obtaining ^{31}P NMR data.

complexes **9** and **10** with the bridging $\eta^2(P,C)$-μ-PPh$_2$CHOMe ligand. The first step in this latter reaction presumably involves methylation of the formyl oxygen to give the methoxymethylene complex **15** (eq 11). The μ-PPh$_2$ and methoxymethylene ligands



must then couple to give the observed product **9**. This coupling may arise via transient dissociation of one PPh$_2$ ligand from Os followed by nucleophilic addition of this ligand to the carbene carbon. Similar coupling reactions also occur during acylation of **4** and **5** to give products similar to **9**. While there are a few other complexes that contain bridging ligands similar to those in **9–12**,[21] none derive by reactions analogous to those reported herein in which μ-PR$_2$ and carbene ligands couple.

We had considered the possibility of deriving complexes containing *bridging* μ-CHO ligands from the binuclear complexes reported herein. However, that does not happen. The formyl complexes **4** and **5** are coordinatively saturated, and a coordination site would have to open on W in order for these ligands to convert from a one-electron terminal CHO to a three-electron μ-CHO ligand. When heated, ligand loss does occur but from the wrong metal (Os). Thus, hydride migration from the formyl to Os occurs preferentially to CO migration from W to Os, and a μ-CHO ligand does not form.

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Registry No. **1**, 91686-43-0; **2**, 91740-97-5; **3**, 91670-64-3; **4**, 88904-52-3; **5**, 91670-65-4; **6**, 91739-99-0; **7**, 91740-00-0; **8**, 91670-66-5; **9**, 91740-01-1; **10a**, 91670-67-6; **10b**, 91740-02-2; **11**, 91670-68-7; **12a**, 91670-69-8; **12b**, 91740-03-3; **13**, 91740-98-6; **14**, 91686-44-1; W(CO)$_4$(PPh$_2$H)$_2$, 70505-43-0; Li$_2$[W(CO)$_4$(PPh$_2$)$_2$], 68829-50-5; Os(CO)$_4$Br$_2$, 18953-16-7; PMePh$_2$, 1486-28-8; PMe$_3$, 594-09-2; Li[BEt$_3$H], 22560-16-3; [(CH$_3$)$_3$O]BF$_4$, 420-37-1; CH$_3$COCl, 75-36-5; W, 7440-33-7; Os, 7440-04-2.

Supplementary Material Available: Tables of anisotropic thermal parameters, complete bond lengths and angles, calculated hydrogen atom positions, and structure factors and a figure showing the complete atom numbering scheme (23 pages). Ordering information is given on any current masthead page.

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(22) Rosenberg, S.; Geoffroy, G. L.; Rheingold, A. L., submitted for publication in *Organometallics*.