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Bidentate and Tridentate Coordination Modes of a Novel Bicyclic Ditertiary Phosphine Ether

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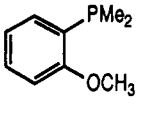
The synthesis and characterization of the new ligand *cis*-1,5-bis[(diphenylphosphino)methyl]-3-oxabicyclo[3.3.0]octane (**6**) is reported. Oxidation of **6** with *t*-BuOOH or S_8 yields the phosphoryl and thiophosphoryl derivatives **10a** and **10b**, respectively. The complexes (**6**-*P,P'*)M(CO)$_4$ (M = Cr, Mo, W), (**6**-*P,P'*)PdCl$_2$, and two diastereomers of *fac*-(**6**-*P,P'*)Mn(CO)$_3$Br have been prepared, in which **6** coordinates in a bidentate (*P,P'*) fashion. ^{1}H NMR spectra suggest a ligand conformational preference in these complexes. A tridentate (*P,P',O*) coordination mode has been established for (**6**-*P,P',O*)M(CO)$_3$ (M = Mo, W) and [(**6**-*P,P',O*)Mn(CO)$_3$]BF$_4$ on the basis of ^{1}H, ^{13}C, ^{31}P, and IR spectroscopic data. Single-crystal X-ray diffraction studies on (**6**-*P,P'*)Mo(CO)$_4$ and (**6**-*P,P',O*)W(CO)$_3$ verify the bidentate and tridentate coordination modes of **6**, respectively. Crystals of (**6**-*P,P'*)Mo(CO)$_4$ are triclinic, space group $P\bar{1}$, with unit cell dimensions $a = 15.321$ (3) Å, $b = 22.371$ (3) Å, $c = 11.376$ (2) Å, $\alpha = 90.52$ (1)°, $\beta = 91.80$ (1)°, $\gamma = 72.07$ (1)°, and $Z = 4$. Crystals of (**6**-*P,P',O*)W(CO)$_3$ are monoclinic, space group $P2_1/c$ (No. 14), with unit cell dimensions $a = 12.262$ (5) Å, $b = 17.38$ (1) Å, $c = 16.285$ (7) Å, $\beta = 92.08$ (4)°, and $Z = 4$. The structures were refined to $R = 0.059$ and $R_w = 0.079$ for 6702 reflections with $I > 3.0\sigma(I)$ for (**6**-*P,P'*)Mo(CO)$_4$ and $R = 0.076$ and $R_w = 0.093$ for 4068 reflections with $I \geq 3.0\sigma(I)$ for (**6**-*P,P',O*)W(CO)$_3$.

Introduction

Because phosphines play an important role in homogeneous transition-metal-catalyzed reactions of both academic and industrial importance, the synthesis of new phosphine ligands continues to be an area of significant activity. Of particular relevance here are phosphines possessing potentially coordinating ether groups. *o*-Anisole–phosphines (and arsines)[1] were the first such ligands shown to coordinate transition metals via the phosphorus and oxygen atoms. Early on, the weak interactions of the ether oxygen of **1** with the metal centers of square-planar rhodium and iridium complexes were shown to increase significantly the rates of oxidative addition of methyl iodide.[2] Knowles[3] studied the related ligands PAMP (**2**), CAMP (**3**) and DiPAMP (**4**) in the rhodium-catalyzed asymmetric hydrogenation of (*N*-acylamino)cinnamic acids as part of the L-DOPA synthesis in the 1970s. A weak interaction of the ether oxygen with Rh has been proposed to play an important role in similar reactions.[4] Coordination of the ether oxygen has now been demonstrated in a variety of metal–ligand systems,[5] and such linkages have been substantiated by X-ray crystallography for [*o*-(diphenylphosphino)anisole]$_2$RuCl$_2$,[6] (CH$_3$OCH$_2$CH$_2$PPh$_2$)$_2$RuCl$_2$,[7] (CH$_3$OCH$_2$CH$_2$PPh$_2$)$_2$Ru(CO)Cl$_2$,[7] [Rh(TMPP)$_2$)]BF$_4$,[8] (TMPP)Mo(CO)$_3$,[9] Rh$_2$(O$_2$CCH$_3$)$_3$(TMPP)(MeOH)[10] (TMPP = (2,4,6-trimethoxyphenyl)phosphine), and [{(Ph$_2$PCH$_2$CH$_2$)$_2$O}Rh(CO)]PF$_6$.[11]



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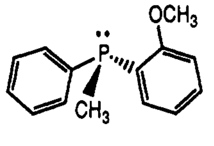

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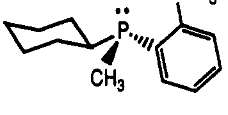

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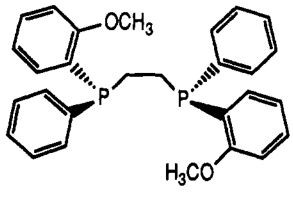

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The oxygen ligands in such complexes are sufficiently labile to be displaced by molecules such as phosphines, phosphites,[5g] nitriles,[5c,7,9] dialkyl sulfides,[5c] and CO.[5b,c,g,7] This property renders ether functional groups in phosphines well suited to stabilizing reactive catalytic intermediates having accessible coordination sites. Recently, Lindner[12] utilized a variety of phosphine ethers in rhodium

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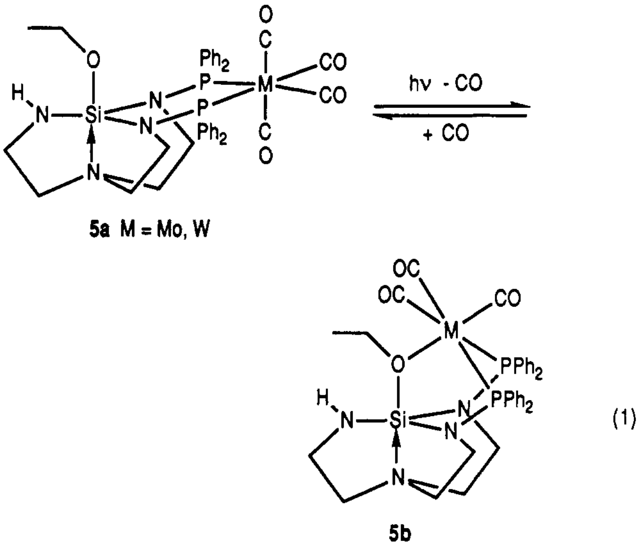
and cobalt-catalyzed methanol carbonylations.

Recently, we reported[13] reversible silyl–ether coordination in group VI metal carbonyl complexes of *N,N'*-bis(diphenylphosphino)azasilatrane (**5a**, **5b**) (reaction 1).

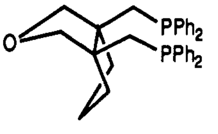


5a M = Mo, W

5b

(1)

Stimulated by this observation, we synthesized the new chelating ligand *cis*-1,5-bis[(diphenylphosphino)methyl]-3-oxabicyclo[3.3.0]octane (**6**) which exhibits much improved stability in solution in comparison to our *N,N'*-bis(diphenylphosphino)azasilatrane system. Unlike the vast majority of previously reported phosphine ethers, **6** is a bis(phosphine) capable of adopting only a *fac* geometry when coordinated to an octahedral metal in a tridentate fashion. Furthermore, **6** forms six-membered chelate rings upon ether coordination, in contrast to previously reported ether phosphines, including our azasilatrane system, which coordinate their ether functional groups with the formation of five-membered chelate rings.[1-12,29] The presence and ring size of chelating ligands as well as the geometry they impose around a metal center are important factors in determining the chemistry of metal complexes. Here we report the synthesis of **6** and its ability to coordinate in either a bi- or tridentate mode in octahedral transition-metal carbonyl complexes.



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Experimental Section

All reactions were performed under an inert atmosphere of argon or nitrogen with standard inert atmosphere techniques. Toluene, pentane, tetrahydrofuran, and diethyl ether were distilled from sodium benzophenone ketyl prior to use. Methylene chloride was distilled from calcium hydride and stored over 4Å molecular sieves. Ph_2PH,[14] $Mn(CO)_5Br$,[15] (η^6-cycloheptatriene)$Mo(CO)_3$,[16] (η^6-cycloheptatriene)$W(CO)_3$,[17] (piperidine)$_2Mo(CO)_4$,[18] (COD)$W(CO)_4$,[19] (NBD)$Cr(CO)_4$,[20] $(PhCN)_2PdCl_2$,[21] and 1,1,2,2-tetrakis(hydroxymethyl)cyclopentane[22] were synthesized as described in the literature. (η^6-cycloheptatriene)$Cr(CO)_3$ was purchased from Aldrich and used without further purification. Solution NMR spectra were recorded on a Nicolet NT 300 (^1H), Bruker WM 200 (^{31}P), Varian VXR 300 (^1H, ^{13}C, ^{31}P), or Varian Unity 500 (^1H, $^1H\{^{31}P\}$) spectrometer using a deuterated solvent as the internal lock. Chemical shifts are reported relative to TMS (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P). Mass spectra were recorded on a Kratos MS-50 (EI, HRMS) or Finnigan 4000 (EI, CI) instrument. The masses of metal-containing fragments are reported for the most abundqant isotope present, viz. ^{98}Mo and ^{184}W, unless otherwise noted. IR spectra were recorded by using an IBM 98 FT-IR spectrometer. Microanalyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

***cis*-1,5-Bis[((methanesulfonyl)oxy)methyl]-3-oxabicyclo[3.3.0]octane (9a).** Trimethylorthoacetate (4.35 mL, 34.1 mmol), 1,1,2,2-tetrakis(hydroxymethyl)cyclopentane (5.02 g, 26.4 mmol), and 2 mL of methanol were added to 30 mL of $CHCl_3$. A few crystals of *p*-toluenesulfonic acid were added as a catalyst, and the reaction mixture was stirred for 30 min to give a clear solution. K_2CO_3 (0.500 g) was added, and the mixture was stirred overnight. This mixture was filtered, and the volatiles were removed in vacuo to leave a thick residue. This residue was dissolved twice in 5 mL of methanol, which was subsequently removed in vacuo. A ^1H NMR spectrum identified the residue so obtained as *cis*-1,5-bis(hydroxymethyl)-3-oxabicyclo[3.3.0]octane (**8b**). This was used in the next step of this synthesis without further purification. ^1H NMR ($CDCl_3$): δ 4.19 (br s, 2 H, OH), 3.87 (d, 2 H, $^2J_{HH}$ = 9.0 Hz, OCH_2), 3.53 (d, 2 H, $^2J_{HH}$ = 9.0 Hz, OCH_2), 3.63 (s, 4 H, CH_2OH), 1.7–1.5 (m, 6 H, CH_2).

Crude **8b** in 30 mL of pyridine was added dropwise to a cooled (0 °C) solution of methanesulfonyl chloride (6.5 mL, 79 mmol) in 50 mL of pyridine. After the addition was complete, the solution was stirred for 1 h at 0 °C and 4 h at room temperature. The solution was then poured onto a slurry of 600 g of ice/150 mL of H_2O/75 mL of HCl with stirring. After 30 min the pale white solid was isolated by filtration, washed with water, and dried in vacuo. Recrystallization from EtOH/CH_3CN (3:1) yielded 5.4 g (62% yield, mp 105 °C) of **9a**. MS (EI): *m/e* (ion, relative intensity) 327 (M^+, 0.3), 136 (100), 123 (9.1), 106 (48), 93 (61), 79 (57). HRMS (EI) calcd for $C_{11}H_{19}O_7S_2$ (M^+): 327.05722. Found: 327.05640. ^{13}C NMR ($CDCl_3$): δ 77.8 (CH_2O), 71.2 ($CH_2OSO_2CH_3$), 56.0 (s, C), 37.4 (OSO_2CH_3), 36.2 ($CH_2CH_2CH_2$), 23.4 ($CH_2CH_2CH_2$). ^1H NMR ($CDCl_3$): δ 4.25 (s, 4 H, $CH_2OSO_2CH_3$), 3.88 (d, 2 H, $^2J_{HH}$ = 9.6 Hz, OCH_2), 3.61 (d, 2 H, $^2J_{HH}$ = 9.6 Hz, OCH_2), 3.06 (s, 6 H, OSO_2CH_3), 1.9–1.6 (m, 6 H, CH_2).

***cis*-1,5-Bis[(diphenylphosphino)methyl]-3-oxabicyclo[3.3.0]octane (6).** A deep red solution of lithium diphenylphosphide was generated by the addition of *n*-BuLi (6.5 mL, 13 mmol) to a solution of diphenylphosphine (2.25 mL, 12.9 mmol) in 125 mL of THF. This was cooled to 0 °C and treated dropwise with a solution of **9a** (2.11 g, 6.42 mmol) in 45 mL of THF. After the addition was complete, the resulting mixture was stirred for 2 h at room temperature followed by refluxing overnight. After cooling to room temperature, excess phosphide was quenched with the addition of 1 mL of a saturated NH_4Cl(aq) solution. The mixture was filtered, and the solvent was removed from the filtrate in vacuo to leave a thick residue. This residue was chromatographed on silica gel with 10% ethyl acetate in toluene to yield a thick oil, which readily crystallized at room temperature. These

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crystals were rinsed with *n*-pentane and dried in vacuo. Yield 2.48 g (76%, mp 110–111 °C). MS (EI): *m/e* (ion, relative intensity) 508 (M^+, 3.6), 431 (100), 323 (23), 183 (31), 108 (19). HRMS (EI) calcd for $C_{33}H_{34}OP_2$ (M^+): 508.20849. Found: 508.20833. IR (KBr): ν (COC) = 1082 cm^{-1}. ^{31}P NMR (toluene): δ −19.8. ^{13}C NMR ($CDCl_3$): δ 139.5 (d, $^1J_{PC}$ = 13.1 Hz, Ph ipso), 139.4 (d, $^1J_{PC}$ = 13.1 Hz, Ph ipso), 133.1 (d, $^2J_{PC}$ = 19.6 Hz, Ph ortho), 133.0 (d, $^2J_{PC}$ = 19.7 Hz, Ph ortho), 128.7 (s, Ph para), 128.5 (d, $^3J_{PC}$ = 7.1 Hz, Ph meta), 81.6 (d, $^3J_{PC}$ = 12.6 Hz, CH_2O), 56.0 (dd, $^2J_{PC}$ = 6.0 Hz, $^3J_{PC}$ = 12.1 Hz, $\mathit{C}C_4$), 40.8 (d, $^3J_{PC}$ = 10.6 Hz, $\mathit{C}H_2CH_2\mathit{C}H_2$), 36.7 (d, $^1J_{PC}$ = 16.6 Hz, $\mathit{C}H_2PPh_2$), 24.3 (s, $CH_2\mathit{C}H_2CH_2$). ^1H NMR ($CDCl_3$): δ 7.50–7.38 (m, Ph), 7.31 (m, Ph), 3.66 (d, $^2J_{HH}$ = 9.2 Hz, CH_2O), 3.48 (d, $^2J_{HH}$ = 9.2 Hz, CH_2O), 2.34 (dd, $^2J_{HH}$ = 13.6 Hz, $^2J_{PH}$ = 2.9 Hz, $C\mathit{H}_2PPh_2$), 2.28 (dd, $^2J_{HH}$ = 13.6 Hz, $^2J_{PH}$ = 3.0 Hz, $C\mathit{H}_2PPh_2$), 1.77 (m, CH_2), 1.6–1.4 (m, CH_2). Anal. Calcd for $C_{33}H_{34}OP_2$: C, 77.94; H, 6.74; P, 12.18. Found: C, 77.90; H, 6.74; P, 12.08.

***cis*-1,5-Bis[(diphenylphosphoryl)methyl]-3-oxabicyclo[3.3.0]octane (10a).** A solution of **6** (0.402 g, 0.791 mmol) in 15 mL of toluene was treated with a solution of *t*-BuOOH in toluene (3.6 M, 0.50 mL) at 0 °C. After stirring at room temperature for 2 h, the volume of the solution was reduced to 5 mL in vacuo. Addition of 5 mL of MeOH followed by the slow addition of 15 mL of hexane yielded the product as a white solid. The product was isolated by filtration, rinsed with 10 mL of pentane and dried in vacuo. Recrystallization from hot MeOH (15 mL) yielded 0.38 g (89%, mp 210 °C) of clear colorless crystals. MS (EI): *m/e* (ion, relative intensity) 540 (M^+, 15), 339 (87), 201 (100). HRMS (EI) calcd for $C_{33}H_{34}O_3P_2$ (M^+): 540.19832. Found: 540.19883. IR (KBr): 1177 cm^{-1} (P=O). ^{31}P NMR ($CHCl_3$): δ 29.6. ^{13}C NMR ($CDCl_3$): δ 134.5 (d, $^1J_{PC}$ = 98.2 Hz, Ph ipso), 134.2 (d, $^1J_{PC}$ = 97.7 Hz, Ph ipso), 131.8 (d, $^4J_{PC}$ = 3.0 Hz, Ph para), 131.7 (d, $^4J_{PC}$ = 3.0 Hz, Ph para), 130.8 (d, $^2J_{PC}$ = 9.6 Hz, Ph ortho), 130.6 (d, $^2J_{PC}$ = 9.1 Hz, Ph ortho), 128.8 (d, $^3J_{PC}$ = 11.6 Hz, Ph meta), 128.7 (d, $^3J_{PC}$ = 12.1 Hz, Ph meta), 80.7 (d, $^3J_{PC}$ = 4.0 Hz, CH_2O), 55.5 (dd, $^2J_{PC}$ = 10.1 Hz, $^3J_{PC}$ = 4.5 Hz, $\mathit{C}C_4$), 39.4 (d, $^3J_{PC}$ = 3.0 Hz, $\mathit{C}H_2CH_2\mathit{C}H_2$), 36.8 (d, $^1J_{PC}$ = 70 Hz, $\mathit{C}H_2P(O)Ph_2$), 24.7 (s, $CH_2\mathit{C}H_2CH_2$). ^1H NMR ($CDCl_3$): δ 7.79 (m, Ph), 7.49 (m, Ph), 3.69 (d, $^2J_{HH}$ = 9.9 Hz, CH_2O), 3.60 (d, $^2J_{HH}$ = 9.9 Hz, CH_2O), 2.60 (dd, $^2J_{HH}$ = 15.0 Hz, $^2J_{PH}$ = 10.5 Hz, $C\mathit{H}_2P(O)Ph_2$), 2.49 (dd, $^2J_{HH}$ = 15.0 Hz, $^2J_{PH}$ = 12.5 Hz, $C\mathit{H}_2P(O)Ph_2$), 1.84 (m, CH_2), 1.7–1.5 (m, CH_2). Anal. Calcd for $C_{33}H_{34}O_3P_2 \cdot 2CH_3OH$: C, 69.52; H, 7.00; P, 10.24. Found: C, 69.74; H, 7.15; P, 10.18.

***cis*-1,5-Bis[(diphenylthiophosphoryl)methyl]-3-oxabicyclo[3.3.0]octane (10b).** A solution of **6** (0.400 g, 0.786 mmol) in 15 mL of toluene was stirred with S_8 (0.0582 g, 0.227 mmol) for 4 h at room temperature. The resulting white precipitate was isolated by filtration, rinsed with 10 mL of hexane, and dried in vacuo. Recrystallization from CH_2Cl_2/ethanol yielded 0.29 g (64%, mp > 250 °C) of fine white needles. MS (EI): *m/e* (ion, relative intensity) 572 (M^+, 17), 539 (80), 507 (43), 431 (32), 355 (57), 323 (45), 217 (100), 185 (52), 139 (50), 108 (57). HRMS (EI) calcd for $C_{33}H_{34}OP_2S_2$ (M^+): 572.15264. Found: 572.15105. ^{31}P NMR (CD_2Cl_2): δ 38.3. ^{13}C NMR (CD_2Cl_2): δ 134.9 (d, $^1J_{PC}$ = 80.1 Hz, Ph ipso), 134.1 (d, $^1J_{PC}$ = 79.0 Hz, Ph ipso), 131.7 (s, Ph para), 131.7 (d, $^2J_{PC}$ = 12.1 Hz, Ph ortho), 131.3 (d, $^2J_{PC}$ = 10.1 Hz, Ph ortho), 129.0 (d, $^3J_{PC}$ = 12.1 Hz, Ph meta), 128.9 (d, $^3J_{PC}$ = 11.6 Hz, Ph meta), 80.5 (d, $^3J_{PC}$ = 4.0 Hz, CH_2O), 56.8 (dd, $^3J_{PC}$ = 4.0 Hz, $^2J_{PC}$ = 10.1 Hz, $\mathit{C}C_4$), 39.6 (d, $^1J_{PC}$ = 55.4 Hz, $\mathit{C}H_2P(S)Ph_2$), 39.2 (d, $^3J_{PC}$ = 3.5 Hz, $\mathit{C}H_2CH_2\mathit{C}H_2$), 25.2 (s, $CH_2\mathit{C}H_2CH_2$). ^1H NMR (CD_2Cl_2): δ 8.02–7.86 (m, Ph), 7.51 (m, Ph), 3.80 (d, $^2J_{HH}$ = 9.9 Hz, CH_2O), 3.68 (d, $^2J_{HH}$ = 9.9 Hz, CH_2O), 3.07 (dd, $^2J_{HH}$ = 14.1 Hz, $^2J_{PH}$ = 12.0 Hz, $C\mathit{H}_2P(S)Ph_2$), 2.78 (dd, $^2J_{HH}$ = 14.1 Hz, $^2J_{PH}$ = 13.0 Hz, $C\mathit{H}_2P(S)Ph_2$), 1.65–1.40 (m, CH_2).

***cis*-[*cis*-1,5-Bis[(diphenylphosphino)methyl]-3-oxabicyclo[3.3.0]octane-*P*,*P*′]dichloropalladium (11).** A solution of **6** (0.403 g, 0.792 mmol) in 10 mL of toluene was slowly added to a solution of $(PhCN)_2PdCl_2$ (0.303 g, 0.790 mmol) in 20 mL of toluene, and the resulting mixture was stirred overnight. The creamy white solid was isolated by filtration, washed with 5 mL of toluene and then 10 mL of hexane, and then dried in vacuo. Yield: 0.53 g (98%). ^{31}P NMR (DMSO-d_6): δ 22.8. ^{13}C NMR (DMSO-d_6): δ 134.9 (at,[23] separation 9.5 Hz, Ph ortho), 133.6 (at, separation 8.5 Hz, Ph ortho), 131.0 (s, Ph para), 128.0 (m, Ph meta), 127.9 (m, Ph meta), 80.7 (m, CH_2O), 53.7 (s, $\mathit{C}C_4$), 34.7 (at, separation 29.7 Hz, $\mathit{C}H_2PPh_2$), 23.6 (s, $CH_2\mathit{C}H_2CH_2$). ^1H NMR (DMSO-d_6): δ 8.07 (m, 4 H, Ph ortho), 7.95 (m, 4 H, Ph ortho), 7.53 (m, Ph meta, para), 3.34 (m, CH_2O), 3.18 (m, $C\mathit{H}_2PPh_2$), 1.40–0.90 (m, 6 H, CH_2).

***cis*-[*cis*-1,5-Bis[(diphenylphosphino)methyl]-3-oxabicyclo[3.3.0]octane-*P*,*P*′]tetracarbonylchromium (12).** A solution of (norbornadiene)tetracarbonylchromium (0.229 g, 0.894 mmol) and **6** (0.455 g, 0.895 mmol) in 20 mL of toluene was refluxed for 3 h, during which time the deep yellow color of the solution almost dissipated. The solvent was removed in vacuo, and the residue was chromatographed on silica gel with CH_2Cl_2. Solvent was removed from the product-containing fractions in vacuo to yield a light yellow solid. Yield: 0.49 g (82%). MS (desorption CI, NH_3): *m/e* (ion, relative intensity) 690 ($M + NH_4^+$, 12), 673 (MH^+, 31), 645 ($MH^+ - CO$, 6.5), 578 (6.4), 560 (7.1), 541 (6.0), 509 (100), 431 (11), 323 (6.3). MS (EI): *m/e* (ion, relative intensity) 588 ($M^+ - 3CO$, 0.3), 560 ($M^+ - 4CO$, 7.3), 508 (16), 431 (100), 323 (44). HRMS (EI) calcd for $C_{34}H_{34}CrO_2P_2$ ($M^+ - 3CO$): 588.14406. Found: 588.14470. Calcd for $C_{33}H_{34}CrOP_2$ ($M^+ - 4CO$): 560.14915. Found 560.15028. ^{31}P NMR (toluene): δ 44.2. ^{13}C NMR (CD_2Cl_2): δ 227.2 (at, separation 20.4 Hz, CO_{eq}) 223.8 (t, $^2J_{PC}$ = 13.9 Hz, CO_{ax}) 217.5 (t, $^2J_{PC}$ = 12.1 Hz, CO_{ax}), 142.4 (m, separation 37.3 Hz, Ph ipso), 138.7 (m, separation 37.3 Hz, Ph ipso), 133.7 (at, separation 10.8 Hz, Ph ortho), 130.9 (at, separation 8.8 Hz, Ph ortho), 130.2 (s, Ph para), 129.1 (s, Ph para), 128.9 (at, separation 8.8 Hz, Ph meta), 128.7 (at, separation 8.4 Hz, Ph meta), 86.2 (at, separation 12.7 Hz, CH_2O), 53.7 (s, $\mathit{C}C_4$), 42.4 (at, separation 8 Hz, $\mathit{C}H_2CH_2\mathit{C}H_2$), 38.4 (at, separation 12.8 Hz, CH_2PPh_2), 24.7 (s, $CH_2\mathit{C}H_2CH_2$). ^1H NMR (CD_2Cl_2): δ 7.86 (m, Ph), 7.50–7.30 (m, Ph), 3.62 (dd, $^2J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 1.2 Hz, CH_2O), 3.57 (d, $^2J_{HH}$ = 9.0 Hz, CH_2O), 3.02 (dd, $^2J_{HH}$ = 15.6 Hz, $^2J_{PH}$ = 10.5 Hz, $C\mathit{H}_2PPh_2$), 2.98 (dd, $^2J_{HH}$ = 15.6 Hz, $^2J_{PH}$ = 2.0 Hz, $C\mathit{H}_2PPh_2$), 1.77 (m, 2 H, H_B), 1.51 (m, 1 H, H_C), 1.42 (m, 1 H, H_D), 1.13 (dd, $^2J_{AB}$ = 12.6 Hz, $^3J_{AC}$ = 5.2 Hz, 2 H, H_A). Anal. Calcd for $C_{37}H_{34}CrO_5P_2$: C, 66.07; H, 5.10; P, 9.21; Found: C, 66.37; H, 5.19; P, 9.13.

***cis*-[*cis*-1,5-Bis[(diphenylphosphino)methyl]-3-oxabicyclo[3.3.0]octane-*P*,*P*′]tetracarbonylmolybdenum (13).** Bis(piperidine)tetracarbonylmolybdenum (0.374 g, 0.983 mmol) and **6** (0.506 g, 0.983 mmol) were refluxed in 25 mL of CH_2Cl_2 for 30 min. The reaction mixture was cooled to room temperature, and the volatiles were removed in vacuo. The resulting white solid was purified by elution on a silica gel column with CH_2Cl_2. The solvent was removed from the product-containing fractions to yield a pure white solid (mp 185 °C dec). MS (desorption CI, NH_3): *m/e* (ion, relative intensity) 719 (MH^+, 64), 691 ($MH^+ - CO$, 64), 509 (29), 262 (31), 187 (100). MS (EI): *m/e* (ion, relative intensity) 690 ($M^+ - CO$, 0.4), 662 ($M^+ - 2CO$, 0.6), 634 ($M^+ - 3CO$, 1.0), 606 ($M^+ - 4CO$, 5.9), 508 (5.1), 431 (100), 323 (29), 183 (52), 108 (41). HRMS (EI) calcd for $C_{36}H_{34}{}^{92}MoO_4P_2$ ($M^+ - CO$): 684.09953. Found: 684.09961. ^{31}P NMR (CD_2Cl_2): δ 22.0. ^{13}C NMR (CD_2Cl_2): δ 215.9 (m, separation 15.1 Hz, CO_{eq}), 212.2 (t, $^2J_{PC}$ = 9.5 Hz, CO_{ax}), 206.0 (t, $^2J_{PC}$ = 7.5 Hz, CO_{ax}), 142.3 (m, separation 35.7 Hz, Ph ipso), 138.4 (m, separation 35.3 Hz, Ph ipso), 134.0 (at, separation 12.3 Hz, Ph ortho), 130.9 (at, separation 10.3 Hz, Ph ortho), 130.3 (s, Ph para), 129.1 (s, Ph para), 128.9 (at, separation 9.1 Hz, Ph meta), 128.7 (at, separation 8.3 Hz, Ph meta), 86.3 (at, separation 12.3 Hz, CH_2O), 53.5 (br s, $\mathit{C}C_4$), 42.8 (br s, $\mathit{C}H_2CH_2\mathit{C}H_2$), 37.1 (at, separation 14.7 Hz, $\mathit{C}H_2PPh_2$), 24.9 (s, $CH_2\mathit{C}H_2CH_2$). ^1H NMR (CD_2Cl_2): δ 7.84 (m, Ph), 7.50–7.30 (m, Ph), 3.60 (dd, $^2J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 2.0 Hz, CH_2O), 3.57 (d, $^2J_{HH}$ = 9.0 Hz, CH_2O), 2.99 (d, $^2J_{PH}$ = 5.7 Hz, $C\mathit{H}_2PPh_2$), 1.81 (m, 2 H, H_B), 1.52 (m, 1 H, H_C), 1.41 (m, 1 H, H_D), 1.12 (dd, $^2J_{AB}$ = 12.3 Hz, $^3J_{AC}$ = 5.4 Hz, 2 H, H_A).

***cis*-[*cis*-1,5-Bis[(diphenylphosphino)methyl]-3-oxabicyclo[3.3.0]octane-*P*,*P*′]tetracarbonyltungsten (14).** A solution of (cyclooctadiene)tetracarbonyltungsten (0.374 g, 0.926 mmol) and **6** (0.466 g, 0.916 mmol) in 25 mL of THF was refluxed for 30 min. The solvent was removed in vacuo, and the residue was chromatographed on silica gel with CH_2Cl_2. Solvent was removed from the product-containing fractions to yield a creamy white solid. Yield: 0.70 g (95%). MS (desorption CI, NH_3): *m/e* (ion, relative intensity) 806 (MH^+, 100), 778 ($MH^+ - CO$, 8.5), 541 (6.5), 525 (6.9), 509 (12), 317 (26), 263 (19). MS (EI): *m/e* (ion, relative intensity) 804 (M^+, 2.4), 776 ($M^+ - CO$, 13), 748 ($M^+ - 2CO$, 3.0), 720 ($M^+ - 3CO$, 9.4), 692 ($M^+ - 4CO$, 6.6), 508 (6.7), 431 (100), 323 (23). HRMS (EI) calcd for $C_{37}H_{34}O_5P_2{}^{184}W$ (M^+): 804.13911.

Found: 804.13910. Calcd for $C_{36}H_{34}O_4P_2{}^{184}W$ (M^+ – CO): 776.14433. Found: 776.14622. ^{31}P NMR (THF): δ 4.5 ($^1J_{PW}$ = 232 Hz). ^{13}C NMR (CD_2Cl_2): δ 206.4 (m, separation 16.2 Hz, CO_{eq}), 204.9 (t, $^2J_{PC}$ = 7.1 Hz, CO_{ax}), 198.9 (t, $^2J_{PC}$ = 5.4 Hz, CO_{ax}), 142.1 (m, separation 42.8 Hz, Ph ipso), 138.0 (m, separation 41.3 Hz, Ph ipso), 134.2 (at, separation 12.0 Hz, Ph ortho), 130.9 (at, separation 9.4 Hz, Ph ortho), 130.5 (s, Ph para), 129.3 (s, Ph para), 129.0 (at, separation 10.0 Hz, Ph meta), 128.7 (at, separation 8.4 Hz, Ph meta), 86.3 (at, separation 12.8 Hz, CH_2O), 53.4 (s, $\mathit{C}C_4$), 42.7 (at, separation 8.0 Hz, $\mathit{C}H_2CH_2\mathit{C}H_2$), 37.4 (m, separation 18.6 Hz, $\mathit{C}H_2PPh_2$), 24.9 (s, $CH_2\mathit{C}H_2CH_2$). ^1H NMR (CD_2Cl_2) δ 7.81 (m, Ph), 7.50–7.30 (m, Ph), 3.60 (dd, $^2J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 1.5 Hz, CH_2O), 3.57 (d, $^2J_{HH}$ = 9.0 Hz, CH_2O), 3.16 (dd, $^2J_{HH}$ = 15.6 Hz, $^2J_{PH}$ = 11.5 Hz, $C\mathit{H}_2PPh_2$), 3.06 (dd, $^2J_{HH}$ = 15.6 Hz, $^2J_{PH}$ = 2.5 Hz, $C\mathit{H}_2PPh_2$), 1.80 (m, 2 H, H_B), 1.52 (m, 1 H, H_C), 1.43 (m, 1 H, H_D), 1.13 (dd, $^2J_{AB}$ = 12.6 Hz, $^3J_{AC}$ = 5.3 Hz, 2 H, H_A).

Reaction of 6 with (η^6-cycloheptatriene)$Cr(CO)_3$. A solution of **6** (0.406 g, 0.798 mmol) in 5 mL of toluene was added to a deep red solution of (η^6-cycloheptatriene)tricarbonylchromium (0.185 g, 0.811 mmol) in 20 mL of toluene. After heating at 70 °C for 12 h, no reaction had occurred, as indicated by ^{31}P NMR spectroscopy. The solution was then refluxed for 8 h, during which time ^{31}P NMR spectra indicated the presence of a small quantity of **12** (δ 44.2) and unreacted **6**. Similarly, refluxing the two starting materials in xylene for 12 h led only to an increase in the quantity of **12** produced. There was no evidence for the formation of a chromium tricarbonyl complex of **6**.

***fac*-[*cis*-1,5-Bis[(diphenylphosphino)methyl]-3-oxabicyclo[3.3.0]octane-*P*,*P′*,*O*]tricarbonylmolybdenum (15).** A solution of **6** (0.410 g, 0.806 mmol) in 5 mL of toluene was added to a red solution of (η^6-cycloheptatriene)tricarbonylmolybdenum (0.2229, 0.815 mmol) in 20 mL of toluene. Stirring at 50 °C for 1 h yielded a yellow precipitate, which was isolated by filtration, washed with 5 mL of toluene, and dried in vacuo. Yield: 0.43 g (78%). MS (desorption CI, NH_3): *m/e* (ion, relative intensity) 691 (MH^+, 7.5), 509 (29), 323 (37), 263 (75), 247 (92), 202 (47), 187 (100). MS (EI): *m/e* (ion, relative intensity) 690 (M^+, 0.2), 662 (M^+ – CO, 0.3) 634 (M^+ – 2CO, 0.7), 606 (M^+ – 3CO, 4.6), 508 (8.1), 431 (100), 323 (41), 183 (54), 108 (39). HRMS (EI) calcd for $C_{36}H_{34}{}^{92}MoO_4P_2$ (M^+): 684.09954. Found: 684.10099. ^{31}P NMR (CD_2Cl_2): δ 12.9. ^{13}C NMR (CD_2Cl_2): δ 229.0 (t, $^2J_{PC}$ = 6.7 Hz, CO_{ax}), 219.9 (m, separation 47 Hz, CO_{eq}), 140.9 (m, separation 34 Hz, Ph ipso), 137.0 (m, separation 35 Hz, Ph ipso), 132.1 (m, separation 12.3 Hz, Ph ortho), 131.5 (m, separation 12.7 Hz, Ph ortho), 129.4 (s, Ph para), 129.3 (s, Ph para), 128.9 (m, separation 9.1 Hz, Ph meta), 128.6 (m, separation 9.1 Hz, Ph meta), 85.4 (m, separation 15.5 Hz, CH_2O), 55.9 (m, separation 6.4 Hz, $\mathit{C}C_4$), 41.7 (m, separation 8.7 Hz, $\mathit{C}H_2CH_2\mathit{C}H_2$), 36.9 (m, separation 12.7 Hz, $\mathit{C}H_2PPh_2$), 22.5 (s, $CH_2\mathit{C}H_2CH_2$). ^1H NMR (CD_2Cl_2): δ 7.72 (m, Ph), 7.40–7.30 (m, Ph), 6.97 (m, Ph), 4.09 (d, $^2J_{HH}$ = 10.5 Hz, CH_2O), 3.32 (dd, $^2J_{HH}$ = 16.0 Hz, $^2J_{PH}$ = 9.5 Hz, $C\mathit{H}_2PPh_2$), 3.29 (br d, $^2J_{HH}$ = 10.5 Hz, CH_2O), 2.88 (br dd, $^2J_{HH}$ = 16.0 Hz, $^4J_{HH}$ = 1.3 Hz, $C\mathit{H}_2PPh_2$), 1.90 (dd, $^2J_{AB}$ = 13.2 Hz, $^3J_{BD}$ = 5.1 Hz, 2 H, H_B), 1.71 (dt, $^2J_{CD}$ = 12.2 Hz, $^3J_{AC}$ = 6.3 Hz, 1 H, H_C), 1.59 (m, 2 H, H_A), 1.48 (m, 1 H, H_D).

***fac*-[*cis*-1,5-Bis[(diphenylphosphino)methyl]-3-oxabicyclo[3.3.0]octane-*P*,*P′*,*O*]tricarbonyltungsten (16).** A solution of **6** (0.413 g, 0.812 mmol) in 5 mL of toluene was added to a solution of (cycloheptatriene)tricarbonyltungsten (0.294 g, 0.818 mmol) in 15 mL of toluene. The solution was stirred at room temperature for 2 h and at 60 °C for 6 h to yield a bright yellow precipitate. This was isolated by filtration, washed twice with 10 mL of toluene, and dried in vacuo. Recrystallization could be achieved from CH_2Cl_2 at –78 °C. Yield: 0.40 g (64%). MS (desorption CI, NH_3): *m/e* (ion, relative intensity) 805 (MH + NH_4^+, 11), 777 (MH^+, 100), 509 (44). MS (EI): *m/e* (ion, relative intensity) 776 (M^+, 1.1), 748 (M^+ – CO, 0.5), 720 (M^+ – 2CO, 2.2), 692 (M^+ – 3CO, 1.6), 431 (26), 221 (59), 108 (100). ^{31}P NMR (CD_2Cl_2): δ 8.4 ($^1J_{PW}$ = 228 Hz). ^{13}C NMR (CD_2Cl_2): δ 218.5 (t, $^2J_{PC}$ = 3.9 Hz, CO_{ax}), 216.0 (dd, $^2J_{cis}$ = 7.3 Hz, $^2J_{trans}$ = 35.7 Hz, CO_{eq}), 140.4 (dd, $^3J_{PC}$ = 7.5 Hz, $^1J_{PC}$ = 33.0 Hz, Ph ipso), 136.8 (d, $^1J_{PC}$ = 39.3 Hz, Ph ipso), 132.0 (d, separation 11.9 Hz, Ph ortho), 131.5 (d, separation 11.9 Hz, Ph ortho), 129.4 (s, Ph para), 128.9 (d, separation 9.5 Hz, Ph meta), 128.6 (d, separation 9.5 Hz, Ph meta), 86.6 (d, separation 15.5 Hz, CH_2O), 55.8 (d, separation 5.9 Hz, $\mathit{C}C_4$), 41.7 (d, separation 9.1 Hz, $CH_2CH_2\mathit{C}H_2$), 37.8 (d, separation 15.8 Hz, $\mathit{C}H_2PPh_2$), 22.4 (s, $CH_2\mathit{C}H_2CH_2$). ^1H NMR (CD_2Cl_2): δ 7.71 (m, Ph), 7.35 (m, Ph), 6.97 (m, Ph), 4.22 (d, $^2J_{HH}$ = 10.5 Hz, CH_2O), 3.65 (dd, $^2J_{HH}$ = 16.2 Hz, $^2J_{HP}$ = 10.5 Hz, $C\mathit{H}_2PPh_2$), 3.46 (br d, $^2J_{HH}$ = 10.5 Hz, CH_2O), 2.95 (br d, $^2J_{HH}$ = 16.2 Hz, $C\mathit{H}_2PPh_2$), 1.93 (dd, $^2J_{AB}$ = 13.0 Hz, $^3J_{BD}$ = 5.4 Hz, 2 H, H_B), 1.75 (dt, $^2J_{CD}$ = 12.5 Hz, $^3J_{AC}$ = 5.5 Hz, 1 H, H_C), 1.59 (m, 2 H, H_A), 1.47 (m, 1 H, H_D). Anal. Calcd for $C_{36}H_{34}O_4P_2W$: C, 55.69; H, 4.41; W, 23.68. Found: C, 55.49; H, 4.63; W, 23.17.

***fac*-[*cis*-1,5-Bis[(diphenylphosphino)methyl]-3-oxabicyclo[3.3.0]octane-*P*,*P′*]bromotricarbonylmanganese (Isomers 17a, 17b).** A solution of **6** (0.520 g, 1.02 mmol) in 10 mL of toluene was added to a suspension of $Mn(CO)_5Br$ (0.268 g, 0.975 mmol) in 5 mL of toluene. This mixture was refluxed for 20 min to yield a yellow precipitate. The mixture was cooled and stirred at room temperature for 30 min. Precipitation was completed with the addition of 20 mL of pentane. The product was isolated by filtration, washed twice with 5 mL of pentane, and dried in vacuo. Yield: 0.56 g (79%). ^1H, ^{13}C, and ^{31}P NMR spectra showed the presence of two facial isomers (4/1 ratio) which were not separated.

Major isomer (**17a**): ^{31}P NMR (CH_2Cl_2) δ 26.9; ^{13}C NMR (CD_2Cl_2) δ 139.4 (m, separation 39.7 Hz, Ph ipso), 137.7 (m, separation 38.5 Hz, Ph ipso), 134.0 (at, separation 9.1 Hz, Ph ortho), 132.0 (at, separation 8.7 Hz, Ph ortho), 130.6 (s, Ph para), 130.3 (s, Ph para), 128.9 (at, separation 8.4 Hz, Ph meta), 128.6 (at, separation 9.1 Hz, Ph meta), 55.4 (s, $\mathit{C}C_4$), 39.6 (at, separation 9.4 Hz, $\mathit{C}H_2CH_2\mathit{C}H_2$), 38.2 (at, separation 14.6 Hz, $\mathit{C}H_2PPh_2$), 22.5 (s, $CH_2\mathit{C}H_2CH_2$); ^1H NMR (CD_2Cl_2) δ 8.02 (br, Ph), 3.45 (br m, CH_2O), 3.05 (br m, CH_2PPh_2), 1.8–1.0 (m, CH_2).

Minor isomer (**17b**): ^{31}P NMR (CH_2Cl_2) δ 28.7; ^{13}C NMR (CD_2Cl_2) δ 133.4 (at, separation 8.3 Hz, Ph ortho), 132.9 (at, separation 9.1 Hz, Ph ortho), 130.6 (s, Ph para), 130.3 (s, Ph para), 128.9 (at, Ph meta), 128.4 (at, separation 8.7 Hz, Ph meta), 55.6 (s, C), 41.2 (m, $\mathit{C}H_2CH_2\mathit{C}H_2$), 37.2 (m, $\mathit{C}H_2PPh_2$), 22.5 (s, $CH_2\mathit{C}H_2CH_2$).

***fac*-[*cis*-1,5-Bis[(diphenylphosphino)methyl]-3-oxabicyclo[3.3.0]octane-*P*,*P′*,*O*]tricarbonylmanganese Tetrafluoroborate (18).** The isomeric mixture **17a**, **17b** (0.296 g, 0.407 mmol) and $AgBF_4$ (0.090 g, 0.462 mmol) were stirred in 15 mL of CH_2Cl_2 for 1.5 h. The resulting mixture was filtered through Celite to leave a bright yellow filtrate. The volume was reduced to 10 mL in vacuo, and the product was precipitated by the addition of 20 mL of pentane. The product was isolated by filtration, washed twice with 10 mL of diethyl ether, and dried in vacuo. Yield: 0.25 g (85%). MS (FAB): *m/e* (ion, relative intensity) 647 (M^+, 71), 591 (M^+ – 2CO, 20), 563 (M^+ – 3CO, 47). ^{31}P NMR (CH_2Cl_2): δ 20.0. ^{13}C NMR (CD_2Cl_2): δ 223.2 (t, CO_{ax}), 214.7 (m, CO_{eq}), 137.0 (d, separation 22.6 Hz, Ph ipso), 136.7 (d, separation 21.8 Hz, Ph ipso), 131.4 (at, separation 9.1 hz, Ph ortho), 131.1 (s, Ph para), 131.0 (s, Ph para), 130.8 (at, separation 9.5 Hz, Ph ortho), 130.0 (at, separation 9.5 Hz, Ph meta), 129.6 (at, separation 9.9 Hz, Ph meta), 86.0 (at, separation 14.6 Hz, CH_2O), 54.8 (s, $\mathit{C}C_4$), 39.6 (at, separation 10.3 Hz, $\mathit{C}H_2CH_2\mathit{C}H_2$), 32.7 (at, separation 18.6 Hz, $\mathit{C}H_2PPh_2$), 22.5 (s, $CH_2\mathit{C}H_2CH_2$). ^1H NMR (CD_2Cl_2, 500 MHz): δ 7.70 (m, Ph ortho), 7.53 (m, Ph meta), 7.48 (m, Ph para), 7.35 (m, Ph ortho), 7.18 (m, Ph para), 7.04 (m, Ph meta), 3.84 (d, $^2J_{HH}$ = 10.5 Hz, 2 H, CH_2O), 3.64 ("filled in" dd, $^2J_{HH}$ = 16.5 Hz, separation 13.5 Hz, 2 H, $C\mathit{H}_2PPh_2$), 3.42 (bd, $^2J_{HH}$ = 16.5 Hz, 2 H, $C\mathit{H}_2PPh_2$), 3.39 (d, $^2J_{HH}$ = 10.5 Hz, 2 H, CH_2O), 2.06 (m, 2 H, H_B), 1.95 (m, 3 H, $H_{A,C}$), 1.55 (m, 1 H, H_D). Λ_M (CH_2Cl_2) = 27.0 Ω^{-1} cm^2 mol^{-1} at 2.29 mM.

Crystal and Molecular Structure Solution of (6)$Mo(CO)_4$ (13). A colorless crystal of the title compound was attached to the tip of a glass fiber, moved into the cold stream of the low-temperature device on the diffractometer, and cooled to –10 °C. The cell constants for data collection were determined from a list of reflections found by an automated search routine. The final cell constants were determined after data collection using 25 well-centered high-angle reflections. Pertinent data collection and reduction information is given in Table I.

A total of 10 108 reflections were collected in the $\pm h,k,\pm l$ hemisphere. Lorentz and polarization corrections and an absorption correction based on a series of ψ-scans were applied. The agreement factor for the averaging of 642 observed reflections was 1.7% (based on *I*).

The centric space group $P\bar{1}$ was initially chosen, as suggested by intensity statistics; this choice was verified by the successful

Table I. Crystallographic Data for (6)Mo(CO)$_4$ (13) and (6)W(CO)$_3$ (16)

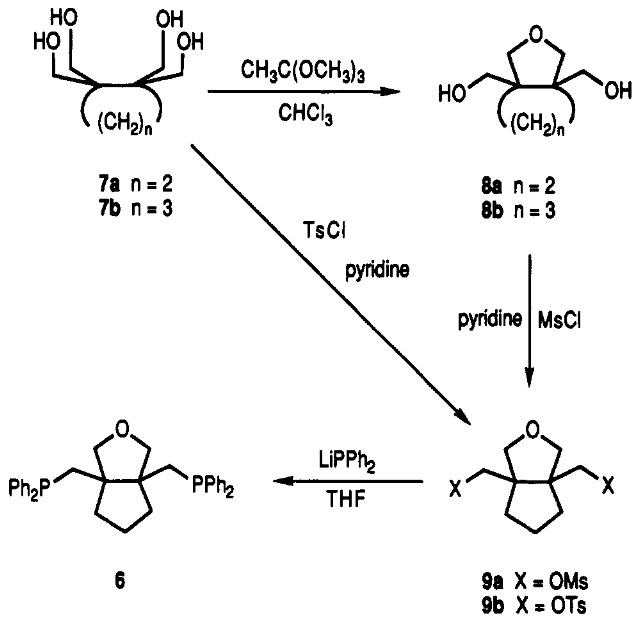
	13	16
formula	$C_{37}H_{34}O_5P_2Mo{\cdot}CH_2Cl_2$	$C_{36}H_{34}O_4P_2W{\cdot}CH_2Cl_2$
fw	801.50	861.39
space group	$P\bar{1}$	$P2_1/c$ (No. 14)
a, Å	15.321 (3)	12.262 (5)
b, Å	22.371 (3)	17.38 (1)
c, Å	11.376 (2)	16.285 (7)
α, deg	90.52 (1)	
β, deg	91.80 (1)	92.08 (4)
γ, deg	72.07 (1)	
V, Å^3	3708 (1)	3468 (3)
Z	4	4
d_{calc}, g/cm^3	1.436	1.650
cryst size, mm	0.48 × 0.24 × 0.18	0.30 × 0.45 × 0.50
μ(Mo Kα), cm^{-1}	6.15	36.85
data collcn instrument	Enraf-Nonius CAD4	Rigaku AFC6R
λ (Mo Kα radiation, monochromated in incident beam), Å	0.71073	0.71069
orientation reflns, no., range (2θ)	25, 21–34	25, 12.5–15.2
temp, °C	-10 (1)	-15
scan method	θ–2θ	ω–2θ
data collcn range, 2θ, deg	4.0–45.0	0–55.2
total no. of unique data	9667	8290
total with $F_o^2 > 3\sigma(F_o^2)$	6702	4068
no. of params refined	615	460
transm factors, max, min (ψ-scans)	0.999,0.947	
R^a	0.059	0.076
R_w^b	0.079	0.093
quality-of-fit indicator^c	2.10	2.53
largest shift/esd, final cycle	0.03	0.36
largest peak, e/Å^3	1.2 (1)	6.09

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = |\sum w(|F_o| - F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}Quality-of-fit $= \sum w(|F_o| - F_c|)^2/(N_{obs} - N_{params})]^{1/2}$.

solution and refinement of the structure. The positions of the two independent Mo atoms were taken from a Patterson map. The remaining non-hydrogen atoms were then found through subsequent sets of difference Fourier maps and least-squares refinement. Two molecules of CH_2Cl_2 were also located in the lattice. The occupancies of the two solvent molecules were included in the refinement; the final occupancy values were 0.80 (2) and 0.88 (2). In the final stages of refinement, all of the non-hydrogen atoms except for the phenyl carbon atoms and the solvent carbon atoms were refined with anisotropic temperature factors. Hydrogen atoms were added in idealized positions with isotropic temperature factors set equal to 1.3 times the isotropic equivalent of the attached carbon atom. An analysis of the environment around each complex verified the independence of the two molecules.

There was a potential ambiguity in the identity of the two unique atoms (one carbon and one oxygen) of the two fused five-membered rings in each complex. The initial identification was made by observation of the refined values of the isotropic thermal parameters. This assignment was later confirmed by using carbon scattering factors for both atoms, fixing isotropic B values at 4.0 for each atom, and refining the positions and occupancy of each atom. For each of the two molecules, the occupancy of the atom previously assigned as oxygen refined to approximately 0.8 and the other occupancy to about 1.2, confirming the initial assignment. Refinement calculations were performed on a Digital Equipment Corp. Micro VAXII computer using the CAD4-SDP programs.[24]

Scheme I



Crystal and Molecular Structure Solution of (6)W(CO)$_3$ (16). A yellow crystal of 16 was mounted on a glass fiber and centered on a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation and a 12-kW rotating anode generator. Cell dimensions and the orientation matrix were obtained from least-squares refinement using setting angles of 25 carefully centered reflections in the range $12.52 < 2\theta < 15.17°$. Since the intensities of three representative reflections measured after every 150 reflections remained constant throughout data collection, no decay correction was applied. Lorentz and polarization corrections were applied to the data. Refinement of the structure was performed by using the TEXSAN crystallographic software package.[25] Scattering factors were obtained from Cromer and Waber.[26]

The space group $P2_1/c$ (No. 14) was initially chosen and subsequently verified by the successful solution and refinement of the structure. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement, which was based on 4068 observed reflections with $I > 3\sigma(I)$ and 460 variable parameters, converged with unweighted and weighted agreement factors of 0.076 and 0.093, respectively.

Refinement of the structure with absorption-corrected data did not yield lower residuals and therefore absorption corrections were omitted, leading to a high residual electron density of 6.09 e/Å^3 in the vicinity of the tungsten atom. When the residual peaks in the difference electron density map were ignored within ~1.0 Å about the tungsten atom, the next largest peak was found near C37 of CH_2Cl_2, which is probably due to the disorder of this solvent molecule.

Results and Discussion

Synthesis of Ligand 6. Previous work from our group[27] showed that reaction of the tetrol **7a** with trimethylorthoacetate in chloroform unexpectedly yielded the diol–ether **8a** in the presence of an acid catalyst. A similar procedure starting with **7b**, followed by reaction with methanesulfonyl chloride in pyridine yielded the dimesylate–ether **9a**. The tosylate derivative **9b** has previously been synthesized[28] directly from **7b**, but in our hands the yield was low.

Substitution of the mesylate groups in **9a** by PPh_2 moieties was achieved by using $LiPPh_2$ in THF. The residue obtained after workup was chromatographed on silica gel with 10% EtOAc/toluene to give pure **6**.

This new diphosphine ether is a crystalline air-stable white solid that is soluble in toluene, tetrahydrofuran, diethyl ether, and CH_2Cl_2. Typical of tertiary phosphines, Scheme II

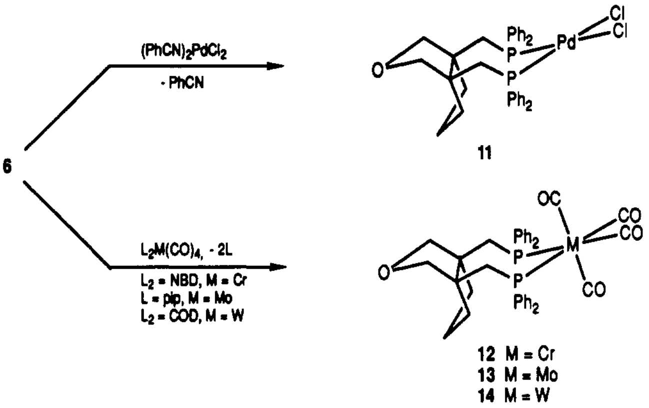
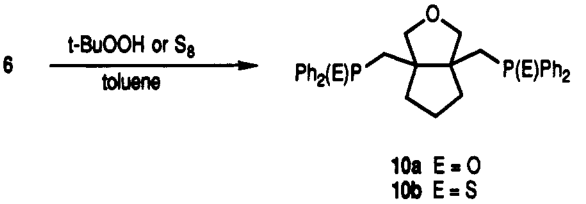


Table II. Infrared (ν_{CO}, cm^{-1}) Spectroscopic Data[a]

12, (**6**)Cr(CO)$_4$	2014	1925	1877	1863
13, (**6**)Mo(CO)$_4$	2027	1934	1886	1869
14, (**6**)W(CO)$_4$	2021	1917	1892	1863
15, (**6**)Mo(CO)$_3$		1921	1826	1763
16, (**6**)W(CO)$_3$		1913	1819	1757
17a,[b] *fac*-(**6**)Mn(CO)$_3$Br	2023	1956	1911	
18,[c] [(**6**)Mn(CO)$_3$]BF$_4$	2044	1981	1931	

[a] Samples prepared as Nujol mulls except where indicated. [b] IR bands for the minor isomer **17b** were not observed in this mixture of isomers. [c] CH$_2$Cl$_2$ solution.

6 is readily oxidized with *t*-BuOOH or S$_8$ in toluene giving **10a** or **10b**, respectively (reaction 2). These compounds



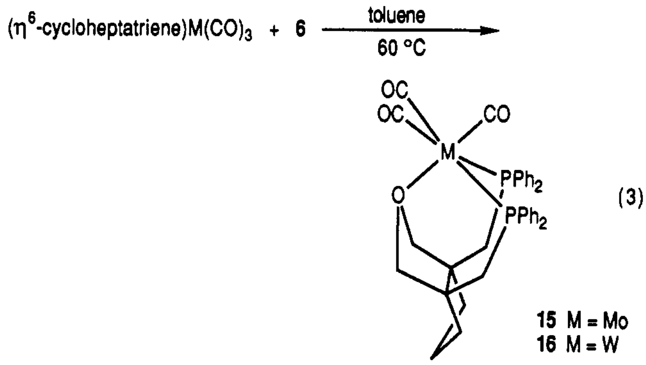
(2)

were isolated as stable white solids, and their constitutions were confirmed by NMR and high-resolution mass spectroscopies.

Coordination Chemistry of 6. Addition of **6** to (PhCN)$_2$PdCl$_2$ in toluene resulted in the precipitation of **11** in Scheme II as a creamy white solid in almost quantitative yield. This compound is insoluble in most organic solvents but exhibits moderate solubility in DMSO. Solutions of **11** in DMSO exhibit a singlet in the ^{31}P NMR spectrum at 22.8 ppm and resonances in the ^{1}H and ^{13}C NMR spectra consistent with the formulation of **11** as a cis square-planar complex wherein **6** is coordinated through the two phosphorus atoms.

Addition of **6** to CH$_2$Cl$_2$ solutions of *cis*-L$_2$Mo(CO)$_4$ (L$_2$ = NBD, (piperidine)$_2$, COD; M = Cr, Mo, W) yields the complexes **12–14** in Scheme II as pale white to light yellow solids. In contrast to **11**, these complexes exhibit high solubility in CH$_2$Cl$_2$ and THF, allowing purification by column chromatography and easy spectroscopic identification. These complexes exhibit singlets in their ^{31}P NMR spectra, except for **14**, which also shows satellites for ^{31}P–^{183}W coupling with a value of 232 Hz. The four strong carbonyl stretches in the infrared spectra of **12–14** (Table II) are in a range consistent with cis phosphine-substituted tetracarbonyls. An X-ray crystallographic study of **13** confirms this assignment. ^{1}H and ^{13}C NMR spectral evidence for these complexes will be discussed later.

In addition to a bidentate phosphine coordination mode (*P,P'*) for **6** as in complexes **11–14**, a tridentate coordination mode (*P,P',O*) is also accessible via coordination of the ether oxygen. Heating solutions of **6** and (η^6-cycloheptatriene)Mo(CO)$_3$ or (η^6-cycloheptatriene)W(CO)$_3$ in toluene at 40–60 °C results in the precipitation of **15** or **16** as bright yellow solids in 70–80% yield (reaction 3).



(3)

These complexes are moderately air stable as solids, but their CH$_2$Cl$_2$ solutions rapidly decompose upon exposure to air.

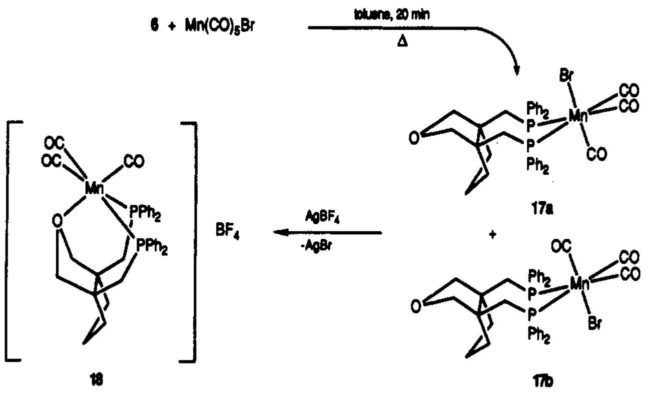
The constitutions of **15** and **16** were confirmed by their mass spectra as well as their IR and NMR spectroscopic properties. Both **15** and **16** show strong molecular ion peaks (MH$^+$) in their desorption CI mass spectra at *m/e* 690 and 777, respectively. In addition, **15** shows a molecular ion peak (M$^+$) in its EI mass spectrum and its molecular formula was confirmed by high-resolution measurement. The appearance of three strong carbonyl stretches in the IR spectra of **15** and **16** supports a facial tricarbonyl species (Table II). Strong evidence for coordination of the ether functionality is also provided by the large shift of carbonyl stretching frequencies to as low as 1763 cm^{-1} for **15** and 1757 cm^{-1} for **16**. Such a shift to lower frequency is expected on the basis of the lack of π acceptor capability of ether donors, resulting in an increase in the strength of M–C back-bonding, especially for the carbonyl trans to the ether oxygen. An attempt was also made to assign the asymmetric ν_{C-O-C} mode for the coordinated ether. Lindner[7,29] has reported that upon ether coordination in metal complexes of ether-substituted phosphines, ν_{C-O-C} shifts to lower frequency by 30–40 cm^{-1}. Although **6** exhibits a weak asymmetric ν_{C-O-C} band at 1082 cm^{-1}, the low intensity of this stretch did not allow for a reliable assignment to be made in the spectra of **15** and **16**.

Attempts to prepare the chromium analogue of **15** and **16** were unsuccessful. No reaction was observed when solutions of (η^6-cycloheptatriene)Cr(CO)$_3$ and **6** were heated in toluene at temperatures up to 100 °C for 12 h. Lower temperatures and longer reaction times also yielded no reaction. Refluxing the two starting materials in xylene yielded only decomposition and disproportionation products. Analysis of this solution by ^{31}P NMR spectroscopy revealed the two major products to be unreacted ligand **6** and the tetracarbonyl derivative **12**.

Mn(CO)$_5$Br was found to react with **6** in refluxing toluene to give (**6**)Mn(CO)$_3$Br as a mixture of two *fac* isomers **17a** and **17b**, which was confirmed by ^{31}P and ^{13}C NMR spectroscopy. Here the isomerism arises from the inequivalency of the two axial sites due to the lack of symmetry of the ligand **6**.

Removal of bromide from a mixture of **17a** and **17b** was achieved by reaction with a slight excess of AgBF$_4$ in CH$_2$Cl$_2$ (Scheme III). Following filtration, precipitation with pentane yielded **18** as a bright yellow solid, which was highly soluble in CH$_2$Cl$_2$. FAB MS revealed a large molecular ion peak (excluding BF$_4^-$) at *m/e* 647. The ionic nature of **18** is shown by its conductivity in CH$_2$Cl$_2$, Λ_m = 27 Ω^{-1} cm^2 mol^{-1}. Although this conductance seems low, it is in the range 20–30 Ω^{-1} cm^2 mol^{-1} observed previously

Scheme III



for other 1:1 electrolytes in CH_2Cl_2.[30] This conductivity, as well as ^1H and ^{13}C NMR data, confirms the coordination of the ether oxygen to manganese. Infrared data are also consistent with a facial tricarbonyl species. Whereas coordination of the ether oxygen in 15 and 16 significantly lowers the carbonyl stretching frequencies to as low as ~1760 cm^{-1}, they remain in the region 2044–1931 cm^{-1} in the case of 18. Presumably, this arises from the formation of a positive charge on manganese, which offsets the expected increase in M–CO back-bonding anticipated for the axial carbonyl upon ether coordination.

Crystallographic Studies. Slow evaporation of a CH_2Cl_2 solution of 13 yielded clear colorless crystals suitable for X-ray analysis. In addition to two solvent molecules, the unit cell contains two independent molecules of the complex, each with the same overall geometry but differing by small variations in bond distances and angles (Figure 1). The distorted octahedral geometry around Mo is comprised of two cis phosphorus atoms from 6 and four carbonyl ligands. The average Mo–P distance of 2.543 (2) Å is in the range reported previously for other phosphine complexes of molybdenum carbonyls.[31] The Mo–C distances for the carbonyls trans to phosphorus average 1.977 (9) Å. This is shorter than the Mo–C distances for the mutually trans axial carbonyls, as is expected for the poorer π acceptor ability of P compared with CO. Furthermore, the mutually trans carbonyls occupy stereochemically nonequivalent axial sites which is reflected in the Mo–C bond distances. The Mo–C distances of 2.061 (9) and 2.048 (8) Å for C(1) and C(5), which occupy the axial positions nearest the two phenyl rings, are significantly elongated compared with 2.021 (8) and 2.011 (7) Å for C(4) and C(8), which are nearest the cyclopentane ring of ligand 6 (See Table III).

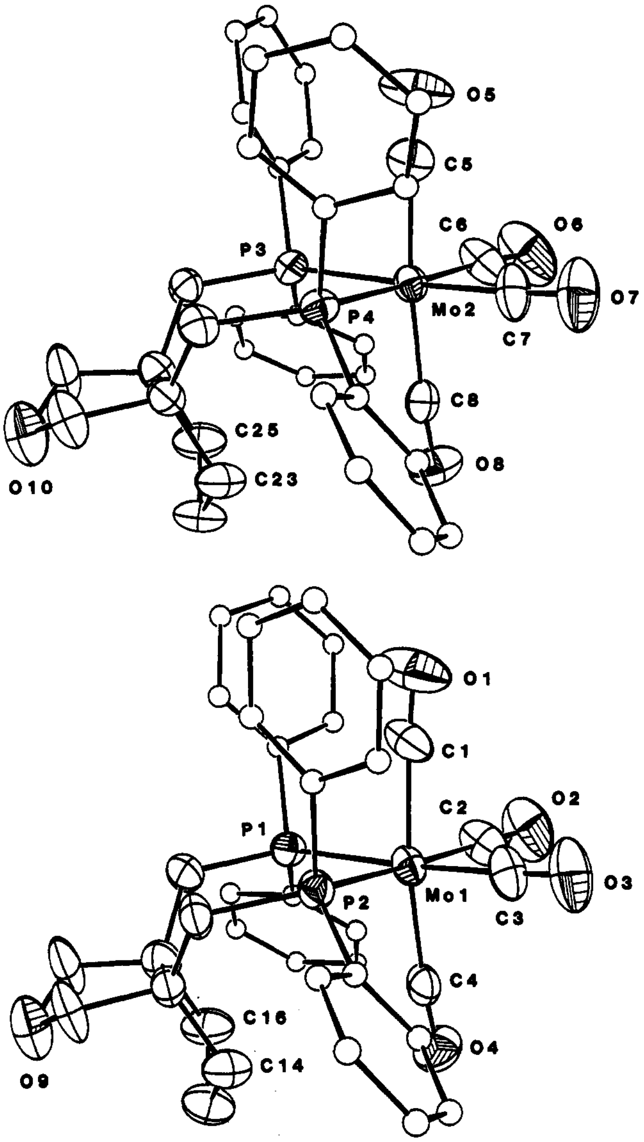


Figure 1. ORTEP drawings of each of the independent molecules of 13 with ellipsoids drawn at the 50% probability level.

Table III. Selected Bond Distances (Å) and Angles (deg) for 13•CH_2Cl_2

	Bond Distances		
Mo(1)–P(1)	2.544 (2)	Mo(1)–C(3)	1.981 (9)
Mo(1)–P(2)	2.546 (2)	Mo(1)–C(4)	2.021 (8)
Mo(2)–P(3)	2.543 (2)	Mo(2)–C(5)	2.048 (8)
Mo(2)–P(4)	2.539 (2)	Mo(2)–C(6)	1.980 (9)
Mo(1)–C(1)	2.061 (9)	Mo(2)–C(7)	1.965 (8)
Mo(1)–C(2)	1.983 (8)	Mo(2)–C(8)	2.011 (7)
	Bond Angles		
P(1)–Mo(1)–P(2)	93.05 (6)	P(3)–Mo(2)–P(4)	94.00 (7)
P(1)–Mo(1)–C(1)	90.0 (3)	P(3)–Mo(2)–C(5)	89.9 (2)
P(1)–Mo(1)–C(2)	92.8 (3)	P(3)–Mo(2)–C(6)	91.4 (3)
P(1)–Mo(1)–C(3)	176.0 (2)	P(3)–Mo(2)–C(7)	177.4 (2)
P(1)–Mo(1)–C(4)	93.2 (2)	P(3)–Mo(2)–C(8)	92.3 (2)
P(2)–Mo(1)–C(1)	89.4 (2)	P(4)–Mo(2)–C(5)	88.5 (3)
P(2)–Mo(1)–C(2)	173.0 (3)	P(4)–Mo(2)–C(6)	173.5 (3)
P(2)–Mo(1)–C(3)	84.8 (2)	P(4)–Mo(2)–C(7)	87.0 (3)
P(2)–Mo(1)–C(4)	96.9 (2)	P(4)–Mo(2)–C(8)	96.8 (2)
C(1)–Mo(1)–C(2)	86.7 (3)	C(5)–Mo(2)–C(6)	88.0 (4)
C(1)–Mo(1)–C(3)	86.6 (4)	C(5)–Mo(2)–C(7)	87.7 (3)
C(1)–Mo(1)–C(4)	172.7 (3)	C(5)–Mo(2)–C(8)	174.1 (4)
C(2)–Mo(1)–C(3)	89.1 (4)	C(6)–Mo(2)–C(7)	87.4 (4)
C(2)–Mo(1)–C(4)	86.6 (3)	C(6)–Mo(2)–C(8)	86.5 (3)
C(3)–Mo(1)–C(4)	90.3 (3)	C(7)–Mo(2)–C(8)	90.0 (3)

The geometry around Mo reveals a distortion of the carbonyls away from the phosphine ligand, presumably due to steric hindrance. The average P–Mo–P angle has been opened up to 93.5°. Most P–Mo–C angles also slightly exceed 90°, with the largest deviations being 96.8 (2) and 96.9 (2)° for P(4)–Mo(2)–C(8) and P(2)–Mo(1)–C(4), respectively. However, P(2)–Mo(1)–C(3) exhibits a much smaller angle of 84.8 (2)°. To offset the slightly larger-than-ideal P–Mo–C angles, the C–Mo–C angles are slightly less than 90° with an average value of 87.9°. The distortion from an idealized octahedral geometry is also readily apparent by noting that the trans C–Mo–C and P–Mo–C angles vary from 172.7 (3) to 177.4 (2)°. An important feature to note in this structure is the orientation of one methylene proton toward the face of a phenyl ring on each of carbons 14, 16 and 23, 25 in the cyclopentane ring. The

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[30] (a) Uguagliati, P.; Deganello, G.; Busetto, L.; Belluco, U. *Inorg. Chem.* **1969**, *8*, 1625. (b) Rosenthal, M. R.; Drago, R. S. *Inorg. Chem.* **1965**, *4*, 840.

[31] Bernal, I.; Reisner, G. M.; Dobson, G. R.; Dobson, C. B. *Inorg. Chim. Acta* **1986**, *121*, 199 and references therein.

Table IV. Selected Bond Distances (Å) and Angles (deg) for 16•CH_2Cl_2

	Bond Distances		
W(1)-P(1)	2.558 (5)	W(1)-C(3)	1.98 (2)
W(1)-P(2)	2.550 (5)	O(1)-C(1)	1.19 (2)
W(1)-O(4)	2.33 (1)	O(2)-C(2)	1.15 (3)
W(1)-C(1)	1.91 (2)	O(3)-C(3)	1.12 (3)
W(1)-C(2)	1.98 (2)		
	Bond Angles		
P(1)-W(1)-P(2)	83.2 (2)	P(2)-W(1)-C(3)	170.5 (6)
P(1)-W(1)-O(4)	88.6 (4)	O(4)-W(1)-C(1)	178.0 (7)
P(1)-W(1)-C(1)	92.1 (7)	O(4)-W(1)-C(2)	91.5 (7)
P(1)-W(1)-C(2)	178.1 (6)	O(4)-W(1)-C(3)	88.9 (7)
P(1)-W(1)-C(3)	91.4 (6)	C(1)-W(1)-C(2)	87.7 (9)
P(2)-W(1)-O(4)	83.2 (3)	C(1)-W(1)-C(3)	89.3 (9)
P(2)-W(1)-C(1)	98.7 (6)	C(2)-W(1)-C(3)	86.7 (9)
P(2)-W(1)-C(2)	98.8 (6)		

implications of such a conformation and its effect on ^1H and ^{13}C NMR spectra of these complexes will be discussed later. Also, of the two five-membered rings in 6, it should be noted that the ether-containing ring is pointed away from the metal center.

Slow evaporation of a CH_2Cl_2 solution of 16 yielded yellow crystals of X-ray quality as a CH_2Cl_2 solvate (Figure 2). The distorted octahedral coordination sphere around tungsten is comprised of three carbonyls in a *fac* arrangement as well as an oxygen and two phosphorus donors, verifying the tridentate coordination mode for 6 in 16. The P(1)-W(1)-P(2) angle has decreased upon ether coordination to 83.2°, an angle considerably less than the 93.5° angle observed in 13. All C-W-C angles between carbonyls as well as P-W-O angles of 6 are less than 90° whereas all P-W-C and O-W-C angles exceed 90°, indicating the expected distortion of the carbonyls away from the steric bulk of 6. The largest deviations from an ideal octahedron are observed for P(2)-W(1)-O(4), P(2)-W(1)-C(1), and P(2)-W(1)-C(2) with angles of 83.2 (3), 98.7 (6), and 98.8 (6)°, respectively (see Table IV).

Two W-C distances are observed for the two types of nonequivalent carbonyls in 16. The two carbonyls trans to phosphorus atoms exhibit a W-C distance of 1.98 (2) Å in agreement with the analogous Mo-C distances in 13.[32] The W-C distance of 1.91 (2) Å observed for the carbonyl trans to the coordinated ether represents a considerable bond shortening when compared to the Mo-C distances for the mutually trans carbonyls in 13, which range from 2.011 (7) to 2.061 (9) Å. This decrease in W-C bond distance in 16 is consistent with an increase in W-C π bonding for the carbonyl trans to the poor π-accepting ether oxygen, as is further substantiated by the low ν_{CO} value of 1757 cm^{-1} in the infrared spectrum. The W-O distance of 2.33 (1) Å is considerably longer than the sum of the covalent radii (2.19 Å), as is expected for a weak ether-metal interaction. This distance is in agreement with Mo-O distances of 2.363 (6) and 2.337 (7) Å reported for (TMPP)$Mo(CO)_3$.[9] The W-P distances of 2.558 (5) and 2.550 (5) Å are quite normal.

^1H NMR Spectroscopic Characterization. Compound 6 exhibits resonances in three distinct regions of its ^1H NMR spectrum that are useful in the characterization of the metal complexes of this ligand. These regions are comprised of the phenyl protons, the CH_2O and CH_2PPh_2 methylene protons, and the methylene protons of the cyclopentane ring. Assignments discussed below were aided by the use of $^1H\{^{31}P\}$ spectra obtained on a

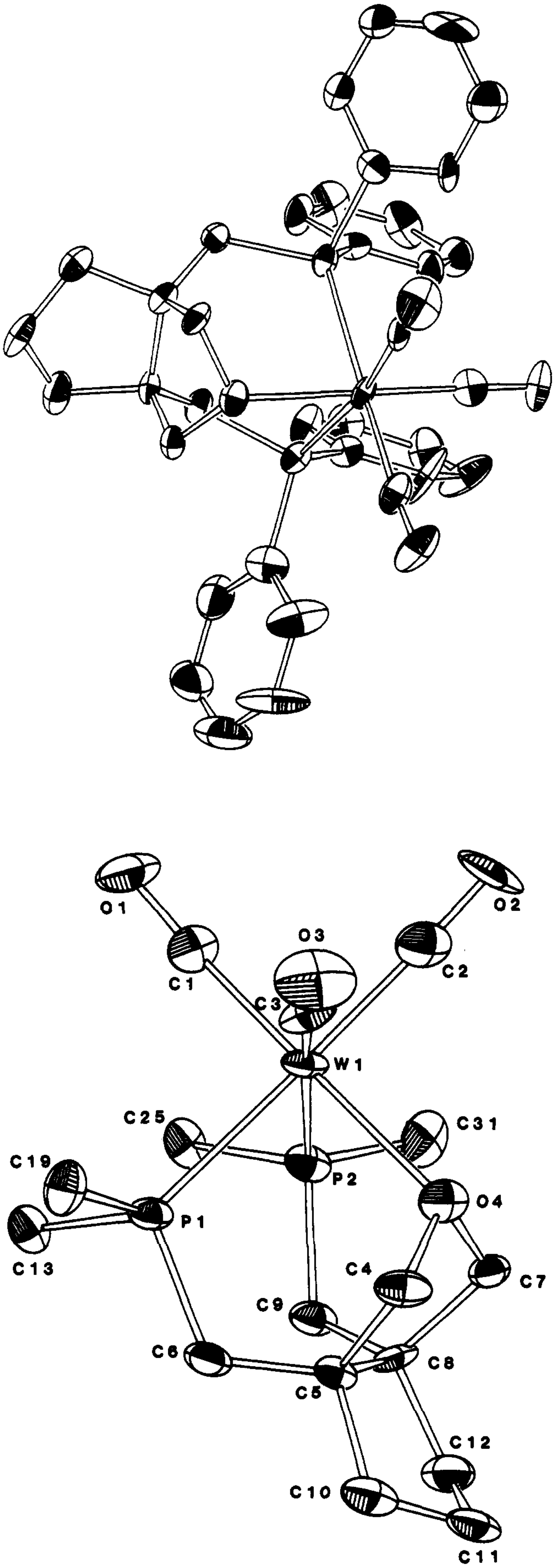

Figure 2. ORTEP drawings of 16 with ellipsoids drawn at the 50% probability level. All phenyl carbons, except for the Ph ipso carbons, have been omitted for clarity in the lower view.

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[32] The covalent radii of tungsten and molybdenum are approximately the same, 1.46 and 1.45 Å, respectively. See: Pauling, L. *Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; pp 224-249.

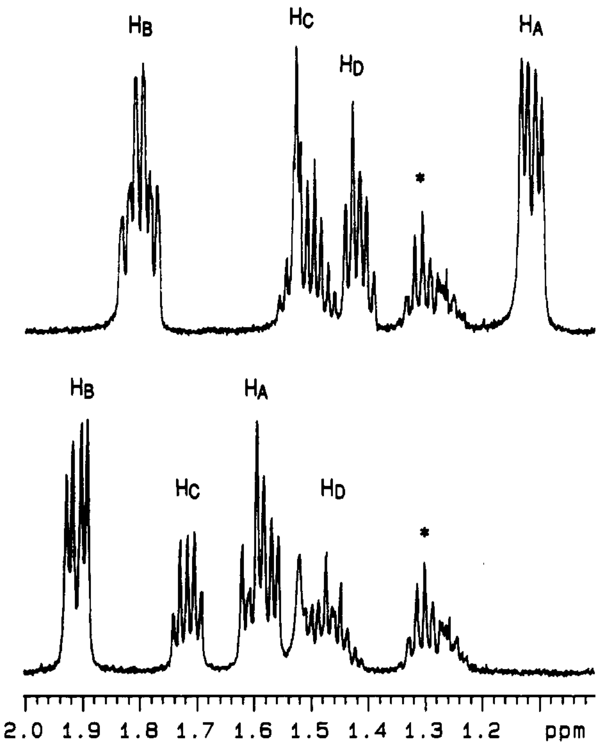


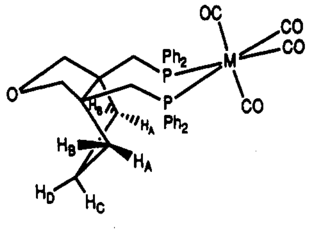
Figure 3. The cyclopentane region of the ^1H NMR (500 MHz) spectra of (6)Mo(CO)$_4$ (13) (above) and (6)Mo(CO)$_3$ (15) (below) in CD_2Cl_2. The asterisks indicate resonances due to pentane present as an impurity.

500-MHz spectrometer to assure correct assignment of couplings due to phosphorus nuclei.

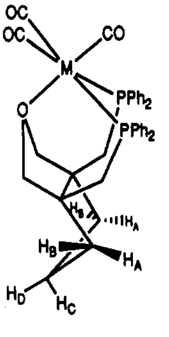
The phenyl region in **6** shows two multiplets, one centered at 7.46 ppm assigned to the ortho protons and the other at 7.31 ppm assigned to the meta and para protons. The multiplet at 7.46 ppm actually corresponds to two sets of inequivalent ortho protons owing to the presence of two sets of stereochemically nonequivalent phenyls, one each per phorphorus atom. In fact, the 500-MHz ^1H NMR spectrum of **10a** shows two well-resolved multiplets at 7.82 and 7.76 ppm for these two types of ortho protons. These multiplets are assigned to the phenyl ortho protons on the basis of integrations and on the collapse of these multiplets to doublets (with fine structure) upon phosphorus irradiation in the $^1H\{^{31}P\}$ NMR spectrum.

Compound **6** also exhibits an AB quartet centered at 3.57 ppm and an ABX pattern (X = P) centered at 2.31 ppm for the diastereotopic methylene protons adjacent to the ether oxygen and the PPh_2 groups, respectively. The region from 1.4 to 1.8 ppm is marked by complex multiplets due to the A_2B_2CD spin system for the six cyclopentane ring protons. The derivatives **10a** and **10b** display the same basic features discussed above for their parent compound **6**.

Upon coordination of **6** to an octahedral metal fragment in **12–14**, the cyclopentane portion of the spectrum features well-separated resonances. In **13** for example, a doublet of doublets at 1.12 ppm and a multiplet at 1.81 ppm are assigned to the geminal protons H_A and H_B, as shown in Figure 3. The resonance at 1.12 ppm for H_A appears as a doublet of doublets due to a strong geminal coupling to H_B of 12.3 Hz and a vicinal cis coupling to H_C of 5.4 Hz. A vicinal trans coupling of H_A to H_D is not observed, as is sometimes the case for cyclopentane rings.[33] These assignments agree with the results of a COSY experiment for **12** and $^1H\{^{31}P\}$ spectra for **12–14**, which show that none of the couplings in this region arise from P–H coupling.

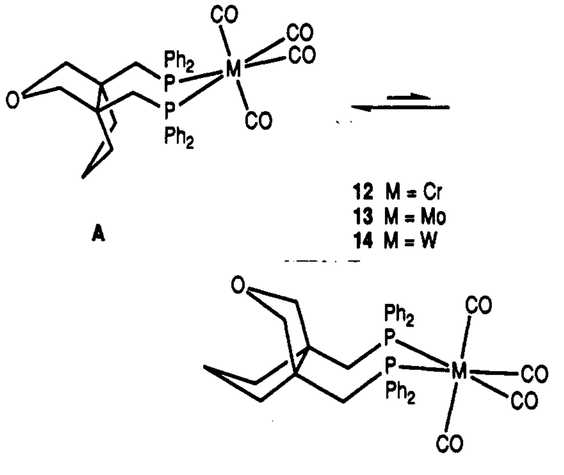


13



15

In Figure 3 it is noted that the position of H_A in **13** has been shifted significantly upfield compared with the chemical shift of H_B and compared with the corresponding resonances for **6**, **10a**, and **10b**. Presumably, this upfield shift has been induced by a neighboring phenyl ring. The crystal structure of **13** indeed shows that H_A is oriented toward the face of a phenyl ring on phosphorus *in the solid state*. In solution one might expect fluxionality between conformations wherein the two five-membered rings switch positions, as in eq 4. If such a conformational equilibrium exists, noticeable shielding should also be observed for two of the four diastereotopic CH_2O protons. However, the ^1H NMR spectrum of **13** shows an AB system centered at 3.59 ppm ($\Delta\delta_{AB}$ = 0.03 ppm) for the CH_2O protons and a partially collapsed ABX pattern at 2.99 ppm for the CH_2PPh_2 protons. Thus no significant shielding in this region is observed, prompting us to speculate that in solution the conformations of **12–14** closely resemble that found in the solid state for **13** where the ether oxygen in **6** is removed as far as possible from the metal center. Variable-temperature ^1H NMR spectra of **14** in pyridine-d_5 lend further support to this argument. As the temperature increases, the doublet of doublets resonance at 1.24 ppm assigned to H_A at 20 °C gradually shifts downfield to 1.38 ppm at 110 °C. Similarly, the difference in chemical shifts for the CH_2O proton resonances steadily increases from 0.07 ppm at 20 °C to 0.20 ppm at 110 °C. This can be explained by a shift in equilibrium toward conformation B with increasing temperature, allowing for decreased shielding at H_A and an increase in shielding for two of the four CH_2O protons.



A

12 M = Cr
13 M = Mo
14 M = W

B

(4)

Upon coordination of the ether oxygen in **15**, a doublet of doublets resonance appears in the ^1H NMR spectrum

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[33] Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley and Sons, New York, 1981; p 209.

at 1.90 ppm ($^2J_{AB}$ = 13.2 Hz, $^3J_{BD}$ = 5.1 Hz) assigned to H_B. H_A has shifted downfield to 1.58 ppm, a change of 0.46 ppm from the resonance for H_A in **13**. This is consistent with structural data for **16**, which show that upon ether coordination, none of the phenyl rings on phosphorus are oriented in a manner conducive to shielding any of the cyclopentane protons. Resonances for the diastereotopic CH_2O protons of **15** are observed as doublets ($^2J_{HH}$ = 10.5 Hz) at 4.09 and 3.29 ppm, a separation of 0.8 ppm compared with a separation of only 0.03 ppm in **13**. Similarly, a much larger separation of the CH_2PPh_2 methylene protons is also observed for **15**, **16**, and **18** compared with **12**–**14**. For example, a separation of 0.44 ppm is observed for the diastereotopic CH_2PPh_2 methylene protons of **15**, whereas in **13** the CH_2PPh_2 methylene resonance appears as a doublet with coupling only to phosphorus.

Coordination of the ether to a metal also increases the resolution of the phenyl protons. $^1H\{^{31}P\}$ spectra of **15**, **16**, and **18** clearly show well-resolved resonances for each of the two nonequivalent ortho, meta, and para protons in a window spanning, for example, from 6.98 to 7.72 ppm for **16**. Overlap of some of these resonances occurs for the non-ether coordinated complexes **12**–**14**.

^{13}C NMR Spectroscopic Characterization. In the free ligand **6**, inequivalence of the two phenyl rings is indicated by the observance of two doublets for the ipso carbons and two doublets for the ortho carbons. The difference between the chemical shifts of the phenyl carbons increases upon oxidation because two doublets each are observed for the ipso, ortho, meta and para carbons in **10a** and **10b**. Also, the oxidation of phosphorus in **10a** and **10b** is supported by the large $^1J_{PC(ipso)}$ values[34] of 98 and 80 Hz, respectively.

In the ^{13}C NMR spectra of **12**–**14**, resonances are also observed for two nonequivalent phenyl rings. The multiplicities of these resonances vary, however. The ortho and meta resonances are "apparent" triplets with two much smaller, but observable, satellites. The couplings in these virtually coupled triplets are reported here as the separation between lines 2 and 4 (counting the smaller two satellites as lines 1 and 5), and these separations represent the sum of two coupling constants, $|^nJ_{PC} + {}^{n+2}J_{PC}|$. Phenyl ipso carbon resonances appear as five-line multiplets[35] for **12** and **13** but as doublets with a small center line for **14**. These multiplicities follow the trend expected for a decreasing value of $J_{PP'}$ for the heavier metals in group VI for an AXX′ spin system.[36] This spin system and its relevance to group VI metal carbonyl complexes[37] have been fully detailed previously. All of the methylene carbons of ligand **6** exhibit similar five-line patterns, usually as apparent triplets, except for the central methylene in the cyclopentane ring which appears as a singlet in all metal complexes reported here.

The symmetry of **6** imposes an inequivalency upon the axial positions of octahedral metal complexes of this ligand. This asymmetry is revealed in the ^{13}C NMR spectra of **12**–**14**. In the spectrum of **13** for instance, three carbonyl resonances are observed. Two triplets of equal intensity at 212.0 and 206.0 ppm are assigned to two nonequivalent axial carbonyls. For the two equatorial carbonyls a five-line multiplet of the virtual type is observed at 215.9 ppm with twice the intensity of an axial carbonyl resonance.

As expected, the phenyl resonances for **15**, **16**, and **18** show the presence of two nonequivalent phenyl rings, with multiplicities similar to those described for **12**–**14**. Also, the carbonyl regions of these spectra show only two resonances. In the ^{13}C NMR spectrum of **15**, a five-line multiplet is observed at 219.9 ppm for the two equatorial carbonyls and a triplet with only half the intensity of the first resonance is observed at 229.0 ppm for the axial carbonyl. This represents a considerable downfield shift of this resonance upon coordination of the ether oxygen compared with the axial carbonyl chemical shifts for **13**. The lack of resonances corresponding to an additional axial carbonyl (or some other additional ligand) supports the assignment of a structure wherein **6** binds in a tridentate (*P,P′,O*) manner. The changes observed in the CH_2O chemical shift upon coordination of the ether oxygen in **12**–**14** to the metal in **15**, **16**, and **18** were small. Thus no diagnostic trend is apparent in these particular resonances for differentiating the bidentate (*P,P′*) from tridentate (*P,P′,O*) coordination modes.

Conclusions. We have synthesized a new diphosphine ether, **6**, capable of coordinating to metal carbonyl complexes in either a bidentate (*P,P′*) or a tridentate (*P,P′,O*) coordination mode, as shown from the analysis of spectroscopic and structural data. The ^{1}H NMR spectra for the (*P,P′*)-coordinated octahedral metal complexes of **6** studied here are consistent with the presence of a ligand whose conformational preference in solution is similar to that observed in the crystal structure of **13**.

The weak metal–O(ether) interactions in complexes such as **15**, **16**, and **18** are expected to be quite labile. Results of substitution reactions of these complexes will be reported shortly. Further studies concerning the chemistry of **6** and its potential in catalytic systems are in progress.

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Supplementary Material Available: ORTEP diagrams with complete labeling schemes and tables of positional and thermal parameters and complete bond lengths and angles for **13** and **16** as well as a table of least-squares planes for **13** and anisotropic thermal parameters for **16** (26 pages); listings of structure factors for **13** and **16** (65 pages). Ordering information is given on any current masthead page.

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[34] (a) Modro, T. A. *Can. J. Chem.* **1977**, *55*, 3681. (b) Albright, T. A.; Freeman, W. J.; Schweizer, E. E. *J. Org. Chem.* **1975**, *40*, 3437.

[35] The small central line of these five-line multiplets is actually composed of two lines that are resolved in some spectra. Six lines are expected for the X portion of an ABX system. See: Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High Resolution Nuclear Magnetic Resonance*; McGraw-Hill Book Co.: New York, 1959; pp 132–135.

[36] (a) Pregosin, P. S.; Kunz, R. W. *NMR: Basic Princ. Progr.* **1979**, *16*, 65. (b) Redfield, D. A.; Nelson, J. H.; Carey, L. W. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 727.

[37] Andrews, G. T.; Colquhoun, I. J.; McFarlane, W. *Polyhedron* **1983**, *2*, 783.