Ligand Substitution Reactions in Group 6 Metal Carbonyl Complexes of a Novel Bicyclic Ditertiary Phosphine Ether

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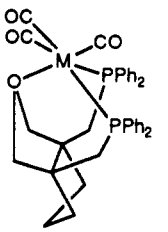
The complexes *fac*-(1-*P*,*P*′,*O*)M(CO)$_3$, where M = Mo or W and 1 is *cis*-1,5-bis((diphenylphosphino)-methyl)-3-oxabicyclo[3.3.0]octane, were found to react with the ligands L = acetonitrile, piperidine, pyridine, and P(OCH$_2$)$_3$CCH$_3$ to yield two diastereomers of *fac*-(1-*P*,*P*′)M(CO)$_3$(L) in each case. ^{1}H and ^{13}C NMR spectroscopic data suggest that the major isomer in each product is that in which the added ligand occupies the site originally occupied by the ether oxygen of 1 and that the minor isomer contains the new ligand in the position trans to this site. Carbon monoxide reacts with the complexes *fac*-(1-*P*,*P*′,*O*)M(CO)$_3$ (M = Mo, W) to yield (1-*P*,*P*′)M(CO)$_4$. Using ^{13}CO, these reactions stereoselectively yield two diastereomers of *fac*-(1-*P*,*P*′)M(CO)$_3$(^{13}CO) in ratios of approximately 5:1 and 7:1 for M = Mo and W, respectively. A scheme involving the isomerization of diastereomeric five-coordinate square-pyramidal intermediates is discussed. The N-donor complexes *fac*-(1-*P*,*P*′)M(CO)$_3$L, where M = Mo and W and L = acetonitrile, pyridine, and piperidine, were observed by infrared and ^{1}H and ^{31}P NMR spectroscopy to partially dissociate in solution, equilibrating with free L and *fac*-(1-*P*,*P*′,*O*)M(CO)$_3$. This equilibrium was further substantiated by monitoring the exchange reaction between free and coordinated CD$_3$CN in the presence of *fac*-(1-*P*,*P*′)Mo(CO)$_3$(NCCH$_3$) using ^{2}H NMR spectroscopy.

Introduction

Considerable interest in phosphines possessing ether functional groups capable of coordinating to transition metals has been generated in recent years.[1-14] This interest is based on the lability of the metal–ether interaction, which can dissociatively liberate metal sites for coordination of additional ligands. Such lability has been demonstrated in several metal systems for a variety of ether-containing phosphines by substitution of the coordinated ether with ethylene (Rh),[2] acetylenes (Rh),[2] phosphites (Mo, W),[3] nitriles (Mo,[4] Ru[5]), dimethyl sulfide (Pt),[6] pyridine (Pt),[6] isocyanides (Ru),[5] and carbon monoxide (Mo,[3] W,[3,7] Rh,[2,8] Ru,[5,9] Pt[6]).

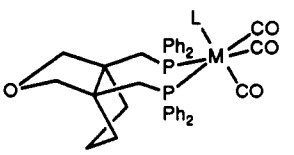
Our investigations of the new ditertiary phosphine ether *cis*-1,5-bis((diphenylphosphino)methyl)-3-oxabicyclo-[3.3.0]octane (1) have recently shown that this ligand coordinates to transition metals in either a tridentate (P,P′,O) or bidentate (P,P′) manner, as demonstrated by spectroscopic and structural data for **2** and **3** (Chart I) and for **4**–**6**, respectively[10] (Chart II). Ligand 1 differs from previously reported ether-containing phosphines in that it is a chelating bidentate phosphine capable of forming

Chart I. P,P′,O Coordination Mode of 1



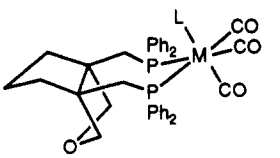
2, M = Mo
3, M = W

Chart II. P,P′ Coordination Mode of 1



A

	M	L
4	Cr	CO
5	Mo	CO
6	W	CO
7a	Mo	P(OCH$_2$)$_3$CCH$_3$
8a	W	P(OCH$_2$)$_3$CCH$_3$
9a	Mo	py
10a	W	py
11a	Mo	NCMe
12a	W	NCMe
13a	W	pip



B

	M	L
7b	Mo	P(OCH$_2$)$_3$CCH$_3$
8b	W	P(OCH$_2$)$_3$CCH$_3$
9b	Mo	py
10b	W	py
11b	Mo	NCMe
12b	W	NCMe
13b	W	pip

(1) (a) Reddy, V. V. S.; Varshney, A.; Gray, G. M. *J. Organomet. Chem.* **1990**, *391*, 259. (b) Chen, S. J.; Dunbar, K. R. *Inorg. Chem.* **1990**, *29*, 588. (c) Lindner, E.; Norz, H. *Chem. Ber.* **1990**, *123*, 459. (d) Lindner, E.; Glaser, E. *J. Organomet. Chem.* **1990**, *391*, C37. (e) Lindner, E.; Speidel, R. *Z. Naturforsch.* **1989**, *44B*, 437. (f) Dunbar, K. R.; Haefner, S. C.; Pence, L. E. *J. Am. Chem. Soc.* **1989**, *111*, 5504. (g) Lindner, E.; Andres, B. *Chem. Ber.* **1988**, *121*, 829. (h) Lindner, E.; Sickinger, A.; Wegner, P. *J. Organomet. Chem.* **1988**, *349*, 75. (i) Lindner, E.; Sickinger, A.; Wegner, P. *J. Organomet. Chem.* **1986**, *312*, C37. (j) Lindner, E.; Meyer, S. *J. Organomet. Chem.* **1988**, *339*, 193. (k) Lindner, E.; Schober, V. *Inorg. Chem.* **1988**, *27*, 212. (l) Lindner, E.; Schober, V.; Stangle, M. *J. Organomet. Chem.* **1987**, *331*, C13. (m) Brown, J. M.; Maddox, P. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1276. (n) Horner, L.; Simmons, G. *Z. Naturforsch.* **1984**, *39B* 497. (o) Lindner, E.; Rauleder, H.; Scheytt, C.; Mayer, H. A.; Hiller, W.; Fawzi, R.; Wegner, P. *Z. Naturforsch.* **1984**, *39B*, 632. (p) Miller, E. M.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1974**, 480. (q) Empsall, H. D.; Hyde, E. M.; Jones, C. E.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1974**, 1980.

(2) Werner, H.; Hampp, A.; Peters, K.; Peters, E. M.; Walz, L.; von Schnering, H. G. *Z. Naturforsch.* **1990**, *45B*, 1548.

(3) Lindner, E.; Mayer, H. A.; Wegner, P. *Chem. Ber.* **1986**, *119*, 2616.

(4) Dunbar, K. R.; Haefner, S. C.; Burzynski, D. J. *Organometallics* **1990**, *9*, 1347.

(5) Jeffrey, J. C.; Rauchfuss, T. B. *Inorg. Chem.* **1979**, *18*, 2658.

(6) Anderson, G. K.; Kumar, R. *Inorg. Chem.* **1984**, *23*, 4064.

(7) Lindner, E.; Meyer, S.; Wegner, P.; Karle, B.; Sickinger, A.; Steger, B. *J. Organomet. Chem.* **1987**, *335*, 59.

(8) Lindner, E.; Andres, B. *Chem. Ber.* **1987**, *120*, 761.

(9) (a) Rauchfuss, T. B.; Patino, F. T.; Roundhill, D. M. *Inorg. Chem.* **1975**, *14*, 652. (b) Lindner, E.; Schober, V.; Fawzi, R.; Hiller, W.; Englert, V.; Wegner, P. *Chem. Ber.* **1987**, *120*, 1621.

(10) Mason, M. R.; Su, Y.; Jacobson, R. A.; Verkade, J. G. *Organometallics* **1991**, *10*, 2335.

(11) Alcock, N. W.; Brown, J. M.; Jeffrey, J. C. *J. Chem. Soc., Dalton Trans.* **1976**, 583.

(12) (a) Knowles, W. S.; Sabacky, M. J.; Vineyard, B. D. *J. Chem. Soc., Chem. Commun.* **1972**, 10. (b) Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J.; Bachman, G. L.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5946. (c) Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106.

(13) (a) Lindner, E.; Bader, A.; Braunling, H.; Reinhard, J. *J. Mol. Catal.* **1990**, *57*, 291. (b) Lindner, E.; Schober, U.; Glaser, H.; Norz, H.; Wegner, P. *Z. Naturforsch.* **1987**, *42B*, 1527.

(14) Mason, M. R.; Verkade, J. G. *J. Am. Chem. Soc.* **1991**, *113*, 6309.

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only *fac* complexes upon coordination of the ether. Most of the ligands in this class are monotertiary phosphines with the exceptions of $(Ph_2PCH_2CH_2)_2O$,[11] DIPAMP,[12] and a few analogues of DIPAMP studied by Lindner.[13] The last groups of ligands are bidentate phosphines which contain one or more ether donors each and are not restricted to *fac* complex formation upon coordination of the ether. Additionally, ligand **1** is unique in that it forms six-membered chelate rings upon ether coordination, in contrast to the vast majority of previously reported ligands, which form five-membered chelate rings (often achieved by making use of a 2-methoxyphenyl substituent on phosphorus). Furthermore, the low symmetry of **1** allows differentiation of the two chemically different axial[15] sites in its octahedral transition-metal complexes (A and B in Chart II) when the P,P′ coordination mode is utilized. These factors may play significant roles in the chemistry of transition-metal complexes of **1**.

On the basis of the literature cited above, it was anticipated that the metal–ether interaction in complexes wherein **1** adopts a P,P′,O coordination mode would be quite weak, thus permitting facile ligand substitution reactions. Here we report the results of ligand substitution reactions of **2** and **3** leading to diastereomeric products **7a–13a** and **7b–13b**, all displaying a *fac* geometry (Chart II). Part of this work has been described in a preliminary publication.[14]

Experimental Section

All reactions were performed under an inert atmosphere of argon using standard inert-atmosphere techniques. Toluene, tetrahydrofuran, pentane, and diethyl ether were distilled from sodium benzophenone ketyl. Methylene chloride, acetonitrile, and pyridine were distilled from calcium hydride prior to use. Compounds **2**, **3**, **5**, and **6**[10] and $P(OCH_2)_3CCH_3$[16] were prepared as previously described. ^{13}CO (99%) was purchased from Cambridge Isotope Laboratories. Solution NMR spectra were recorded on Bruker WM200 (^{31}P), Varian VXR 300 (^1H, ^2H, ^{13}C, ^{31}P) or Varian Unity 500 (^1H, $^1H\{^{31}P\}$) spectrometers using a deuterated solvent as the internal lock. ^2H NMR spectra were obtained by locking on the ^1H resonance of CH_2Cl_2. The natural abundance resonance for $CHDCl_2$ (5.3 ppm, $^2J_{HD}$ = 0.9 Hz) was used as the reference and internal standard for the ^2H NMR experiment. All chemical shifts are reported relative to TMS (^1H, ^2H, ^{13}C) or 85% H_3PO_4 (^{31}P). Mass spectra were recorded on a Finnegan 4000 instrument using chemical ionization and ammonia as the carrier gas. The masses of metal-containing fragments are reported for the most abundant isotope present, viz. ^{98}Mo and ^{184}W, unless otherwise noted. IR spectra were recorded using an IBM 98 FT-IR spectrometer and CaF_2 cells. Microanalyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

***fac*-(*cis*-1,5-Bis((diphenylphosphino)methyl)-3-oxabicyclo[3.3.0]octane-*P,P′*)tricarbonyl(1-methyl-4-phospha-3,5,8-trioxabicyclo[2.2.2]octane-*P*)molybdenum (7a,b).** The ligand $P(OCH_2)_3CCH_3$ (0.0421 g, 0.284 mmol) in 5 mL of CH_2Cl_2 was added to a solution of **2** (0.183 g, 0.266 mmol) in 10 mL of CH_2Cl_2. The reaction mixture was stirred for 20 min, during which time the yellow solution became colorless. The solution was filtered through Celite to remove traces of insoluble material. The solvent was removed in vacuo from the clear filtrate to leave a white solid. Spectral data clearly showed the presence of two facial isomers in a 4:1 ratio by integration of CH_3 and CH_2OP resonances in the ^1H NMR spectrum. Recrystallization from CH_2Cl_2 yielded fine white needles of the product as an isomeric mixture. Anal. Calcd for $C_{41}H_{43}O_7P_3Mo$: C, 58.86; H, 5.18; Mo, 11.47. Found: C, 59.18; H, 5.23; Mo, 11.54.

Major Isomer (7a): MS (desorption CI, NH_3) *m/e* (relative intensity) 811 (MH^+ – CO, 4.9), 719 (6.4), 691 (66), 509 (100); ^{31}P NMR (CD_2Cl_2) δ 86.9 (t, $^2J_{PP}$ = 32 Hz, $POCH_2$), 20.2 (d, $^2J_{PP}$ = 32 Hz, PPh_2); ^{13}C NMR (CD_2Cl_2) δ 220.5 (dt, $^2J_{PC\text{-}trans}$ = 49 Hz, $^2J_{PC\text{-}cis}$ = 9.5 Hz, CO_{ax}), 218.3 (m, CO_{eq}), 144.3 (m, Ph ipso), 139.6 (m, Ph ipso), 134.3 (at,[17] separation 12.3 Hz, Ph ortho), 132.1 (at, separation 9.6 Hz, Ph ortho), 129.7 (s, Ph para), 128.6 (at, separation 9.1 Hz, Ph meta), 127.8 (s, Ph para), 127.3 (at, separation 7.9 Hz, Ph meta), 87.6 (at, separation 12.3 Hz, CH_2OCH_2), 73.3 (d, $^2J_{PC}$ = 6.0 Hz, $POCH_2$), 41.7 (at, separation 8.4 Hz, $CH_2CH_2CH_2$), 35.8 (at, separation 12.7 Hz, CH_2PPh_2), 31.6 (d, $^3J_{PC}$ = 32.1 Hz, $POCH_2C$), 24.6 (s, $CH_2CH_2CH_2$), 15.6 (s, CH_3); ^1H NMR (CD_2Cl_2) δ 7.90 (m, Ph), 7.44–7.15 (m, Ph), 3.69 (d, $^2J_{HH}$ = 9.0 Hz, CH_2OCH_2), 3.63 (dd, $^2J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 1.5 Hz, CH_2OCH_2), 3.15 (d, $^3J_{PH}$ = 3.9 Hz, CH_2OP), 2.9 (m, CH_2PPh_2), 1.64 (m, CCH_2C), 1.35 (m, CCH_2C), 0.81 (dd, $^2J_{HH}$ = 12.9 Hz, $^3J_{HH\text{-}cis}$ = 5.4 Hz, CCH_2C), 0.31 (s, CH_3).

Minor Isomer (7b): ^{31}P NMR (CD_2Cl_2) δ 85.9 (t, $^2J_{PP}$ = 31.8 Hz, $POCH_2$), 18.9 (d, $^2J_{PP}$ = 31.8 Hz, PPh_2); ^{13}C NMR (CD_2Cl_2) δ 133.7 (at, separation 12.3 Hz, Ph ortho), 132.0 (at, separation 9.5 Hz, Ph ortho), 129.9 (s, Ph para), 128.8 (at, separation 9.1 Hz, Ph meta), 127.9 (s, Ph para), 127.4 (at, separation 7.8 Hz, Ph meta), 81.4 (at, separation 10.3 Hz, CH_2O), 73.6 (d, $^2J_{PC}$ = 5.6 Hz, $POCH_2$), 49.3 (at, separation 8.3 Hz, $CH_2CH_2CH_2$), 36.8 (at, separation 11.1 Hz, CH_2PPh_2), 26.2 (s, $CH_2CH_2CH_2$), 15.4 (s, CH_3); ^1H NMR[18] (CD_2Cl_2) δ 3.25 (d, $^3J_{PH}$ = 3.9 Hz, CH_2OP), 0.36 (s, CH_3).

***fac*-(*cis*-1,5-Bis((diphenylphosphino)methyl)-3-oxabicyclo[3.3.0]octane-*P,P′*)tricarbonyl(1-methyl-4-phospha-3,5,8-trioxabicyclo[2.2.2]octane-*P*)tungsten (8a,b).** A solution of $P(OCH_2)_3CCH_3$ (0.0622 g, 0.420 mmol) in 5 mL of CH_2Cl_2 was added to a solution of **3** (0.257 g, 0.331 mmol) in 10 mL of CH_2Cl_2, resulting in a loss of color within 10 min. After 1 h the volume was reduced to 5 mL in vacuo and pentane (10 mL) was added to complete the precipitation. The white solid was isolated by filtration, washed with 5 mL of pentane, and dried in vacuo (yield 0.24 g, 78%). Spectral data showed the presence of two *fac* isomers in a ratio of 6:1. Recrystallization from CH_2Cl_2 yielded fine white needles of the product as an isomeric mixture. Anal. Calcd for $C_{41}H_{43}O_7P_3W$: C, 53.26; H, 4.69; W, 19.88. Found: C, 52.95; H, 4.67; W, 19.69.

Major Isomer (8a): ^{31}P NMR (CD_2Cl_2) δ 111.8 (t, $^2J_{PP}$ = 25 Hz, $^1J_{PW}$ = 382 Hz, $POCH_2$), 1.4 (d, $^2J_{PP}$ = 25 Hz, $^1J_{PW}$ = 225 Hz, PPh_2); ^{13}C NMR (CD_2Cl_2) δ 212.2 (m, CO_{ax}), 209.2 (m, CO_{eq}), 144.4 (m, Ph ipso), 139.3 (m, Ph ipso), 134.6 (at, separation 10.7 Hz, Ph ortho), 132.1 (at, separation 9.1 Hz, Ph ortho), 129.9 (s, Ph para), 128.6 (at, separation 9.5 Hz, Ph meta), 127.9 (s, Ph para), 127.2 (at, separation 8.4 Hz, Ph meta), 87.6 (at, separation 12.7 Hz, CH_2OCH_2), 73.6 (d, $^2J_{PC}$ = 6.0 Hz, $POCH_2$), 53.3 (s, CC_4), 41.5 (at, separation 7.5 Hz, $CH_2CH_2CH_2$), 36.2 (at, separation 17.1 Hz, CH_2PPh_2), 31.5 (d, $^3J_{PC}$ = 33.0 Hz, $POCH_2C$), 24.6 (s, $CH_2CH_2CH_2$), 15.7 (s, CH_3); ^1H NMR (CD_2Cl_2) δ 7.89 (m, Ph), 7.41 (m, Ph), 7.32–7.15 (m, Ph), 3.69 (d, $^2J_{HH}$ = 9.0 Hz, 2 H, CH_2OCH_2), 3.63 (dd, $^2J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 2.0 Hz, 2 H, CH_2OCH_2), 3.15 (d, $^3J_{PH}$ = 4.2 Hz, 6 H, $POCH_2$), 3.13 (dd, $^2J_{HH}$ = 15.0 Hz, $^2J_{PH}$ = 12.5 Hz, CH_2PPh_2), 2.96 (d, $^2J_{HH}$ = 15.0 Hz, CH_2PPh_2), 1.6 (m, 2 H, CH_2), 1.4–1.2 (m, 2 H, CH_2), 0.82 (dd, $^2J_{HH}$ = 12.6 Hz, $^3J_{HH\text{-}cis}$ = 5.4 Hz, 2 H, CH_2), 0.31 (s, 3 H, CH_3).

Minor Isomer (8b): ^{31}P NMR (CD_2Cl_2) δ 113.0 (t, $^2J_{PP}$ = 24 Hz, $POCH_2$), 0.1 (d, $^2J_{PP}$ = 24 Hz, PPh_2); ^{13}C NMR (CD_2Cl_2) δ 134.1 (at, Ph ortho), 131.9 (at, separation 9.1 Hz, Ph ortho), 130.1 (s, Ph para), 128.8 (at, separation 9.6 Hz, Ph meta), 128.0 (s, Ph para), 127.3 (Ph meta), 81.1 (at, separation 9.6 Hz, Ph meta), 73.8 (d, $^2J_{PC}$ = 6.0 Hz, $POCH_2$), 53.5 (s, CC_4), 49.7 (at, separation 9.5 Hz, $CH_2CH_2CH_2$), 37.1 (at, separation 13.5 Hz, CH_2PPh_2), 26.6 (s, $CH_2CH_2CH_2$), 15.7 (s, CH_3); ^1H NMR[18] (CD_2Cl_2) δ 3.48 (d, $^2J_{HH}$ = 9.0 Hz, CH_2OCH_2), 3.28 (dd, $^2J_{HH}$ = 15.5 Hz, $^3J_{PH}$ = 12.5 Hz, CH_2PPh_2), 3.22 (d, $^3J_{PH}$ = 3.9 Hz, $POCH_2$), 3.09 (d, $^2J_{HH}$ = 15.5 Hz, CH_2PPh_2), 2.90 (d, $^2J_{HH}$ = 9.0 Hz, CH_2OCH_2), 0.34 (s, CH_3).

***fac*-(*cis*-1,5-Bis((diphenylphosphino)methyl)-3-oxabicyclo[3.3.0]octane-*P,P′*)tricarbonyl(η¹-pyridinio)molybdenum (9a,b).** This product was prepared as described below for the

(15) In this context axial refers to a site *cis* to both phosphorus donors and equatorial refers to a site *trans* to a phosphorus donor.

(16) Heitsch, C. W.; Verkade, J. G. *Inorg. Chem.* **1962**, *1*, 392.

(17) The five-line multiplets of an AXX′ (A = ^{13}C; X, X′ = ^{31}P) spin system which resemble triplets are denoted here as "apparent" triplets, at.

(18) Due to the overlap of some resonances for the two diastereomers present, not all assignments could be made in the phenyl and cyclopentane methylene regions of the ^1H NMR spectra for the minor isomers.

tungsten analogues **10a** and **10b**.

Major Isomer (9a): ^{31}P NMR (CD_2Cl_2) δ 20.7 (s); ^{13}C NMR (CD_2Cl_2) δ 226.3 (t, $^2J_{PC}$ = 8 Hz, CO_{ax}), 219.9 (m, separation 24 Hz, CO_{eq}), 154.9 (t, $^3J_{PC}$ = 3 Hz, pyridine C1), 139.2 (m, separation 35 Hz, Ph ipso), 138.1 (m, separation 26 Hz, Ph ipso), 134.9 (s, pyridine C3), 134.7 (at, separation 12 Hz, Ph ortho), 131.6 (at, separation 10 Hz, Ph ortho), 129.6 (s, Ph para), 128.5 (at, separation 9.1 Hz, Ph meta), 128.2 (s, Ph para), 128.1 (at, separation 7 Hz, Ph meta), 122.5 (s, pyridine C2), 87.8 (at, separation 12 Hz, CH_2OCH_2), 41.5 (at, separation 8 Hz, $CH_2CH_2CH_2$), 35.8 (at, separation 13 Hz, CH_2PPh_2), 24.8 (s, $CH_2CH_2CH_2$); ^1H NMR (CD_2Cl_2) δ 8.02 (m, Ph ortho), 7.6–7.2 (m, Ph), 6.90 (m, Ph), 6.15 (m, pyridine C2), 3.74 (d, $^2J_{HH}$ = 9.3 Hz, CH_2OCH_2), 3.69 (dd, $^2J_{HH}$ = 9.3 Hz, $^4J_{HH}$ = 1.8 Hz, CH_2OCH_2), 3.00 (dd, $^2J_{HH}$ = 15.3 Hz, CH_2PPh_2), 2.80 (d, $^2J_{HH}$ = 15.3 Hz, CH_2PPh_2), 2.13 (m, CH_2), 0.90 (dd, $^2J_{HH}$ = 12.0 Hz, $^3J_{HH\text{-}cis}$ = 5.4 Hz, CH_2).

Minor Isomer (9b): ^{31}P NMR (CD_2Cl_2) δ 19.4 (s); ^{13}C NMR (CD_2Cl_2) δ 134.4 (at, separation 12 Hz, Ph ortho), 131.4 (at, Ph ortho), 122.6 (s, pyridine C2), 81.1 (m, CH_2OCH_2), 50.4 (at, $CH_2CH_2CH_2$), 26.2 (s, $CH_2CH_2CH_2$); ^1H NMR[18] (CD_2Cl_2) δ 4.05 (d, $^2J_{HH}$ = 9.0 Hz, CH_2OCH_2), 3.17 (dd, $^2J_{HH}$ = 15.3 Hz, $^2J_{PH}$ = 11.3 Hz, CH_2PPh_2), 2.91 (d, $^2J_{HH}$ = 15.3 Hz, CH_2PPh_2).

***fac*-(*cis*-1,5-Bis((diphenylphosphino)methyl)-3-oxabicyclo[3.3.0]octane-*P*,*P'*)tricarbonyl(η^1-pyridinio)tungsten (10a,b).** To a solution of **3** (0.305 g, 0.393 mmol) in 10 mL of CH_2Cl_2 was added 0.5 mL of pyridine. The addition resulted in an immediate color change to a pale lemon yellow. A ^{31}P NMR spectrum of this solution showed only the presence of **10a** and **10b**. After 20 min at room temperature, stirring was discontinued. Diethyl ether (30 mL) was slowly layered on top of the CH_2Cl_2, and the reaction flask was cooled in the freezer overnight to yield light yellow crystals, which were collected by filtration and dried in vacuo (yield 0.22 g, 65%). Anal. Calcd for $C_{41}H_{39}NO_4P_2W$: C, 57.56; H, 4.59; W, 21.49. Found: C, 57.12; H, 4.55; W, 21.50.

Major Isomer (10a): ^{31}P NMR (CD_2Cl_2) δ 12.9 (s), $^1J_{PW}$ = 232 Hz; ^{13}C NMR (CD_2Cl_2) δ 217.2 (t, $^2J_{PC}$ = 9.9 Hz, CO_{ax}), 214.1 (dd, $^2J_{PC\text{-}trans}$ = 37 Hz, $^2J_{PC\text{-}cis}$ = 10.0 Hz, CO_{eq}), 156.1 (t, $^3J_{PC}$ = 7.1 Hz, pyridine C1), 139.1 (m, separation 42.0 Hz, Ph ipso), 137.6 (m, separation 34.2 Hz, Ph ipso), 135.1 (at, separation 11.9 Hz, Ph ortho), 134.8 (s, pyridine C3), 131.6 (br, Ph ortho), 129.8 (s, Ph para), 128.7 (at, separation 9.5 Hz, Ph meta), 128.5 (s, Ph para), 128.3 (at, separation 7.5 Hz, Ph meta), 123.2 (s, pyridine C2), 87.8 (at, separation 12.7 Hz, CH_2OCH_2), 53.3 (at, separation 3.2 Hz, CC_4), 41.3 (at, separation 7.5 Hz, $CH_2CH_2CH_2$), 36.2 (m, separation 17.4 Hz, CH_2PPh_2), 24.8 (s, $CH_2CH_2CH_2$); ^1H NMR (CD_2Cl_2, 500 MHz) δ 7.99 (m, 4 H, Ph ortho), 7.68 (m, 2 H, pyridine C1), 7.42–7.28 (m, Ph), 6.91 (m, Ph), 6.10 (m, 2 H, pyridine HC2), 3.74 (d, $^2J_{HH}$ = 9.0 Hz, 2 H, CH_2OCH_2), 3.69 (dd, $^2J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 2.0 Hz, 2 H, CH_2OCH_2), 3.18 (dd, $^2J_{HH}$ = 15.0 Hz, $^2J_{PH}$ = 12.6 Hz, 2 H, CH_2PPh_2), 2.83 (d, $^2J_{HH}$ = 15.0 Hz, 2 H, CH_2PPh_2), 2.11 (m, 2 H, CH_2), 1.50 (m, 1 H, CH_2), 1.45 (m, 1 H, CH_2), 0.91 (dd, $^2J_{HH}$ = 12.5 Hz, $^3J_{HH\text{-}cis}$ = 5.5 Hz, 2 H, CH_2).

Minor Isomer (10b): ^{31}P NMR (CD_2Cl_2) δ 11.6 (s), $^1J_{PW}$ = 232 Hz; ^{13}C NMR (CD_2Cl_2) δ 123.2 (s, pyridine C2), 81.0 (at, separation 9.5 Hz, CH_2OCH_2), 50.4 (at, separation 9.1 Hz, $CH_2CH_2CH_2$), 37.5 (m, CH_2PPh_2); ^1H NMR[18] (CD_2Cl_2, 500 MHz) δ 4.04 (dd, $^2J_{HH}$ = 9.5 Hz, $^4J_{HH}$ = 1.5 Hz, CH_2OCH_2), 3.35 (dd, $^2J_{HH}$ = 15.5 Hz, $^2J_{PH}$ = 12.5 Hz, CH_2PPh_2), 2.99 (d, $^2J_{HH}$ = 9.5 Hz, CH_2OCH_2), 2.93 (d, $^2J_{HH}$ = 15.5 Hz, CH_2PPh_2).

***fac*-(Acetonitrile)(*cis*-1,5-((diphenylphosphino)methyl)-3-oxabicyclo[3.3.0]octane-*P*,*P'*)tricarbonylmolybdenum (11a,b).** This product was prepared as described below for the tungsten analogues **12a** and **12b**.

Major Isomer (11a): ^{31}P NMR (CH_2Cl_2) δ 27.1 (s); ^{13}C NMR (CD_2Cl_2) δ 223.2 (t, $^2J_{PC}$ = 8.4 Hz, CO_{ax}), 219.8 (m, separation 23.0 Hz, CO_{eq}), 139.8 (m, separation 27.4 Hz, Ph ipso), 138.8 (m, separation 35.7 Hz, Ph ipso), 135.4 (at, separation 12.7 Hz, Ph ortho), 131.4 (at, separation 9.1 Hz, Ph ortho), 130.0 (s, Ph para), 128.6 (at, separation 9.5 Hz, Ph meta), 128.2 (at, separation 7.1 Hz, Ph meta), 127.9 (s, Ph para), 120.8 (s, CH_3CN), 87.4 (at, separation 12.3 Hz, CH_2OCH_2), 53.4 (s, CC_4), 41.3 (at, separation 8.7 Hz, $CH_2CH_2CH_2$), 36.8 (at, separation 13.9 Hz, CH_2PPh_2), 24.8 (s, $CH_2CH_2CH_2$), 1.5 (s, CH_3CN); ^1H NMR (CD_2Cl_2) δ 8.01 (m, Ph ortho), 7.40 (m, Ph), 7.35–7.15 (m, Ph), 3.64 (d, $^2J_{HH}$ = 9.0 Hz, CH_2OCH_2), 3.56 (dd, $^2J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 1.8 Hz, CH_2OCH_2), 2.87 (d, $^3J_{PH}$ = 5.4 Hz, CH_2PPh_2), 2.06 (m, CH_2), 1.44 (m, CH_2), 0.91 (dd, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH\text{-}cis}$ = 4.5 Hz, CH_2), 0.80 (s, CH_3CN).

Minor Isomer (11b): ^{31}P NMR (CD_2Cl_2) δ 25.4 (s); ^{13}C NMR (CD_2Cl_2) δ 134.8 (at, Ph ortho), 130.2 (s, Ph para), 128.7 (at, Ph meta), 81.5 (m, CH_2OCH_2), 49.3 (m, $CH_2CH_2CH_2$), 37.9 (at, separation 11.1 Hz, CH_2PPh_2), 26.0 (s, $CH_2CH_2CH_2$), 1.7 (s, CH_3CN); ^1H NMR[18] (CD_2Cl_2) δ 3.96 (d, $^2J_{HH}$ = 9.3 Hz, CH_2OCH_2), 3.02 (d, $^2J_{HH}$ = 9.3 Hz, CH_2OCH_2), 2.98 (br s, CH_2PPh_2), 0.93 (s, CH_3CN).

***fac*-(Acetonitrile)(*cis*-1,5-bis((diphenylphosphino)methyl)-3-oxabicyclo[3.3.0]octane-*P*,*P'*)tricarbonyltungsten (12a,b).** To a solution of **3** (0.227 g, 0.292 mmol) in 5 mL of CH_2Cl_2 was added 0.5 mL of CH_3CN, which resulted in a decrease in color to yield a very pale yellow solution. ^{31}P NMR spectroscopy showed only the presence of **12a** and **12b** in this solution. After the reaction mixture was stirred at room temperature for 10 min, pentane (10 mL) was slowly added. Within 10 min a creamy white precipitate had formed, and an additional 10 mL of pentane was added to complete the precipitation. The solid was isolated by filtration, washed with 5 mL of pentane, and dried in vacuo (yield 0.23 g, 96%). The product was obtained as pale yellow crystals by layering diethyl ether onto a CH_2Cl_2 solution of the complex and cooling overnight in the refrigerator.

Major Isomer (12a): ^{31}P NMR (CH_2Cl_2) δ 14.8 (s), $^1J_{PW}$ = 231 Hz; ^{13}C NMR (CD_2Cl_2) δ 213.9 (t, $^2J_{PC}$ = 5.9 Hz, CO_{ax}), 212.5 (m, separation 24.9 Hz, CO_{eq}), 139.0 (m, separation 32.9 Hz, Ph ipso), 138.3 (m, separation 38.8 Hz, Ph ipso), 135.7 (at, separation 12.2 Hz, Ph ortho), 131.3 (at, separation 8.7 Hz, Ph ortho), 130.1 (s, Ph para), 128.6 (at, separation 9.9 Hz, Ph meta), 128.3 (at, separation 7.5 Hz, Ph meta), 128.1 (s, Ph para), 119.0 (s, CH_3CN), 87.4 (at, separation 13.0 Hz, CH_2OCH_2), 41.1 (at, separation 8.3 Hz, $CH_2CH_2CH_2$), 37.3 (m, separation 17.8 Hz, CH_2PPh_2), 24.8 (s, $CH_2CH_2CH_2$), 1.5 (s, CH_3CN); ^1H NMR (CD_2Cl_2) δ 8.00 (m, Ph), 7.45 (m, Ph), 7.31 (m, Ph), 7.20 (m, Ph), 3.64 (d, $^2J_{HH}$ = 8.7 Hz, CH_2OCH_2), 3.57 (dd, $^2J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.2 Hz, CH_2OCH_2), 3.08 (dd, $^2J_{HH}$ = 15.6 Hz, $^3J_{PH}$ = 13.3 Hz, CH_2PPh_2), 2.92 (d, $^2J_{HH}$ = 15.6 Hz, CH_2PPh_2), 2.09 (m, CH_2), 1.47 (m, CH_2), 0.94 (m, CH_2), 0.83 (t, $^5J_{PH}$ = 1.5 Hz, CH_3CN).

Minor Isomer (12b): ^{31}P NMR (CH_2Cl_2) δ 13.4 (s), $^1J_{PW}$ = 229 Hz; ^{13}C NMR (CD_2Cl_2) δ 135.3 (at, Ph ortho), 131.2 (m, Ph ortho), 130.2 (s, Ph para), 125.6 (s, CH_3CN), 81.1 (at, CH_2OCH_2), 49.7 (m, $CH_2CH_2CH_2$), 38.4 (m, CH_2PPh_2), 26.4 (s, $CH_2CH_2CH_2$), 1.7 (s, CH_3CN); ^1H NMR[18] (CD_2Cl_2) δ 4.00 (d, $^2J_{HH}$ = 9.3 Hz, CH_2OCH_2), 3.22 (dd, $^2J_{HH}$ = 15.6 Hz, $^3J_{PH}$ = 12.3 Hz, CH_2PPh_2), 3.06 (d, $^2J_{HH}$ = 15.6 Hz, CH_2PPh_2), 2.99 (d, $^2J_{HH}$ = 9.3 Hz, CH_2OCH_2), 0.92 (s, CH_3CN).

***fac*-(*cis*-1,5-Bis((diphenylphosphino)methyl)-3-oxabicyclo[3.3.0]octane-*P*,*P'*)tricarbonyl(η^1-piperidino)tungsten (13a,b).** To a deep yellow solution of **3** (0.214 g, 0.275 mmol) in 5 mL of CH_2Cl_2 was added 0.15 mL of piperidine, which resulted in an immediate change of color to a light lemon yellow. This solution was stirred for 10 min and then treated with 10 mL of pentane. Within 10 min a pale yellow precipitate began to appear, and an additional 15 mL of pentane was added to complete the precipitation. The solid was isolated by filtration, rinsed with 5 mL of pentane, and dried in vacuo (yield 0.22 g, 98%).

Major Isomer (13a): ^{31}P NMR ($CDCl_2$) δ 10.9 (s), $^1J_{PW}$ = 230 Hz; ^{13}C NMR (CD_2Cl_2) δ 215.3 (t, $^2J_{PC}$ = 5.1 Hz, CO_{ax}), 214.4 (m, separation 26.6 Hz, CO_{eq}), 141.5 (m, separation 27.8 Hz, Ph ipso), 138.7 (d, separation 42.4 Hz, Ph ipso), 135.1 (at, separation 9.9 Hz, Ph ortho), 131.2 (at, separation 8.4 Hz, Ph ortho), 129.8 (s, Ph para), 129.3 (at, separation 7.1 Hz, Ph meta), 129.1 (s, Ph para), 128.6 (at, separation 9.5 Hz, Ph meta), 87.6 (at, separation 12.7 Hz, CH_2OCH_2), 56.1 (t, $^3J_{PC}$ = 2.0 Hz, pip C1), 41.3 (at, separation 7.2 Hz, $CH_2CH_2CH_2$), 37.0 (at, separation 16.3 Hz, CH_2PPh_2), 28.6 (s, pip C2), 24.7 (s, $CH_2CH_2CH_2$), 22.9 (s, pip C3); ^1H NMR (CD_2Cl_2) δ 8.01 (m, Ph ortho), 7.53 (m, Ph ortho), 7.50–7.25 (m, Ph), 3.70 (d, $^2J_{HH}$ = 9.0 Hz, 2 H, CH_2O), 3.63 (dd, $^2J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 1.5 Hz, 2 H, CH_2O), 3.24 (dd, $^2J_{HH}$ = 15.0 Hz, $^2J_{PH}$ = 12.6 Hz, 2 H, CH_2PPh_2), 2.83 (d, $^2J_{HH}$ = 15.0 Hz, 2 H, CH_2PPh_2), 2.75 (m, uncoordinated pip NCH_2 groups), 2.0–1.0 (m, pip CH_2 groups), 0.80 (dd, $^2J_{HH}$ = 12.9 Hz, $^3J_{HH}$ = 5.4 Hz, 2 H, CH_2).

Minor Isomer (13b): ^{31}P NMR (CD_2Cl_2) δ 9.4 (s), $^1J_{PW}$ = 230 Hz; ^{13}C NMR (CD_2Cl_2) δ 134.7 (at, Ph ortho), 131.1 (at, Ph ortho), 130.0 (s, Ph para), 128.9 (at, separation 9.1 Hz, Ph meta), 80.9 (at, separation 8.7 Hz, CH_2O), 50.2 (at, separation 9.1 Hz,

$CH_2CH_2CH_2$), 37.9 (at, separation 13.8 Hz, CH_2PPh_2), 26.6 (s, $CH_2CH_2CH_2$); ^1H NMR[18] (CD_2Cl_2) δ 3.72 (d, $^2J_{HH}$ = 9.0 Hz, CH_2O), 2.87 (d, $^2J_{HH}$ = 9.0 Hz, CH_2O), 3.40 (m, CH_2PPh_2), 2.92 (d, $^2J_{HH}$ = 15.3 Hz, CH_2PPh_2).

Attempted Thermolysis of (1)W(CO)$_4$ (6). Complex **6** (0.206 g, 0.256 mmol) was dissolved in 15 mL of toluene, and the solution was refluxed for 16 h, during which time no precipitate had formed. A ^{31}P NMR spectrum of this reaction solution showed only the presence of the starting complex, **6** (δ 4.5 (s), $^1J_{PW}$ = 232 Hz).

Photolysis of (1)Mo(CO)$_4$ (5) and (1)W(CO)$_4$ (6). Complex **5** (0.050 g, 0.070 mmol) was dissolved in 2 mL of THF, and the solution was irradiated at 254 nm for 4 h. A very faint yellowing of the solution occurred, but ^{31}P NMR spectroscopy showed only the presence of the starting complex, **5** (δ 22.0 (s)). Similarly, a solution of complex **6** (0.218 g, 0.272 mmol) in 15 mL of toluene was irradiated with a 275-W UV lamp for 3 h, during which time the solution became brown and a brown decomposition product had precipitated. A ^{31}P NMR spectrum of the supernatant showed the present of unreacted starting material as the only phosphorus-containing species in solution.

Exchange Reaction between *fac*-(1)W(CO)$_3$(NCCH$_3$) and CD$_3$CN. Approximately 25 mg of *fac*-(1)W(CO)$_3$(NCCH$_3$) (**12a**, **12b**) was dissolved in 0.5 mL of CH_2Cl_2 in a 5-mm NMR tube. CD_3CN was then added and the tube immediately placed in the spectrometer. The exchange reaction was monitored by ^2H NMR spectroscopy over the course of 2 h.

Reaction of ^{13}CO with *fac*-(1)M(CO)$_3$, Where M = Mo (2) and W (3). Compounds **2** and **3** (~20–30 mg) were dissolved in CD_2Cl_2 in separate 5-mm NMR tubes under argon. ^{13}CO was bubbled through the yellow solutions for 10 min, resulting in near-colorless solutions. A small quantity of decomposition product precipitated initially for the reaction involving **2**, but ^1H and ^{13}C NMR spectroscopy revealed only the presence of *fac*-(1)Mo(CO)$_3$(^{13}CO). The NMR tubes were then sealed, and the reactions were monitored by ^{13}C NMR spectroscopy.

Results and Discussion

Substitution by Phosphorus and Nitrogen Donors. Reaction of **2** or **3** with $P(OCH_2)_3CCH_3$ proceeds cleanly in CH_2Cl_2 at room temperature by displacement of the coordinated ether, yielding products of the stoichiometry (1)M(CO)$_3$[P(OCH$_2$)$_3$CCH$_3$], where M = Mo (**7a**, **7b**) and W (**8a**, **8b**), as shown by mass spectral and analytical data. In both cases two isomeric products were obtained. From complex **2**, the two products **7a** and **7b** were isolated as a mixture in approximately a 4:1 ratio as shown by ^1H NMR spectroscopy. Attempts to separate these two products by column chromatography and fractional recrystallization were unsuccessful. In the ^{31}P NMR spectrum of this product mixture, a triplet at 86.9 ppm ($^2J_{PP}$ = 32 Hz) for the phosphite resonance and a doublet at 20.2 ppm ($^2J_{PP}$ = 32 Hz) for the phosphine resonance of the major isomer and similar resonances for the minor product suggest a *fac* geometry for both. A *fac* geometry for **7a** is also substantiated in the ^{13}C NMR spectrum by a doublet of triplets resonance at 220.5 ppm ($^2J_{PC\text{-}trans}$ = 49 Hz, $^2J_{PC\text{-}cis}$ = 9.5 Hz) for the axial carbonyl and a complex multiplet at 218.3 ppm for the two equivalent equatorial carbonyls. The signal-to-noise ratio of the spectrum was insufficient to assign the carbonyl resonances of the minor isomer **7b**. Remaining ^{13}C NMR resonances for both isomers indicate the presence of a plane of symmetry consistent with a *fac*, but not a *mer*, arrangement of ligands. On this basis the compounds **7a** and **7b** are assigned as a pair of *fac* diastereomers.

Two diastereomers of *fac* geometry may arise because of the inequivalence of the two axial sites in octahedral metal complexes of ligand **1**. The axial sites above and below the P_2M plane are differentiated by the symmetry of **1**. This has been demonstrated previously[10] for the complexes (1)M(CO)$_4$, where M = Cr (**4**), Mo (**5**), and W (**6**), by the presence of two axial carbonyl resonances in the ^{13}C NMR spectra of these complexes. Analysis of the ^{31}P and ^{13}C NMR spectra for the tungsten analogues **8a** and **8b** reveals the same features noted above for **7a** and **7b**, and hence they are assigned as two *fac* diastereomers of (1)W(CO)$_3$[P(OCH$_2$)$_3$CCH$_3$].

Table I. Infrared Spectroscopic Data[a]

		ν_{CO}, cm^{-1}		
fac-(1)Mo(CO)$_3$ (**2**)[b]		1921	1826	1763
fac-(1)W(CO)$_3$ (**3**)[b]		1913	1819	1757
(1)Mo(CO)$_4$ (**5**)[b]	2027	1934	1886	1869
(1)W(CO)$_4$ (**6**)[b]	2021	1917	1892	1863
fac-(1)Mo(CO)$_3$[P(OCH$_2$)$_3$CCH$_3$] (**7a**)		1942	1850	
fac-(1)W(CO)$_3$[P(OCH$_2$)$_3$CCH$_3$] (**8a**)		1942	1846	1828
fac-(1)Mo(CO)$_3$(py) (**9a**)		1929	1830	1801
fac-(1)W(CO)$_3$(py) (**10a**)		1921	1825	1796
fac-(1)W(CO)$_3$(NCCH$_3$) (**12a**)		1929	1836	1805
fac-(1)W(CO)$_3$(pip) (**13a**)		1923	1825	1790

[a] Spectra were obtained on CH_2Cl_2 solutions, except where noted. [b] Spectra were obtained on Nujol mulls.

The reactions of **2** and **3** with acetonitrile, pyridine, and piperidine also yield two *fac* diastereomers in each case (**9a–13a**, **9b–13b**). Piperidine was included in this study in the hope that intramolecular hydrogen bonding between the N–H of piperidine and the ether of ligand **1** would be favorable in one of the two *fac* diastereomers **13a** and **13b**, thus aiding in their separation. Darensbourg has previously noted hydrogen bonding between the N–H of piperidine and the oxygen of P(OMe)$_3$ in the X-ray structure of *cis*-Mo(CO)$_4$(pip)[P(OMe)$_3$][19] as well as hydrogen bonding to THF in solution.[20] Unfortunately complexes **13a** and **13b** are labile to piperidine dissociation, as will be discussed shortly, thus precluding separation.

The products **9a–13a** and **9b–13b** exhibit singlets in their ^{31}P NMR spectra, thus ruling out substitution in an equatorial site to yield *mer* complexes, for which an AB pattern would be expected for the phosphorus nuclei. The ^{31}P NMR resonances of the tungsten complexes exhibit satellites due to $^1J_{^{31}P\text{-}^{183}W}$ in the range 229–232 Hz. The ^{13}C NMR spectra of **9a–13a** and **9b–13b** indicate the presence of a plane of symmetry in these molecules as discussed above for **7a** and **7b** and **8a** and **8b**. The major isomers **9a–13a** also each exhibit a triplet resonance and a five-line multiplet for the single axial carbonyl and the two equivalent equatorial carbonyls, respectively, as expected for an AXX′ spin system.[21]

The major substitution products **7a–13a** all exhibit three strong carbonyl stretches in their infrared spectra, consistent with their assignment as *fac* tricarbonyl complexes (see Table I). Unfortunately, the carbonyl stretches for the minor diastereomers could not be resolved from those of the major products in these spectra. Thus, on the basis of infrared and ^{31}P and ^{13}C NMR spectroscopic data, all of the substitution products discussed above are assigned a *fac* geometry.

Stereochemical Assignment of the *fac* Diastereomeric Products. Although spectroscopic data confirm a *fac* geometry for all diastereomeric products **7a–13a** and **7b–13b**, there are important spectroscopic criteria that differentiate the major diastereomers **7a–13a** from the minor diastereomers **7b–13b** (Table II). Previously, our X-ray structural analysis of (1)Mo(CO)$_4$ (**5**) revealed a

(19) Atwood, J. L.; Darensbourg, D. J. *Inorg. Chem.* **1977**, *16*, 2314.
(20) Ewen, J.; Darensbourg, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 6874.
(21) (a) Pregosin, P. S.; Kunz, R. W. *NMR: Basic Princ. Prog.* **1979**, *16*, 65. (b) Redfield, D. A.; Nelson, J. H.; Carey, L. W. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 727. (c) Andrews, G. T.; Colquhoun, I. J.; McFarlane, W. *Polyhedron* **1983**, *2*, 783.

Table II. Selected ^1H and ^{13}C NMR Spectroscopic Data[a]

	$\delta(O-(CH_2)_2)$	$\delta(CH_2-(CH_2)_2)$	$\delta(O-(CH_2)_2)$	$\Delta\delta(O-(CH_2)_2)$
Major Isomers				
(1)Mo(CO)$_4$ (**5**)	86.3	42.8	3.60, 3.57	0.03
(1)W(CO)$_4$ (**6**)	86.3	42.7	3.60, 3.57	0.03
fac-(1)Mo(CO)$_3$[P(OCH$_2$)$_3$CCH$_3$] (**7a**)	87.6	41.7	3.69, 3.63	0.06
fac-(1)W(CO)$_3$[P(OCH$_2$)$_3$CCH$_3$] (**8a**)	87.6	41.5	3.69, 3.63	0.06
fac-(1)Mo(CO)$_3$(py) (**9a**)	87.8	41.5	3.74, 3.69	0.05
fac-(1)W(CO)$_3$(py) (**10a**)	87.8	41.3	3.74, 3.69	0.05
fac-(1)Mo(CO)$_3$(NCCH$_3$) (**11a**)	87.4	41.3	3.64, 3.56	0.08
fac-(1)W(CO)$_3$(NCCH$_3$) (**12a**)	87.4	41.1	3.64, 3.57	0.08
fac-(1)W(CO)$_3$(pip) (**13a**)	87.6	41.3	3.70, 3.63	0.07
Minor Isomers				
fac-(1)Mo(CO)$_3$[P(OCH$_2$)$_3$CCH$_3$] (**7b**)	81.4	49.3	*b*	*b*
fac-(1)W(CO)$_3$[P(OCH$_2$)$_3$CCH$_3$] (**8b**)	81.1	49.7	3.48, 2.90	0.58
fac-(1)Mo(CO)$_3$(py) (**9b**)	81.1	50.4	*b*	*b*
fac-(1)W(CO)$_3$(py) (**10b**)	81.0	50.4	4.04, 2.99	1.05
fac-(1)Mo(CO)$_3$(NCCH$_3$) (**11b**)	81.5	49.3	3.96, 3.02	0.94
fac-(1)W(CO)$_3$(NCCH$_3$) (**12b**)	81.1	49.7	4.00, 2.99	1.01
fac-(1)W(CO)$_3$(pip) (**13b**)	80.9	50.2	3.72, 2.87	0.85

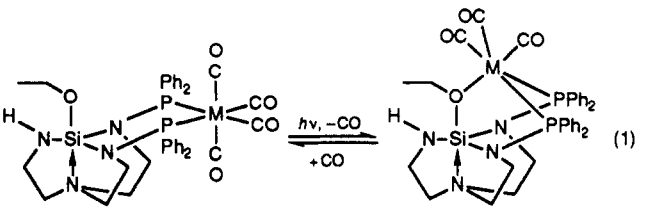
[a] Data were taken on CD_2Cl_2 solutions at 20 °C. [b] Due to overlap of some of the resonances, definite assignments could not be made.

conformation as illustrated for A in the Chart II (L = CO), wherein the ether oxygen of **1** is oriented away from the metal center.[10] In addition, a strong ring current effect was observed in the ^1H NMR spectrum of **5** for two methylene protons adjacent to the bridgehead carbons of the C_5 ring, which strongly argued for a similar conformation in solution. Analogously, the ^1H NMR spectrum for each of the major diastereomers contains a doublet of doublets in the vicinity of 1.0 ppm, also consistent with shielding of two C_5 methylene protons by neighboring phenyl substituents on phosphorus. Furthermore, the CH_2OCH_2 region in the ^1H NMR spectra of the major diastereomers exhibits resonances analogous to those found for **5** and **6** with no indication of a ring current effect.

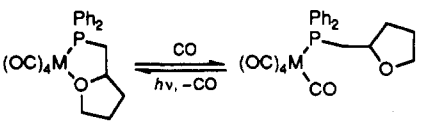
In the ^{13}C NMR spectra of **7a–13a** and **7b–13b**, differences between the groups of major and minor products are observed only in the CH_2OCH_2 and $CH_2CH_2CH_2$ resonances. All the other ^{13}C NMR resonances of these complexes are quite similar. The CH_2OCH_2 and $CH_2CH_2CH_2$ resonances of the major diastereomers are analogous to those found in the ^{13}C NMR spectra of **5** and **6**. On the basis of the similarity of ^1H and ^{13}C NMR spectral data for **7a–13a** to those for **5** and **6**, the major diastereomers are assigned structure A, wherein the new ligand occupies the axial site previously occupied by the ether oxygen of **1** in the starting materials **2** and **3**.

In contrast to the major diastereomers, the minor diastereomers **7b–13b** differ significantly in their ^1H and ^{13}C NMR spectra from those of **5** and **6**. These compounds experience a downfield shift of 7.6–9.1 ppm for their $CH_2CH_2CH_2$ ^{13}C NMR resonances and an upfield shift of 6.0–6.5 ppm for their CH_2OCH_2 resonances in comparison to the major isomers. Again, no significant differences are found for the other carbon resonances. Molecular models reveal these two carbons to be closest to neighboring phenyl rings, allowing these carbons to experience ring current effects. These spectroscopic differences suggest a change in configuration from A to B where the new ligand now occupies an axial site trans to that previously occupied by the ether oxygen in the starting complexes **2** and **3**. Of the two five-membered rings in the ligand **1**, the ether-containing ring is now the closest one to the metal center. Shielding is thus experienced at the CH_2OCH_2 sites and not at the $CH_2CH_2CH_2$ positions. ^1H NMR spectroscopy provides some additional evidence for this conclusion. ^1H and $^1H\{^{31}P\}$ NMR spectra (500 MHz) have allowed accurate assignments for the CH_2OCH_2 protons for the minor isomers **8b**, **10b**, **11b**, and **12b**. For **10b**, two doublet resonances are observed at 4.04 and 2.99 ppm, a substantial separation of 1.05 ppm. Similarly for **8b**, **11b**, and **12b**, these resonances are separated by 0.58, 0.94, and 1.01 ppm, respectively, with the upfield resonances occurring between 2.90 and 3.02 ppm in all cases. In contrast, the major diastereomers **7a–13a** exhibit AB quartets with resonances separated by only 0.06–0.08 ppm. This large chemical shift separation for the minor isomers as well as the upfield shift of one of the two CH_2OCH_2 resonances strongly argues for a shielding effect at this position caused by a neighboring phenyl ring. Such shielding for two of the four CH_2OCH_2 protons is plausible only for structure B.

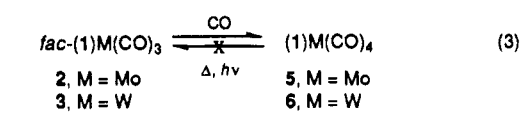
Reactions with Carbon Monoxide. We have reported[22] earlier that the *N,N'*-bis(diphenylphosphino)azasilatrane complexes **14a** and **14b** react with carbon monoxide to form the tetracarbonyl species **15a** and **15b** (reaction 1). This reaction was found to be reversible under photolytic as well as thermal conditions. Similarly, Rauchfuss[5] reported reversible CO binding for ruthenium complexes of *o*-(diphenylphosphino)anisole under both thermal and photolytic conditions, and Lindner[3] reported reaction 2 to be reversible under photolytic conditions. When carbon monoxide was bubbled through a CH_2Cl_2 solution of **2** or **3**, substitution of the coordinated ether was completed within 10 min as indicated by loss of the yellow color of the solution (reaction 3). ^{31}P NMR and IR spectroscopic data allowed identification of the products as the previously characterized complexes **5** and **6**.[10] In contrast to the above-cited examples, however, this reaction is not reversible. Refluxing **5** or **6** in toluene for as long as 16 h or photolyzing **5** in THF for 4 h yielded no spectroscopic evidence for reaction. Photolysis of **6** in toluene did result in the precipitation of some decomposition products, but only starting material was identified in the supernatant by ^{31}P NMR spectroscopy.



(1)



(2)



(3)

We recently reported[14] the results of a ^{13}CO labeling study which probed the stereoselectivity of reaction 3. Reaction of **2** with ^{13}CO was found to proceed with stereoselective incorporation of ^{13}CO into axial sites, yielding two diastereomers of *fac*-(1)Mo(CO)$_3$(^{13}CO) as the sole products. Monitoring the reaction by ^{13}C NMR spec-

(22) Gudat, D.; Daniels, L. M.; Verkade, J. G. *Organometallics* **1990**, *9*, 1464.

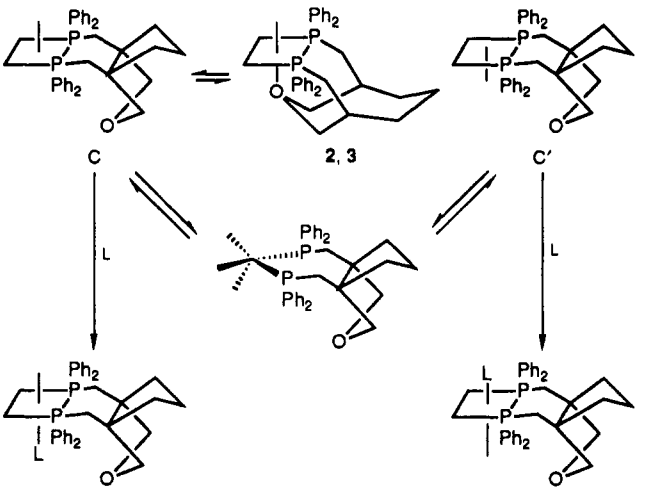
troscopy revealed no ^{13}CO incorporation into an equatorial site, with the approximately 4:1 ratio of diastereomers remaining stable over a period of 17 days.

Darensbourg has reported[23] that reaction of *fac*-(dppm)$W(CO)_3(NCCH_3)$ with ^{13}CO stereospecifically yields *fac*-(dppm)$W(CO)_3(^{13}CO)$ by incorporation of the ^{13}CO into an axial site. Over the course of 2 weeks, however, a subsequent intramolecular rearrangement process led to scrambling of the ^{13}CO between equatorial and axial sites. Thus, it was of interest to extend our ^{13}CO labeling study to include the tungsten analogue **3**.

^{13}CO was bubbled through a solution of **3** in CD_2Cl_2 for 10 min during which time the characteristic yellow color of **3** had dissipated. The ^{13}C NMR spectrum of this solution showed two intense carbonyl resonances at 204.7 and 198.8 ppm with an intensity ratio of 0.16:1.00. The triplet resonance at 198.8 ppm showed well-resolved tungsten satellites with $^1J_{^{183}W-^{13}C} = 124$ Hz.[24] The natural-abundance spectrum of (1)$W(CO)_4$ (**6**) exhibits carbonyl resonances at 206.4, 204.9, and 198.9 ppm with the last two assigned to the two nonequivalent axial carbonyls. The relative intensities of these resonances are 1.0:0.47:0.52, respectively. As in our molybdenum case, this result demonstrates stereoselective introduction of ^{13}CO exclusively into either of the two axial sites, yielding two diastereomers of *fac*-(1)$W(CO)_3(^{13}CO)$. Over the course of 2 weeks, ^{13}C NMR spectroscopy revealed a slow equilibration of ^{13}CO between axial and equatorial sites. After 27 days, however, the relative intensities of the equatorial and axial carbonyl resonances had only attained a ratio of 1:1.2:3.4, far from the ratio observed in the natural-abundance ^{13}C NMR spectrum of (1)$W(CO)_4$. As in Darensbourg's case, our system apparently undergoes a slow *fac* to *mer* intramolecular rearrangement process, but at a rate much slower than that observed for *fac*-(dppm)$W(CO)_3(^{13}CO)$. This large difference in rates for the two systems is most likely related to the presence of a seven- versus a four-membered chelate ring. This isomerization may proceed via a slow dissociation of a chelating PPh_2 group, followed by subsequent isomerization and rechelation, in which case the stability of the chelated form is expected to determine the rate of equilibration.

Previous ^{13}CO labeling studies on ligand substitution reactions of metal carbonyl complexes have also demonstrated stereospecificity in such reactions.[25] In addition to the work by Darensbourg cited above, Angelici reported[26] that the reaction of $[(Ph_2PCH_2CH_2)_2NEt]Mo(CO)_3$ with ^{13}CO stereospecifically yielded *fac*-$[(Ph_2PCH_2CH_2)_2NEt]Mo(CO)_3(^{13}CO)$. Our study differs from these previous examples in that for metal complexes wherein 1 coordinates as a bidentate (P,P′) ligand, a plane of symmetry does not exist in the P_2M plane, thus differentiating the two axial sites. Our results demonstrate

Scheme I



that the incoming ^{13}CO not only has access to the axial site vacated by the dissociated ether group of **1** but also has access to the other nonequivalent axial site, thus accounting for the minor diastereomeric products *fac*-(1)$Mo(CO)_3(^{13}CO)$ (ca. 20%) and *fac*-(1)$W(CO)_3(^{13}CO)$ (~14%).

The pathway we propose to account for this result is outlined in Scheme I. Dissociation of the ether donor of **1** in **2** or **3** yields the five-coordinate intermediate C of approximately square-pyramidal geometry. Unsaturated five-coordinate intermediates, such as $[Cr(CO)_5]$, have been shown to be solvated within picoseconds after their formation.[27,28] On the basis of calculations by Davy and Hall,[29] this process is too rapid to allow isomerization of C to provide an equatorial vacancy. Thus, no *mer* products should be formed in accord with the observed stereospecificity in this type of substitution reaction.[30] Lichtenberger and Brown[31] have proposed a mechanism whereby, in a five-coordinate intermediate, the vacant site may be interchanged between two sites cis to a noncarbonyl ligand, but trans to each other, without the intermediate formation of a vacant site trans to the noncarbonyl ligand. In Scheme I, inversion of the vacant site to the position trans to itself would involve the migration of the axial carbonyl trans to the vacant site, to an equatorial site with the simultaneous migration of the equatorial carbonyl to the initially vacant axial site. Calculations by Davy and Hall[29] show that such a rearrangement has an activation barrier of less than 1 kcal/mol for $Cr(CO)_4PH_3$ and can occur within the time frame of solvation. In our case, this rearrangement would isomerize the two five-coordinate intermediates C and C′. These two in-

(23) Darensbourg, D. J.; Zalewski, D. J.; Plepys, C.; Campana, C. *Inorg. Chem.* **1987**, *26*, 3727.

(24) $^1J_{^{183}W-^{13}C}$ values typically range from 120 to 145 Hz for carbonyl ligands in tungsten complexes. We believe that the $^1J_{^{183}W-^{13}C}$ values of 70.4 and 62.5 Hz reported in ref 23 may have been misstated and are probably 140.8 and 125 Hz, respectively. See: (a) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135. (b) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1.

(25) (a) Darensbourg, D. J.; Kudaroski, R.; Schenk, W. *Inorg. Chem.* **1982**, *21*, 2488. (b) Darensbourg, D. J. *Inorg. Chem.* **1979**, *18*, 2821. (c) Dobson, G. R.; Asali, K. J.; Marshall, J. L.; McDaniel, C. R. *J. Am. Chem. Soc.* **1977**, *99*, 8100. (d) Darensbourg, D. J.; Kump, R. L. *J. Organomet. Chem.* **1977**, *140*, C29. (e) Darensbourg, D. J.; Dobson, G. R.; Muradi-Araghi, A. *J. Organomet. Chem.* **1976**, *116*, C17. (f) Hyde, C. L.; Darensbourg, D. J. *Inorg. Chem.* **1973**, *12*, 1286. (g) Darensbourg, D. J.; Graves, A. H. *Inorg. Chem.* **1979**, *18*, 1257.

(26) Knebel, W. J.; Angelici, R. J.; Gansow, O. A.; Darensbourg, D. J. *J. Organomet. Chem.* **1974**, *66*, C11.

(27) Simon, J. D.; Peters, K. S. *Chem. Phys. Lett.* **1983**, *98*, 53.

(28) Simon, J. D.; Xie, X. *J. Phys. Chem.* **1986**, *90*, 6715.

(29) Davy, R. D.; Hall, M. B. *Inorg. Chem.* **1989**, *28*, 3524.

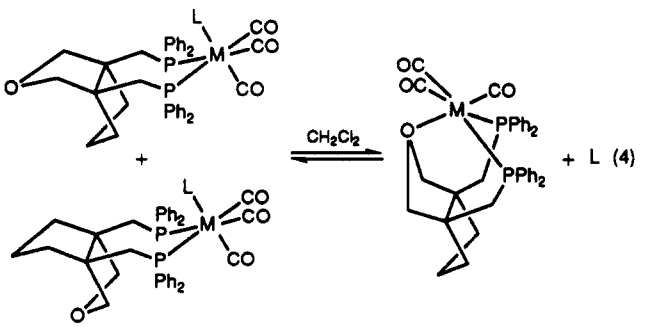
(30) As an alternative rationale, a reviewer has suggested that the preference of the five-coordinate intermediate to possess the two phosphine ligands in the equatorial plane of the square-pyramidal structures (B and B′) precludes the formation of *mer* products. Dobson, however, has shown that $Mo(CO)_4$(diphos) reacts with phosphites, phosphines, and amines via rate-determining CO loss to yield either *fac*- or *mer*-(L)$Mo(CO)_3$(diphos), depending on the ligand employed. Although *fac* products are preferred, *mer* products may be obtained when bulky ligands are used. See: (a) Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557. (b) Faber, G. C.; Dobson, G. R. *Inorg. Chim. Acta* **1968**, *2*, 479. (c) Dobson, G. R.; Houk, L. W. *Inorg. Chim. Acta* **1967**, *1*, 287.

(31) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366.

termediates are diastereomeric and should not be degenerate in energy. Thus, the rate of interconversion of C and C′ relative to their rates of reaction with additional ligands may account for the unequal ratio of diastereomeric products observed.

The results of the reactions of **2** and **3** with acetonitrile, pyridine, piperidine, and $P(OCH_2)_3CCH_3$ also indicate stereoselective incorporation of these ligands into axial sites to yield two *fac* diastereomers in each case. Thus, the proposed scheme seems to be general for the ligands we have investigated.

Lability of the N-Donor Complexes. As discussed earlier, reaction of **2** or **3** with $P(OCH_2)_3CCH_3$ cleanly yields the fac diastereomeric products **7a**, **7b**, **8a**, and **8b**. The results obtained with pyridine, piperidine, and acetonitrile were analogous with one notable distinction. The products obtained with these N-donor ligands partially dissociate in solution unless excess N-donor ligand is present. For example, **3** reacts with excess pyridine, yielding only the two *fac* diastereomers **10a** and **10b**, which are isolated as an analytically pure stable yellow solid. However, ^{31}P NMR and IR spectroscopy shows not only the presence of **10a** and **10b** but also the presence of the starting complex **3** when this solid sample is redissolved in methylene chloride. Additionally, a ^1H NMR spectrum of a solution of this redissolved material shows not only resonances due to a small quantity of **3** but also resonances assigned to an equimolar amount of uncoordinated pyridine. ^{31}P NMR spectra of redissolved samples **9a**, **9b**, **11a–13a**, and **11b–13b** also display the presence of the ether-coordinated complexes **2** or **3** unless excess N-donor ligand is present. For the complex *fac*-(**1**)$W(CO)_3$(pip) (**13a**, **13b**), piperidine dissociation occurs to such an extent that **3** accounts for approximately 40% of the mixture in solution as shown by ^{31}P NMR spectroscopy. These results suggest equilibrium 4, wherein the ether of **1**, aided by chelation, effectively competes with the N-donor ligands for coordination sites on the metal.



M = Mo, W
L = py, pip, CH_3CN, CD_3CN

This equilibrium is supported by the results of an exchange reaction involving **12a** and **12b** and CD_3CN monitored by ^2H NMR spectroscopy. A solution of *fac*-(**1**)$W(CO)_3(NCCH_3)$ in CH_2Cl_2 was treated with an excess of CD_3CN. ^2H NMR spectroscopy of the reaction solution after 5 min showed, in addition to free CD_3CN at 1.93 ppm, two singlets at 0.88 and 0.78 ppm in approximately a 1:4 ratio assigned to coordinated CD_3CN. The proton resonances for coordinated CH_3CN in the ^1H NMR spectrum of **12a** and **12b** experience an upfield shift due to neighboring phenyl rings and appear at 0.83 and 0.92 ppm, respectively. This assignment is substantiated by the splitting of the resonance for **12a** into a well-resolved triplet with $^5J_{PH}$ = 1.5 Hz. Monitoring this exchange reaction over a period of 2 h by ^2H NMR spectroscopy shows a steady increase in the intensity of the coordinated CD_3CN resonances compared with the intensity of the $CHDCl_2$ resonance. Although the reaction was monitored for 2 h, it appears to reach completion within approximately 50 min. This confirms that an exchange process does occur between coordinated and noncoordinated acetonitrile and that analogous exchange processes presumably occur for our piperidine and pyridine complexes, as indicated by the ^{31}P and ^1H NMR spectroscopic data presented above.

Regarding equilibrium 4, it should be noted that neither **2** nor **3** reacts with PPh_3 at ambient temperatures, in contrast to results obtained by Darensbourg[23] and Dobson[25c] for the reactions of PPh_3 with *fac*-(dppm)$W(CO)_3(NCCH_3)$ and *fac*-(dppe)$Mo(CO)_3$(pip), respectively. Thus, in addition to steric crowding at the axial site hindering reaction of **2** or **3** with PPh_3, the ether of ligand **1** may also effectively compete with PPh_3 for coordination to the metal. We also note that neither **2** nor **3** reacts with ethylene or THF.

Conclusions. We have demonstrated that the metal–ether interactions of **2** and **3** are indeed labile to displacement by a variety of ligands. However, the coordinated ether is not as labile as might initially be expected for such a ligand, presumably because of a favorable chelation effect. Evidence for this conclusion is the presence of an equilibrium for the N-donor ligands, wherein the ether of **1** effectively competes for coordination sites on the metal. We have also shown that all of the substitution reactions studied here are stereoselective, yielding two *fac* diastereomers in each case with the major substitution product arising from coordination of the new ligand to the site vacated by the ether of **1**. Now that we have achieved a better understanding of the basic coordination modes and substitution reactions of these group 6 metal complexes, we plan to explore the chemistry of **1** in metal systems that are potentially more significant catalytically.

Acknowledgment. We thank the National Science Foundation and the Mallinckrodt Chemical Co. for grant support of this research to J.G.V. We also thank Drs. Winfried Plass and Martina Schmidt for experimental assistance in the ^{13}CO labeling experiments.

Registry No. **2**, 134848-44-5; **3**, 134848-45-6; **5**, 134848-42-3; **6**, 134848-43-4; **7**, 139242-50-5; **7a**, 139344-43-7; **7b**, 139344-44-8; **8**, 139242-51-6; **8a**, 139344-45-9; **8b**, 139344-46-0; **9**, 139242-52-7; **9a**, 139344-47-1; **9b**, 139344-48-2; **10**, 139242-53-8; **10a**, 139344-49-3; **10b**, 139344-50-6; **11**, 139242-54-9; **11a**, 139344-51-7; **11b**, 139344-52-8; **12**, 139242-55-0; **12a**, 139344-53-9; **12b**, 139344-54-0; **13**, 139242-56-1; **13a**, 139344-55-1; **13b**, 139344-56-2.