the connecting thread shared by this array of donors and by the present thio acids as well. It now appears that the initial 1e act involving Cr(V) is, in all systems, an inner-sphere process, but in each case, the radical intermediate must depart from the site at which it is generated. Its release is not unexpected, for removal of an electron from a donor center generally makes it a much less effective ligating species. Nevertheless, the radical is, in each instance, consumed preferentially by Cr(V) (again by an inner-sphere transaction), rather than by the stronger oxidant, Cr(IV). Its preference for Cr(V) may reflect an accommodation, by this coordinatively unsaturated center, of the weakened ligand, which, however, competes less effectively with water or carboxylate for a site at hexacovalent chromium(IV).[39]

Acknowledgment. We thank Drs. James Espenson and David Stanbury for valuable discussions and Arla White for technical assistance.

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[39] There is uncertainty concerning the ligand configuration about Cr(IV) in aqueous solution. Although formal similarity to V(IV) suggests that it may be a 5-coordinate oxo ion, an octahedral configuration appears, at this time, to be more likely. See, for example: Espenson, J. H. *Acc. Chem. Res.* **1970**, *3*, 347.

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Synthesis, Reactivity, and X-ray Structure of *fac*-$W(CO)_3(dppm)(CH_3CN)$. Stereoselective Preparation of *fac*-$W(CO)_3(^{13}CO)(dppm)$ and Subsequent Intramolecular Rearrangement Processes

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The reaction of *fac*-$W(CO)_3(CH_3CN)_3$ with an equimolar quantity of bis(diphenylphosphino)methane (dppm) results in the quantitative formation of *fac*-$W(CO)_3(dppm)(CH_3CN)$. The solid-state structure of *fac*-$W(CO)_3(dppm)(CH_3CN)$ was established by X-ray diffraction [$P2_1/c$ (monoclinic), $a = 10.937$ (2) Å, $b = 18.399$ (4) Å, $c = 15.194$ (3) Å, $\beta = 108.33$ (1)°, $Z = 4$]. This compound reacts with ^{13}CO to afford stereoselective *fac*-$W(CO)_3(^{13}CO)(dppm)$. The reaction proceeds by a dissociative pathway, with activation parameters for loss of CH_3CN being $\Delta H^{\ddagger} = 23.5$ kcal/mol and $\Delta S^{\ddagger} = -6.0$ eu. In a subsequent, intramolecular ligand rearrangement facial $\rightleftharpoons$ meridional isomerization occurs. Reaction of *fac*-$W(CO)_3(dppm)(CH_3CN)$ with an additional 1 mol of dppm leads initially to formation of *fac*-$W(CO)_3(dppm)_2$, which contains both bidentate and monodentate dppm ligands. Isomerization and oxidation of the unattached phosphine eventually provided *mer*-$W(CO)_3(dppm)(Ph_2PCH_2P(O)Ph_2)$. The structure of the latter species was determined by X-ray diffraction [$P4_1$ (tetragonal), $a = 11.186$ (4) Å, $c = 40.498$ (9) Å, $Z = 4$].

Introduction

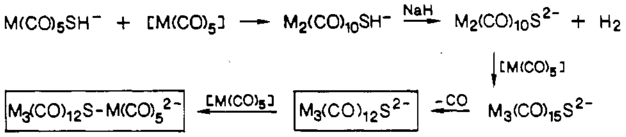
We have been interested in cluster synthesis of group 6 metal carbonyl species utilizing a thiolate ligand as the nucleating agent.[2,3] The reaction sequence provided below in Scheme I has afforded routes into tri- and tetranuclear derivatives. Attempts to prepare phosphine-substituted derivatives by means of CO displacement in the polynuclear species have been unsuccessful. An alternative synthetic approach is apparent in that the unsaturated $[M(CO)_5]$ moiety is prominent in Scheme I. Hence, it should be possible to introduce phosphine ligands into these anionic clusters by using substituted $[M(CO)_{5-n}L_n]$ species.

In this regard we have examined the chemistry of $W(CO)_3(dppm)(CH_3CN)$, where dppm = bis(diphenylphosphino)methane, with respect to ligand substitution processes involving the labile acetonitrile ligand. These investigations have allowed for an assessment of the kinetic parameters for CH_3CN dissociation from an unencumbered transition-metal center. In addition, stereoselective substitution with ^{13}CO was achieved to provide *fac*-$W(CO)_3(dppm)(^{13}CO)$, and its subsequent intramolecular ligand rearrangement process is reported upon herein.

Experimental Section

Methods and Materials. All manipulations were performed on a double-manifold Schlenk vacuum line under an atmosphere of dry nitrogen or in an argon-filled glovebox. Solvents were dried and deoxygenated by distillation from the appropriate reagent under a nitrogen atmosphere. Infrared spectra were recorded in 0.10-mm CaF_2 cells on an IBM IR/32 spectrometer. ^1H, ^{31}P, and ^{13}C NMR spectra were obtained on a Varian XL-200 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Scheme I



$W(CO)_6$, PPh_3, PMe_3, and $H_2C(PPh_2)_2$ were purchased from Strem Chemicals, Inc., and were used without further purification. Carbon monoxide (99 atom % ^{13}C) was obtained from Isotec, Inc. $W(CO)_3(CH_3CN)_3$ was prepared by refluxing $W(CO)_6$ in acetonitrile according to the published procedure.[4]

Syntheses. *fac*-$W(CO)_3(CH_3CN)(dppm)$. $W(CO)_3(CH_3CN)_3$ (0.583 g, 1.49 mmol) and bis(diphenylphosphino)methane (0.586 g, 1.52 mmol) were placed in a 50-mL Schlenk flask containing a magnetic stirring bar. The flask was fitted with a rubber septum, evacuated, and backfilled with a nitrogen atmosphere. Fifteen milliliters of dry acetonitrile was added to the flask, and the mixture was allowed to stir for 5 h. During this time period, all of the $W(CO)_3(CH_3CN)_3$ was consumed and a yellow precipitate of *fac*-$W(CO)_3(dppm)(CH_3CN)$ was formed when the reaction mixture was allowed to stand overnight at subambient temperatures. The yellow product was isolated by removing the solution with a cannula. The product was washed with 10 mL of diethyl ether and dried under vacuum to afford 0.646 g of *fac*-$W(CO)_3(CH_3CN)(dppm)$. The mother solution was evaporated under vacuum to provide a yellow solid, which was washed with diethyl ether and recrystallized from CH_2Cl_2/hexane to give an additional 0.113 g of product (73.5% total yield). IR (cm^{-1} in THF): 1930.0 (vs), 1837.4 (s), 1823.0 (sh). ^1H NMR ($CDCl_3$): 7.4 (multiplet), 5.5 (dt; $J_{P-H} = 8$ Hz, $J_{H-H} = 15.2$ Hz), 4.2 ppm (dt; $J_{P-H} = 10$ Hz, $J_{H-H} = 15.2$ Hz). ^{31}P NMR (THF/acetone-d_6): −11.06 ppm(s). Anal. Calcd: C, 51.97; H, 3.63; P, 8.93. Found: C, 51.90; H, 3.82; P, 9.08.

fac-$W(CO)_3(PPh_3)(dppm)$. *fac*-$W(CO)_3(CH_3CN)(dppm)$ (0.264 g, 0.38 mmol) and PPh_3 (0.132 g, 0.50 mmol) were added to a 50-mL Schlenk flask along with a magnetic stirring bar. The flask was fitted with a rubber septum, evacuated, and backfilled with a nitrogen atmo-

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[1] Nicolet Instrument Corp., Madison, WI 53711.

[2] (a) Darensbourg, D. J.; Zalewski, D. J. *Organometallics* **1984**, *3*, 1598. (b) Darensbourg, D. J.; Zalewski, D. J.; Delord, T., submitted for publication in *Inorg. Chem.*

[3] Hoefler, M.; Tebbe, K.-F.; Veit, H.; Weiler, N. E. *J. Am. Chem. Soc.* **1983**, *105*, 6338.

[4] (a) Tate, C. P.; Knipple, W. R.; Augi, J. M. *Inorg. Chem.* **1962**, *1*, 433. (b) King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *5*, 1837.

sphere. Ten milliliters of THF was added to the flask, and the solution was stirred overnight at ambient temperature. Following this reaction period the solution contained only *fac*-W(CO)$_3$(PPh$_3$)(dppm), as indicated by infrared spectroscopy, where the ν(CO) bands appeared at 1930.0 (s) and 1838.4 cm^{-1} (s, br).

***mer*-W(CO)$_3$(PPh$_3$)(dppm).** A THF solution of *fac*-W(CO)$_3$(PPh$_3$)(dppm) was heated at 50 °C for 20 h. During this time period, the facial isomer was completely converted into the meridional isomer. This isomer was precipitated upon addition of hexane to afford a 94.5% yield of product. IR (cm^{-1} in THF): 1966.7 (w), 1868.3 (s), 1845.1 (m). Anal. Calcd for W(CO)$_3$(PPh$_3$)(dppm)·CH$_3$CN: C, 60.33; H, 4.22; P, 9.72. Found: C, 59.71; H, 4.25; P, 9.54.

***mer*-W(CO)$_3$(dppm)(Ph$_2$PCH$_2$P(O)Ph$_2$).** *fac*-W(CO)$_3$(CH$_3$CN)(dppm) and a slight excess of dppm were dissolved in THF under a nitrogen atmosphere in a Schlenk flask. The solution was stirred overnight at ambient temperature with *fac*-W(CO)$_3$(dppm)$_2$, where one phosphine ligand is unbound to the tungsten center, being afforded, as revealed by infrared spectroscopy. During prolonged (4 days) stirring of *fac*-W(CO)$_2$(dppm)$_2$ in THF at ambient temperature, isomerization to the meridional isomer occurred with concurrent oxidation of the uncoordinated phosphine ligand by adventitious oxygen. X-ray-suitable crystals were obtained by slow recrystallization from THF/hexane.

W(CO)$_4$(dppm). Method A. W(CO)$_6$ (0.979 g, 2.78 mmol) and dppm (1.19 g, 3.10 mmol) in 80 mL of THF were photolyzed for 1 h. The solvent was removed under vacuum, and the product was recrystallized from chloroform and methanol upon cooling to $\simeq$0 °C. The yield of W(CO)$_4$(dppm) was 1.77 g (2.60 mmol) or 93.7%.

Method B. *fac*-W(CO)$_3$(CH$_3$CN)(dppm) (0.102 g) was placed in a 50-mL Schlenk flask fitted with a rubber septum. The flask was evacuated and backfilled with a carbon monoxide atmosphere and 15-mL of THF. The solution was heated at 50 °C overnight, following which its infrared spectrum indicated the presence of W(CO)$_4$(dppm) as the sole product. IR (cm^{-1} in THF): 2016.8 (m), 1906.9 (vs), 1878.9 (s). ^{1}H NMR (CDCl$_3$): 7.45 (multiplet), 4.92 ppm (t; $J_{\text{P-H}}$ = 8.8 Hz). ^{31}P NMR (THF/acetone-d_6): −18.26 ppm. ^{13}C NMR (CDCl$_3$): 210.3 (t; $J_{\text{P-C}}$ = 7.8 Hz, $J_{\text{W-C}}$ = 70.4 Hz), 202.7 (t; $J_{\text{P-C}}$ = 6.7 Hz, $J_{\text{W-C}}$ = 62.5 Hz), 130.0 (m), 51.87 ppm (t; $J_{\text{P-C}}$ = 24.0 Hz).

***fac*-W(CO)$_3$(^{13}CO)(dppm).** This complex is best synthesized by reacting a THF solution of *fac*-W(CO)$_3$(CH$_3$CN)(dppm) with ^{13}CO at 65 °C for 2 h. Under these conditions all of the W(CO)$_3$(CH$_3$CN)(dppm) is converted to W(CO)$_3$(^{13}CO)(dppm), with a minimal quantity of the meridional isomer being formed. IR (cm^{-1} in THF): 2003.3 (m), 1910.7 (s), 1878.9 (vs). An equilibrium mixture of facial and meridional isomers is obtained upon allowing a THF solution of *fac*-W(CO)$_3$(^{13}CO)(dppm) to stand at ambient temperature for 2 weeks. The infrared bands ascribed to the *mer*-W(CO)$_3$(^{13}CO)(dppm) isomer appear at 2012.0 (m), 1909.8 (s), and 1849.0 (m) cm^{-1} in THF solution.

Kinetic Measurements. In a typical experiment, under a nitrogen atmosphere, approximately 40 mg of *fac*-W(CO)$_3$(CH$_3$CN)(dppm) was placed in a 50-mL Schlenk flask fitted with a rubber septum. THF (5 mL) was added to dissolve the complex, and the flask was evacuated and backfilled with an atmosphere of 99% ^{13}CO. The reaction flask was placed in a Haake A81 constant-temperature bath set at a predetermined temperature. The reaction was followed by intermittently withdrawing samples with a hypodermic syringe and monitoring the infrared spectra in the ν(CO) region. The concentration of *fac*-W(CO)$_3$(CH$_3$CN)(dppm) was determined by measuring the height of the band at 1930.0 cm^{-1} recorded in absorbance units.

Crystallographic Studies. Crystallographic analyses were carried out at the Nicolet XRD Corp. (Madison, WI). Crystallographic data for the complexes *fac*-W(CO)$_3$(dppm)(CH$_3$CN) (I) and *mer*-W(CO)$_3$(dppm)(Ph$_2$PCH$_2$P(O)Ph$_2$)(THF) (II) have been tabulated in Table I. The intensity measurements were carried out with a Nicolet R3 or R3V diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) for crystals of dimensions 0.40 mm × 0.30 mm × 0.30 mm (I) or 0.25 mm × 0.20 mm × 0.20 mm (II). A total of 4156 reflections having $4.0 \leq 2\theta \leq 45°$ were measured for I and 3948 reflections having $3.0 \leq 2\theta \leq 45°$ were measured for II. The 1.0° wide ω-scan technique was used with a variable scan speed of 3.98–29.30°/min in 2θ and a background-to-scan ratio equal to 1.0. During the data collection, three standard reflections were monitored every 97 reflections for I and two standard reflections were monitored every 48 reflections for II.

Lorentz and polarization corrections were applied to the data. The unit cell parameters and the systematic absences are consistent with the monoclinic system, space group $P2_1/c$, for I and the tetragonal system, space group $P4_1$, for II. The number of reduced data with $I/\sigma(I)$ = 3.0 is 2780 (I) and 2073 (II).

Table I. Crystal, Data Collection, and Refinement Parameters for *fac*-W(CO)$_3$(dppm)(CH$_3$CN) (I) and *mer*-W(CO)$_3$(dppm)(Ph$_2$PCH$_2$P(O)Ph$_2$)THF (II)

	I	II
	Crystal Data	
empirical formula	$C_{30}H_{25}N_1O_3P_2W_1$	$C_{57}H_{48}O_4P_4W$
color and habit	yellow prisms	pale yellow prisms
size, mm^3	0.40 × 0.30 × 0.30	0.25 × 0.20 × 0.20
space group	monoclinic, $P2_1/c$	tetragonal, $P4_1$
unit cell dimens		
a, Å	10.937 (2)	11.186 (4)
b, Å	18.399 (4)	
c, Å	15.194 (3)	40.498 (9)
β, deg	108.33 (1)	
vol, Å^3	2902 (1)	5067 (5)
molecules/cell	4	4
mol wt	693	1104
density (calcd), g/cm^3	1.59	1.45
F(000), e	1360	2160
	Data Collection	
diffractometer	Nicolet R3	Nicolet R3/V
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp, °C	22	22
monochromator	highly oriented graphite cryst	highly oriented graphite cryst
2θ range, deg	4.0–45.0	3.0–45.0
scan type	Wyckoff ω scan	$\theta/2\theta$
scan speed, deg/min	variable: 3.98–29.30	variable: 3.98–29.30
bkgd measmt	stationary cryst and stationary counter at beginning and end of scan, each for half of total scan time	stationary cryst and stationary counter at beginning and end of scan, each for half of total scan time
std reflcns	3 measd every 97 reflcns	2 measd every 48 reflcns
no. of reflcns collcd	4156 (3783 independent)	3948 (3365 independent)
no. of reflcns obsd	2780 ($I > 3\sigma(I)$)	2073 ($I > 3\sigma(I)$)
abs coeff, cm^{-1}	42.0	24.6
min/max transmission	1.24	N/A
	Solution and Refinement	
system used	Nicolet EXTL (SHELXTL 5.1)	Nicolet SHELXTL PLUS (MicroVAX II)
soln	direct methods (SOLV 1.2)	direct methods
final residuals: R_1, R_2	2.68%, 2.68%	4.36%, 4.71%
goodness of fit	1.29	1.27
largest Δ/σ	0.20	1.00
data:parameter	8.3:1	5:1
largest diff peak, e/Å^3	0.57	1.00

The positions of the W and P atoms were derived with use of the Nicolet EXTL (SHELXTL 5.1) or SHELXTL PLUS direct-methods software. The remaining positions of the non-hydrogen atoms were obtained from a Fourier synthesis based or refined parameters for the tungsten and phosphorus atoms. Anomalous dispersion corrections and scattering factors were taken from ref 5.

The positions of the hydrogen atoms were calculated by using an idealized sp^2- or sp^3-hybridized geometry and a C–H bond length of 0.960 Å. Refinement with a data:parameter ratio equal to 8.3 gave R_1 and R_2 values of 2.68% with a goodness of fit of 1.29 for I and a data: parameter ratio equal to 5 gave R_1 and R_2 values of 4.36% and 4.71% with a goodness of fit of 1.27 for II. The final atomic coordinates for all non-hydrogen atoms are provided in Tables II and V. The anisotropic thermal parameters for all non-hydrogen atoms and the calculated atomic coordinates for the hydrogen atoms in crystalline *fac*-W(CO)$_3$(dppm)(CH$_3$CN) and *mer*-W(CO)$_3$(dppm)(Ph$_2$PCH$_2$P(O)Ph$_2$) are available as supplementary material. Bond lengths and bond angles are presented in Tables III and IV for I and Tables VI and VII for II.

Results and Discussion

Reaction of *fac*-W(CO)$_3$(CH$_3$CN)$_3$ with an equimolar quantity of bis(diphenylphosphino)methane (dppm) results in the quantitative formation of *fac*-W(CO)$_3$(dppm)(CH$_3$CN). The facial geometry is indicated by the infrared band pattern observed in

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(5) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for I

	x	*y*	*z*	*U*(eq)[a]
W	3252 (1)	1999 (1)	3010 (1)	39 (1)
C(1)	4687 (7)	1439 (4)	2824 (4)	49 (3)
O(1)	5508 (5)	1064 (3)	2760 (4)	76 (2)
C(2)	2022 (7)	1548 (3)	1918 (5)	51 (3)
O(2)	1282 (5)	1262 (3)	1285 (3)	77 (2)
C(3)	3001 (6)	1183 (3)	3732 (4)	47 (3)
O(3)	2831 (5)	675 (3)	4161 (3)	77 (2)
N(1)	3497 (5)	2973 (3)	2254 (3)	49 (2)
C(4)	3572 (6)	3522 (4)	1925 (4)	51 (3)
C(5)	3632 (8)	4226 (4)	1505 (5)	82 (4)
C(6)	3044 (5)	2881 (3)	4823 (4)	45 (2)
P(1)	4472 (2)	2653 (1)	4477 (1)	41 (1)
C(7)	5276 (7)	3515 (4)	4406 (4)	50 (3)
C(8)	4587 (8)	4140 (4)	4104 (5)	71 (3)
C(9)	5246 (10)	4754 (4)	3960 (5)	98 (5)
C(10)	6505 (10)	4757 (5)	4089 (6)	121 (6)
C(11)	7159 (10)	4134 (5)	4382 (7)	121 (6)
C(12)	6580 (8)	3513 (5)	4553 (6)	83 (4)
C(13)	5572 (6)	2204 (3)	5479 (4)	47 (3)
C(14)	5973 (6)	1504 (4)	5416 (5)	55 (3)
C15)	6772 (7)	1151 (4)	6170 (6)	75 (4)
C(16)	7198 (7)	1503 (5)	7007 (6)	77 (4)
C(17)	6800 (8)	2194 (5)	7097 (5)	86 (4)
C(18)	6000 (7)	2550 (4)	6334 (5)	68 (3)
P(2)	1793 (2)	2687 (1)	3702 (1)	41 (1)
C(19)	1046 (6)	3565 (3)	3298 (4)	45 (3)
C(20)	734 (6)	3731 (4)	2360 (5)	57 (3)
C(21)	135 (7)	4387 (4)	2038 (5)	68 (3)
C(22)	−111 (7)	4877 (4)	2632 (6)	71 (4)
C(23)	188 (7)	4720 (4)	3553 (6)	69 (4)
C(24)	784 (6)	4076 (4)	3887 (4)	57 (3)
C(25)	497 (6)	2205 (3)	3962 (5)	47 (3)
C(26)	−212 (7)	1714 (4)	3319 (6)	71 (3)
C(27)	−1222 (7)	1335 (5)	3469 (6)	92 (4)
C(28)	−1486 (7)	1430 (4)	4276 (6)	87 (4)
C(29)	−812 (7)	1907 (5)	4921 (5)	82 (4)
C(30)	169 (7)	2293 (4)	4763 (5)	69 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Lengths (Å) for I

W–C(1)	1.970 (8)	W–C(2)	1.962 (6)
W–C(3)	1.929 (6)	W–N(1)	2.190 (5)
W–P(1)	2.514 (2)	W–P(2)	2.512 (2)
C(1)–O(1)	1.162 (9)	C(2)–O(2)	1.169 (8)
C(3)–O(3)	1.187 (8)	N(1)–C(4)	1.140 (9)
C(4)–C(5)	1.455 (10)	C(6)–P(1)	1.845 (7)
C(6)–P(2)	1.854 (5)	P(1)–C(7)	1.834 (7)
P(1)–C(13)	1.816 (6)	P(2)–C(19)	1.827 (6)
P(2)–C(25)	1.818 (7)		

Table IV. Selected Bond Angles (deg) for I

C(1)–W–C(2)	91.3 (3)	C(1)–W–C(3)	86.4 (3)
C(2)–W–C(3)	88.2 (3)	C(1)–W–N(1)	96.8 (3)
C(2)–W–N(1)	93.9 (2)	C(3)–W–N(1)	176.1 (2)
C(1)–W–P(1)	98.8 (2)	C(2)–W–P(1)	169.6 (2)
C(3)–W–P(1)	89.9 (2)	N(1)–W–P(1)	87.5 (1)
C(1)–W–P(2)	164.3 (2)	C(2)–W–P(2)	102.1 (2)
C(3)–W–P(2)	86.1 (2)	N(1)–W–P(2)	90.3 (2)
P(1)–W–P(2)	67.5 (1)	W–C(1)–O(1)	174.3 (6)
W–C(2)–O(2)	177.9 (6)	W–C(3)–O(3)	178.6 (4)
W–N(1)–C(4)	172.5 (6)	N(1)–C(4)–C(5)	178.4 (8)
P(1)–C(6)–P(2)	98.1 (3)	W–P(1)–C(6)	95.8 (2)
W–P(1)–C(7)	119.5 (2)	W–P(2)–C(6)	95.7 (2)
W–P(1)–C(13)	123.6 (2)	C(6)–P(1)–C(7)	106.5 (3)
W–P(2)–C(19)	125.5 (2)	C(6)–P(1)–C(13)	105.2 (3)
W–P(2)–C(25)	119.1 (2)	C(6)–P(2)–C(19)	105.1 (3)
		C(6)–P(2)–C(25)	107.2 (3)

the CO stretching region (Table VIII). In this instance one CO group is slightly different from the other two. Because of this disruption of the C_3 symmetry of the W(CO)$_3$ moiety (and its concomitant A$_1$ + E ν(CO) vibrational modes), three intense infrared bands are anticipated of symmetry designations 2 A′ + A″. The ^{31}P NMR spectrum is also consistent with the formation of the facial isomer, where only one resonance at −11.06 ppm (downfield from H$_3$PO$_4$) is observed. The meridional isomer is expected to display two ^{31}P resonances.[6] The proton spectrum of *fac*-W(CO)$_3$(CH$_3$CN)(dppm) is more informative with the acetonitrile ligand disrupting the symmetry of the dppm moiety, causing the methylene protons to be diastereotopic. Each proton resonance appears as a doublet of triplets, being mutually coupled to each other and to the two phosphorus atoms of the dppm ligand.

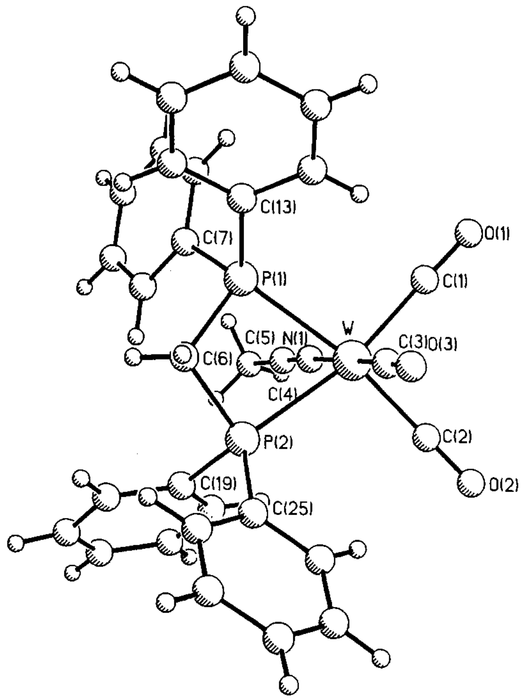

Figure 1. Atom labeling for the *fac*-W(CO)$_3$(dppm)(CH$_3$CN) complex.

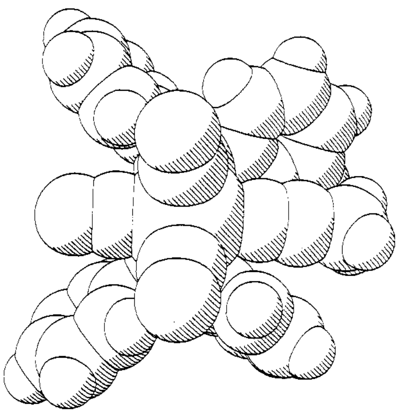

Figure 2. Space-filling diagram of the *fac*-W(CO)$_3$(dppm)(CH$_3$CN) molecule.

The solid-state structure of the *fac*-W(CO)$_3$(dppm)(CH$_3$CN) molecule was established by X-ray crystallography. Crystals suitable for X-ray structural analysis were obtained by slow diffusion of hexane into a concentrated methylene chloride solution of the title compound. The coordination geometry of the complex is that of a regular octahedron (Figure 1). This ligand arrangement is only slightly distorted due to the small bite angle of the dppm ligand of 67.5 (1)°. There does not appear to be significant steric interaction between the phenyl rings of the dppm ligand and the acetonitrile group. This is best seen in the space-filling plot illustrated in Figure 2. The axial CH$_3$CN and CO ligands possess nearly identical bond angles with the dppm ligand, with the average values being 88.9 (0.2) and 88.5 (0.2)°,

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(6) (a) Issacs, E. E.; Graham, W. A. G. *Inorg. Chem.* **1975**, *14*, 2560. (b) Bond, A. M.; Colton, R.; McGregor, K. *Inorg. Chem.* **1986**, *25*, 2378.

Table V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for II

	x	*y*	*z*	*U*(eq)[a]
W	8622.1 (5)	7102.3 (5)	1827	39 (1)
P(1)	6848 (3)	6286 (4)	1527 (1)	44 (1)
P(2)	9062 (4)	6605 (4)	1252 (1)	45 (1)
P(3)	7714 (3)	7373 (3)	2375 (1)	43 (1)
P(4)	5985 (4)	5836 (4)	2849 (1)	53 (2)
C(1)	10185 (20)	7724 (18)	1950 (5)	79 (8)
O(1)	11150 (14)	8024 (17)	2028 (4)	120 (8)
C(2)	9137 (20)	5472 (19)	1973 (4)	88 (8)
O(2)	9401 (16)	4545 (13)	2060 (4)	117 (8)
C(3)	8156 (18)	8785 (17)	1683 (4)	65 (7)
O(3)	7877 (14)	9706 (11)	1611 (3)	87 (6)
C(4)	7531 (14)	6161 (15)	1130 (4)	54 (6)
C(5)	6534 (13)	6264 (13)	2444 (3)	46 (5)
C(11)	5494 (13)	7156 (14)	1463 (4)	53 (6)
C(12)	5187 (14)	8008 (15)	1677 (4)	60 (6)
C(13)	4102 (19)	8659 (21)	1657 (5)	95 (9)
C(14)	3392 (21)	8442 (19)	1393 (6)	90 (9)
C(15)	3687 (17)	7559 (20)	1178 (5)	90 (9)
C(16)	4736 (16)	6907 (17)	1200 (5)	75 (7)
C(21)	6287 (16)	4763 (15)	1613 (4)	58 (6)
C(22)	7019 (20)	3808 (15)	1549 (5)	75 (8)
C(23)	6623 (26)	2684 (19)	1639 (6)	94 (11)
C(24)	5570 (29)	2504 (20)	1767 (6)	111 (12)
C(25)	4814 (18)	3472 (20)	1833 (6)	90 (8)
C(26)	5161 (16)	4596 (16)	1749 (4)	66 (7)
C(31)	9542 (15)	7676 (18)	948 (4)	62 (7)
C(32)	9309 (22)	7559 (20)	613 (5)	89 (9)
C(33)	9693 (30)	8368 (29)	386 (6)	133 (15)
C(34)	10311 (23)	9348 (28)	482 (6)	106 (12)
C(35)	10557 (18)	9495 (22)	810 (7)	105 (12)
C(36)	10196 (15)	8677 (18)	1030 (5)	68 (7)
C(41)	10058 (12)	5362 (14)	1155 (3)	43 (5)
C(42)	11169 (14)	5377 (14)	1299 (5)	62 (6)
C(43)	12026 (16)	4517 (19)	1210 (5)	80 (8)
C(44)	11714 (18)	3624 (18)	986 (5)	73 (8)
C(45)	10615 (18)	3592 (19)	853 (5)	75 (8)
C(46)	9771 (15)	4461 (15)	930 (4)	60 (6)
C(51)	8652 (15)	7276 (13)	2746 (3)	46 (6)
C(52)	9703 (16)	6621 (17)	2738 (4)	58 (7)
C(53)	10398 (17)	6536 (17)	3021 (5)	71 (8)
C(54)	10111 (20)	7097 (18)	3293 (5)	72 (8)
C(55)	9049 (19)	7775 (16)	3309 (4)	66 (7)
C(56)	8349 (16)	7840 (14)	3038 (4)	55 (6)
C(61)	6990 (15)	8812 (14)	2444 (4)	52 (6)
C(62)	5796 (18)	8985 (16)	2508 (4)	69 (7)
C(63)	5317 (23)	10092 (26)	2527 (5)	100 (10)
C(64)	5995 (29)	11108 (22)	2497 (5)	104 (12)
C(65)	7174 (25)	10912 (17)	2441 (5)	87 (10)
C(66)	7707 (18)	9842 (15)	2406 (4)	66 (7)
C(71)	7157 (14)	4886 (14)	3009 (4)	54 (6)
C(72)	7721 (18)	4056 (16)	2806 (5)	74 (7)
C(73)	8679 (20)	3437 (17)	2926 (6)	89 (9)
C(74)	9081 (19)	3618 (18)	3250 (6)	86 (9)
C(75)	8503 (19)	4419 (17)	3450 (5)	75 (8)
C(76)	7536 (19)	5003 (17)	3326 (5)	75 (8)
C(81)	4710 (15)	4901 (17)	2763 (4)	61 (7)
C(82)	3747 (19)	5406 (23)	2595 (5)	90 (9)
C(83)	2796 (29)	4757 (40)	2545 (10)	165 (22)
C(84)	2598 (39)	3666 (51)	2632 (14)	226 (34)
C(85)	3549 (30)	3092 (27)	2821 (8)	137 (15)
C(86)	4574 (22)	3736 (20)	2882 (5)	94 (10)
O(4)	5665 (11)	6807 (11)	3071 (3)	75 (5)
O(1S)	288 (40)	1610 (32)	2026 (14)	299 (29)
C(1S)	1335 (66)	1590 (78)	2083 (17)	334 (75)
C(2S)	2025 (41)	1261 (50)	1936 (16)	209 (34)
C(3S)	1667 (60)	1250 (35)	1616 (11)	243 (34)
C(4S)	511 (44)	1690 (46)	1666 (10)	210 (29)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

respectively. The three W–CO bond lengths are 1.970 (8), 1.962 (6), and 1.929 (6) Å, where the shortest distance represents the carbonyl ligand located trans to the acetonitrile group. The W–P bond distances at 2.514 (2) and 2.512 (2) Å are quite similar to those found in other tungsten phosphine derivatives containing sterically unencumbering phosphine ligands.[7] The W–N bond distance is 2.190 (5) Å.

Table VI. Selected Bond Lengths (Å) for II

W–P(1)	2.500 (3)	W–P(2)	2.445 (3)
W–P(3)	2.458 (3)	W–C(1)	1.947 (19)
W–C(2)	2.001 (19)	W–C(3)	2.039 (18)
P(1)–C(4)	1.783 (15)	P(1)–C(11)	1.818 (13)
P(1)–C(21)	1.849 (15)	P(2)–C(4)	1.850 (13)
P(2)–C(31)	1.799 (16)	P(2)–C(41)	1.824 (13)
P(3)–C(5)	1.833 (13)	P(3)–C(51)	1.836 (13)
P(3)–C(61)	1.823 (13)	P(4)–C(5)	1.817 (13)
P(4)–C(71)	1.807 (15)	P(4)–C(81)	1.803 (16)
P(4)–O(4)	1.455 (11)	C(1)–O(1)	1.173 (19)
C(2)–O(2)	1.135 (18)	C(3)–O(3)	1.115 (17)

Table VII. Selected Bond Angles (deg) for II

P(2)–W–P(1)	67.2 (1)	P(3)–W–P(1)	99.0 (1)
P(3)–W–P(2)	166.1 (1)	C(1)–W–P(1)	165.4 (5)
C(1)–W–P(2)	98.3 (5)	C(1)–W–P(3)	95.5 (5)
C(2)–W–P(1)	92.2 (5)	C(2)–W–P(2)	90.9 (5)
C(2)–W–P(3)	88.0 (5)	C(2)–W–C(1)	89.5 (8)
C(3)–W–P(1)	89.7 (5)	C(3)–W–P(2)	89.3 (4)
C(3)–W–P(3)	92.3 (5)	C(3)–W–C(1)	88.5 (8)
C(3)–W–C(2)	178.0 (8)	C(4)–P(1)–W	97.3 (4)
C(11)–P(1)–W	122.3 (5)	C(11)–P(1)–C(4)	105.8 (7)
C(21)–P(1)–W	120.9 (5)	C(21)–P(1)–C(4)	104.1 (7)
C(21)–P(1)–C(11)	103.7 (7)	C(4)–P(2)–W	97.4 (5)
C(31)–P(2)–W	124.0 (6)	C(31)–P(2)–C(4)	105.9 (8)
C(41)–P(2)–W	120.1 (4)	C(41)–P(2)–C(4)	107.7 (6)
C(41)–P(2)–C(31)	100.2 (6)	C(5)–P(3)–W	110.6 (4)
C(51)–P(3)–W	119.7 (5)	C(51)–P(3)–C(5)	104.2 (6)
C(61)–P(3)–W	115.6 (5)	C(61)–P(3)–C(5)	104.7 (7)
C(61)–P(3)–C(51)	100.4 (6)	C(71)–P(4)–C(5)	103.4 (6)
C(81)–P(4)–C(5)	104.2 (7)	C(81)–P(4)–C(71)	107.6 (7)
O(4)–P(4)–C(5)	116.4 (6)	O(4)–P(4)–C(71)	113.4 (7)
O(4)–P(4)–C(81)	110.0 (7)	O(1)–C(1)–W	175.7 (18)
O(2)–C(2)–W	178.1 (20)	O(3)–C(3)–W	177.8 (16)
P(2)–C(4)–P(1)	97.8 (6)	P(4)–C(5)–P(3)	124.1 (7)

Table VIII. Carbonyl Stretching Frequencies of Several $W(CO)_3(dppm)L$ Complexes

stereochemistry	L	ν(CO), cm^{-1} [a]			
	CO	2017 (m)	1916 (sh)	1907 (vs)	1879 (s)
facial	CH_3CN	1930 (vs)	1837 (s)	1823 (sh)	
facial	^{13}CO	2003 (m)	1911 (m)	1879 (s)	
meridional	^{13}CO	2012 (m)	1910 (vs)	1849 (m)	
facial	PPh_3	1930 (vs)	1838 (s)		
meridional	PPh_3	1967 (vw)	1868 (vs)	1845 (m)	
meridional	$Ph_2PCH_2P(O)Ph_2$	1968 (vw)	1868 (vs)	1844 (m)	
facial	PMe_3	1936 (s)	1838 (vs)		

[a] Infrared spectra were recorded in 0.1-mm CaF_2 cells with THF as solvent.

The acetonitrile ligand in *fac*-$W(CO)_3(dppm)(CH_3CN)$ is readily replaced by carbon monoxide according to eq 1. W-

$$fac\text{-}W(CO)_3(dppm)(CH_3CN) + CO \rightarrow W(CO)_4(dppm) + CH_3CN \quad (1)$$

$(CO)_4(dppm)$ was identified as the sole reaction product in quantitative yield by comparisons of its ν(CO) vibrational modes with that of an authetic sample of $W(CO)_4(dppm)$ prepared photochemically from $W(CO)_6$ and dppm. The kinetic parameters for the displacement of CH_3CN in *fac*-$W(CO)_3(dppm)(CH_3CN)$ by CO in THF were determined as a function of temperature over a range of 25 °C, and these data are presented in Table IX. An Arrhenius plot for this process is shown in Figure 3.

Reaction 1 was observed to be first order in metal substrate and zero order in carbon monoxide concentration at pressures close to 1 atm. The activation parameters, $\Delta H^{\ddagger} = 23.5$ kcal/mol and $\Delta S^{\ddagger} = -6$ eu, are consistent with dissociation of CH_3CN without

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(7) Cotton, F. A.; Darensbourg, D. J.; Klein, S.; Kolthammer, B. W. S. *Inorg. Chem.* **1982**, *21*, 2661.

Table IX. Temperature Dependence of the Rate of Reaction of *fac*-$W(CO)_3(CH_3CN)(dppm)$ with ^{13}CO[a]

temp, °C	10^4k, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
41.0	0.400 ± 0.030	23.5 ± 1.4	−6.0 ± 4.4
51.0	1.45 ± 0.10		
58.3	2.87 ± 0.26		
62.8	5.02 ± 0.18		
65.6	6.91 ± 0.60		

[a] Reactions were measured in tetrahydrofuran solution. Error limits represent 90% confidence level.

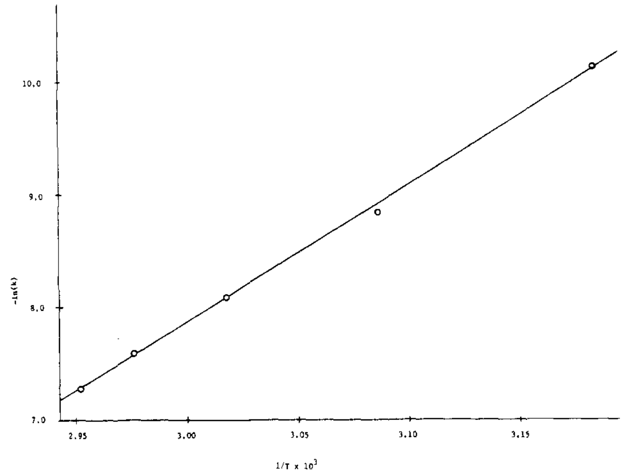

Figure 3. Arrhenius plot for the reaction of *fac*-$W(CO)_3(dppm)(CH_3CN)$ with CO to provide $W(CO)_4(dppm)$.

major assistance by the solvent THF molecule. A lower $\Delta H^{\ddagger}$ value and a more negative $\Delta S^{\ddagger}$ value are anticipated for THF-assisted ligand displacement processes.[8] Nevertheless, *cis*-$W(CO)_3(dppm)(THF)$ is expected to be the initially afforded product, with rapid THF substitution by CO subsequently occurring. The activation parameters determined herein are similar to those noted for amine dissociation in a $W(CO)_5$–amine complex carried out in noninteracting solvents.[9] It is of interest to note that, in $W(CO)_5L$ ($L = CH_3CN$, NHC_5H_{10}), gas-phase bond energies have been reported to be quite similar (42.7 and 44.7 kcal/mol, respectively) to that of W–CO in $W(CO)_6$.[10]

When ^{13}CO is used in reaction 1, stereoselective formation of *fac*-$W(CO)_3(^{13}CO)(dppm)$ is accomplished (eq 2). Figure 4

$$fac\text{-}W(CO)_3(dppm)(CH_3CN) + {}^{13}CO \rightarrow fac\text{-}W(CO)_3({}^{13}CO)(dppm) + CH_3CN \quad (2)$$

$$fac\text{-}W(CO)_3({}^{13}CO)(dppm) \rightleftharpoons mer\text{-}W(CO)_3({}^{13}CO)(dppm) \quad (3)$$

depicts the progress of the reaction as monitored by infrared spectroscopy in the $\nu(CO)$ region. The initially afforded facial isomer is converted into the meridional isomer in a subsequent, slower intramolecular ligand rearrangement process. The intramolecular nature of reaction 3 is seen by the lack of ligand exchange between $W(CO)_4(dppm)$ and free carbon monoxide in solution on the time scale of ligand rearrangement. Reaction 3 occurs slowly at ambient temperature and is readily followed by either infrared or ^{13}C NMR spectroscopy. After 2 weeks at 25 °C, a solution composed originally of *fac*-$W(CO)_3(^{13}CO)(dppm)$ contains an equilibrium mixture of the two isomers. Figure 5 illustrates the infrared spectral changes in the $\nu(CO)$ region observed during this transformation.

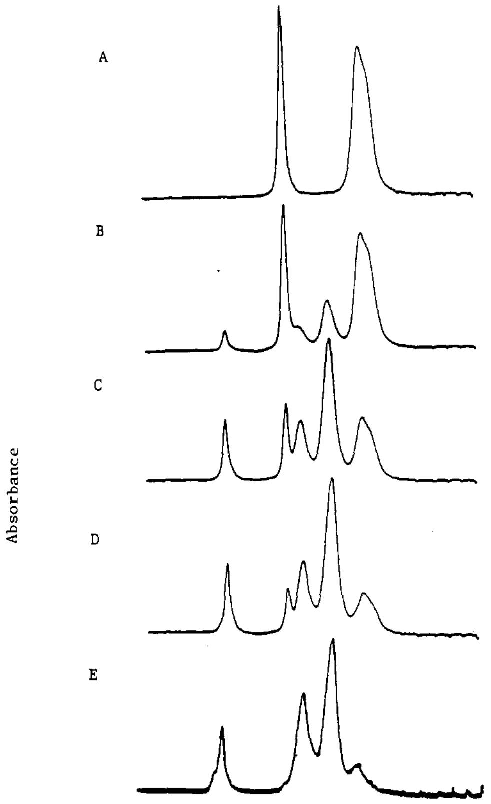

Figure 4. Infrared monitoring of $\nu(CO)$ modes for the reaction between *fac*-$W(CO)_3(dppm)(CH_3CN)$ and ^{13}CO in THF at 62.8 °C: (A) initial spectrum; (B) spectrum at $t = 4.5$ min; (C) spectrum at $t = 23$ min; (D) spectrum at $t = 40$ min; (E) spectrum at reaction completion.

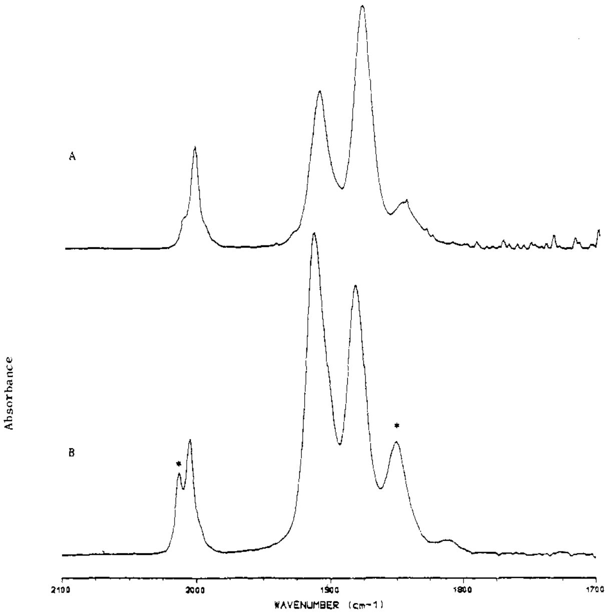

Figure 5. Infrared spectra of $\nu(CO)$ modes during the intramolecular ligand rearrangement process, *fac*-$W(CO)_3(^{13}CO)(dppm) \rightleftharpoons$ *mer*-$W(CO)_3(^{13}CO)(dppm)$, at 25 °C in THF (peaks indicated with an asterisk are due exclusively to the meridional isomer): (A) initial spectrum; (B) spectrum for equilibrium mixture of facial and meridional isomers.

^{13}C NMR spectroscopy is as well useful in assessing the progress of this intramolecular reaction. The natural-abundance ^{13}C NMR spectrum of $W(CO)_4(dppm)$ displays resonances for the equatorial and axial CO ligands at 210.5 and 203.0 ppm, respectively, of intensity ratio 0.90:1.00. Freshly prepared *fac*-$W(CO)_3(^{13}CO)(dppm)$ exhibits peaks at 210.5 and 203.0 ppm in an in-

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(8) For example, substitution of carbon monoxide in $W(CO)_5O_2CCH_3^-$ by phosphine ligands in THF occurs via a process independent of phosphine concentration and first order in $W(CO)_5O_2CCH_3^-$. The activation parameters determined in this system were $\Delta H^{\ddagger} = 17.8$ kcal/mol and $\Delta S^{\ddagger} = -17.6$ eu.: unpublished results from our laboratories (Holly C. Pickner).

(9) (a) Dobson, G. R. *Inorg. Chem.* **1974**, *13*, 1790. (b) Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557 and references therein.

(10) Bernstein, M.; Simon, J. D.; Peters, K. S. *Chem. Phys. Lett.* **1983**, *100*, 241.

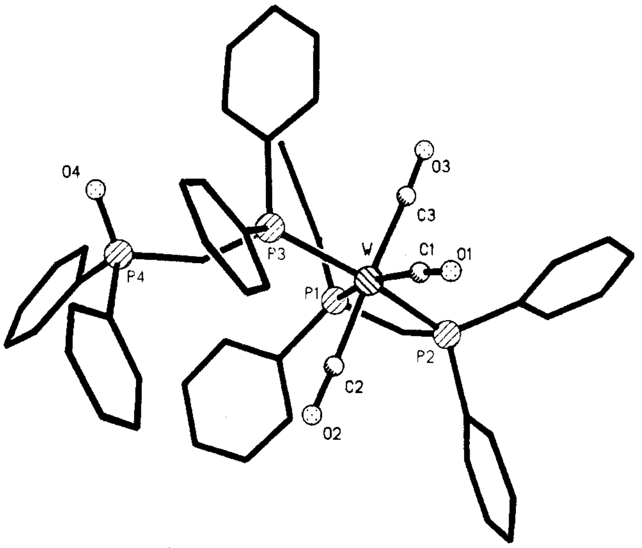

Figure 6. Molecular structure of the *mer*-W(CO)$_3$(dppm)(Ph$_2$PCH$_2$P(O)Ph$_2$) molecule.

tensity ratio of 0.18:1.00. When a solution of *fac*-W(CO)$_3$(^{13}CO)(dppm) is allowed to stand for approximately 2 weeks at ambient temperature, the ratio of the two ^{13}C signals is 0.89:1.00, indicating that reaction 3 has reached equilibrium. After the ligand rearrangement, no ^{13}CO–^{13}CO coupling was observed in the resulting W(CO)$_4$(dppm) product, an observation consistent with an intramolecular exchange process.[11]

The reaction of *fac*-W(CO)$_3$(dppm)(CH$_3$CN) with triphenylphosphine in THF at ambient temperature affords *fac*-W(CO)$_3$(dppm)(PPh$_3$). However, because of the steric requirements of the PPh$_3$ ligand, when a THF solution of *fac*-W(CO)$_3$(dppm)(PPh$_3$) is heated at 50 °C, isomerization to the meridional isomer readily takes place. Once formed, the meridional isomer is quite resistant to ligand dissociation; for example, it is stable to reaction with ^{13}CO at 50 °C for 3 days. Similarly, the reaction of *fac*-W(CO)$_3$(dppm)(CH$_3$CN) with Ph$_2$PCH$_2$PPh$_2$ at ambient temperature in THF afforded what was initially assumed to be *fac*-W(CO)$_3$(dppm)$_2$ with a dangling phosphine ligand on the basis of the ν(CO) stretching band pattern. After prolonged standing in solution at room temperature this complex exhibited facial $\rightleftharpoons$ meridional isomerization.

More detailed examination by X-ray crystallography of crystals presumed to be *mer*-W(CO)$_3$(dppm)$_2$ revealed this complex to contain an uncoordinated phosphine oxide group. The coordination geometry of the complex is that of a regular octahedron (Figure 6) with a dppm bite angle of 67.2°. The three W–CO bond lengths are 1.947 (19), 2.001 (19), and 2.039 (18) Å, where the shortest distance corresponds to the carbonyl ligand located trans to the phosphine ligand. Concomitantly, the W–P bond distance trans to the carbonyl ligand is the longest at 2.500 (3) Å, with the remaining W–P distances being 2.445 (3) and 2.458 (3) Å for the dppm and Ph$_2$PCH$_2$P(O)Ph$_2$ groups, respectively. Although the origin of the phosphine oxide has not been clearly established, since we started with pure dppm, oxidation of the PPh$_2$ moiety by adventitious oxygen presumably occurred during the prolonged *fac–mer* isomerization process.

Acknowledgment. The financial support of the Robert A. Welch Foundation is greatly appreciated.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates, and complete bond distances and angles (9 pages); listings of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

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[11] (a) Darensbourg, D. J. *J. Organomet. Chem.* **1979**, *174*, C70. (b) Darensbourg, D. J. *Adv. Organomet. Chem.* **1982**, *21*, 113. (c) Dobson, G. R.; Asali, K. J. *Inorg. Chem.* **1981**, *20*, 3563 and references therein.

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Digonally Coordinated Halide within an Octametal Cage. Crystal and Solution Structures of [XCd$_8$(SCH$_2$CH$_2$OH)$_{12}$X$_3$], X = Cl, Br, I[1]

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The complexes [ClCd$_8$(SCH$_2$CH$_2$OH)$_{12}$Cl$_3$] (**5**) and [BrCd$_8$(SCH$_2$CH$_2$OH)$_{12}$Br$_3$] (**6**) are formed in the reaction of 2-hydroxyethanethiol with cadmium acetate and excess sodium halide in water, similarly to the formation of [ICd$_8$(SCH$_2$CH$_2$OH)$_{12}$I$_3$] (**2**). **5** and **6** contain [XCd$_8$(SCH$_2$CH$_2$OH)$_{12}$X$_3$] molecules with threefold symmetry in the rhombohedral space group *R*3 with *Z* = 1 (**5**, *a* = 11.700 (1) Å, α = 103.57 (1)°, 1594 reflections (Mo Kα), *R* = 0.028; **6**, *a* = 11.681 (1) Å, α = 102.38 (1)°, 1587 reflections (Mo Kα), *R* = 0.029), in which an oblate Cd$_8$ hexahedron (compressed along the threefold axis) intersects an axially prolate S$_{12}$ icosahedron. Three four-coordinate (S$_3$CdX) and three five-coordinate (chelated S$_3$Cd(–OH)$_2$) Cd atoms lie outside the faces of the icosahedra in both structures. In **5** the other two Cd atoms on the threefold axis lie inside the faces of the icosahedron, creating symmetric linear digonal coordination of the central Cl atom (Cl–Cd = 2.69 (2), 2.69 (2) Å). In **6** only one axial Cd atom is inside the icosahedron, while the other is almost coplanar with its icosahedral face, thereby creating dissymmetric linear digonal coordination of the internal Br atom (Br–Cd = 2.754 (8), 3.008 (9) Å). ^{113}Cd NMR spectra (natural abundance, 66.6 MHz) of **5**, **6**, and **2** in DMF solution are in the slow-Cd-exchange regime at 220 K and reveal all distinct Cd coordination environments, without evidence of Cd–Cd coupling. At room temperature and above the Cd sites are interchanged rapidly.

Introduction

There exists the established class of molecular aggregates [XM$_8$Y$_{12}$] (**1**), in which a cube of metal atoms contains a halide ion X at or close to the body center and doubly bridging ligands across the 12 edges. The donor atoms Y of the 12 bridging ligands constitute an icosahedron. Examples are (μ_8-I)Cd$_8$(SCH$_2$CH$_2$OH)$_{12}$I$_3$ (**2**)[2] and [(μ_8-Cl)M$^1_8$(L---L)$_6$]^z (**3**), in which M is Cu or Ag and L---L is a square-planar chelate moiety containing another metal M′ and providing two cis bridging sulfur

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[1] Applications of Cadmium NMR to Polycadmium Compounds. 5. Part 4: Dance, I. G.; Garbutt, R. G.; Craig, D. C. *Aust. J. Chem.* **1986**, *39*, 1449.

[2] Burgi, H. B.; Gehrer, H.; Strickler, P.; Winkler, F. K. *Helv. Chim. Acta* **1976**, *59*, 2558.