Inorg. Chem. **1984,** *23,* 3181-3183

Contribution from Los Alamos National Laboratory,
University of California, Los Alamos, New Mexico 87545

Reduction of Sulfur Dioxide by Cp_2MH_2 (M = Mo, W) to $Cp_2M(S_2O_3)$ and Water. Molecular Structure and Reaction with Acids of an Organometallic Molybdenum–Thiosulfate Complex

G. J. KUBAS* and R. R. RYAN

Received September 28, 1983

Treatment of Cp_2MH_2 (M = Mo, W) solutions with SO_2 has been found to rapidly and quantitatively give $Cp_2M(S_2O_3)$ and water. Single-crystal X-ray studies of the Mo product at −95 °C revealed bidentate coordination of thiosulfate to molybdenum [Mo–O = 2.134 (4) Å; Mo–S = 2.450 (2) Å] with a dihedral angle between the Cp planes of 46.8° and a planar $MoOS_2$ ring. The thiosulfate complexes were found to react with aqueous HCl and HBr to produce SO_2, H_2O, and new metal–sulfur complexes of apparent stoichiometry $[Cp_2M(S)(X)]X$ (X = Cl, Br), characterized by infrared and proton NMR spectroscopy. Crystallographic data for $Cp_2Mo(S_2O_3)$: space group $P2_1/n$, $a = 13.600$ (4) Å, $b = 10.623$ (2) Å, $c = 7.610$ (1) Å, $\beta = 100.08$ (2)°; $Z = 4$, $R = 0.023$ for 1722 reflections with $I \geq 2\sigma(I)$ and $2\theta \leq 50°$.

Reduction of SO_2 by transition-metal hydride complexes to sulfur (or metal–sulfur complexes) and water is currently being investigated in relation to devising methods for homogeneous catalytic reduction of this pollutant to innocuous products. Hydrogen reduction of SO_2 to sulfur and water has been catalyzed heterogeneously[1] under mild conditions, but thus far this type of conversion has not been carried out homogeneously. Although several examples of simple addition of SO_2 to monohydride complexes or displacement of H_2 from dihydride complexes by SO_2 are known, no actual reaction of a transition-metal hydride with SO_2 has been reported that proceeded with the formation of water and reduced sulfur species.[2] We have found that SO_2 is rapidly and quantitatively reduced by Cp_2MH_2 (M = Mo, W) to yield water and an organometallic thiosulfate, $Cp_2M(S_2O_3)$. This paper reports the synthesis, structure, and novel reaction of this complex with strong acids.

Experimental Section

The complexes Cp_2MH_2 (M = Mo, W) were prepared by the method of King[3] and purified by sublimation. Other reagents were used as received, and reactions were carried out in a nitrogen atmosphere. Infrared spectra were recorded on a Perkin-Elmer 683 (Nujol mulls), NMR spectra were measured on a Varian EM-390, and elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Conductivity measurements were carried out on a Barnstead Model PM 70CB conductivity bridge and electrochemical experiments on a Princeton Applied Research Model 170 electrochemistry system with conventional three-electrode configurations.

Reaction of SO_2 with Cp_2MH_2. Preparation of $Cp_2M(S_2O_3)$. A solution of 0.5 mmol of Cp_2MH_2 (M = Mo, W) in 5 mL of toluene was treated with excess SO_2, giving an immediate brown precipitate of $Cp_2M(S_2O_3)$. The latter was collected by filtration, washed with toluene and then diethyl ether, and dried in vacuo. Yields were nearly quantitative (94–98%), and water was identified to be a coproduct. Anal. Calcd for $C_{10}H_{10}O_3S_2Mo$: C, 35.5; H, 3.0; O, 14.2; S, 19.0; Mo, 28.4. Found: C, 35.7; H, 3.2; O, 14.3; S, 18.0; Mo, 28.6. Calcd for $C_{10}H_{10}O_3S_2W$: C, 28.2; H, 2.4; S, 15.0. Found: C, 27.9; H, 2.4; S, 14.2.

The complexes were soluble in Me_2SO and nitromethane but were nearly insoluble in most other solvents.

When the reaction of Cp_2MoH_2 with SO_2 was carried out in Me_2SO, a deep brown solution was obtained that slowly yielded well-formed crystals of $Cp_2Mo(S_2O_3)$ upon standing. Use of methanol as solvent gave several uncharacterized brown products and very little thiosulfate complex.

Table I. Crystallographic Data

temp, °C	room temp	−95[a]
a, Å	13.620 (3)	13.600 (4)
b, Å	10.418 (2)	10.623 (2)
c, Å	7.924 (1)	7.610 (1)
β, deg	99.96 (2)	100.08 (2)
space group	$P2_1/n$	
Z	4	
μ(Mo Kα), cm^{-1}	15.1	
developed faces (dist from origin, mm)	{100} (0.025), {011} (0.078)	
max, min transmission[4]	0.95, 0.88	
data colled	$2\theta \leqslant 50°$	
no. of unique reflcns	1914	
no. of obsd reflcns with $I \geqslant 2\sigma(I)$	1722	
unweighted *R* value	2.3%	
diffractometer	Picker FACS-1, P. G. Lenhert's disk operating system,[5] Wang encoders, graphite monochromator, 3.5° takeoff angle (1.5° + dispersion), continuous scans, 20 s symm bkgd counts, Mo Kα radiation (λ 0.709 30 Å).	

[a] The temperature was maintained by using the nitrogen boil-off system as designed by Strouse.[6]

Reaction of Cp_2WH_2 with SO_2 (1:1) at −78 °C. A solution of Cp_2WH_2 (0.118 g, 0.373 mmol) in 4 mL of toluene was treated with SO_2 (0.34 mmol) on a vacuum line at dry ice–acetone bath temperature. Immediate formation of a red precipitate took place. On warming of the mixture, the latter became browner, becoming totally brown at ambient temperature. Solvent was removed, and the residue was analyzed by IR and NMR methods, showing the presence of $Cp_2W(S_2O_3)$, unreacted Cp_2WH_2, and several other minor species. Attempts to isolate the initial red precipitate by low-temperature filtration failed.

Reaction of $Cp_2M(S_2O_3)$ with Aqueous HCl and HBr. The addition of $Cp_2W(S_2O_3)$ to concentrated aqueous HCl or HBr (but not HPF_6) gave intense green homogeneous solutions that yielded green solids upon evaporation (HCl) or standing (HBr). Mass spectral analysis showed SO_2 to be produced also. For M = Mo, a red-brown product was observed, which displayed a strong broad infrared peak at 325 cm^{-1} apparently due to ν(Mo–Cl). The tungsten products gave IR bands due to Cp, low-frequency bands at 385, 365, and 327 cm^{-1}, and a peak at 300 cm^{-1} assignable to ν(W–Cl), since this peak was absent in the HBr reaction product. Elemental analysis of the latter was consistent with the composition Cp_2WSBr_2. Anal. Calcd: C, 23.7; H, 2.0; Br, 31.6; S, 6.3. Found: C, 23.3; H, 2.1; Br, 32.6; S, 5.7. The complexes were water soluble with slow decomposition. Addition of NH_4PF_6 (0.11 g in 4 mL of H_2O) to the green solution

---

(1) Moody, D. C.; Ryan, R. R.; Salazar, K. V. *J. Catal.* **1981,** *70,* 221 and references therein.

(2) Reactions yielding other products have been reported: Ghatak, I.; Mingos, D. M. P.; Hursthouse, M. B.; Abdul Malik, K. M. *Transition Met. Chem. (Weinheim, Ger.)* **1979,** *4,* 260. Komiya, S.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1976,** *49,* 784.

(3) King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; p 79.

0020-1669/84/1323-3181$01.50/0 © 1984 American Chemical Society

Table II. Fractional Coordinates and Thermal Parameters

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Mo1	0.22140 (4)	0.20885 (5)	−0.00403 (6)	*a*	O1	0.1250 (3)	0.1810 (4)	0.1857 (5)	*a*
S1	0.0562 (1)	0.2964 (1)	0.1770 (2)	*a*	O2	−0.0473 (3)	0.2579 (4)	0.1329 (6)	*a*
O3	0.0801 (3)	0.3696 (4)	0.3395 (5)	*a*	S2	0.1034 (1)	0.3850 (1)	−0.0328 (2)	*a*
C1	0.3901 (5)	0.1915 (6)	0.0509 (9)	*a*	C2	0.3560 (5)	0.1697 (7)	0.2126 (9)	*a*
C3	0.3167 (5)	0.2847 (7)	0.2610 (9)	*a*	C4	0.3250 (5)	0.3751 (6)	0.1322 (9)	*a*
C5	0.3688 (5)	0.3180 (6)	−0.0010 (9)	*a*	C6	0.0974 (5)	0.1166 (6)	−0.2001 (8)	*a*
C7	0.1491 (5)	0.0176 (6)	−0.1034 (9)	*a*	C8	0.2446 (5)	0.0162 (6)	−0.1404 (9)	*a*
C9	0.2531 (5)	0.1136 (7)	−0.2650 (9)	*a*	C10	0.1619 (5)	0.1751 (6)	−0.3040 (8)	*a*
H1	0.4203 (47)	0.1394 (62)	−0.0067 (82)	1.5 (14)	H2	0.3658 (50)	0.0995 (64)	0.2696 (86)	1.8 (15)
H3	0.2886 (53)	0.2949 (64)	0.3574 (94)	2.3 (15)	H4	0.3026 (47)	0.4592 (66)	0.1343 (82)	1.9 (14)
H5	0.3810 (53)	0.3495 (67)	−0.0904 (91)	2.1 (16)	H6	0.0420 (47)	0.1396 (59)	−0.1982 (80)	1.0 (14)
H7	0.1291 (47)	−0.0316 (58)	−0.0234 (81)	1.2 (13)	H8	0.2931 (56)	−0.0313 (74)	−0.0999 (97)	3.2 (18)
H9	0.3088 (45)	0.1293 (56)	−0.2993 (75)	0.8 (12)	H10	0.1450 (49)	0.2361 (62)	−0.3754 (85)	1.6 (14)

[a] Anisotropic thermal parameters are published as supplementary data.

formed from 0.2 g of $Cp_2W(S_2O_3)$ dissolved in 2 mL of HCl yielded 0.217 g of a green precipitate of a PF_6^- salt. Elemental analysis of a sample recrystallized from CH_3NO_2–ether indicated the composition $[Cp_2WS(Cl)][PF_6]$. Anal. Calcd: C, 22.8; H, 1.9; S, 6.1; Cl, 6.7; W, 34.9; P, 5.9; F, 21.6. Found: C, 22.9; H, 2.1; S, 6.3; Cl, 6.6; W, 35.3; P, 5.9; F, 20.6. Conductivity of a 4.2×10^{-4} M solution in CH_3NO_2 at 22 °C: 42.1 μmho (cf. 40.7 μmho for a similar solution of $[Bu_4N]I$). The IR peak at 300 cm^{-1} was still present, evidence for a W–Cl bond.

X-ray Measurements, Solution, and Refinements. Crystals of $Cp_2Mo(S_2O_3)$ were obtained by SO_2 addition to Me_2SO solutions of Cp_2MoH_2. Pertinent information concerning the cell, crystal morphology, and intensity measurements is given in Table I. Two standard reflections measured after every 50 reflections varied by ca. 20% over the period of the data collection process. Correction curves for this decrease were estimated by least-squares refinement of a polynomial to the standards and applied to the data. The variance for $\overline{F^2}$ (denotes the average of $\overline{F^2}$ over equivalent reflections) was computed from $\sigma^2(\overline{F^2}) = \sigma_c^2(\overline{F^2}) + \sigma_N^2(\overline{F^2})^2$ where σ_c^2 is the variance due to counting statistics and σ_N is taken to be 0.015.

Data were collected at room temperature, and the structure was solved by standard Patterson and Fourier techniques. The function minimized in the least-squares refinements was $\sum w(|F_o| - |F_c^*|)^2$, where $w = 4F_o^2/\sigma(\overline{F^2})^2$ and F^* includes a correction for secondary extinction.[7] All atoms heavier than hydrogen were located and refined by using neutral-atom scattering factors and appropriate anomalous scattering terms[8] to an R value of 12% with isotropic temperature factors. Difference maps revealed severe disorder of the cyclopentadienyl rings; residual electron density of 2–3 e/Å^3 appeared in the region of C–C bonds. Accordingly, a data set was taken at −95 °C, and the atom coordinates from the room-temperature refinements were used as starting values for the refinement of the low-temperature structure. Hydrogen atom positions were located from the difference maps and were refined with isotropic thermal parameters. Final refinements with anisotropic thermal parameters for all atoms heavier than hydrogen converged to an R value of 2.3%. Final difference maps indicated no further problems with the refinement of the low-temperature data. Final parameters are given in Table II. Table III contains selected distances and angles.

Results and Discussion

Preparation and Properties of $Cp_2M(S_2O_3)$ and $[Cp_2M(S)(X)]^+$ Complexes. The following reaction has been found to readily occur:

$$Cp_2MH_2 + 2SO_2 \xrightarrow{\text{toluene}} Cp_2M(S_2O_3) + H_2O$$
$$M = Mo, W$$

Table III. Selected Distances and Angles

Inner Coordination Sphere Distances (Å)

Mo–O1	2.134 (4)	Mo–C5	2.313 (6)
Mo–S2	2.450 (2)	Mo–C6	2.269 (6)
Mo–C1	2.267 (6)	Mo–C7	2.325 (6)
Mo–C2	2.278 (6)	Mo–C8	2.341 (6)
Mo–C3	2.341 (6)	Mo–C9	2.335 (6)
Mo–C4	2.380 (6)	Mo–C10	2.312 (6)

Thiosulfate Distances (Å)

	$Cp_2Mo(S_2O_3)$	$Ni(tu)_4S_2O_3\cdot H_2O$[13]	$Na_2S_2O_3\cdot 5H_2O$[14]
S1–S2	2.051 (2)	2.01 (1)	2.024 (4)
S1–O1	1.536 (4)	1.50 (1)	1.459 (3)
S1–O2	1.447 (4)	1.46 (1)	1.461 (3)
S1–O3	1.449 (4)	1.43 (1)	1.481 (3)
S1–Mo	2.982 (2)		

Angles (deg)

	$Cp_2Mo(S_2O_3)$	$Ni(tu)_4S_2O_3\cdot H_2O$	$Na_2S_2O_3\cdot 5H_2O$
S2–Mo–O1	72.3 (1)		
Mo–O1–S1	107.6 (2)		
Mo–S2–S1	82.5 (1)		
S2–S1–O1	97.4 (2)	104.8 (0.4)	108.5 (2)
S2–S1–O3	111.3 (2)	110.6 (5)	108.9 (2)
O1–S1–O2	110.2 (2)	110.4 (7)	111.4 (2)
O2–S1–O3	114.4 (3)	111.6 (7)	111.2 (2)
S2–S1–O2	111.9 (2)	108.6 (5)	107.0 (2)
O1–S1–O3	110.4 (2)	110.7 (6)	109.7 (2)

Immediately upon addition of excess SO_2, a brown air-stable precipitate of $Cp_2M(S_2O_3)$ formed in nearly quantitative yield (e.g. 98% for M = W), and water was identified to be a coproduct. The reaction is relatively rapid even below room temperature, although at −78 °C interaction of 1:1 amounts of SO_2 and Cp_2WH_2 in toluene initially gave a red precipitate. The latter was thermally unstable and gradually decomposed on warming to room temperature, eventually yielding $Cp_2W(S_2O_3)$, H_2O, Cp_2WH_2, and several uncharacterized Cp-containing species. Attempts to isolate the incipient species were unsuccessful.

Spectral data for $Cp_2M(S_2O_3)$ were recorded, and the IR frequencies of the Mo complex (ν(SO) = 1247, 1137, 1128, and 652 cm^{-1}) were in agreement with those for a known complex of this stoichiometry prepared by metathesis of Cp_2MoCl_2 and $Na_2S_2O_3$.[9] It is quite likely that the complexes possess identical structures as well. Infrared frequencies due to ν(SO) were located for $Cp_2W(S_2O_3)$ at positions (1262, 1128, and 656 cm^{-1}) similar to those of the Mo analogue.

Proton NMR spectra of $Cp_2M(S_2O_3)$ in Me_2SO-d_6 displayed a single sharp peak due to the Cp protons at τ 4.32 for

---

(4) (a) deMeulenaer, J.; Tompa, H. *Acta Crystallogr.* **1964**, *19*, 1014. (b) Templeton, L. K.; Templeton, D. H. American Crystallographic Association, Summer Meeting, Storrs, CT, June 1973, Abstract No. E10.

(5) Lenhert, P. G. *J. Appl. Crystallogr.* **1975**, *8*, 568.

(6) Strouse, C. E. *Rev. Sci. Instrum.* **1976**, *47*, 871.

(7) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558. Larson, A. C. *Acta Crystallogr.* **1969**, *23*, 664.

(8) Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A. D. T. Cromer *Ibid.*, Table 2.3.1.

(9) Green, M. L. H.; Lynch, A. H.; Swanwick, M. G. *J. Chem. Soc., Dalton Trans.* **1972**, 1445.

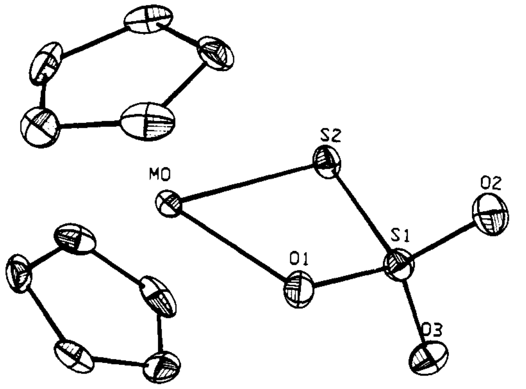

Figure 1. ORTEP projection of $Cp_2Mo(S_2O_3)$.

M = Mo and τ 4.36 for M = W, indicating equivalence of the Cp groups.

The complexes $Cp_2M(S_2O_3)$ were found to decompose in acid much like ionic thiosulfates. The reaction of $Cp_2W(S_2O_3)$ with aqueous concentrated HBr yielded SO_2, H_2O, and metal-coordinated sulfur instead of free sulfur as for ionic $S_2O_3^{2-}$ decomposition. The reaction immediately gave an intensely green solution, followed by slow precipitation of a dark green sulfur complex of apparent stoichiometry Cp_2WSBr_2. This species as well as the chloro analogue reacted with NH_4PF_6 to form PF_6^- salts $[Cp_2W(S)(X)]PF_6$, as indicated by elemental analysis and conductivity measurements (X = Cl). The reaction of $Cp_2M(S_2O_3)$ with acids containing noncoordinating anions (e.g. HPF_6) did not yield these types of complexes. This fact, plus the observation of IR bands characteristic of metal–chloride stretches, strongly argues for the formulation of metal–halide bonding in these complexes. A single sharp proton NMR resonance at 6.46 ppm for CD_3NO_2 solutions indicated that $[Cp_2W(S)(Cl)]PF_6$ is diamagnetic. The complex possesses reversible redox properties, since reaction with strong oxidants such as $NOSbF_6$ in CH_3NO_2 produce a violet color, reverting back to green upon $NaBH_4$ reduction. Cyclic voltammetry confirmed this, since two closely spaced reversible waves were observed at –0.11 and +0.09 V in CH_3NO_2 (0.1 M $[Bu_4N][SbF_6]$ supporting electrolyte; 200 mV/s scan rate; SCE reference).

The fact that the compound can be oxidized suggests that it is an S_2^{2-}-bridged dimer, since if S^{2-} were present, the metal would already be in its highest oxidation state (+6). In any event, the complex appears to be unprecedented.

Structure of $Cp_2Mo(S_2O_3)$. An ORTEP projection of $Cp_2Mo(S_2O_3)$ is given in Figure 1. The structure exhibits an approximately staggered conformation for the two Cp rings. Maximum deviation of the Cp carbon atoms for their least-squares planes is 0.01 Å; the angle between the plane normals is 133.2°. The relationship between the tipping angle of the Cp rings and the LML′ angle has been extensively reviewed for Cp_2MLL' complexes by Prout, Cameron, et al.,[10] who suggest that the equilibrium conformation of the molecular structures is determined by repulsions (a) between the ligands L and L′, (b) between the ligands L and the cyclopentadienyl rings, and (c) between the hydrogen atoms of the Cp rings. It is suggested that smaller L ligands, lead to smaller L–M–L′ angles, larger ring-normal angles, and shorter distances between the metal atom and the Cp plane.

In the present structure the L–Mo–L′ angle is, by virtue of the constraint imposed by the bite angle of the thiosulfate ion, the smallest (except for $[Cp_2Mo(OH)(NH_2CH_3)]PF_6$[10]) observed for a complex of this general type, and this complex should exhibit an angle between the Cp normals that is among the largest of these. This is not the case; the angle between the ring normals falls midway between the extremes established by Cp_2MoD_2[11] (148°) and Cp_2ZrI_2 (126°).[12]

Although many structural investigations of the thiosulfate ion have been carried out, including neutron diffraction investigations, structural studies for which the ion is coordinated to a metal center in a bidentate fashion are sparse. To our knowledge the only previous example of bidentate (O, S) bonding is the structure of $Ni(tu)_4S_2O_3{\cdot}H_2O$ (tu = thiourea).[13] The distances and angles of the thiosulfate ion in the present structure are compared (Table III) with those for $Ni(tu)_4S_2O_3{\cdot}H_2O$ and $Na_2S_2O_3{\cdot}5H_2O$, the latter being the results from a recent neutron diffraction investigation.[14] Obviously one would expect significant distortion of the thiosulfate ion upon coordination to a metal center although this is not evident in the $Ni(tu)_4S_2O_3{\cdot}H_2O$ structure. The magnitude of these distortions is evident from inspection of Table III. One should notice that the S2–S1–O1 angle is significantly smaller and the O2–S1–O3 angle is larger than in either $Na_2S_2O_3{\cdot}5H_2O$ (for which the thiosulfate ion is perturbed only by hydrogen bonding) or $Ni(tu)_4S_2O_3{\cdot}H_2O$. Also, significant lengthening of the S2–S1 and O1–S1 bonds and shortening of the O2–S1 and O3–S1 bonds are evident. The Mo–S1–S2–O1 moiety is essentially planar; the dihedral angle about the O1–S2 vector is 4.7°, compared to 2.2° for $Ni(tu)_4S_2O_3{\cdot}H_2O$.

The nature of the thermally unstable intermediate observed at –78 °C is worthy of speculation. Since Cp_2MoH_2 is known[15] to form an adduct with BF_3, it would not be unreasonable to suggest the same possibility for SO_2. Also, in light of our recent isolation of the complex $CpMo(CO)_3(SO_2H)$[16] from the reaction of $CpMo(CO)_3H$ with SO_2, it is possible that the intermediate is an insertion product. Since the identification of the intermediate would no doubt make a valuable comment on the mechanism of SO_2 reduction by metal hydrides, further attempts to isolate it are under way.

Acknowledgment. This work was performed under the auspices of the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Science.

Registry No. $Cp_2Mo(S_2O_3)$, 37298-37-6; $Cp_2W(S_2O_3)$, 91670-54-1; Cp_2WSBr_2, 91670-55-2; $[Cp_2WS(Cl)][PF_6]$, 91670-57-4; Cp_2MoH_2, 1291-40-3; Cp_2WH_2, 1271-33-6; SO_2, 7446-09-5.

Supplementary Material Available: Listings of observed and calculated structure factors and anisotropic thermal parameters (8 pages). Ordering information is given on any current masthead page.

---

(10) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2290.

(11) Schultz, A. J.; Stearly, K. L.; Williams, J. M.; Mink, R.; Stucky, G. D. *Inorg. Chem.* **1977**, *16*, 3303.

(12) Bush, M. A.; Sim, G. A. *J. Chem. Soc. A* **1971**, 2225.

(13) Gasparri, G. F.; Mangia, A.; Musatti, A.; Nardelli, M. *Acta Crystallogr., Sect. B* **1969**, *B25*, 203.

(14) (a) Lisensky, G. C.; Levy, H. A. *Acta Crystallogr., Sect. B* **1978**, *B34*, 1975. (b) Uraz, A. A.; Ormagan, N. *Acta Crystallogr., Sect. B* **1977**, *B33*, 1396.

(15) Johnson, M. J.; Shriver, D. F. *J. Am. Chem. Soc.* **1966**, *88*, 301.

(16) Kubas, G. J.; Ryan, R. R.; Wasserman, H. J., manuscript in preparation.