Inorg. Chem. **1981**, *20*, 3577–3579 **3577**

Contribution from the Department of Chemistry,
Tulane University, New Orleans, Louisiana 70118,
and Crystalytics Company, Lincoln, Nebraska 68501

Crystal and Molecular Structure of Dicarbonyl(η^5-cyclopentadienyl)(formato)iron(II)

Donald J. Darensbourg,*[1a] Cynthia S. Day,[1b]
and Mark B. Fischer[1a]

Received March 19, 1981

Recently we have become interested in the chemistry of organometallic derivatives containing the formate ligand bonded in a monodentate fashion.[2,3] The impetus for this concern arises from the potential occurrence of these type complexes as reaction intermediates in catalysis of the water–gas shift reaction by metal carbonyls in alkaline solution. This suggestion is possible in view of the known ability of both monodentate and bidentate metalloformates to undergo decarboxylation to metal hydrides and carbon dioxide.[4,5] For example, the title compound has been shown to proceed smoothly according to reaction 1 in hydrocarbon solvents.[2a]

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2O_2CH \xrightarrow{\Delta} (\eta^5\text{-}C_5H_5)Fe(CO)_2H + CO_2 \rightarrow {}^1/_2[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 + {}^1/_2H_2 \quad (1)$$

We report here details of the structure analysis of (η^5-C_5H_5)Fe(CO)$_2$(O_2CH), a preliminary account of which has been given elsewhere.[2a]

Experimental Section

Synthesis of (η^5-C_5H_5)Fe(CO)$_2O_2$CH. The synthesis of (η^5-C_5H_5)Fe(CO)$_2O_2$CH is a modified version of that previously reported by Dombek and Angelici.[6] [(η^5-C_5H_5)Fe(CO)$_2$(THF)][BF_4][7] (2.8 g, 0.010 mol) was placed in a 100-mL round-bottom flask under nitrogen. A solution of 13.7 g (0.186 mol) of NaO_2CH in 34 mL of deionized water was syringed into the flask, and the mixture was stirred for 2.5 h at ambient temperature. The H_2O was then removed under vacuum, and the resulting residue was extracted twice with 50-mL portions of CH_2Cl_2. After filtration of the combined extracts under nitrogen, the volume was reduced to approximately 2 mL, and 45 mL of hexane was added. The solution was cooled to −10 °C to afford the red-brown product which was collected by filtration and vacuum dried. The infrared spectrum in the ν(CO) region displayed two bands at 2055 and 2016 cm^{-1} and at 2058 and 2012 cm^{-1} in hexane and chloroform, respectively. Single crystals suitable for X-ray analysis were grown for CH_2Cl_2/hexane.

Table I. Atomic Coordinates in Crystalline (η^5-C_5H_5)(O_2CH)Fe(CO)$_2$[a]

atom type[b]	fractional coordinates x	y	z
Fe	0.02763 (5)	0.17145 (3)	0.24063 (3)
O1	−0.14616 (36)	0.15620 (19)	0.46414 (22)
O2	−0.35378 (31)	0.11044 (21)	0.04109 (23)
O3	−0.00263 (28)	0.32766 (14)	0.20722 (20)
O4	−0.28086 (31)	0.35397 (17)	0.27672 (27)
C1	−0.08278 (38)	0.16853 (22)	0.37586 (25)
C2	−0.20837 (39)	0.13767 (21)	0.11877 (26)
C3	−0.14480 (41)	0.38406 (22)	0.23221 (31)
Cp1	0.33440 (38)	0.19153 (23)	0.23278 (31)
Cp2	0.33394 (42)	0.14670 (28)	0.35649 (30)
Cp3	0.22466 (46)	0.04688 (26)	0.32936 (34)
Cp4	0.15962 (43)	0.03198 (23)	0.19102 (33)
Cp5	0.22688 (40)	0.12244 (24)	0.13020 (29)

atom type[b]	fractional coordinates x	y	z	B_{iso},[c] Å^2
H3	−0.12691 (492)	0.46489 (277)	0.21302 (327)	4.74 (72)
Hp1	0.39319 (504)	0.25881 (269)	0.22215 (324)	4.29 (70)
Hp2	0.39592 (493)	0.17657 (261)	0.44240 (346)	4.52 (72)
Hp3	0.19263 (542)	0.00077 (314)	0.39275 (370)	5.76 (86)
Hp4	0.07175 (504)	−0.02847 (297)	0.14531 (341)	5.37 (82)
Hp5	0.20140 (481)	0.13101 (271)	0.03890 (340)	4.43 (72)

[a] The figures in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 2. [c] Isotropic thermal parameter.

Crystallographic Studies. A spherical-shaped orange-red crystal, 0.44 mm in diameter, was glued to the inside of a thin glass capillary under nitrogen. This crystal was then accurately centered optically on a computer-controlled four-circle Nicolet autodiffractometer, and a total of 15 high-angle ($2\theta_{Mo\ K\bar{\alpha}} > 25°$) reflections were used to align the crystal and calculate angular settings for each reflection. A least-squares refinement of the diffraction geometry for these 15 reflections recorded at ambient laboratory temperature of 20 ± 1 °C with graphite-monochromated Mo K$\bar{\alpha}$ radiation (λ = 0.71073 Å) showed the crystal to belong to the monoclinic system with lattice constants a = 6.799 (2) Å, b = 12.325 (4) Å, c = 10.440 (3) Å, and β = 106.84 (2)°. Systematic absences indicated the space group to be $P2_1/n$ (a special setting of $P2_1/c$—C_{2h}^5 (No. 14)).[8] A unit cell of four (C_5H_5)Fe(CO)$_2O_2$CH molecules per 837.3 (5) Å^3 afforded a calculated density of 1.76 g cm^{-3}. The linear absorption coefficient of the crystal for Mo K$\bar{\alpha}$ radiation is 1.82 mm^{-1}.[9a]

Intensity measurements utilized graphite-monochromated Mo K$\bar{\alpha}$ radiation and the ω scanning technique with a 4° takeoff angle and a normal-focus X-ray tube. A total of 2480 independent reflections having $2\theta \leq 60.4°$ were measured in three shells. A scanning rate of 4°/min was employed for the scan between settings 0.50° respectively above and below the calculated K$\bar{\alpha}$ doublet value for those reflections having $3.0° < 2\theta_{Mo\ K\bar{\alpha}} \leq 43.0°$, and a scanning rate of 3°/min was used for reflections having $43° < 2\theta_{Mo\ K\bar{\alpha}} \leq 60.4°$. Each of these 1.0° scans was divided into 19 equal time intervals, and those 13 contiguous intervals which had the highest single accumulated count at their midpoint were used to calculate the net intensity for scanning. Background counts, each lasting for half the total time used for the net scan, were measured at ω settings 1° above and below the calculated value for each reflection as a monitor for possible disalignment and/or deterioration of the crystal, gave no indication of either. The intensities were reduced without absorption corrections to relative squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections.

Of the 2480 reflections examined, 698 were eventually rejected as unobserved by applying the rejection criterion, $I < 3.0\sigma(I)$, and $\sigma(I)$ is the standard deviation in the intensity computed from $\sigma^2(I) = (C_t + k^2B)$ where C_t is the total scan count, k is the ratio of scan time to background time, and B is the total background count.

The iron atom was located from a Patterson synthesis; the remaining nonhydrogen atoms appeared in a single difference Fourier synthesis based on refined parameters for the Fe atom (R_1 = 0.370 for 834 independent reflections having $2\theta_{Mo\ K\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$). Isotropic unit-weighted full-matrix least-squares refinement for the 13 nonhydrogen atoms gave R_1 (unweighted, based on F) = 0.067 and R_2 (weighted) = 0.067 (eq 2), where anisotropic refinement converged

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$$
$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2} \quad (2)$$

to R_1 = 0.036 and R_2 = 0.042 for 834 reflections having $2\theta_{Mo\ K\bar{\alpha}}$ <

---

(1) (a) Tulane University. (b) Crystalytics Co.

(2) (a) Darensbourg, D. J.; Fischer, M. B.; Schmidt, R. E., Jr.; Baldwin, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 1297. (b) Darensbourg, D. J.; Rokicki, A. *ACS Symp. Ser.* **1981**, *No. 152*, 107.

(3) Darensbourg, D. J.; Rokicki, A.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 3223.

(4) See, e.g., the review by: Eisenberg, R.; Hendriksen, D. E. in *Adv. Catal.* **1979**, *28*, 79.

(5) See, e.g., the review by: Kolomnikov, I. S.; Grigoryan, M. Kh. *Russ. Chem. Rev.* (*Engl. Transl.*) **1978**, *47*, 334.

(6) Dombek, D. B.; Angelici, R. J. *Inorg. Chim. Acta* **1973**, *7*, 345.

(7) Reger, D. L.; Coleman, C. *J. Organomet. Chem.* **1977**, *131*, 153.

(8) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I.

(9) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) pp 55–66; (b) pp 149–150; (c) pp 99–101.

0020-1669/81/1320-3577$01.25/0

Table II. Anisotropic Thermal Parameters in Crystalline $(\eta^5\text{-}C_5H_5)(O_2CH)Fe(CO)_2$[a]

atom type[b]	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	2.17 (1)	2.26 (1)	2.70 (1)	−0.08 (1)	1.04 (1)	0.03 (1)
O1	5.54 (11)	5.71 (12)	4.26 (9)	−0.18 (9)	2.98 (9)	0.35 (9)
O2	3.16 (8)	6.31 (13)	4.58 (10)	−0.53 (8)	0.22 (7)	−0.71 (9)
O3	4.09 (8)	2.41 (6)	5.15 (9)	0.13 (6)	2.54 (7)	0.38 (7)
O4	3.14 (8)	3.86 (10)	8.02 (15)	0.20 (7)	2.27 (9)	−0.30 (9)
C1	3.20 (9)	3.11 (9)	3.22 (10)	−0.13 (8)	1.21 (8)	0.08 (8)
C2	2.92 (9)	3.43 (10)	3.27 (10)	0.18 (8)	1.36 (8)	0.08 (8)
C3	3.37 (11)	2.57 (10)	4.58 (13)	0.17 (8)	0.97 (10)	0.03 (9)
Cp1	2.34 (8)	3.68 (12)	4.93 (13)	−0.35 (8)	1.66 (9)	−0.34 (10)
Cp2	2.71 (10)	5.58 (16)	3.52 (12)	0.67 (10)	0.44 (9)	−0.39 (11)
Cp3	3.75 (12)	4.20 (13)	4.91 (15)	1.58 (10)	1.78 (11)	1.65 (11)
Cp4	3.30 (11)	2.77 (10)	5.59 (15)	0.37 (8)	1.74 (10)	−0.68 (10)
Cp5	2.87 (10)	4.15 (12)	3.62 (11)	0.28 (9)	1.53 (9)	−0.32 (9)

[a] The numbers in parentheses following each B_{ij} value are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 2.

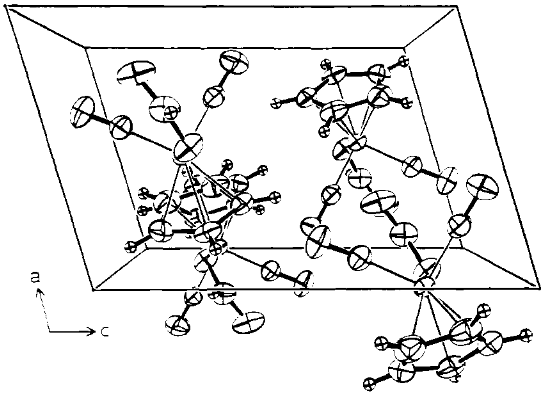

Figure 1. View of the monoclinic unit cell of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(O_2CH)$.

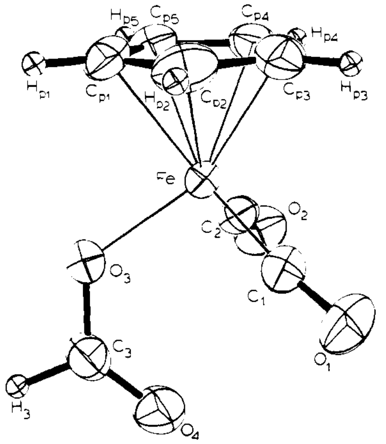

Figure 2. A perspective ORTEP drawing of the $(C_5H_5)Fe(CO)_2(O_2CH)$ molecule. All nonhydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density. Hydrogen atoms are represented by arbitrarily small spheres which are in no way representative of their true thermal motion.

Table III. Bond Distances (Å) in $(\eta^5\text{-}C_5H_5)Fe(CO)_2O_2CH$[a]

atom 1	atom 2	dist[b]	atom 1	atom 2	dist[b]
Fe	O3	1.957 (2)	Cp1	Cp2	1.406 (4)
			Cp1	Cp5	1.397 (4)
Fe	C1	1.781 (3)	Cp2	Cp3	1.423 (5)
Fe	C2	1.784 (3)	Cp3	Cp4	1.395 (5)
			Cp4	Cp5	1.423 (4)
Fe	Cp1	2.125 (3)			
Fe	Cp2	2.106 (3)	C3	H3	1.03 (3)
Fe	Cp3	2.071 (3)			
Fe	Cp4	2.073 (3)	Cp1	Hp1	0.94 (3)
Fe	Cp5	2.106 (3)	Cp2	Hp2	0.95 (3)
			Cp3	Hp3	0.94 (4)
O1	C1	1.135 (3)	Cp4	Hp4	0.99 (4)
O2	C2	1.133 (4)	Cp5	Hp5	0.92 (3)
O3	C3	1.277 (3)			
O4	C3	1.208 (4)			

[a] The atoms are labeled in agreement with Figure 2. [b] The figures in parentheses are the estimated standard deviations in the last significant digit.

43° and $I > 3\sigma(I)$.[10] These and all subsequent structure factor calculations employed the atomic form factors compiled by Cromer and Mann[11] and an anomalous dispersion correction to the scattering factor of the iron atom.[9b]

A different Fourier synthesis based on this fully refined anisotropic model contained peaks which corresponded to chemically anticipated positions of the six hydrogen atoms. Further unit-weighted least-squares refinement, which employed isotropic thermal parameters for hydrogen atoms but was otherwise anisotropic, gave $R_1 = 0.022$ and $R_2 = 0.023$ for 834 reflections. An additional cycle of unit-weighted full-matrix least-squares refinement with those reflections having $2\theta_{Mo\,K\alpha} < 60.4°$ resulted in $R_1 = 0.029$ and $R_2 = 0.030$ for 1782 reflections having $I > 3\sigma(I)$.

The final cycle of empirically weighted[12,13] least-squares refinement which employed isotropic thermal parameters for hydrogen atoms and anisotropic thermal parameters for all others converged to $R_1 = 0.029$, $R_2 = 0.034$, and GOF = 1.31[14] for 1782 reflections. During the final cycle of refinement, no parameter (including those of the hydrogen atoms) shifted by more than $0.14\sigma_p$ with the average shift being less than $0.01\sigma_p$ where σ_p is the estimated standard deviation of the parameter. A final difference Fourier synthesis revealed no peaks present above the noise level (0.25 e/Å³).

All calculations were performed on a Data General Eclipse S-200 computer with 64K of 16-bit words, a parallel floating-point processor for 32- and 64-bit arithmetic, and a Data General disk with 10 million 16-bit words using versions of the Nicolet (Syntex) E-XTL or SHELXTL interactive crystallographic software package as modified at Crystalytics Company.

Results and Discussion

The crystal structure of $(\eta^5\text{-}C_5H_5)Fe(CO)_2O_2CH$ consists of a discrete racemic mixture of molecules arranged in the monoclinic unit cell as illustrated in Figure 1. There are no unusually short intermolecular contacts in this structure. The shortest contact (2.42 (4) Å) involves atoms O4 and Hp1 for which the sum of the van der Waals radii is 2.60 Å.[15] The

---

(10) The anisotropic thermal parameter is of the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

(11) Cromer, D. T.; Mann, J. L. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.

(12) The weighting scheme used in the least-squares minimization of the function $\sum w(|F_o| - |F_c|)^2$ is defined as $w = 1/\sigma_F^2$.

(13) For empirical weights $\sigma_F = \sum_0^3 a_n|F_o|^n = a_0 + a_1|F_o| + a_2|F_o|^2 + a_3|F_o|^3$, with the a_n being coefficients from the least-squares fitting of the curve $||F_o| - |F_c|| = \sum_0^3 a_n|F_o|^n$. In this case, $a_0 = 0.49$, $a_1 = -6.7 \times 10^{-3}$, $a_2 = 2.52 \times 10^{-4}$, and $a_3 = -6.07 \times 10^{-7}$.

(14) GOF = $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ where NO is the number of observations and NV is the number of variables.

Table IV. Bond Angles (Deg) for (η^5-C_5H_5)Fe(CO)$_2$O$_2$CH)[a]

atom 1	atom 2	atom 3	angle[b]
O3	Fe	C1	96.6 (1)
O3	Fe	C2	94.4 (1)
O3	Fe	Cp1	86.1 (1)
O3	Fe	Cp2	106.3 (1)
O3	Fe	Cp3	146.1 (1)
O3	Fe	Cp4	143.3 (1)
O3	Fe	Cp5	103.6 (1)
C1	Fe	C2	93.6 (1)
Cp1	Fe	Cp2	38.8 (1)
Cp1	Fe	Cp5	38.6 (1)
Cp2	Fe	Cp3	39.8 (1)
Cp3	Fe	Cp4	39.3 (1)
Cp4	Fe	Cp5	39.8 (1)
Cp1	Fe	Cp3	65.7 (1)
Cp2	Fe	Cp4	66.2 (1)
Cp3	Fe	Cp5	66.2 (1)
Cp4	Fe	Cp1	65.6 (1)
Cp5	Fe	Cp2	65.6 (1)
Fe	O3	C3	123.1 (2)
Fe	C1	O1	173.1 (3)
Fe	C2	O2	176.1 (3)
O3	C3	O4	128.4 (3)
O3	C3	H3	110 (2)
O4	C3	H3	121 (2)
Cp5	Cp1	Cp2	109.0 (3)
Cp2	Cp1	Hp1	125 (2)
Cp5	Cp1	Hp1	126 (2)
Cp1	Cp2	Cp3	107.3 (3)
Cp1	Cp2	Hp2	127 (2)
Cp3	Cp2	Hp2	126 (2)
Cp2	Cp3	Cp4	108.1 (3)
Cp2	Cp3	Hp3	126 (2)
Cp4	Cp3	Hp3	125 (2)
Cp3	Cp4	Cp5	108.2 (3)
Cp3	Cp4	Hp4	124 (2)
Cp5	Cp4	Hp4	127 (2)
Cp4	Cp5	Cp1	107.5 (3)
Cp4	Cp5	Hp5	124 (2)
Cp1	Cp5	Hp5	128 (2)

[a] The atoms are labeled in agreement with Figure 2. [b] The figures in parentheses are the estimated standard deviation in the last significant digit.

final atomic coordinates and thermal parameters are collected in Tables I and II. Figure 2 presents a perspective view of the structure and defines the atomic numbering scheme employed. Interatomic distances and angles are provided in Tables III and IV.

It is clear from Figure 2 that the complex contains a monodentate formate ligand which is oriented such as to place its uncoordinated oxygen atom in the direction of the carbonyl ligands and 3.172 Å away from the iron center. This distal oxygen of the formate ligand to iron distance is considerably longer than the sum of their van der Waals radii (2.67 Å).[15] On the other hand, the formate's distal oxygen is tilted toward C1, having a nonbonding distance of 2.702 (3) Å (van der Waals contact = 3.00 Å) as compared with the distance to C2 to 3.246 (3) Å. This observation is suggestive of a nonbonding interaction analogous to intermolecular nucleophilic addition to a carbonyl carbon atom. The formate carbon-oxygen bond distances are consistent with the conventional description for the M—OC(O)H linkage, i.e., (Fe)O—C and C═O. The average Fe—C and C—O bond lengths in the metal carbonyl fragment are 1.783 (3) and 1.134 (4) Å, respectively. The cyclopentadienyl ring, inclusive of hydrogen atoms, is fairly planar (see Table V) with the Fe–C bond distances displaying only slight variations (range 2.071 (3)–2.125 (3) Å) with an average value of 2.096 (3) Å. Bonding parameters within the cyclopentadienyl ring are normal.

Table V. Best Least-Squares Plane for the Cyclopentadienyl Group[a]

atom	dev from plane, Å	atom	dev from plane, Å
Cp1	−0.0032	Hp1	0.0237
Cp2	0.0019	Hp2	−0.0028
Cp3	0.0001	Hp3	0.0544
Cp4	−0.0020	Hp4	0.0623
Cp5	0.0032	Hp5	0.0074

[a] Defined by $-0.8749X + 0.4820Y + -0.0475Z = -0.3427$, where X, Y, and Z are orthogonal coordinates measured along $\vec{a}$, $\vec{b}$, and $\vec{c}^*$ of the unit cell, respectively.

Acknowledgment. The financial support of this research at Tulane University by the National Science Foundation (Grant CHE 80-09233) is greatly appreciated.

Registry No. (η^5-C_5H_5)Fe(CO)$_2$O$_2$CH, 42870-99-5; [(η^5-C_5H_5)Fe(CO)$_2$(THF)][BF$_4$], 63313-71-3.

Supplementary Material Available: A listing of the observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

---

[15] Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

Contribution from the Department of Chemistry,
The University of Utah, Salt Lake City, Utah 84112

Deprotonation of Pentaborane(9) with Solid Potassium Hydroxide

Mansel A. Nelson and Goji Kodama*

Received April 21, 1981

Since the preparation of octahydropentaborate(1−) was reported by Gaines[1] and by Shore[2] in 1967, the anion has been used for the syntheses of various B_5H_8 derivatives.[3] Furthermore, a variety of novel metallaborane and metallacarborane compounds have been prepared by the reactions involving the $B_5H_8^-$ ion.[4] The anion has usually been prepared by deprotonating pentaborane(9) with alkali metal hydrides or alkyls.[1,2]

$$B_5H_9 + MQ \xrightarrow[R_2O]{\text{low temp}} M^+B_5H_8^- + HQ$$

$$MQ = \text{Li alkyls, NaH, KH}$$

Earlier, Jolly employed solid potassium hydroxide to deprotonate extremely weak acids and, at the same time, to dehydrate the reaction mixtures.[5] The task of preparing compounds such as $CH_3Mo(CO)_3C_5H_5$, ferrocene, and methylphosphines has become less laborious by incorporating the KOH method in the procedures of the syntheses. In this note we report the deprotonation of pentaborane(9) with potassium hydroxide powder in tetrahydrofuran. The resulting solution of KB_5H_8 would be of use for various syntheses as the source of the $B_5H_8^-$ anion.

---

(1) Gaines, D. F.; Iorns, T. V. *J. Am. Chem. Soc.* **1967**, *89*, 3375.
(2) Geanangel, R. A.; Shore, S. G. *J. Am. Chem. Soc.* **1967**, *89*, 6771.
(3) (a) Gaines, D. F. in "Boron Chemistry 4"; Parry, R. W., Kodama, G., Eds.; Pergamon Press: Elmsford, NY, and Oxford, 1980; p 73 and references therein; *Acc. Chem. Res.* **1973**, *6*, 416 and references therein. (b) Greenwood, N. N.; Kennedy, J. D.; Staves, J. *J. Chem. Soc., Dalton Trans.* **1978**, 1146 and references therein. (c) Hosmane, N. S.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 2886.
(4) (a) Weiss, R.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 3291. (b) Miller, V. R.; Weiss, R.; Grimes, R. N. *J. Am. Chem. Soc.* **1977**, *99*, 5646.
(5) (a) Jolly, W. L. *Inorg. Synth.* **1968**, *11*, 113. (b) *J. Chem. Educ.* **1967**, *44*, 304.

0020-1669/81/1320-3579$01.25/0 © 1981 American Chemical Society