pyruvate decarboxylase activity (using the standard assay).[18] Using a range of concentrations of **2** (from sample B) from 1 to 53 μM, we find no activity due to its presence, although enzyme-bound **2** is an obligatory intermediate in the catalytic cycle.

Although the apoenzyme does not appear to bind **2**, it is activated by the *tert*-butyl ester of **2** (**3**) and the ethyl ester of **2** (**5**). These results are summarized in Figure 1. Presumably **3** and **5** are converted to the respective pyruvate esters and enzyme-bound TDP.[10] The different TDP derivatives give Lineweaver–Burk plots with different K_m values and $V_{\max}$ values that are identical within experimental error.

Scheme I shows a kinetic mechanism to account for the results in Figure 1. The species "X-TDP" are the active C(2) adducts **3**, **4**, and **5**. Assays of activity are done under conditions where a steady-state concentration of E·TDP has evolved.

Scheme I

$$\text{X—TDP} + \text{E} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{E·X—TDP}$$

$$\text{E·X—TDP} \xrightarrow{k_2} \text{E·TDP} + \text{X}$$

$$\text{E·TDP} \xrightarrow{k_3} \text{E} + \text{TDP}$$

Using steady-state equations for [E·TDP] and [E·X—TDP] and with $k_2 \gg k_3$ (since TDP dissociates very slowly from the holoenzyme), we obtain the Michaelis–Menten expression

$$1/v = (V_{\max}/K_m)(1/s) + 1/V_{\max}$$

where $K_m = k_1k_2/[k_3(k_{-1} + k_2)]$, v is a measure of [E·TDP], and $V_{\max}$ is a measure of $[E_{tot}]$. It is likely that $k_2 \gg k_{-1}$, making $K_m = k_1/k_3$. Since k_3 is independent of X, differences in K_m are due to differences in k_1.

Our observation of an apparent lack of affinity of the apoenzyme for **2** indicates either that the enzyme form which binds **2** during catalysis is not in equilibrium with the apoenzyme to a significant extent or there is a large kinetic barrier to its association with **2**. We find that the rate of association of **2** and apoenzyme must be slower than the rate of the nonenzymic decarboxylation of **2** ($t_{1/2}$ = 5 h,[10] yielding **4** which activates the enzyme) under our conditions.

Physical studies indicate that the TDP binding site of related enzymes is hydrophobic.[19-21] The order of K_m values for **3** and **5** suggests this also applies to wheat germ pyruvate decarboxylase apoenzyme. That is, large alkyl groups on the ester moiety promote association with the apoenzyme.

Lienhard has presented evidence, from model studies,[12] that suggests that the enzymic decarboxylation of **2** should occur most rapidly if its enzyme-binding site is hydrophobic. However, a polar site must be available initially to bind pyruvate and give **2**. This implies that the enzyme must assume at least two forms with different active-site polarities. We have suggested that the formation of **2** on an enzyme should be highly exergonic.[10] The energy that is thus made available could promote isomerization of the enzyme intermediate complex to the catalytically active form (for decarboxylation), placing **2** in a hydrophobic environment. Decarboxylation of enzyme-bound **2** would return the enzyme to another form which then catalyzes the release of acetaldehyde from **4**. This form is what binds **3**, **4**, and **5** and converts them to TDP. Thus, conclusions drawn from studies with **3** and **5** (and from other studies of apoenzymes that bind TDP)[19-21] should apply to the form of the enzyme that binds **4** (not **2**). Our results with **2**, however, suggest that in the normal catalytic cycle the pyruvate adduct is bound to a different, externally inaccessible, high-energy form of the enzyme which promotes decarboxylation of **2**.[22] It remains probable that hydrophobic catalysis is involved, but this has yet to be proven.

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(19) Gutowski, J. A.; Lienhard, G. E. *J. Biol. Chem.* **1976,** *251,* 2863.

(20) Wittorf, J. H.; Gubler, C. J. *Eur. J. Biochem.* **1970,** *14,* 53.

(21) O'Brien, T. A.; Gennis, R. B. *J. Biol. Chem.* **1980,** *255,* 3302.

(22) The possibility of a situation in which a transition state would be bound to a "closed" form of an enzyme had been predicted by Wolfenden (Wolfenden, R. *Mol. Cell. Biochem.* **1974,** *3,* 207).

Isolation of a C,N-Bonded Formamido Complex and Its Isomerization to a C,O-Bonded Form on the Edge of a Triosmium Cluster. Crystal and Molecular Structure of a Urethane Derivative of the C,N-Bonded Formamido Complex

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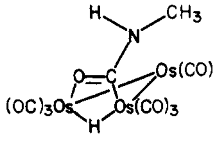
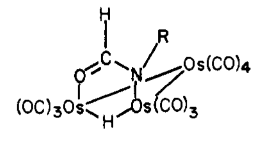
η²-Bonded carbonyl groups either in mononuclear[1] or in polynuclear[2-4] systems are believed to be important in the homologation of carbon monoxide by metal catalysts. We have recently observed formation of a μ-η²-carboxamido complex (**1**) in the treatment of $Os_3(CO)_{12}$ with primary aliphatic amines.[5,6] By contrast, an isomeric O,N-bonded formamido complex (**2a**) has been isolated as the principal product from the reaction of *p*-tolyl isocyanate with $H_2Os_3(CO)_{10}$.[7] We were interested in obtaining the methyl isocyanate complex (**2b**) to determine whether **1** and **2b** were thermally interconvertible and, if so, which would be the more stable.



1



2a, R = *p*-$CH_3C_6H_4$
b, R = Me

The reaction of methyl isocyanate with $H_2Os_3(CO)_{10}$ at room temperature for 40 min in neat isocyanate was carried out under N_2 atmosphere by using Schlenk techniques. Solvent was removed from the mixture under vacuum. Hexane was then added to the dried powder to make a yellow solution which was subjected to column chromatography using a silica gel support. Starting with pure hexane and going in four stages to 80:20 hexane/dichloromethane, four bands were eluted.[8a] The first consists of a trace

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(1) (a) Huffman, J. C.; Stone, J. G.; Krusell, W. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1977,** *99,* 5829. (b) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976,** *98,* 6733.

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(4) (a) Shriver, D. F.; Alich, A., Sr. *Coord. Chem. Rev.* **1972,** *8,* 15. (b) Kristoff, J. S.; Shriver, D. F. *Inorg. Chem.* **1974,** *13,* 499. (c) Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1980,** *102,* 5093.

(5) (a) Kaesz, H. D.; Szostak, R.; Lin, Y. C.; Van Buskirk, G.; Humphries, A. P. "Abstracts of Papers", American Chemical Society/Chemical Society of Japan Chemical Congress, Honolulu, Hawaii, April 1979; American Chemical Society: Washington, DC; INOR 174. (b) A similar O,C-bonded complex was obtained from benzylamine and $Os_3(CO)_{12}$ in refluxing octane: Azam, K. A.; Yin, C. C.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1978,** 1201.

(6) The conventional vector between metal atoms of the double-bridged edge is omitted from our structure representations of trinuclear cluster complexes because we believe this better reflects the octahedral coordination around the metal atoms in question. Bonding interactions between metal atoms of a double-bridged edge are believed to take place through orbitals involving the bridging atoms. See: (a) Mason, R.; Mingos, D. W. P. *J. Organomet. Chem.* **1973,** *50,* 53. (b) Teo, B. K.; Hall, M. B.; Fenske, R. F.; Dahl, L. F. *Ibid.* **1974,** *70,* 413.

(7) Adams, R. D.; Golembeski, N. *J. Organomet. Chem.* **1979,** *171,* C21.

(8) (a) Since some of the products are related by proton shifts (see below), a reviewer asked whether the silica gel used in separation serves as a catalyst for interconversion. ¹H NMR spectrum of the crude reaction mixture demonstrates that the products and their distribution are unaffected by the chromatography. (b) For $t_{1/2}$ measurements the ratio of three different pairs of corresponding resonances in **3a** and **1**, namely, those of the methyl group, the bridging hydrogen atoms, and the OH and NH groups (see ref 15), were measured at the same time; all give consistent results.

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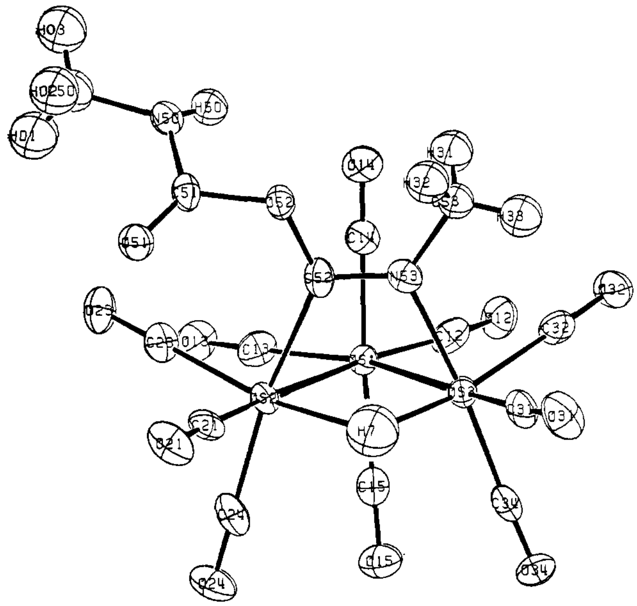
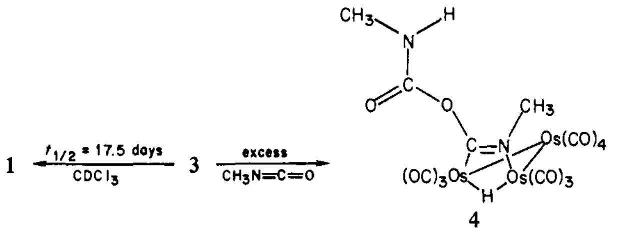


Figure 1. ORTEP projection of **4**, $HOs_3(C(OR){=}NCH_3)(CO)_{10}$, R = $C(O)N(H)CH_3$; thermal ellipsoids at 50% probability.

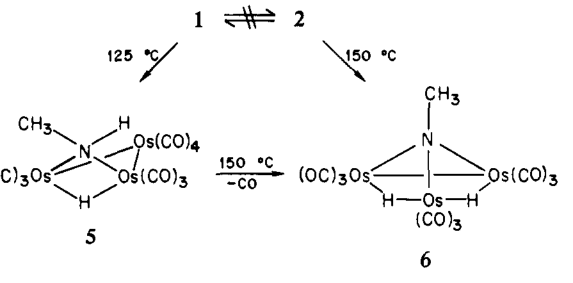
(i.e., less than 3% by weight of starting material); this substance has as yet not been identified. The second band consists of the O,N-bonded complex (**2b**), obtained in 80% yield, analogous to the complex obtained by Adams and Golembeski. The third and fourth bands consist of two new complexes, **3** and **4**, isolated,



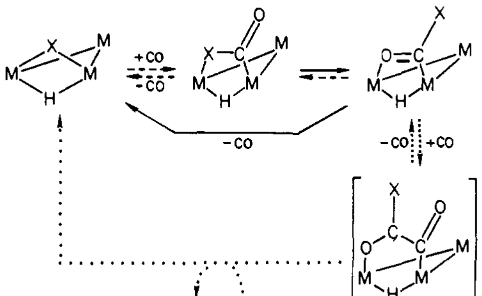
respectively, in yields of 6% and 10% by weight of starting material. Complex **3** proved to be unstable, slowly converting to **1** ($t_{1/2}$ = 17.5 days, $CDCl_3$ solution).[8b] Assignment of its structure follows a discussion of **4**.

For **4** single crystals were obtained and a structure determination was undertaken at −158 °C.[9,10] An ORTEP projection of the molecule is shown in Figure 1. This consists of an isosceles triangle of osmium atoms bridged on the longest edge by an (RO)C=NMe group [R=C(O)-N(H)Me]. This edge is also bridged by a hydrogen atom.[10] The separation C(52)-N(53) is close to that expected for a double bond ($d_{C=N}$ = 1.27 Å)[11] and is similar to that found in other triosmium cluster complexes containing the RC=NR′ group.[12] The urethane group (OR) may be visualized as an adduct of the OH group of an enol tautomer of **3** (**3a**; see discussion below) with excess methyl isocyanate used as solvent.

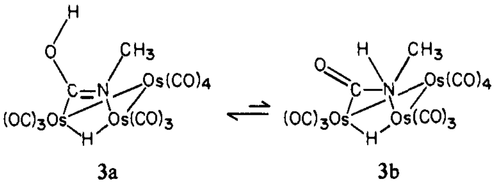
Scheme I



Scheme II



We were not able to obtain single crystals of **3**; however, its structure and the existence of a tautomeric mixture **3a** ⇌ **3b** may



be elucidated from spectroscopic data. Interpretation of these data is assisted by corresponding data from complex **4** whose structure has been determined in this work.

Molecular weight of **3** was determined from the parent ion peak in the mass spectrum.[13] This indicates the presence of ten CO groups from ten individual CO-loss fragments.[14a] The presence of the OH group is indicated by IR [ν_{OH} 3595 cm^{-1} (s), $\nu_{OH\cdots O}$ 3313 cm^{-1} (br)].[14b] An IR absorption is observed at 1617 cm^{-1}, assigned as $\nu_{C=N}$, parallel to one at 1590 cm^{-1} in **4** of the same origin. A peak is also seen for **3** at 1795 cm^{-1} in a hexane solution which diminishes in intensity in C_2Cl_4; we attribute this to $\nu_{C=N}$ of tautomer **3b**, differing in equilibrium concentration in solvents of different polarity. For **4**, $\nu_{C=O}$ of the urethane group is seen at 1776 cm^{-1} (hexane solution); this derivative also displays ν_{NH} at 3465 cm^{-1}. ^1H NMR for **3** confirms the existence of tautomers.[15,16] Relative intensity measurements of the singlet of the

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[9] Strouse, C. E. *Rev. Sci. Instrum.* **1976**, *47*, 871.

[10] Space group $P2_1/c$, a = 13.413 (2), b = 16.712 (3), c = 9.400 (3) Å; β = 95.011 (2)°; Z = 4; ρ = 3.06 g cm^{-3} 3721 reflections were collected at −158 °C of which 2936 reflections [$I > 3\sigma(I)$] were used in the structure solution and refinement. The structure was solved by the heavy atom method and difference Fourier maps. Absorption correction was applied (μ 199.57 cm^{-1}). All calculations were performed on the UCLA Office of Academic Computing's IBM 3033. Refinement converged at R = 0.030 and R_w = 0.037. The crystal consists of discrete molecules. After all but two atoms (methyl carbon) were refined anisotropically, the metal hydride was located; these two methyl carbon atoms were included in the refinement as members of a rigid methyl group. H7 and H50 were located and included in the structure factor calculation but were not refined. Details including tables of positional and thermal parameters and structure factor amplitudes will accompany the full report of this work (to be submitted to *Inorg. Chem.*). Selected bond distances (Å): Os(1)–Os(2) = 2.882 (1), Os(1)–Os(3) = 2.881 (1), Os(2)–Os(3) = 2.923 (1), H(7)–Os(2) = 1.94, H(7)–Os(3) = 1.77, C(52)–N(53) = 1.27(3), C(51)–O(51) = 1.21 (2), C(52)–O(52) = 1.36 (2), C(51)–O(52) = 1.40 (2), Os(2)–C(52) = 2.13 (2), and Os(3)–N(53) = 2.12 (2). Selected bond angles (deg): C(21)–Os(2)–Os(3) = 117, C(31)–Os(3)–Os(2) = 116, C(23)–Os(2)–Os(1) = 90, C(32)–Os(3)–Os(2) = 85, C(23)–Os(3)–H(7) = 169, and C(32)–Os(2)–H(7) = 168.

[11] *Spec. Publ. Chem. Soc.* **1965**, *No. 18.*

[12] Adams, R. D.; Golembeski, N. *Inorg. Chem.* **1978**, *17*, 1969.

[13] Mass spectra were obtained on an AEI MS-9 spectrometer using a direct inlet probe temperature of 90–100 °C and an ionizing voltage of 70 eV.

[14] (a) The carbonyl absorptions in the stretching region of the IR spectra in hexane solution are, respectively (cm^{-1}), **3**: 2107 (m), 2065 (s), 2055 (s), 2024 (s), 2012 (s), 2006 (w, sh), 1992 (s), 1977 (m), and 1953 (vw). **4**: 2107 (m), 2069 (vs), 2056 (s), 2025 (s), 2010 (m, sh), 2003 (m), 1995 (m), 1987 (w, sh), and 1979 (m). For these and infrared absorptions mentioned further down in the text we employed a Nicolet FT-IR, MX-1 instrument. (b) For precedents to these assignments, see: Bellamy, L. J., "Advances in Infrared Group Frequencies"; Chapman and Hall: London, 1975; p 49 ff.

[15] **3a**: ^1H NMR δ 6.57 (br, NH), 3.05 (s, CH_3), and −15.45 (s, Os–H–Os). **3b**: δ 6.32 (br, NH), 2.94 (d, CH_3, J_{H-H} = 4.82 Hz), and −13.99 (s, Os–H–Os). **4**: δ 4.94 (br, NH), 3.11 (s, CH), 2.86 (d, 3 H, J_{H-H} = 5.62 Hz), and −15.20 (s, Os–H–Os).

methyl group in **3a** compared to the doublet of the methyl group in **3b** indicate **3a** is the predominant isomer, approximately 95%, in CDCl$_3$.

Complexes **1** and **2** are not thermally interconvertible in hydrocarbon solution.[17] Complex **1** is stable up to 125 °C, whereupon it is decarbonylated to the edge-bridged amido complex **5**, similar to observations previously noted for the *N*-benzylformamido complex.[5b] Complex **2** is stable up to 150 °C, whereupon it is decarbonylated to the methylnitrene complex, **6** (Scheme I).

The relationship of the transformations observed in this work to a general syngas conversion on polynuclear centers is summarized in Scheme II; transformations observed in this work are represented by solid arrows with X = NHMe. The top portion of Scheme II indicates a possible role for the C,X-bonded species in the decarbonylation of the O,C-bonded species to a μ-X bridged species (analogous to transformation **1** → **5** in Scheme I). The dotted arrows represent possible extension to C$_2$ species based on the greater stability of the three-atom bridging unit (analogous to complex **2**, in Scheme I). These proposals supplement those recently advanced by Wilkinson and co-workers for syngas conversions at binuclear ruthenium centers.[18] Such transformations may occur in systems containing a polynuclear species as a principal component or in other systems[19] where such may exist only as a minor *but very active* constituent.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-79-08406); computing costs were supported in part by an intramural grant from the UCLA Academic Computing Center. We thank Dr. Andreas Mayr for valuable discussions and Professor R. D. Adams for a preliminary copy of the paper cited in ref 17.

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(16) The chemical shift of hydrogen bridging an edge of the metal cluster also bridged by a RC═NR′ group is characteristically found from −14.95 to −15.16 ppm: δ −15.02 in HOs$_3$(μ-PhC═NMe)(CO)$_{10}$. See: (a) Yin, C. C.; Deeming, A. J. *J. Organomet. Chem.* **1977**, *133*, 123. δ −15.15 in HOs$_3$(μ-HC═NMe)(CO)$_{10}$ −15.16 in HOs$_3$(μ-HC═NPh)(CO)$_{10}$, and −14.95 in HOs$_3$(μ-HC═NPh)(CO)$_9$(P(OMe)$_3$). See: (b) Adams, R. D.; Golembeski, N. *J. Am. Chem. Soc.* **1979**, *101*, 2579. This provides additional support for the structure assignment in **3a**.

(17) This observation has also been made independently by R. D. Adams, N. M. Golembeski, and J. P. Selegue (private communication from R. D. Adams). These workers have isolated an O,C-bonded formamido cluster complex as a minor product in the reaction of *p*-tolyl isocyanate with H$_2$-Os$_3$(CO)$_{10}$. They noted also that phosphine substitution in the starting cluster can markedly affect the product distribution in its reaction with isocyanate, an observation which we confirm in our work.

(18) Daroda, R. J., Blackborow, J. R.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1980**, 1101.

(19) Dombek, B. D. *J. Am. Chem. Soc.* **1980**, *102*, 6855.

A New Mo(IV) Thioanion Containing the Mo═S$_t$ Unit. Synthesis and Structural Characterization of (Et$_4$N)$_2$MoS$_9$

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Structural information concerning the Mo-containing site of nitrogenase has become available recently. Analyses of the Mo X-ray absorption fine structure in the Fe–Mo protein component of nitrogenase[1] and the nitrogenase cofactor[1,2] have established the existence of Mo–S coordination and the presence of two or three iron atoms at close proximity (~2.7 Å) to the molybdenum atom.

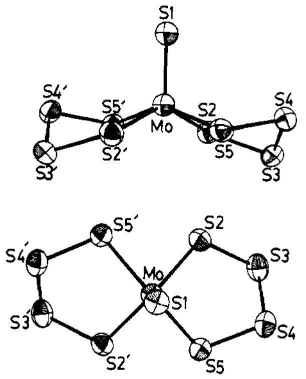

Figure 1. Two views of the MoS$_9^{2-}$ anion. Thermal ellipsoids as drawn by ORTEP (C. K. Johnson, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965) represent the 50% probability surfaces.

This information has stimulated an interest in the synthesis of polynuclear Fe–Mo–S complexes, several of which have been isolated and structurally characterized.[3,4] In our approach toward the synthesis of these polynuclear complexes, we have used effectively the tetrathiomolybdate anion, MoS$_4^{2-}$, as a chelating ligand for iron.[4]

The use of other molybdenum sulfur complexes as "reagents" for the synthesis of polynuclear aggregates containing Mo–S coordination is hindered by the limited availability of binary Mo–S complexes. With the exception of MoS$_4^{2-}$ and polymeric molybdenum sulfides, the only other binary Mo–S complexes characterized, to date, are members of a series of polynuclear molybdenum complexes which contain the disulfide (S$_2^{2-}$) ligands.[5] One of the these complexes, Mo$_2$S$_{12}^{2-}$, recently has been reported to be an excellent reagent for the generation of the Mo$_2$S$_4^{2+}$ core and the subsequent synthesis of various complexes containing this core.[6] In this communication we report on the synthesis and structural characterization of *the first mononuclear Mo(IV) complex, with a MoS$_5$ coordination sphere, containing the MoS^{2+} group.*

The reaction of (Et$_4$N)$_2$MoS$_4$ with dibenzyl trisulfide, (C$_7$H$_7$)$_2$S$_3$, under dinitrogen in acetonitrile, CH$_3$CN, solution at ambient temperature is rapid, and red-brown crystals of (Et$_4$N)$_2$MoS$_9$ (I) are deposited almost instantly in 90% yield. Anal. Calcd for MoS$_9$C$_{16}$H$_{40}$N$_2$ (M_r = 645.1): C, 29.79; H, 6.26; N, 4.34; S, 44.73; Mo, 14.87. Found: C, 30.52; H, 6.40; N, 4.45; S, 44.08; Mo, 14.61. The synthesis of I can also be accomplished in excellent yields (ca. 70%) by the reaction of (Et$_4$N)$_2$MoS$_4$ with an equimolar amount of elemental sulfur in CH$_3$CN at ambient temperatures in a dinitrogen atmosphere. The electronic spectrum of I in dimethylformamide (DMF) solution shows a strong ab-

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(1) (a) Cramer, S. P.; Hodgson, K. O.; Gillum, W. O.; Mortenson, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 3398. (b) Cramer, S. P.; Gillum, W. O.; Hodgson, K. O.; Mortenson, L. E.; Stiefel, E. I.; Chisnell, J. R.; Brill, W. E.; Shah, V. K. *Ibid.* **1978**, *100*, 3814.

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(3) (a) Wolff, T. E.; Berg, J. M.; Warrick, C.; Hodgson, K. O.; Holm, R. H.; Frankel, R. B.; *J. Am. Chem. Soc.* **1978**, *100*, 4630. (b) Wolff, T. E.; Berg, J. M.; Hodgson, K. O.; Frankel, R. B.; Holm, R. H.; *Ibid.* **1979**, *101*, 4140. (c) Wolff, T. E.; Power, P. P.; Frankel, R. B.; Holm, R. H. *Ibid.* **1980**, *107*, 4694. (d) Christou, G.; Garner, C. D.; Mabbs, F. E.; King, T. J. *J. Chem. Soc., Chem. Commun.* **1978**, *740*. (e) Christou, G.; Garner, C. D.; Mabbs, F. E.; *Inorg. Chem. Acta* **1978**, *28*, L189. (f) Christou, G.; Garner, C. D.; Mabbs, F. E.; Drew, M. G. B. *J. Chem. Soc., Chem. Commun.* **1979**, *91*.

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(5) (a) Müller, A.; Nolte, W. O.; Krebs, B. *Angew Chem., Int. Ed. Engl.* **1978**, *17*, 279. (b) Müller, A.; Sarkar, S.; Bhattacharyya, R. G.; Pohl, S.; Dartmann, M.; *Ibid.* **1978**, *17*, 535. (c) Müller, A.; Eltzner, W.; Mohan, W. *Ibid.* **1979**, *18*, 168. (d) Rittner, W.; Müller, A.; Newman, A.; Bäther, W.; Sharma, R. C. *Ibid.* **1979**, *18*, 530. (e) Müller, A.; Nolte, W. O.; Krebs, B. *Inorg. Chem.* **1980**, *19*, 2835.

(6) Miller, K. F.; Bruce, A. E.; Corbin, J. L.; Wherland, S.; Stiefel, E. *J. Am. Chem. Soc.* **1980**, *102*, 5102.

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