Inorg. Chem. **1992**, *31*, 5053–5055

Synthesis and Structure of a Ni_3Fe Cluster Featuring Single and Double Thiolato Bridges

Gerard J. Colpas, Roberta O. Day,* and Michael J. Maroney*

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

Received June 5, 1992

The reaction of the Ni(II) complex of *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)-1,3-propanediamine, [Ni(dmpn)], with $[Fe(H_2O)_6](ClO_4)_2$ in methanol leads to the formation of $\{[Ni(dmpn)]_3Fe\}(ClO_4)_2$ (**1**), which contains novel Ni_3Fe cluster dications. Crystals of **1** form from methanol solution in the triclinic space group $P\bar{1}$ with $a = 15.936$ (6) Å, $b = 16.842$ (8) Å, $c = 17.335$ (5) Å, $\alpha = 102.32$ (3)°, $\beta = 106.27$ (3)°, $\gamma = 89.88$ (4)°, $V = 4355$ (3) Å^3, and $Z = 4$. The structure was refined to final values of $R = 0.074$ and $R_w = 0.096$. The crystals contain two independent cluster dications in the asymmetric unit that are essentially structurally identical. The cluster dications consist of a central high-spin Fe^{2+} ion ($\mu = 4.9\ \mu_B$) surrounded by five thiolate S-donors, which form bridges to the three Ni centers. The remaining thiolate is not bonded to the Fe atom. The Ni centers are in planar four-coordinate environments similar to those found in the Ni(dmpn) complex. This structure is a model for structural elements that have been proposed for the metal sites of Ni metalloenzymes that also contain Fe,S clusters (e.g. hydrogenase and carbon monoxide dehydrogenase).

Interest in clusters containing Ni and Fe with S-donor ligands has been stimulated by the possibility that such clusters exist in the active sites of the enzymes hydrogenase (H_2ase)[1] and carbon monoxide dehydrogenase (COdase).[2] Evidence supporting the existence of Ni,Fe,S clusters in these enzymes has been obtained from EPR,[3] ENDOR,[4] Mössbauer,[2] and EXAFS[1,5] investigations. Herein we report the synthesis and structure of a novel Ni_3Fe cluster. The cluster provides an unusual example of an isolated high-spin ferrous FeS_5 center and also contains examples of both mono- and dithiolato bridges to Ni sites. In this respect, it constitutes a structural model that is useful for examining a possible Ni–S–Fe linkage between a Ni center and an Fe,S cluster that has been suggested by the spectroscopic studies of the Ni sites in H_2ase and COdase.

Experimental Section

The Ni(II) complex of *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)-1,3-propanediamine (dmpn), Ni(L), was prepared as previously described.[6] All manipulations involving solutions of the compounds were performed anaerobically under a N_2 atmosphere using standard Schlenk techniques. A solution of $[Fe(H_2O)_6](ClO_4)_2$ (363 mg, 1.0 mmol) in methanol (10 mL) was added to a solution of Ni(dmpn) (837 mg, 3.0 mmol) in methanol (40 mL). (Note: It is critical that no Fe(III) be present.) Upon standing overnight, 951 mg (87%) of green-brown crystalline $\{[Ni(dmpn)]_3Fe\}(ClO_4)_2$ (**1**) formed. The product was isolated by filtration, washed with EtOH, dried in vacuo, and stored under N_2.[7,8] Magnetic susceptibility measurements were made at 21 °C with a Johnson-Matthey susceptibility balance and are uncorrected for diamagnetic contributions. The error in the measurement is <±2%.

Table I. Crystallographic Data for **1**

formula	$C_{27}H_{60}N_6S_6Ni_3FeCl_2O_8$	γ, deg	89.88 (4)
fw	1092.08	V, Å^3	4355 (3)
cryst system	triclinic	Z	4
space group	$P\bar{1}$ (No. 2)	T, °C	23 ± 2
a, Å	15.936 (6)	λ, Å	0.710 73
b, Å	16.842 (8)	D_{calc}, g/cm^3	1.666
c, Å	17.335 (5)	μ, cm^{-1}	20.616
α, deg	102.32 (3)	$R(F_o)^a$	0.074
β, deg	106.27 (3)	$R_w(F_o)^a$	0.096

^{a} $R = \sum\|F_o| - |F_c\|/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

The best crystals of **1** were obtained directly from the methanol reaction mixture, and these were of poor diffraction quality.[8] The irregular crystal used for data collection was cut to approximate dimensions of 0.12 × 0.30 × 0.40 mm. A total of 9318 independent reflections ($+h,\pm k,\pm l$) were measured by use of an Enraf-Nonius CAD-4 diffractometer and graphite-monochromated Mo radiation. Data were collected by use of the θ–2θ scan mode ($2\theta_{max} = 42°$). An empirical absorption correction based on ψ scans was applied (relative transmission factors from 0.7250 to 0.9987 on I). The structure was solved by use of direct methods and difference Fourier techniques. The oxygen atoms of the ClO_4^- anions were poorly defined. Full-matrix least-squares refinement[9] on F (Fe, Ni, S, Cl, and N atoms anisotropic; O and C atoms isotropic; H atoms omitted) gave $R = 0.074$ and $R_w = 0.096$ for the 5141 reflections with $I \geq 3\sigma_I$. All computations were performed on a Microvax II computer by using the Enraf-Nonius SDP system of programs. Crystallographic data are summarized in Table I.

Results and Discussion

The structures of the two independent Ni_3Fe cluster dications in **1** are essentially identical. The structure of one representative dication is shown in Figure 1, and selected atomic coordinates and distances and angles are listed in Tables II and III, respectively. The cluster consists of a central high-spin Fe^{2+} center surrounded by five thiolate S-donors, which form bridges to three planar Ni^{2+} centers. The remaining thiolate is not within a distance consistent with a strong covalent bond (Fe1–S1 = 3.197 (8) Å). Consequently, the geometry about the Fe center is five-coordinate. When the noncoordinated S atom is included (Figure 2), the geometry about the Fe atom can be viewed as a distorted octahedron, where the distortion is toward a trigonal prism due to the small bite of the N_2S_2 ligands. The two three-atom planes defined by S1, S4, S6 and S2, S3, S5 are nearly parallel (dihedral angle = 2.2°), and the Fe atom lies between these planes at distances of 1.285 Å from the former and 1.334

---

(1) Maroney, M. J.; Colpas, G. J.; Bagyinka, C.; Baidya, N.; Mascharak, P. K. *J. Am. Chem. Soc.* **1991**, *113*, 3962.

(2) Lindahl, P. A.; Munck, E.; Ragsdale, S. W. *J. Biol. Chem.* **1990**, *265*, 3873.

(3) Lindahl, P. A.; Ragsdale, S. W.; Munck, E. *J. Biol. Chem.* **1990**, *265*, 3880.

(4) Fan, C.; Gorst, C. M.; Ragsdale, S. W.; Hoffman, B. M. *Biochemistry* **1991**, *30*, 431.

(5) Bastian, N. R.; Diekert, G.; Niderhoffer, E. C.; Teo, B. K.; Walsh, C. T.; Orme-Johnson, W. H. *J. Am. Chem. Soc.* **1988**, *110*, 5581.

(6) Colpas, G. J.; Kumar, M.; Day, R. O.; Maroney, M. J. *Inorg. Chem.* **1990**, *29*, 4779.

(7) *Caution*! *Perchlorate salts are known explosives.* Although this compound has not posed any hazard to date, it should be synthesized only in small quantities, and due care should be employed in its isolation and manipulation.

(8) Anal. Calcd for $C_{27}H_{60}N_6O_8S_6Cl_2Ni_3Fe$: C, 29.78; H, 5.56; N, 7.72. Found: C, 28.43; H, 5.54; N, 7.15. Ni:Fe = 3.05:1.00 by ICP spectroscopy. IR (cm^{-1}): 1305m, 1180vs (ClO_4^-), 970m, 940m, 785m, 751m, 722m, 621s (ClO_4^-).

(9) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$.

0020-1669/92/1331-5053$03.00/0

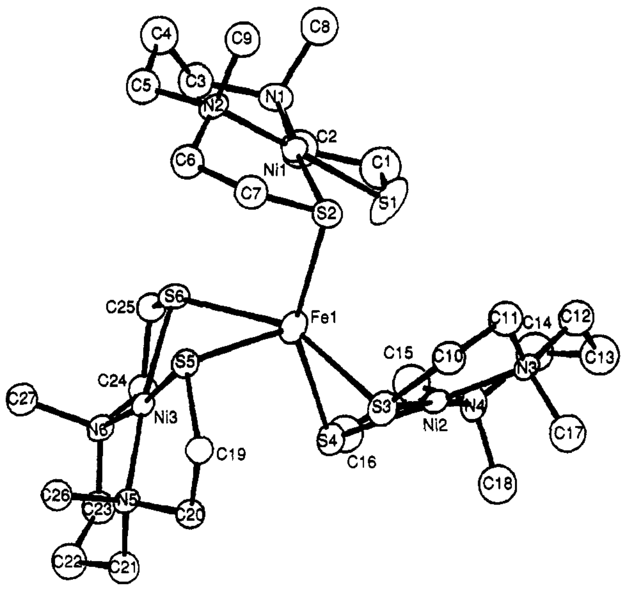

Figure 1. ORTEP plot of one of the two independent Ni_3Fe cluster dications in **1** with thermal ellipsoids at the 30% probability level.

Table II. Selected Atomic Coordinates and B_{equiv} Values for $\{Fe[Ni(L)_3]\}(ClO_4)_2$[a]

atom	*x*	*y*	*z*	B_{equiv}, Å^2
Ni1	0.7128 (2)	0.5116 (1)	0.1525 (1)	3.12 (6)
Ni2	0.5570 (1)	0.2935 (1)	0.2508 (1)	2.72 (5)
Ni3	0.8282 (1)	0.4810 (1)	0.4675 (1)	2.38 (5)
Ni4	–0.2098 (2)	0.1697 (1)	–0.1506 (1)	2.96 (6)
Ni5	–0.0544 (2)	–0.0957 (1)	–0.2435 (1)	2.95 (6)
Ni6	–0.3271 (1)	–0.0035 (1)	–0.4632 (1)	2.50 (5)
Fe1	0.7171 (2)	0.4019 (2)	0.2879 (2)	3.95 (7)
Fe2	–0.2134 (2)	0.0014 (2)	–0.2835 (2)	4.07 (7)
S1	0.5835 (4)	0.4617 (4)	0.1392 (5)	7.7 (2)
S2	0.7471 (1)	0.3875 (3)	0.1531 (3)	4.6 (1)
S3	0.6846 (3)	0.2449 (3)	0.2647 (3)	4.1 (1)
S4	0.6209 (3)	0.3733 (3)	0.3689 (3)	4.0 (1)
S5	0.8695 (3)	0.3965 (3)	0.3741 (3)	3.1 (1)
S6	0.7799 (3)	0.5461 (3)	0.3701 (3)	3.4 (1)
S7	–0.0839 (4)	0.1227 (4)	–0.1501 (4)	5.5 (2)
S8	–0.2418 (4)	0.0459 (3)	–0.1482 (3)	4.7 (1)
S9	–0.1832 (3)	–0.1484 (3)	–0.2582 (4)	4.6 (1)
S10	–0.1165 (3)	–0.0663 (3)	–0.3611 (3)	4.0 (1)
S11	–0.3681 (3)	–0.0434 (3)	–0.3679 (3)	3.4 (1)
S12	–0.2797 (3)	0.1061 (3)	–0.3675 (3)	3.3 (1)
N1	0.665 (1)	0.6204 (9)	0.1509 (9)	4.1 (4)
N2	0.836 (1)	0.5404 (9)	0.1606 (9)	3.7 (4)
N3	0.514 (1)	0.2166 (8)	0.1436 (9)	3.5 (4)
N4	0.4462 (9)	0.3449 (9)	0.2544 (9)	3.8 (4)
N5	0.8725 (9)	0.4067 (8)	0.5420 (8)	3.0 (4)
N6	0.7931 (9)	0.5701 (8)	0.5456 (9)	3.1 (4)
N7	–0.164 (1)	0.2795 (8)	–0.1507 (9)	3.9 (4)
N8	–0.331 (1)	0.197 (1)	–0.150 (1)	4.5 (4)
N9	–0.013 (1)	–0.1248 (9)	–0.135 (1)	4.4 (4)
N10	0.0590 (9)	–0.0484 (9)	–0.2483 (9)	3.8 (4)
N11	–0.3706 (9)	–0.1115 (8)	–0.5361 (9)	3.6 (4)
N12	–0.2926 (9)	0.0488 (8)	–0.5422 (8)	3.1 (4)

[a] Numbers in parentheses are estimated standard deviations. Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Å from the latter. Thus, in the absence of S1, the geometry about the Fe atom is best described as a distorted octahedron with one ligand missing. The structure cannot be adequately described in terms of either a trigonal bipyramid or a rectangular pyramid, nor does it lie on the coordinate connecting these two geometries. The distortions involved in describing the structure in terms of either limiting five-coordinate geometry are so large as to render the description meaningless.

Table III. Selected Distances (Å) and Angles (deg) for $\{Fe[Ni(L)]_3\}(ClO_4)_2$[a]

Distances			
Fe1–S1	3.197 (8)	Fe1–S2	2.477 (7)
Fe1–S3	2.619 (6)	Fe1–S4	2.459 (7)
Fe1–S5	2.484 (5)	Fe1–S6	2.581 (5)
Ni1–S1	2.158 (7)	Ni1–S2	2.160 (6)
Ni1–N1	1.99 (2)	Ni1–N2	1.98 (2)
Ni2–S3	2.160 (6)	Ni2–S4	2.168 (5)
Ni2–N3	1.97 (1)	Ni2–N4	1.98 (2)
Ni3–S5	2.166 (5)	Ni3–S6	2.167 (6)
Ni3–N5	1.98 (1)	Ni3–N6	1.99 (1)
Fe1–Ni1	3.269 (4)	Fe1–Ni2	2.976 (4)
Fe1–Ni3	3.123 (3)	Ni1–Ni2	5.257 (4)
Ni1–Ni3	5.388 (3)	Ni2–Ni3	5.355 (3)
Angles			
S2–Fe1–S3	92.6 (2)	S2–Fe1–S4	149.6 (2)
S2–Fe1–S5	98.3 (2)	S2–Fe1–S6	105.3 (2)
S3–Fe1–S4	69.2 (2)	S3–Fe1–S5	92.7 (2)
S3–Fe1–S6	156.3 (2)	S4–Fe1–S5	106.4 (2)
S4–Fe1–S6	99.8 (2)	S5–Fe1–S6	69.7 (2)
S1–Ni1–S2	82.9 (3)	S1–Ni1–N1	89.3 (5)
S1–Ni1–N2	171.5 (5)	S2–Ni1–N1	172.2 (5)
S2–Ni1–N2	88.8 (5)	N1–Ni1–N2	99.0 (7)
S3–Ni2–S4	83.6 (2)	S3–Ni2–N3	89.3 (5)
S3–Ni2–N4	172.1 (4)	S4–Ni2–N3	172.9 (5)
S4–Ni2–N4	88.8 (4)	N3–Ni2–N4	98.3 (6)
S5–Ni3–S6	83.9 (2)	S5–Ni3–N5	87.4 (4)
S5–Ni3–N6	172.3 (5)	S6–Ni3–N5	170.9 (4)
S6–Ni3–N6	89.5 (5)	N5–Ni3–N6	99.3 (6)
Ni1–S1–C1	100.3 (9)	Ni1–S2–C7	101.1 (6)
Ni1–S2–Fe1	89.4 (2)	Fe1–S2–C7	107.6 (7)
Ni2–S3–C10	101.1 (6)	Ni2–S3–Fe1	76.4 (2)
Fe1–S3–C10	116.5 (7)	Ni2–S4–C16	101.1 (7)
Ni2–S4–Fe1	79.8 (2)	Fe1–S4–C16	119.7 (9)
Ni3–S5–C19	101.5 (6)	Ni3–S5–Fe1	84.1 (2)
Fe1–S5–C19	113.3 (6)	Ni3–S6–C25	99.8 (6)
Ni3–S6–Fe1	81.8 (2)	Fe1–S6–C25	129.7 (6)

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 1.

The formation of an FeS_5 center is surprising since geometric constraints would appear to favor six equivalent Fe–S bonds. The Fe center is unique in that it is an example of a magnetically isolated high-spin ferrous center with five thiolate ligands. Magnetic susceptibility measurements provide a value of $\mu = 4.9$ μ_B for the cluster at 21 °C. This value is consistent with the expected formulation of the cluster as containing an isolated high-spin Fe^{2+} ion[10] and three diamagnetic Ni^{2+} centers. Other examples of Fe^{2+} in an S_5 coordination environment fall into two classes: Fe,S clusters with bidentate S-donor ligands[11] and dimers composed of FeS_4 units.[12]

The geometry about the three Ni^{2+} centers in the Ni_3Fe cluster does not deviate significantly from planarity, and no significant difference between the Ni center with one bridging thiolate and the two $(\mu\text{-}S)_2Ni$ centers is observed. In fact, the NiN_2S_2 units in **1** are more planar (to within ±0.01 to ±0.06 Å) than those in crystals of [Ni(dmpn)] (within ±0.07 Å).[6] The Ni–S and Ni–N distances are slightly shorter in **1** than those found in the isolated Ni(dmpn) complex.[6]

Three Ni–Fe distances characterize the cluster (Table III). The largest of these distances (Ni1–Fe1 = 3.269 (4) Å) is associated with the Ni center that has only a single bridge to Fe. However, this distance is not very different from the other Ni–Fe distances because the metal–S bond lengths and the angles about the bridging S atoms are similar. The Ni–Fe distances are

---

(10) Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders: Philadelphia, PA, 1977; p 425.

(11) (a) Kanatzidis, M. G.; Coucouvanis, D.; Simopoulous, A.; Kostikas, A.; Papaefthymiou, V. *J. Am. Chem. Soc.* **1985**, *107*, 4925. (b) Inomata, S.; Tobita, H.; Ogino, H. *J. Am. Chem. Soc.* **1990**, *112*, 6145. (c) Liu, Q.; Huang, L.; Liu, H.; Lei, X.; Wu, D.; Kang, B.; Lu, J. *Inorg. Chem.* **1990**, *29*, 4131.

(12) (a) Sawyer, D. T.; Srivatsa, G. S.; Bodini, M. E.; Schaefer, W. P.; Wing, R. M. *J. Am. Chem. Soc.* **1986**, *108*, 936. (b) Ileperuma, O. A.; Feltham, R. D. *Inorg. Chem.* **1975**, *14*, 3042.

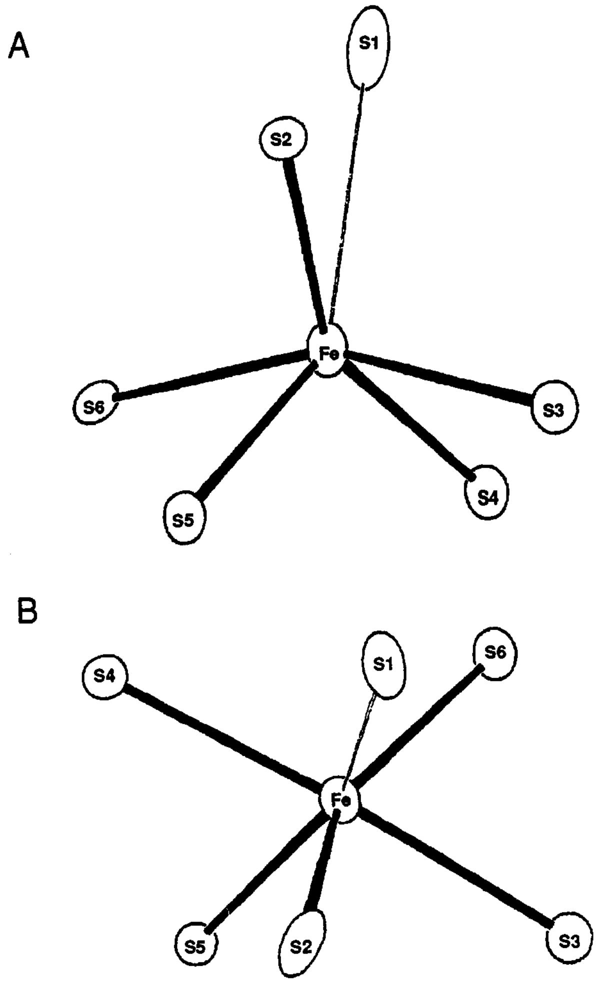

Figure 2. ORTEP plots showing the coordination geometry at Fe1 and including the noncoordinated S1 atom: (A) Viewed perpendicular to the plane defined by S2, S3, and S5; (B) viewed parallel to the plane defined by S2, S3, and S5.

comparable to those found in the analysis of EXAFS data from COdase (3.25 (5) Å)[5] but are much shorter than those suggested for the H_2ase active site cluster (4.3 (1) Å).[1] Neither EXAFS analysis supports a structure in which Ni is incorporated into an Fe,S cluster. The structure of **1** illustrates the point that it is the M–S–M angle and not the number of bridging S atoms that is the more important factor in determining the M–M distance in these clusters. Thus, it is not possible to distinguish the nature of the bridge(s) from distances obtained from EXAFS.

The ability of complexes with terminal thiolate ligands to form clusters by bridging to additional metal ions is well-documented.[13] The synthesis of **1** also takes advantage of the well-known tendency of planar Ni thiolate complexes to form dimers, trimers, tetramers, and higher polymers involving bridging thiolates.[6,14] Typically, Ni^{2+} complexes of chelating ligands that feature two terminal thiolates in a cis orientation will form trinuclear complexes with an additional Ni^{2+} ion, where the additional Ni atom is bound in an S_4 site composed of bridging thiolates from two Ni(L) units.[14s,15] The monomeric Ni(dmpn) complex is no exception and readily forms a trimeric complex upon addition of 0.5 equiv of Ni^{2+}.[6]

A recent example of a Ni,Fe,S cluster, $[Ni(L)FeCl_2]_2$, synthesized using a similar strategy has been reported.[16] This cluster is a dimer that contains only di-μ-S units. Since $FeCl_2$ was used as a source of Fe^{2+}, the resulting cluster features Fe–Cl as well as Fe–S bonds, which precludes the formation of the clusters analogous to those in **1**. Neither the Ni_3Fe nor the $[Ni(L)FeCl_2]_2$ cluster is sterically congested, and both structures contain five-coordinate Fe^{2+} centers with essentially identical Fe–S bond lengths. Thus, the difference in the overall structures is due in part to the anions employed.

Supplementary Material Available: Tables of crystallographic data, atomic coordinates, anisotropic thermal parameters, and distances and angles for **1** (16 pages). Ordering information is given on any current masthead page.

---

(13) (a) Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41. (b) Wark, T. A.; Stephan, D. W. *Organometallics* **1989**, *8*, 2836.

(14) (a) Watson, A. D.; Rao, Ch. P.; Dorfman, J. R.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 2820. (b) Nicholson, J. R.; Christou, G.; Huffman, J. C.; Folting, K. *Polyhedron* **1987**, *6*, 863. (c) Snyder, B. S.; Rao, Ch. P.; Holm, R. H. *Aust. J. Chem.* **1986**, *39*, 963. (d) Barclay, G. A.; McPartlin, E. M.; Stephenson, N. C. *Acta Crystallogr.* **1969**, *B25*, 1262. (e) Baker, D. J.; Goodall, D. C.; Moss, D. S. *Chem. Commun.* **1969**, 325. (f) Villa, A. C.; Manfredotti, A. G.; Nardelli, M.; Pelizzi, C. *Chem. Commun.* **1970**, 1322. (g) Fackler, J. P., Jr.; Zegarski, W. J. *J. Am. Chem. Soc.* **1973**, *95*, 8566. (h) Schwarzenbach, G. *Chem. Zvesti* **1965**, *19*, 200. (i) Tremel, W.; Kriege, M.; Krebs, B.; Henkel, G. *Inorg. Chem.* **1988**, *27*, 3886. (j) Tremel, W.; Krebs, B.; Henkel, G. *Chem. Commun.* **1986**, 1527. (k) Tremel, W.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Eng.* **1984**, *23*, 634. (l) White, G. S.; Stephan, D. W. *Organometallics* **1988**, *7*, 903. (m) Kriege, M.; Henkel, G. *Z. Naturforsch., B* **1987**, *42B*, 1121. (n) Gaete, W.; Ros, J.; Solans, X.; Font-Altaba, M.; Briansó, J. L. *Inorg. Chem.* **1984**, *23*, 39. (o) Woodward, P.; Dahl, L. F.; Abel, E. W.; Crosse, B. C. *J. Am. Chem. Soc.* **1965**, *87*, 5251. (p) Gould, R. O.; Harding, M. M. *J. Chem. Soc. A* **1970**, 875. (q) Dance, I. G.; Scudder, M. L.; Secomb, R. *Inorg. Chem.* **1985**, *24*, 1201. (r) Wark, T. A.; Stephan, D. W. *Organometallics* **1989**, *8*, 2836. (s) Wei, C. H.; Dahl, L. F. *Inorg. Chem.* **1970**, *8*, 1878. (t) Vance, T. B., Jr.; Warner, L. G.; Seff, K. *Inorg. Chem.* **1977**, *16*, 2106. (u) Barrera, H.; Suades, J.; Perucaud, M. C.; Briansó, J. L. *Polyhedron* **1984**, *3*, 839. (v) Mikuriya, M.; Kida, S.; Murase, I. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1180. (w) Rosenfield, S. G.; Wong, M. L. Y.; Stephan, D. W.; Mascharak, P. K. *Inorg. Chem.* **1987**, *26*, 4119. (x) Ali, M. A.; Livingstone, S. E. *Coord. Chem. Rev.* **1974**, *13*, 101. (y) Handa, M.; Mikuriya, M.; Okawa, H.; Kida, S. *Chem. Lett.* **1988**, 1555.

(15) (a) Jicha, D. C.; Busch, D. H. *Inorg. Chem.* **1962**, *1*, 872. (b) Turner, M. A.; Driessen, W. L.; Reedijk, J. *Inorg. Chem.* **1990**, *29*, 3331.

(16) Mills, D. K.; Hsiao, Y. M.; Farmer, P. J.; Atnip, E. V.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1991**, *113*, 1421.