As usual, the axial P–N bonds are longer than the equatorial bonds; however, the P–N(3) axial bond is 1.940 (4) Å, 0.15 Å longer than the P–N(1) axial bond. This significant difference may be due to the greater polarizing effect of the proton, relative to $ZnCl_3$. Interestingly, both of the P–N axial bonds in cyclenPH$_3^{2+}$ are only about 1.87 Å.[8] The $NZnCl_3$ geometry is comparable to that in other derivatives.[11,12] Species **3** and **4** can be viewed as zwitterionic molecules with positive charges on the two quaternized nitrogens and a 2– charge on the zinc.

The conformations of the rings show some asymmetry when viewed down the plane containing the N(1), P, and N(3) atoms (Figure 2): C(5) and C(8) lie "below" the P–C(6)–C(7) plane, while C(1) and C(4) lie "above" the P–C(2)–C(3) plane. This conformation has been observed before in cyclenPH$_3^{2+}$ and referred to as an "S" pattern. Such a geometry should lead to similarly directionalized lone pairs on the axial nitrogens, which is apparent from the similar torsion angles the N(1)–Zn and N(3)–H(3n) bonds make with the P–H(1p) bond [19.9 (1.7) and 17.6 (3.9)°, respectively] (see Figure 2). Similar torsion angles were not found for the two N–H hydrogens in cyclenPH$_3^{2+}$. This was attributed to the fact that hydrogen bonding only occurred between one of the hydrogens and one of the counterions, CF_3COO^-. The other N–H hydrogen was not involved in such an interaction.

The structure of **3** and [Li(THF)cyclenP]$_x$ (above) demonstrate the tendency for cyclenPH (or cyclenP) to bind primarily through both axial nitrogens under suitable conditions, i.e., with harder metallic Lewis acids such as Li^+ and Zn^{2+}.[3] The fact that [Li(THF)cyclenP]$_x$ polymerizes rather than dimerizes may be due to the steric repulsion of the two phosphoranide lone pairs that would face each other in a dimer similar to **3** (where the cyclenP units would only be separated by a lithium atom). This suggests that the structures of **1** and **2** may also be polymeric (to avoid P–H repulsions) via N–M–N linkages. However, this conjecture needs to be substantiated by structural data on related metal complexes of cyclenPH.[13]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Robert A. Welch Foundation, and SMU (Seed Grant), for generous financial support. We also thank Professor A. Dean Sherry for obtaining the 125.8-MHz ^{13}C NMR data and David Brand for assistance in preparing the cyclen.

Supplementary Material Available: Tables of anisotropic thermal parameters, bond distances, bond angles, torsion angles, hydrogen atom coordinates, and full crystallographic data and a crystal packing diagram for **3** (6 pages); a table of observed and calculated structure factors for **3** (9 pages). Ordering information is given on any current masthead page.

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(12) See, for example: (a) Purnell, L. G.; Hodgson, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 3651. (b) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1978**, *17*, 1338. (c) Mazzanti, M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1986**, *25*, 2308.

(13) Attempts at obtaining reliable molecular weight data for these complexes in Me_2SO, from either commercial or our laboratories, proved unsuccessful.

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$[Fe_6S_6(PEt_3)_6]^+$: Extension of Stabilization of the Basket Core Topology to the $[Fe_6S_6]^+$ Oxidation Level

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The influence of terminal ligands on Fe–S cluster structures formed in self-assembly systems is evident. In recent work it has been shown that systems containing Fe(II), Et_3P, and L = halide or thiolate assemble the clusters $Fe_6S_6(PEt_3)_4L_2$ (**1**, **2**), whose $[Fe_6S_6]^{2+}$ cores possess a C_{2v} basket-type stereochemistry with the bridging modalities $Fe_6(\mu_2\text{-}S)(\mu_3\text{-}S)_4(\mu_4\text{-}S)$. In order to determine the nature of the cluster formed when the only possible terminal ligand is a tertiary phosphine, the assembly system 1:4:1 $[Fe(OH_2)_6](BF_4)/Et_3P/Li_2S$ in THF was investigated. The compound $[Fe_6S_6(PEt_3)_6](BF_4)$ was isolated in 14% purified yield. It crystallizes in monoclinic space group $P2_1/m$ with a = 12.370 (5) Å, b = 16.745 (6) Å, c = 15.151 (4) Å, β = 93.76 (3)°, and Z = 2. The crystal structure contains the cluster $[Fe_6S_6(PEt_3)_6]^+$ (**4**), which has imposed C_s symmetry but closely approaches C_{2v} symmetry. Cluster **4** has the basket stereochemistry of **1** and **2** with only relatively minor dimensional differences. As in the latter two clusters, the six Fe sites of **4** divide into two that have tetrahedral stereochemistry and four that exhibit distorted trigonal-planar coordination. The tetrahedral sites are those that bind halide and thiolate in **1** and **2**. Retention of this geometry in **4** indicates that it is intrinsic to the basket core topology, which has now been shown to stabilize the (reduced) $[Fe_6S_6]^+$ oxidation level. Thus far, the basket structure has been observed only in the oxidation levels $[Fe_6S_6]^{2+,+}$ and only with four or six Et_3P ligands. Cluster **4** does not show clean electrochemical reactions but does react with chloride or chlorinated solvents to give $Fe_6S_6(PEt_3)_4Cl_2$, and with dioxygen and elemental sulfur to afford the known species $[Fe_6S_8(PEt_3)_6]^{2+}$ and $[Fe_6S_8(PEt_3)_6]^+$, respectively. The two oxidation reactions are further examples of core conversions of basket clusters, in this case affording a stellated octahedral cluster product. The characterization of **4** raises to 5 the number of characterized *hexa*nuclear Fe–S clusters. Those of the type $[Fe_6S_6L_6]^{2-,3-}$ (L = RO^-, RS^-, halide), with more oxidized cores than in **1**, **2**, and **4**, have been shown earlier to have the prismane stereochemistry.

Introduction

In addition to the usual variables of solvent and stoichiometry, it is now evident that the products generated in iron–sulfur cluster self-assembly systems are influenced by the terminal ligand reactant(s) present. With systems containing an Fe(II,III) salt, a sulfide source, and thiolate as the sole terminal ligand, the principal or exclusive product is $[Fe_2S_2(SR)_4]^{2-}$, $[Fe_4S_4(SR)_4]^{2-}$, or $[Fe_6S_9(SR)_2]^{4-}$, depending on the particular experimental conditions.[1-4] When the terminal ligand is chloride or bromide, the product is $[Fe_nS_nX_4]^{2-}$ (n = 2, 4).[5-7] The system Fe(0), S, and I_2 affords the clusters $[Fe_nS_nI_4]^{2-}$ (n = 2, 4) or $[Fe_6S_6I_6]^{2-}$.[8-10]

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(1) Hagen, K. S.; Reynolds, J. G.; Holm, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 4054 and references therein.

(2) Christou, G.; Sabat, M.; Ibers, J. A.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 3518.

(3) Hagen, K. S.; Watson, A. D.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 3905.

(4) Strasdeit, H.; Krebs, B.; Henkel, G. *Inorg. Chem.* **1984**, *23*, 1816.

(5) Cleland, W. E., Jr.; Averill, B. A. *Inorg. Chem.* **1984**, *23*, 4192.

(6) Müller, A.; Schladerbeck, N.; Bögge, H. *Chimia* **1985**, *39*, 24.

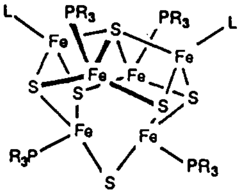
(7) Rutchik, S.; Kim, S.; Walters, M. A. *Inorg. Chem.* **1988**, *27*, 1515.

(8) Saak, W.; Henkel, G.; Pohl, S. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 150.

(9) Saak, W.; Pohl, S. *Z. Naturforsch.* **1985**, *40B*, 1105.

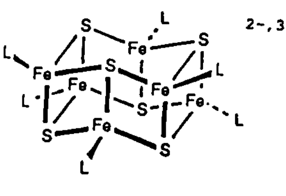
0020-1669/90/1329-0274$02.50/0

With combinations of triethylphosphine and halide or thiolate as the terminal ligand, several cluster types are formed separately. One of these is $Fe_7S_6(PEt_3)_4Cl_3$, whose $[Fe_7S_6]^{3+}$ core has a monocapped-prismane configuration.[11] The other clusters are of the type $Fe_6S_6(PEt_3)_4L_2$ (**1**,[12-14] **2**[15]), whose $[Fe_6S_6]^{2+}$ core has a "basket" structure and is topologically isomeric (but not isoelectronic) with the cores of the prismane clusters $[Fe_6S_6L_6]^{2-,3-}$ (**3**).[8,16,17] When the only potential terminal ligands present are chloride and the acetanilide anion, the unique cyclic cluster $[Na_2Fe_{18}S_{30}]^{8-}$, with *no* terminal ligands, is formed in good yield.[18]



1 (L = Cl⁻, Br⁻, I⁻)

2 (L = RS⁻)



3 (L = Cl⁻, Br⁻, I⁻, RO⁻, RS⁻)

In most cluster assembly systems we have investigated, product formation is dependent primarily on reactant stoichiometry and the nature of the terminal ligand, and to a lesser extent on solvent and temperature. The results of Fenske and co-workers[19] make evident, often in quite dramatic fashion, the role of these variables and also the nature of the chalcogenide source, on the formation of high-nuclearity clusters. Whatever may be the exact pathways leading to the formation of different cluster types, which are summarized elsewhere,[15] the fact remains that basket clusters have been assembled thus far only in the presence of tertiary phosphines and halide or thiolate. Therefore, one question which arises at this point pertains to the nature of the cluster formed in a Fe–S assembly system containing a tertiary phosphine as the *only* component that could function as a terminal ligand. Precedents for an all-phosphine Fe–S cluster of this sort are limited to the species $[Fe_6S_8(PEt_3)_6]^{+,2+}$, which are formed in a system containing $[Fe(OH_2)_6](BF_4)_2$, excess PEt_3 and H_2S, and $NaBPh_4$ in dichloromethane/ethanol solution.[20,21] These clusters contain the stellated octahedral $[Fe_6(\mu_3\text{-}S)_8]^{+,2+}$ cores with square-pyramidal FeS_4P coordination units, quite different from the FeS_3P units in **1** and **2**. In this work we show that an assembly system in THF containing PEt_3 and lacking uncombined halide and thiolate yields a new cluster, $[Fe_6S_6(PEt_3)_6]^+$, which retains the basket core topology of **1** and **2**.

Experimental Section

Preparation of $[Fe_6S_6(PEt_3)_6](BF_4)$ (4). All operations were performed under a pure dinitrogen atmosphere. THF was freshly distilled from Na/benzophenone; all other solvents were anhydrous and were stored under dinitrogen. Triethylphosphine was a gift from the Cyanamid Corp. and was purified by distillation.

Table I. Crystallographic Data for $[Fe_6S_6(PEt_3)_6](BF_4)$

formula	$C_{36}H_{90}BF_4Fe_6P_6S_6$	space group	$P2_1/m$
fw	1322.71	T, K	297
a, Å	12.370 (5)	λ, Å	0.71069 (Mo Kα)
b, Å	16.745 (6)	ρ_{calc},^{a} g/cm^3	1.40
c, Å	15.151 (4)	μ, cm^{-1}	17.0
β, deg	93.76 (3)	$R(F_o)$	6.00
V, Å^3	3131 (2)	$R_w(F_o^2)$	7.88
Z	2		

[a] Density not determined because of the sensitivity of the compound to halogenated solvents.

A solution of 1.00 g (2.96 mmol) of $[Fe(OH_2)_6](BF_4)_2$ in 50 mL of THF was treated with 1.75 mL (11.8 mmol) of Et_3P, resulting in the precipitation of a pale flocculent solid. After the reaction mixture was allowed to stand for 1 h, 0.136 g (2.96 mmol) of Li_2S was added. The mixture rapidly turned deep brown. It was stirred overnight and filtered, and ether (100 mL) was layered onto the filtrate. After 1 day, a heterogeneous mass, consisting of black and pale crystals, was separated by filtration and washed with ether. Fractional crystallization was achieved by vapor diffusion of ether into a concentrated THF solution of the mixture. Initial crops consisted entirely of white needles, shown to be $(Et_3PH)(BF_4)$ by ^1H and ^{31}P NMR spectroscopy. Subsequent crops included white needles and black plates. The final crop consisted entirely of 0.095 g (14%) of black platelike crystals. Absorption spectrum (THF): featureless 800–270 nm with end absorption. ^1H NMR (CD_3CN): δ 1.04 (3), 0.64 (3), 0.30 + 0.21 (5), −0.74 (2), −1.85 (2). Anal. Calcd for $C_{36}H_{90}BF_4Fe_6P_6S_6$: C, 32.64; H, 6.85; Fe, 25.38; P, 14.05; S, 14.51. Found: C, 33.08; H, 6.81; Fe, 25.18; P, 14.15; S, 14.39.

Collection and Reduction of X-ray Data. Single crystals of $[Fe_6S_6(PEt_3)_6](BF_4)$ with diffraction quality were grown by layer diffusion of ether into a THF solution. A black plate was mounted in a glass capillary under a dinitrogen atmosphere. Data collection was carried out at ambient temperature on a Nicolet P3F automated four-circle diffractometer equipped with graphite monochromator. Unit cell parameters were obtained from 25 machine-centered reflections ($20° \le 2\theta \le 25°$). Intensities of three check reflections monitored every 123 reflections indicated no significant decay over the course of data collection. Data sets were processed with the program XTAPE of the SHELXTL program package (Nicolet XRD Corp., Madison, WI 53711), and an empirical absorption correction was applied with the program PSICOR. Axial photographs and the observed systematic absences $0k0$ ($k = 2n + 1$) are consistent with the space group $P2_1$ or $P2_1/m$. Simple E statistics indicated the centrosymmetric space group as the correct choice. Subsequent structure solution and refinement corroborated this choice. Crystal data are summarized in Table I.

Structure Solution and Refinement. Atomic scattering factors were taken from a standard source.[22] All heavy atoms were located by direct methods using the program MULTAN. All carbon atoms were located in successive difference Fourier maps and refined by using the program CRYSTALS. Isotropic refinement converged at R = 15.8%. The tetrafluoroborate anion and the carbon atoms of three triethylphosphine ligands whose phosphorus atoms lie in a mirror plane exhibited varying degrees of disorder. All well-ordered atoms were refined anisotropically, while those evidencing disorder were retained as isotropic. Hydrogen atoms were included on well-ordered carbon atoms at a distance of 0.95 Å. The final difference Fourier map revealed three peaks between 0.5 and 0.85 e. Two of these were associated with the disordered anion and the other with a disordered ethyl group. Final R factors are given in Table I; positional parameters are listed in Table II.[23]

Other Physical Measurements. Determination of electrochemical, magnetic, and Mössbauer spectroscopic properties were made by the methods and with the equipment described elsewhere.[13,24] All measurements were made under anaerobic conditions. Isomer shifts of ^{57}Fe are referenced to Fe metal at 4.2 K.

Results and Discussion

Preparation. The basket clusters $Fe_6S_6(PR_3)_4L_2$ (**1**, **2**) are prepared in purified yields of ≥50% in assembly systems consisting of equimolar quantities of $Fe(PEt_3)_2L_2$ (which may be generated

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(10) Pohl, S.; Saak, W. *Z. Naturforsch.* **1988**, *43B*, 457.
(11) Noda, I.; Snyder, B. S.; Holm, R. H. *Inorg. Chem.* **1986**, *25*, 3851.
(12) Snyder, B. S.; Reynolds, M. S.; Noda, I.; Holm, R. H. *Inorg. Chem.* **1988**, *27*, 595.
(13) Snyder, B. S.; Holm, R. H. *Inorg. Chem.* **1988**, *27*, 2339.
(14) Snyder, B. S.; Reynolds, M. S.; Papaefthymiou, G. C.; Holm, R. H. Results to be published.
(15) Reynolds, M. S.; Holm, R. H. *Inorg. Chem.* **1988**, *27*, 4494.
(16) Kanatzidis, M. G.; Hagen, W. R.; Dunham, W. R.; Lester, R. K.; Coucouvanis, D. *J. Am. Chem. Soc.* **1985**, *107*, 953.
(17) Kanatzidis, M.; Salifoglou, A.; Coucouvanis, D. *Inorg. Chem.* **1986**, *25*, 2460.
(18) You, J.-F.; Snyder, B. S.; Holm, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 6589.
(19) Fenske, D.; Ohmer, J.; Hachgenei, J.; Merzweiler, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1296.
(20) Agresti, A.; Bacci, M.; Cecconi, F.; Ghilardi, C. A.; Midollini, S. *Inorg. Chem.* **1985**, *24*, 689.
(21) (a) Cecconi, F.; Ghilardi, C. A.; Midollini, S. *J. Chem. Soc., Chem. Commun.* **1981**, 640. (b) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1987**, 831.
(22) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974.
(23) See the paragraph at the end of this article concerning supplementary material available.
(24) Carney, M. J.; Papaefthymiou, G. C.; Spartalian, K.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 6084.

Table II. Atom Coordinates ($\times 10^4$) for $[Fe_6S_6(PEt_3)_6](BF_4)$

atom	*x/a*	*y/b*	*z/c*
Fe(1)	7672 (2)	2500	1418 (1)
Fe(2)	5211 (2)	2500	3246 (1)
Fe(2)	7159 (2)	2500	4093 (1)
Fe(4)	5534 (1)	2500	1549 (1)
Fe(5)	6861 (1)	3386.4 (9)	2664.9 (8)
S(1)	6562 (2)	3540 (2)	1229 (2)
S(2)	4006 (3)	2500	2153 (3)
S(3)	6050 (2)	3533 (2)	3898 (2)
S(4)	8194 (3)	2500	2902 (2)
P(1)	9036 (4)	2500	380 (3)
P(2)	3854 (4)	2500	4186 (3)
P(3)	8077 (4)	2500	5510 (3)
P(4)	4579 (4)	2500	199 (3)
P(5)	7611 (3)	4629 (2)	2779 (2)
B(1)	11255 (27)	2500	7879 (23)
F(1)[a]	11881 (51)	2500	7126 (42)
F(2)[a]	12360 (27)	2500	7871 (22)
F(3)[a]	10483 (15)	1954 (12)	7736 (13)
F(4)[a]	11379 (16)	2007 (13)	8587 (14)
F(5)[a]	11274 (24)	3035 (19)	7160 (20)
C(11)[a]	8701 (27)	2973 (20)	−654 (22)
C(12)[a]	9456 (28)	3489 (22)	26 (23)
C(13)	8568 (19)	3868 (17)	−555 (13)
C(14)	10336 (20)	2917 (19)	721 (16)
C(15)	10903 (21)	2500	1511 (20)
C(21)	4288 (24)	2500	5342 (17)
C(22)	3641 (31)	2500	6053 (20)
C(23)[a]	2759 (21)	3170 (17)	4007 (17)
C(24)[a]	3247 (34)	3535 (28)	4330 (26)
C(25)	3042 (21)	3943 (16)	3842 (23)
C(30)	9559 (37)	2906 (37)	5426 (30)
C(31)[a]	10172 (43)	2500	4979 (35)
C(32)	8181 (33)	3236 (24)	6217 (26)
C(33)	7153 (23)	3490 (19)	6328 (21)
C(34)[a]	7746 (47)	3714 (39)	6318 (46)
C(35)[a]	10150 (52)	3139 (42)	4811 (42)
C(41)	3673 (18)	1687 (14)	−23 (11)
C(42)	3697 (24)	970 (16)	304 (16)
C(43)	5409 (20)	2500	−721 (14)
C(44)	5019 (30)	2500	−1590 (17)
C(51)	6663 (16)	5409 (9)	2369 (12)
C(52)	5583 (17)	5371 (11)	2695 (16)
C(53)	8088 (16)	4944 (13)	3903 (12)
C(54)	8727 (21)	5443 (28)	4137 (19)
C(55)	8750 (15)	4863 (12)	2105 (12)
C(56)	9763 (21)	4499 (20)	2411 (19)

[a] Disordered atoms.

in situ) and Li_2S or $(Me_3Si)_2S$ in THF solution.[13-15] Here, the system consisting of 1:4:1 $[Fe(OH_2)_6](BF_4)_2/Et_3P/Li_2S$, also in THF, afforded black $[Fe_6S_6(PEt_3)_6](BF_4)$ (**4**). The modest purified yield (14%) is due in part to the difficulty in separating the product from noncluster byproducts of the system. However, this yield is comparable to those (15–20%) for the formation of black $[Fe_6S_8(PEt_3)_6]^{2+,+}$ in the related assembly system 1:3 $[Fe(OH_2)_6](BF_4)_2/Et_3P + H_2S$ in ethanol/dichloromethane (ca. 1:1 v/v) followed by the addition of $NaBPh_4$ or n-$Bu_4N(PF_6)$ as a precipitant for the cluster cations.[20,21] Inasmuch as these clusters are much more highly oxidized than $[Fe_6S_6(PEt_3)_6]^+$, the formation of different products in the two systems may be due to different sulfide sources and to differing controls on the anaerobicity of the preparations and the purification steps.[25]

Description of the Structure. The crystal structure of $[Fe_6S_6(PEt_3)_6](BF_4)$ consists of discrete cations and anions. The anion resides on a mirror plane and is disordered but otherwise unexceptional. Selected metric data for the cluster cation are collected in Table III, and the structure of its $Fe_6S_6P_6$ portion is

Table III. Selected Distances (Å) and Angles (deg) for $[Fe_6S_6(PEt_3)_6](BF_4)$

Fe(1)–Fe(4)	2.665 (3)	Fe(1)–S(1)	2.224 (3)
Fe(1)–Fe(5)	2.651 (2)	Fe(2)–S(3)	2.217 (3)
Fe(2)–Fe(3)	2.654 (3)	Fe(3)–S(3)	2.216 (3)
Fe(2)–Fe(4)	2.627 (3)	Fe(4)–S(1)	2.229 (3)
Fe(2)–Fe(5)	2.716 (2)	Fe(5)–S(1)	2.198 (3)
Fe(3)–Fe(5)	2.629 (2)	Fe(5)–S(3)	2.192 (3)
Fe(4)–Fe(5)	2.719 (2)	mean	2.213
Fe(5)–Fe(5′)	2.969 (3)	Fe(1)–S(4)	2.299 (4)
Fe(2)–S(2)	2.153 (4)	Fe(3)–S(4)	2.279 (4)
Fe(4)–S(2)	2.153 (4)	Fe(5)–S(4)	2.231 (3)
Fe(1)–P(1)	2.381 (5)	mean	2.270
Fe(2)–P(2)	2.271 (4)	S(1)···S(1)	3.483 (6)
Fe(3)–P(3)	2.363 (5)	S(1)···S(2)	3.946 (4)
Fe(4)–P(4)	2.293 (4)	S(1)···S(3)	4.134 (3)
Fe(5)–P(5)	2.281 (4)	S(1)···S(4)	3.586 (4)
Fe(1)···Fe(2)	4.248 (3)	S(2)···S(3)	3.936 (4)
Fe(1)···Fe(3)	4.142 (3)	S(3)···S(3)	3.461 (6)
Fe(3)···Fe(4)	4.227 (3)	S(3)···S(4)	3.582 (4)
S(1)–Fe(1)–S(1)	103.06 (16)	P(3)–Fe(3)–S(3)	112.16 (11)
S(3)–Fe(2)–S(3)	102.63 (15)	P(3)–Fe(3)–S(4)	117.22 (17)
S(1)–Fe(4)–S(1)	102.76 (16)	P(4)–Fe(4)–S(1)	94.24 (11)
S(3)–Fe(3)–S(3)	102.71 (16)	P(4)–Fe(4)–S(2)	87.93 (16)
S(1)–Fe(1)–S(4)	104.90 (10)	P(5)–Fe(5)–S(1)	90.53 (12)
S(3)–Fe(3)–S(4)	105.67 (10)	P(5)–Fe(5)–S(3)	92.30 (12)
S(1)–Fe(4)–S(2)	128.47 (8)	P(5)–Fe(5)–S(4)	107.58 (13)
S(2)–Fe(2)–S(3)	128.53 (8)	Fe(4)–S(2)–Fe(2)	75.18 (14)
S(3)–Fe(5)–S(1)	140.75 (12)	Fe(4)–S(1)–Fe(1)	73.54 (10)
S(4)–Fe(5)–S(1)	108.17 (13)	Fe(5)–S(1)–Fe(1)	73.69 (10)
S(4)–Fe(5)–S(3)	108.17 (13)	Fe(5)–S(1)–Fe(4)	75.78 (10)
P(1)–Fe(1)–S(1)	111.92 (10)	Fe(2)–S(3)–Fe(3)	73.57 (10)
P(1)–Fe(1)–S(4)	118.72 (17)	Fe(5)–S(3)–Fe(3)	73.24 (10)
P(2)–Fe(2)–S(2)	88.81 (17)	Fe(5)–S(3)–Fe(2)	76.06 (10)
P(2)–Fe(2)–S(3)	93.67 (11)	Fe(3)–S(4)–Fe(1)	129.63 (17)
		Fe(5)–S(4)–Fe(1)	71.64 (10)
		Fe(5)–S(4)–Fe(3)	71.32 (11)
		Fe(5)–S(4)–Fe(5)	83.45 (14)

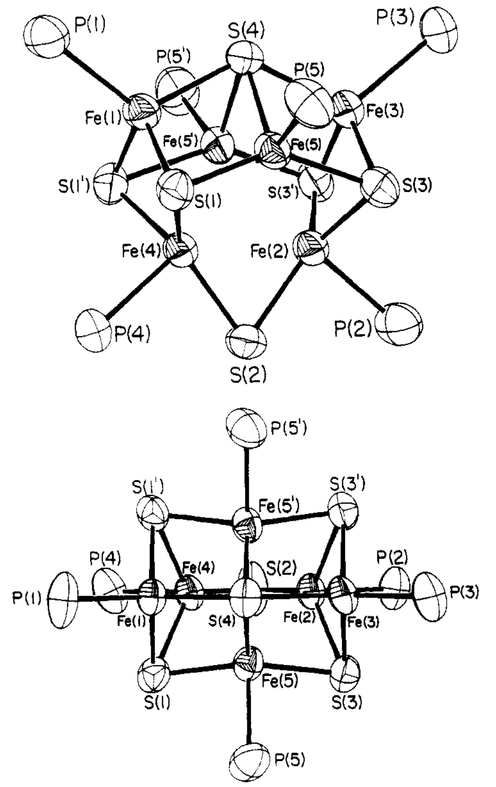

Figure 1. Structure of the $Fe_6S_6P_6$ portion of $[Fe_6S_6(PEt_3)_6]^+$, showing 50% probability ellipsoids and the atom-labeling scheme. The lower view is down the idealized C_2 axis containing S(2,4).

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(25) The preparations of $[Fe_6S_8(PEt_3)_6]^{2+,+}$ are described as being performed under a dinitrogen atmosphere with degassed solvents. The 2+ cluster is air-stable[20] whereas the 1+ cluster is oxidized in solution by atmospheric dioxygen to the 2+ cluster.[21] The lowest oxidation level of the Fe_6S_8 core that can be reached electrochemically, $[Fe_6S_8]^0$ (−1.0 V vs. SCE, $Fe^{2.67+}$), is still much more oxidized than $[Fe_6S_6(PEt_3)_6]^+$ ($Fe^{2.17+}$), which is decomposed by dioxygen. We surmise that the Fe_6S_6 core can be formed only under rigorously anaerobic and neutral conditions. Solvent difference may also play a role, if for no other reason than $[Fe_6S_6(PEt_3)_6]^+$ is oxidized to $Fe_6S_6(PEt_3)_4Cl_2$ in chlorinated solvents.

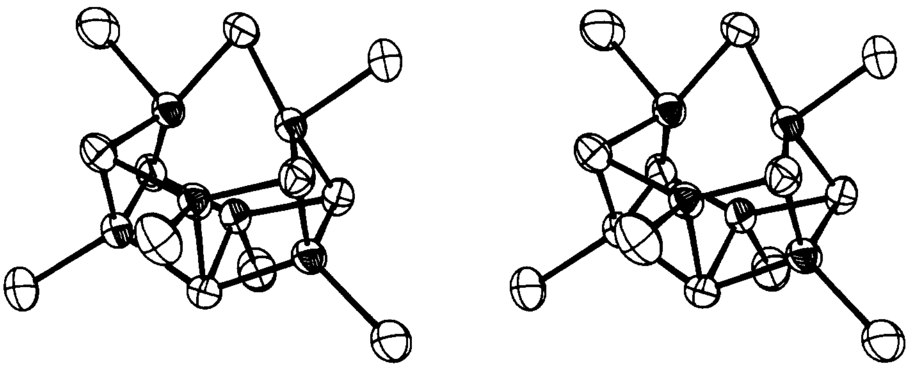

Figure 2. Stereoview of the $Fe_6S_6P_6$ portion of $[Fe_6S_6(PEt_3)_6]^+$.

Table IV. Magnetic and Mössbauer Spectroscopic Properties of $[Fe_6S_6(PEt_3)_6](BF_4)$

Magnetic Data	
$\chi^M = C(T - \Theta)$	
T range, K	6–30
C, emu K/mol	0.380[b]
Θ, K	−0.85
μ_{eff}, μ_B (T, K)	
solid[a]	1.74 (8.00), 1.76 (20.00), 1.88 (50.00), 2.00 (80.10), 2.08 (100.0), 2.10 (141.3), 2.25 (180.4)
CH_3CN soln	2.40 (298)

Mössbauer Data[c,d] (4.2 K)

	site 1	site 2	site 3
δ, mm/s	0.41	0.41	0.38
ΔE_Q, mm/s	0.53	0.88	1.25
Γ, mm/s	0.28	0.24	0.30

[a] Data at $H_0 = 1$ kOe; selected moments given. [b] 0.375 for $S = {}^1/_2$. [c] Fit with three doublets of constrained 1:1:1 intensity ratio and asymmetry parameter $\eta = 0$ (sites 1 and 2) and 1 (site 3). [d] $Fe_6S_6(PEt_3)_4Cl_2$ (4.2 K): δ (ΔE_Q) = 0.63 (0.60), 0.34 (0.87), 0.32 (1.10) mm/s.

presented in Figure 1. A stereoview of this portion is provided in Figure 2. It is immediately apparent that the $[Fe_6S_6]^+$ core of the cluster has the basket stereochemistry recently precedented in clusters **1** and **2**.[12,13,15] The cluster has crystallographically imposed C_s symmetry, with the mirror plane containing Fe(1–4), S(2,4), and P(1–4), and approaches idealized C_{2v} symmetry. Six nonplanar Fe_2S_2 rhombs are fused to form the basket itself, and the Fe(2)–S(2)–Fe(4) fragment (bond angle 75.2 (1)°) serves as the basket handle. This structural arrangement has the uncommon property of three different bridge modalities, μ_2-S(2), μ_3-S(1,1′,3,3′) and μ_4-S(4), as well as three unique types of Fe sites, each terminally ligated by triethylphosphine. This species and clusters **1** and **2**, with the $[Fe_6S_6]^{2+}$ core, differ by one electron. Corresponding dimensions of the two cores are quite similar, with several exceptions. Because the basket topology in $Fe_6S_6(P\text{-}n\text{-}Bu_3)_4Cl_2$[13] and $Fe_6S_6(PEt_3)_4(S\text{-}p\text{-}C_6H_4Br)_2$,[15] whose cores are essentially congruent, has been described at some length earlier,[13,15] we concentrate here on the most important comparative features of clusters in the two different oxidation levels. In this discussion, Fe sites in clusters **1**, **2**, and **4** are designated as in Figure 1, and the appropriate ranges and mean values of metric parameters refer to the structurally determined examples of both **1** and **2**.

(1) Terminal Ligation. In clusters **1** and **2**, chloride or thiolate and the more bulky phosphine ligands are arranged such that there is only one phosphine ligand per Fe_2S_2 rhomb, thus minimizing the steric interactions between them. However, in $[Fe_6S_6(PEt_3)_6]^+$ this cannot be the case and phosphines are necessarily opposite each other in every rhomb. Their interactions are evident in the Fe(n)–P(n) distances of 2.381 (5) Å (n = 1) and 2.363 (5) Å (n = 3), which are markedly elongated compared to 2.282 (9) Å for the other four Fe–P bond distances. Also, the S(4)–Fe(5)–P(5) angle of 107.6 (1)° is ca. 8–9° larger than in **1** and **2** and reflects a displacement of phosphines P(5,5′) away from P(1,3) and toward the open faces of the basket core.

(2) Core. $[Fe_6S_6(PEt_3)_6]^+$ and clusters **1** and **2**, with the $[Fe_6S_6]^{2+}$ core, differ by one electron. Corresponding dimensions of the two cores are quite similar, with only several exceptions. In **1** and **2**, the bond distances Fe–(μ_4-S) divide into two long (2.31–2.34 Å, to Fe–L) and two short (2.20–2.23 Å, to Fe–P). In the present cluster, these dimensions are biased in the same directions but are far more regular, with a difference of only 0.06 Å between the smallest and largest values. The Fe(5)–Fe(5′) separation of 2.969 (3) Å is >0.1 Å longer than in **1** and **2** (2.84–2.86 Å). Also in these clusters, the sites Fe(1,3), which bind chloride or thiolate, have a trigonally distorted tetrahedral stereochemistry with the Fe atom 0.95–0.98 Å above the S_3 plane. The remaining four sites, which bind phosphine, have an unusual distorted trigonal-pyramidal coordination with a small displacement of the Fe atom above the S_3 plane (0.06–0.14 Å) and one or two markedly obtuse angles (127–140°). The same pattern of site stereochemistry is observed in $[Fe_6S_6(PEt_3)_6]^+$. Atoms Fe(1,3) and Fe(2,4,5) are 0.98 and 0.14 Å above their S_3 planes, respectively.

With respect to an interpretation of the preceding structural features, it is difficult to separate the effects of all-phosphine terminal ligation from those of a one-electron difference in core oxidation levels. However, the structural results do afford several important conclusions. The Fe_6S_6 basket core can exist in (at least) two stable oxidation levels (2+, 1+) with four to six tertiary phosphines as terminal ligands. Tetrahedral coordination at Fe(1,3) appears to be intrinsic to the basket topology inasmuch as it is preserved with chloride, thiolate, and phosphine ligands. We lack the compounds to test the matters of retention of the basket structure with ligands other than phosphine at the remaining Fe sites and the correlation of trigonal-pyramidal sites and terminal phosphine ligation. This coordination is found at all phosphine-ligated sites in the monocapped prismanes $Fe_7S_6(PEt_3)_4Cl_3$[11] and $Co_7S_6(PPh_3)_5Cl_2$.[26]

Magnetic and Mössbauer Spectroscopic Properties. These properties of $[Fe_6S_6(PEt_3)_6](BF_4)$ are summarized in Table IV. Presented in Figure 3 is the magnetization behavior of **4** at three field strengths. The data are reasonably well fit by a $S = {}^1/_2$ Brillouin function, indicating a spin-doublet ground state. This assignment is supported by the Curie constant evaluated from Curie–Weiss behavior at 6–30 K. Further, an essentially isotropic EPR signal at $\langle g \rangle = 1.990$ is observed in THF solution at ca. 19 K. The oxidized basket clusters **1** and **2** have $S = 1$ ground states.[14] The zero-field Mössbauer spectrum, displayed in Figure 4, can be treated in terms of three equally intense quadrupole doublets with different splittings (ΔE_Q) but nearly equal isomer shifts (δ). Probable site assignments follow from the spectral assignments of $Fe_6S_6(PEt_3)_4L_2$ (L = Cl^-, Br^-, I^-).[14] On this basis, sites 2 and 3 correspond to phosphine-bound, distorted trigo-

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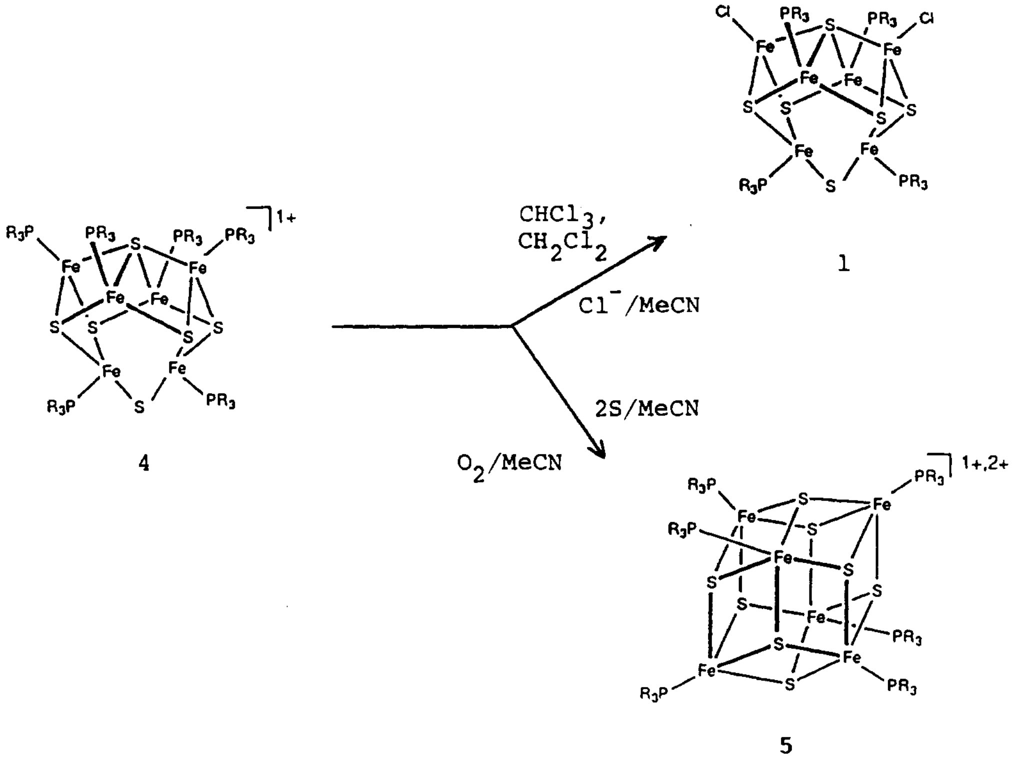
[26] Fenske, D.; Hachgenei, J.; Ohmer, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 706.

Scheme I



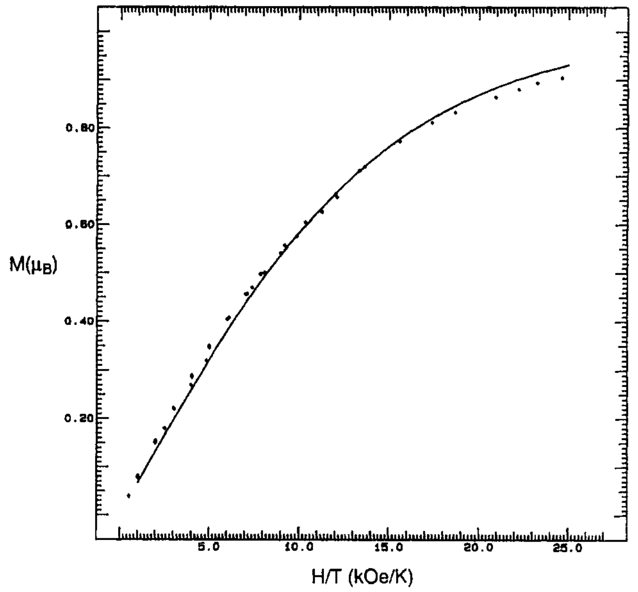


Figure 3. Magnetization behavior of $[Fe_6S_6(PEt_3)_6](BF_4)$. Experimental points were obtained at applied fields of 12.5, 25, and 50 kOe. The solid line corresponds to a $S = {}^1/_2$ Brillouin function.

nal-pyramidal Fe(2,4,5,5′) and site 1, with the smallest quadrupole splitting, to tetrahedral Fe(1,3). Both the structural and Mössbauer data indicate that the mixed-valence cluster is largely delocalized electronically.

Solution Structure and Reactions. The ^1H NMR spectrum of $[Fe_6S_6(PEt_3)_6]^+$ in Figure 5 reveals isotropically shifted and broadened signals for methyl groups at 1.04, 0.64, and 0.30 ppm and for methylene groups at +0.21, −0.74, and −1.85 ppm. The presence of three inequivalent phosphine ligands in equal amounts is consistent with retention of the C_{2v} basket stereochemistry in solution. Under the same criterion, we have shown that **1** and **2** also retain the basket configuration in solution.[13,15]

In contrast to clusters **1** and **2**, $[Fe_6S_6(PEt_3)_6]^+$ does not exhibit any well-defined electrochemical oxidation or reduction. It is, however, otherwise reactive as shown in Scheme I (R = Et). In chlorinated solvents such as dichloromethane or in polar organic

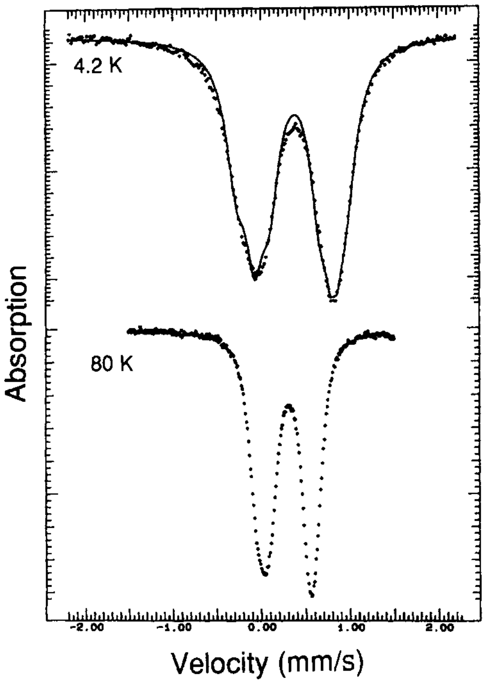


Figure 4. Zero-field Mössbauer spectra of $[Fe_6S_6(PEt_3)_6](BF_4)$ at 4.2 and 80 K. The solid line is a theoretical fit to the data using the parameters in Table IV.

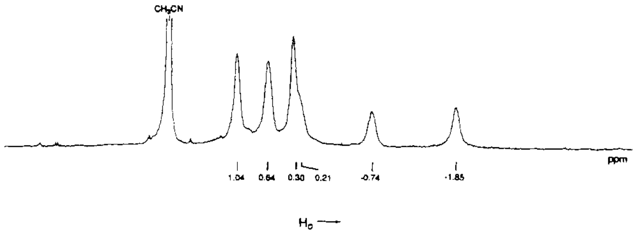


Figure 5. ^1H NMR spectrum of $[Fe_6S_6(PEt_3)_6]^+$ in CD_3CN solution at 298 K. Chemical shifts (δ) are indicated.

solvents to which chloride has been added, the cluster undergoes an immediate reaction to afford $Fe_6S_6(PEt_3)_4Cl_2$, identified by its characteristic ^1H NMR spectrum,[13] and an unidentified black insoluble material. Aerial oxidation of $[Fe_6S_6(PEt_3)_6]^+$ or treatment with elemental sulfur in acetonitrile solution leads to the formation of $[Fe_6S_8(PEt)_6]^{2+}$ or $[Fe_6S_8(PEt_3)_6]^+$ (**5**), respectively. These clusters were identified by their ^1H NMR spectra.[27] The two oxidation reactions are further examples of core conversion reactions[12,13] in which the prismane- (**3**) and cubane-type Fe_4S_4 clusters may be recovered from the basket cluster $Fe_6S_6(PEt_3)_4Cl_2$, which itself is obtainable by a core conversion reaction of $Fe_7S_6(PEt_3)_4Cl_3$. In the present case, the conversion products are the stellated octahedral clusters **5** of established structure.[20,21]

Summary. This work has demonstrated that an Fe–S assembly system with triethylphosphine as the only terminal ligand affords $[Fe_6S_6(PEt_3)_6]^+$. This cluster also possesses the $Fe(\mu_2\text{-}S)(\mu_3\text{-}S)_4(\mu_4\text{-}S)$ basket core topology first observed in **1** and **2**, which are more oxidized by one electron. Tetrahedral stereochemistry at the sites Fe(1,3), also found in the preceding two clusters, appears to be an intrinsic feature of the stable basket cores $[Fe_6S_6]^{2+,+}$. In both oxidation levels, the other four Fe sites exhibit distorted trigonal-pyramidal coordination. $[Fe_6S_6(PEt_3)_6]^+$ has an electronically delocalized core structure, with only small dimensional differences relative to **1** and **2**. It undergoes oxidative core conversion reactions, affording the known clusters $[Fe_6S_8(PEt)_6]^{2+,+}$. Because of the absence of necessary compounds, it is not yet known whether the relative stabilities of basket and prismane (**3**) stereochemistries are dependent on core oxidation level or terminal ligand, or both.

Known Fe–S clusters of nuclearity 6 now include the set $[Fe_6S_6L_6]^{2-,3-}$ (**3**), $Fe_6S_6(PR_3)_4L_2$ (**1**, **2**), $[Fe_6S_6(PEt_3)_6]^+$ (**4**), $[Fe_6S_8(PEt)_6]^{2+,+}$ (**5**), and $[Fe_6S_9(SR)_2]^{4-}$.[2-4] None of the core units of these clusters have as yet been found to occur in proteins, but at least one 6-Fe cluster with a different stoichiometry may exist in certain hydrogenases.[28,29] A future report[14] will describe the electronic properties of **1**, **2**, and **4**. Further reactivity properties of $[Fe_6S_6(PEt_3)_6]^+$ are under examination.

Acknowledgment. This research was supported by NIH Grant GM 28856. X-ray diffraction equipment was obtained by NIH Grant 1 S10 RR02247. We thank Dr. G. C. Papaefthymiou for assistance with Mössbauer spectroscopic measurements.

Supplementary Material Available: Tables of crystallographic data for $[Fe_6S_6(PEt_3)_6](BF_4)$, including a summary of data collection parameters, thermal parameters, calculated hydrogen atom positional parameters, and interatomic distances and angles (7 pages); a listing of calculated and observed structure factors (23 pages). Ordering information is given on any current masthead page.

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[27] ^1H NMR (CD_3CN, 298 K): $[Fe_6S_8(PEt_3)_6]^+$, δ −11.4 (CH_3); $[Fe_6S_8(PEt_3)_6]^{2+}$, δ −44.9 (CH_2), −6.9 (CH_3).

[28] George, G. N.; Prince, R. C.; Stockley, K. E.; Adams, M. W. W. *Biochem. J.* **1989**, *259*, 597.

[29] Adams, M. W. W.; Eccleston, E.; Howard, J. B. *Proc. Natl. Acad. Sci. U.S.A.* **1989**, *86*, 4932.

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Coupling of Thionitrosyls and Nitrosyls on Rhenium Fragments: A Molecular Orbital Analysis

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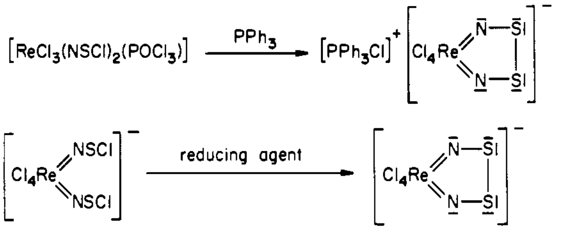
The electronic structure and bonding in complexes of the $[ReCl_4(N_2S_2)]^-$ type have been studied by using extended Hückel calculations. The reaction path and the electronic requirements for the possible coupling of two NS ligands, bonded to the same framework, were studied. The results are then compared with the hypothetical coupling of NO ligands and analyzed for two different types of coupling, involving either (a) the formation of a S–S (O–O) bond or (b) the formation of a N–N-bonded species.

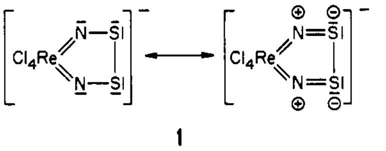
Introduction

Thionitrosyl complexes of transition metals were first discovered in 1974.[1] Compared to the vast number of nitrosyl complexes, only a small number of thionitrosyl complexes have been investigated. The reactivity pattern of NO compounds are complex,[2] and one might anticipate the same for NS compounds. However, the scarcity of complexes containing two or more NS ligands[3] has limited reactivity studies. Interestingly, a few complexes have been recently isolated and characterized,[4] in which apparently two NS ligands have been coupled on a transition-metal center forming a sulfur–sulfur bond, an observation previously unprecedented for NS complexes.

The reaction of (chlorothio)nitrene complexes $[ReCl_3(NSCl)_2(POCl_3)]$ or $[ReCl_4(NSCl)_2]^-$ with reducing agents such as PPh_3, $SbPh_3$, diphenylacetylene, or $BrSiMe_3$ gives the complexes $[ReCl_4(N_2S_2)]^-$. These have been crystallographically characterized in three examples by Dehnicke et al.[4] (**1**). In this reaction a reductive dehalogenation is likely to occur prior to the formation of a new sulfur–sulfur bond.



Reducing agent = PPh_3, $SbPh_3$, Ph−C≡C−Ph, $BrSiMe_3$



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Thus, it may be suggested that during this reaction step a complex with two separate NS ligands cis to each other is formed

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[1] (a) Wilkinson, G.; Gillard, R. D.; McCleverty, J. A. *Comprehensive Coordination Chemistry*; Pergamon Press: Oxford, England, New York, 1987; Vol. 2, Chapter 13.3.3, p 118. (b) Roesky, H. W.; Pandey, K. K. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 337. (c) Herberhold, M. *Nachr. Chem., Tech. Lab.* **1981**, *29*, 365.

[2] (a) Reference 1a, Vol. 2, Chapter 13.3.2, p 101. (b) McCleverty, J. A. *Chem. Rev.* **1979**, *79*, 53. (c) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339. (d) Johnson, B. F. G.; McCleverty, J. A. *Prog. Inorg. Chem.* **1966**, *7*, 277.

[3] (a) Weber, R.; Müller, U.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1983**, *504*, 13. (b) Demant, U.; Willing, W.; Müller, U.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1986**, *532*, 175.

[4] (a) Hiller, W.; Mohyla, J.; Strähle, J.; Hauck, H. G.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1984**, *514*, 72. (b) Conradi, E.; Hauck, H. G.; Müller, U.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1986**, *539*, 39.

0020-1669/90/1329-0279$02.50/0