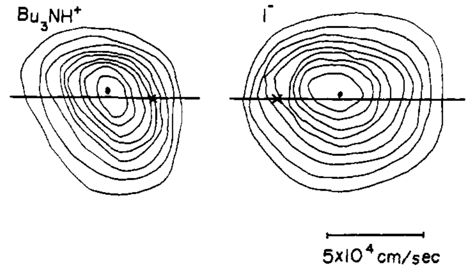

Figure 1. Cartesian probability contours for both ion products in the reaction of HI and tri-*n*-butylamine at a relative energy of 3.65 eV. The relative velocity is 3.65×10^5 cm/s. The lines are a portion of the relative velocity vector; × is the position of the center of mass. The contour diagrams are shown side by side for clarity, but the center of mass is the same point in space for both diagrams. ● is the position of maximum intensity, and the contours are 90%, 80%, 70%, ... of the maximum. The HI beam goes to the right and the amine beam to the left. The spread in the two beam velocities is roughly 1.3×10^4 cm/s (hwhm).

detector pass through a retarding potential energy analyser, an ion lens, and a quadrupole mass filter before they are detected by an electron multiplier. In a typical experiment we first take the angular distribution of one of the product ions with the retarding potential off to collect all the ions at a particular angle. Then, at each angle, the voltage on the retarding grid is scanned to obtain the energy distribution. This then is normalized to the raw angular distribution. There are several coordinate systems that can be used, but we prefer a Cartesian distribution[3] with an origin at the center of mass, $P_C(u_x,u_y,u_z)$, where **u** is the product velocity.

Figure 1 shows the Cartesian contour diagrams for the product ions at an initial relative energy of 3.65 eV. The straight line is the initial relative velocity vector which extends well beyond both edges of the two diagrams. × is the position of the center of mass, and ● is the position of the maximum in the product intensity. The curves surrounding the maximum are contours at 90%, 80%, ... of the intensity of the maximum. The reaction occurs by way of a direct, modified stripping process so that the I^- is found in the direction of the HI beam and the ammonium ion along the amine beam. If the reaction were to proceed by way of a collision complex whose lifetime was comparable to or longer than the duration of a rotation, product intensity would be symmetric about the center of mass, which is not observed. The heat of the reaction is readily computed from the proton affinity of tri-*n*-butylamine,[4] the dissociation energy of HI,[5] the ionization potential of H, and the electron affinity of I to be 79.5 kcal/mol (3.45 eV). The reactants thus have 4.6 kcal/mol in excess of the heat of the reaction. At the 100% contour the final translational energy is 3.0 kcal/mol so that most of the energy of the products is found in translation. It should be noted however, that the energy spread of the two beams is larger than this so that there is a considerable uncertainty in the fraction of energy that appears in translation vs. internal modes. Since the tri-*n*-butylamine is tetrahedral as is the final ammonium ion, one would expect little if any vibrational energy in the N–C bending or stretching modes. One might expect vibrational energy in the N–H stretch, but this is apparently not so. The reaction may occur on two or more potential energy surfaces.

A simple model of the reaction is that the HI passes near the tri-*n*-butylamine, and the proton jumps from the I to the N. The product ions are then gradually decelerated by the Coulombic attraction as they separate. The reaction is direct in that the reactive intermediate lives less than one rotational period.

Acknowledgment. Research support from the National Science Foundation is gratefully acknowledged.

Registry No. $(n\text{-Bu})_3N$, 102-82-9; HI, 10034-85-2.

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(3) Wolfgang, R.; Cross, R. J. *J. Phys. Chem.* **1969**, *73*, 743.

(4) Aue, D. H.; Bowers, M. T. "Gas-Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979.

(5) Bartmess, J. E. McIver, R. T. "Gas-Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979.

2-Azaadamant-1-ene and 4-Azaprotoadamant-3-ene

Juliusz G. Radziszewski,[1a] John W. Downing,[1a]
Curt Wentrup,[1a,b] Piotr Kaszynski,[1a] Mikolaj Jawdosiuk,[1c]
Peter Kovacic,[1c] and Josef Michl*[1a,d]

Departments of Chemistry, University of Utah
Salt Lake City, Utah 84112
University of Wisconsin—Milwaukee
Milwaukee, Wisconsin 53201

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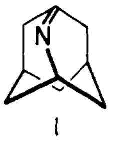
We report the preparation of matrix-isolated 2-azaadamant-1-ene (**1**), the most highly twisted bridgehead imine observed so far, and some of its unusual properties. Two byproducts, 4-azaprotoadamant-3-ene (**2**) and 3-noradamantylnitrene (**3**), have also been identified.



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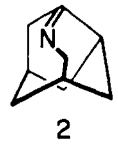

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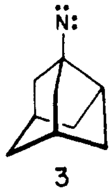

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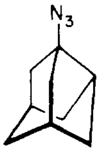

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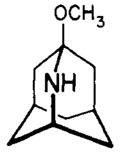

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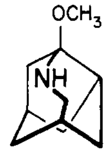

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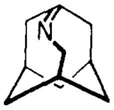

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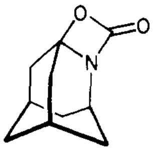

8

Irradiation of 3-azidonoradamantane (**4**) in methanol solution at room temperature produces the methanol adducts **5** and **6**, presumably originating in **1** and **2**, respectively.[2,3] When **4**, isolated in solid argon or polyethylene at 12 K,[4] is irradiated at 308 nm,[5] its UV and IR peaks gradually disappear and a new set of peaks appears. Concurrently, N_2 is formed (Raman).

The new IR and UV peaks belong to two distinct ESR-inactive species, one red and one colorless. The spectra are readily separated (Figures 1 and 2) since the red species is slowly destroyed by irradiation at 488 nm (Ar^+ laser) or rapidly at 254 nm (low-pressure Hg arc). Visible light has no effect on the colorless species, but UV irradiation slowly destroys it. Both species are stable indefinitely in the matrix in the dark (in polyethylene matrix at least up to 100 K) and are destroyed upon warm-up. The structures of the secondary photoproducts and warm-up products are not known.

Irradiation (308 nm) of **4** in a methanol-doped Ar matrix yields the same two products (UV, IR). On subsequent warm-up to ~36 K the red species disappears and several IR bands characteristic

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(1) (a) University of Utah. (b) On sabbatical leave from the University of Marburg, Marburg, West Germany. (c) University of Wisconsin—Milwaukee. (d) Presented at the 187th National American Chemical Society Meeting, St. Louis, MO, April 1984.

(2) Sasaki, T.; Eguchi, S.; Okano, T.; Wakata, Y. *J. Org. Chem.* **1983**, *48*, 4067.

(3) The use of ethanol and dibutylamine as trapping reagents produced similar results: Jawdosiuk, M.; Kovacic, P. *J. Chem. Soc., Perkin Trans. 1* in press.

(4) The characteristic IR bands of **4** (Ar, 12 K) are 2099 (*as* N_3 stretch), 1258 (*sym* N_3 stretch), 721 and 564 (N_3 bend) cm^{-1}. The UV spectrum (polyethylene, 12 K) shows maxima at 216 and 288 nm. ^{13}C NMR ($CDCl_3$) δ 34.1, 37.4, 43.0, 43.4, 47.9, 72.1.

(5) XeCl excimer laser.

0002-7863/84/1506-7996$01.50/0

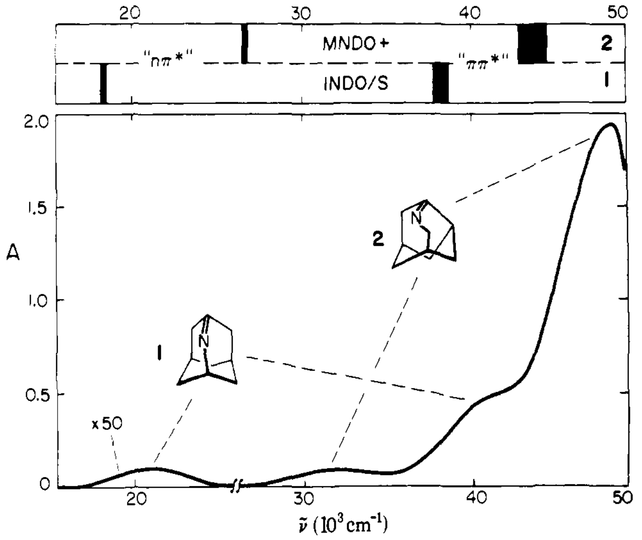

Figure 1. UV-visible absorption spectrum of Ar matrix-isolated products from irradiation of **4** (12 K). On top, INDO/S-vertical transition energies calculated at MNDO-optimized ground-state geometries. Line width indicates calculated intensity (Table I).

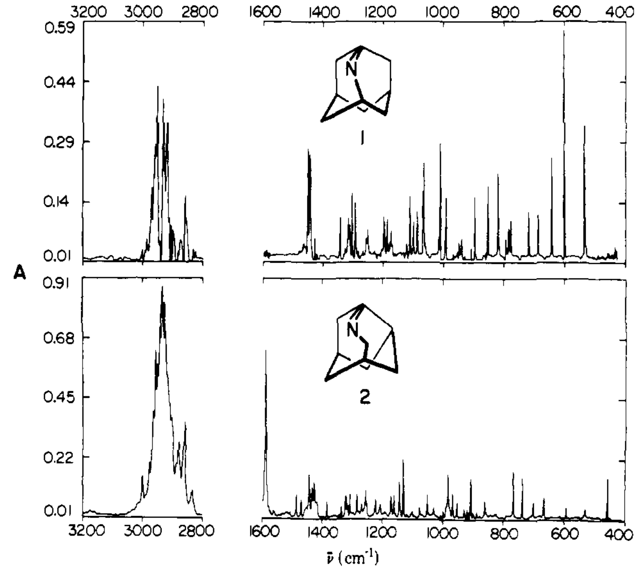

Figure 2. IR spectra of **1** and **2** isolated in Ar matrix (12 K).

of **5** appear. The colorless species remains detectable by IR up to 90 K. After warming to room temperature, the only two major products are the methanol adducts **5** and **6** (capillary column GLC, DB-17-01, comparison with authentic samples[2]). When the red species was first destroyed by irradiation, leaving the colorless one intact, and the methanol-doped argon matrix was only then warmed up, **6** was still produced, but **5** was not. Thus, **5** is derived from the red species and **6** from the colorless species: the former is 2-azaadamant-1-ene (**1**) and the latter is its isomer, 4-azaprotoadamant-3-ene,[6] most likely present as isomer **2** rather than the more highly strained isomer with the *trans* linkage in the six-membered ring.

The UV and IR spectra, both measured on the same matrix, agree very well with the assignments of **1** and **2**. This is illustrated in Figures 1 and 2 and Table I, which show the comparisons with expectations based on the MNDO model[7] (equilibrium geometries and C=N stretching frequencies) and the INDO/S model[8] (UV absorption spectra). These models work well for the related strained imine **7**.[9] The identification of the C=N stretching vibration is based on ^{15}N isotopic shifts.[10]

Table I. Spectroscopic and Computational Data for Imines

	1	**2**	**7**[9]	$(CH_3)_2$-C=NCH$_3$
$\tilde{\nu}_{C=^{14}N}$, cm^{-1}				
exptl	1451	1591	1600	1669[a]
calcd[b]	1472	1585	1595	(1669)
$\tilde{\nu}_{C=^{15}N}$, cm^{-1}				
exptl	1432	1573	1582	
calcd[b]	1454	1564	1575	
$\tilde{\nu}$("nπ*"), 10^3 cm^{-1}				
exptl[c]	20.2	31.9	33.1	41.7[d]
	(w)	(w)	(245)	(~200)
calcd[e]	17.4	26.6	26.3	30.0
	(0.04)	(0.04)	(0.03)	(0.01)
$\tilde{\nu}$("ππ*"), 10^3 cm^{-1}				
exptl[c]	39.7 (s)	49.0 (s)	46.7	~55[d]
			(3000)	(~10 000)
calcd[e]	38.2	43.6	44.2	56.4
	(0.1)	(0.2)	(0.2)	(0.4)
C=N bond length, Å[b]	1.33	1.30	1.30	1.29
pyramidalization at C, deg[b,f]	12	11	8	0
C=N—C angle, deg[b]	110	115	118	126
torsion angle, deg[b,g]	77	51	52	0
charge on C, |e|[b,h]	0.041	0.028	0.040	0.022
charge on N, |e|[b]	−0.327	−0.271	−0.298	−0.285
dipole moment, debye[b]	1.02	1.07	1.08	0.99
$\Delta H_f°$, kcal/mol[b]	66.9	55.9	35.6	0.5

[a] Dunkin, I. R.; Thompson, P. C. P. *Tetrahedron Lett.* **1980**, *21*, 3813. [b] MNDO geometry optimization and force field calculations. The calculated IR frequencies were corrected by using a scaling factor of 0.854, obtained[9b] by fitting the experimental value of $\tilde{\nu}_{C=^{14}N}$ for *N*-methyl-2-propanimine. [c] Peak maxima; extinction coefficient or relative strength in parentheses. [d] Reference 11. [e] INDO/S vertical excitation energies at ground-state MNDO equilibrium geometries. [f] Defined as θ–90°, where θ is any one of the three equal angles between the three bonds originating in the imine carbon and an axis chosen to pass through it. [g] Defined as the dihedral angle between the planes defined by the C=N bond and (i) the axis described under *f* and (ii) the N–C bond. [h] Double-bonded carbon.

The spectral properties of **1**, such as its red color and a C=N stretching vibration at 1451 cm^{-1}, are quite extraordinary for an isolated C=N bond. At planarity, this moiety is associated with an nπ* absorption band at 240 nm and a C=N stretching vibration near 1660 cm^{-1}.[11] An investigation of the chemical properties of **1** has only begun but they promise to be no less out of the ordinary, as a single example will demonstrate: **1** undergoes a rapid cycloaddition reaction with CO$_2$ at 36 K in Ar, while **2** is inert to it. At low concentrations of CO$_2$ (0.2% in Ar) the oxazetidinone **8** is formed. This stable heterocycle[12] also results in a yield of up to 90% of the statistical one-third upon irradiation

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(6) A room-temperature photolysis of **4** in CH$_3$OD (quartz tube; high-pressure Hg lamp) followed by gated ^{13}C NMR analysis of the products confirmed that only the NH groups in **5** and **6** become deuterated.

(7) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907. Dewar, M. J. S.; Ford, G. P.; McKee, M. L.; Rzepa, H. S.; Thiel, W.; Yamaguchi, Y. *J. Mol. Struct.* **1978**, *43*, 135. (b) So far, we have not found an MNDO minimum with the trans double bond in the six-membered ring of 4-azaprotoadamant-3-ene.

(8) Ridley, J.; Zerner, M. *Theor. Chim. Acta* **1973**, *32*, 111.

(9) (a) Michl, J.; Radziszewski, J. G.; Downing, J. W.; Wiberg, K. B.; Walker, F. H.; Miller, R. D.; Kovacic, P.; Jawdosiuk, M.; Bonačić-Koutecký, V. *Pure Appl. Chem.* **1983**, *55*, 315. (b) Radziszewski, J. G.; Jawdosiuk, M.; Downing, J. W.; Kovacic, P.; Michl, J. *J. Am. Chem. Soc.*, in press.

(10) Labeled **4** was obtained by treatment of noradamantane-3-carboxylic acid with Na^{15}N^{14}N^{14}N and concentrated H$_2$SO$_4$. The resulting 3-noradamantylamine (50% ^{15}N) was converted with tosyl azide and NaH in THF to **4**, labeled with 50% ^{15}N at N-1. The ^{15}N-labeled azide has IR bands (Ar, 12 K) at 2094, 1224, 712, and 561 cm^{-1}. Irradiation produces a mixture of **1** and **2**, each 50% labeled at nitrogen. In ^{15}N-labeled **1** all bands below 1450 cm^{-1} are shifted by 0.5–10 cm^{-1} relative to unlabeled **1**, implying considerable coupling of the C=N vibration with the framework. Such coupling is much less evident in **2**.

(11) Sandorfy, C. In "The Chemistry of the Carbon–Nitrogen Double Bond"; Patai, S., Ed.; Interscience: London, 1970; p 38.

(12) **8**: IR (KBr) 1815 and 1829 cm^{-1}; ^{13}C NMR (CDCl$_3$) δ 30.4, 33.7, 34.5, 39.3, 48.1, 98.9 (quaternary C), 156.4 (C=O); mass spectrum, *m/e* 179 (M$^+$, 9.6), 151 ([M − CO]$^+$, 25), 135 ([M − CO$_2$]$^+$, 20), 96 (19), 95 (21), 94 (33), 85 (67), 83 (100); high-resolution mass spectrum, calcd for C$_{10}$H$_{13}$NO$_2$, 179.0946; found, 179.0939.

of a room-temperature solution of **4** in CO_2-saturated benzene or hexafluorobenzene (medium-pressure Hg lamp, Vycor filter).

The reactivity and the spectroscopic properties outlined above clearly indicate that **1** is more highly strained than **2**, in agreement with MNDO calculations (Table I). The opposite ordering of strain energies has been suggested on qualitative grounds.[2,13]

Although **1** and **2** are the only major photoproducts of **4** initially detectable by UV and IR, traces of two triplet products are readily detected by ESR. The ESR signal at 0.8143 T (9.3 GHz) identifies one of these species as a triplet nitrene, assigned as **3**.[14] The other triplet has $|D/hc| = 0.091$ cm^{-1} and $|E/hc| = 0.022$ cm^{-1}, compatible[15] with a localized 1,3-biradical structure. It might originate in a 1,2-H shift to the nitrogen in **1**, but a positive identification has yet to be accomplished.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE 81-21122).

Registry No. 1, 85616-65-5; **2**, 85616-66-6; **3**, 93184-35-1; **4**, 85616-64-4; **8**, 93184-36-2; CO_2, 124-38-9.

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[13] Sasaki, T.; Eguchi, S.; Okano, T. *Tetrahedron Lett.* **1982**, *23*, 4969.

[14] (a) Assuming $E = 0$, one calculates[14b] $|D/hc| = 1.66$ cm^{-1}. (b) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763. Wasserman, E. *Prog. Phys. Org. Chem.* **1971**, *8*, 319. (c) The ESR signal appears to correlate with a weak, sharp UV absorption peak at 302 nm. (d) The structure assignment is supported by a photochemical trapping experiment; in a CO-doped Ar matrix **1**–**3** are still formed from **4** and are stable in the dark, but subsequent irradiation (254 nm) at 36 K, where CO is mobile, produces a weak peak at 2265 cm^{-1} in the IR spectrum. Authentic 1-noradamantyl isocyanate has its strongest peak at 2265 cm^{-1} in Ar matrix. Precedent for photochemical addition of CO to a nitrene is found in ref 9b and: Dunkin, I. R.; Thompson, P. C. P. *J. Chem. Soc., Chem. Commun.* **1982**, 1192.

[15] Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688.

Oxidative Transformation of the $[Fe_4S_4X_4]^{2-}$ "Cubanes" to the $[Fe_6S_6X_6]^{2-}$ "Prismane" Clusters (X = Cl, Br). The Crystal and Molecular Structure of $[(C_6H_5)_4P]_2Fe_6S_6Cl_6$

D. Coucouvanis,* M. G. Kanatzidis, W. R. Dunham, and W. R. Hagen

Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48109

Received August 21, 1984

The existence of 3Fe centers in a number of Fe/S proteins is now well documented.[1] Identification of such centers is based on their characteristic "signatures" in the Mössbauer,[2] magnetic circular dichroism, (MCD),[3] and EPR[4] spectra. The exact nature of the Fe/S cores in the 3Fe ferredoxins is not entirely clear. The spectroscopic data on a number of these proteins and X-ray absorption fine structure (EXAFS) analyses on *D. gigas* FdII[5] and aconitase[6] suggest the presence of 3Fe-4S cores with structural features (Fe–Fe, ~2.70 Å) similar to those found in "conventional" 2Fe or 4Fe ferredoxins. An X-ray structure determination of FdI from *A. vinelandii* shows,[7] however, a 3Fe-3S core with a slightly puckered hexagonal ring structure and "unorthodox" structural features (Fe–Fe, ~4.1 Å; Fe–S–Fe, 126°, 131°, and 113°). These rather unique features had not been found previously in any of the synthetic Fe/S molecular clusters.

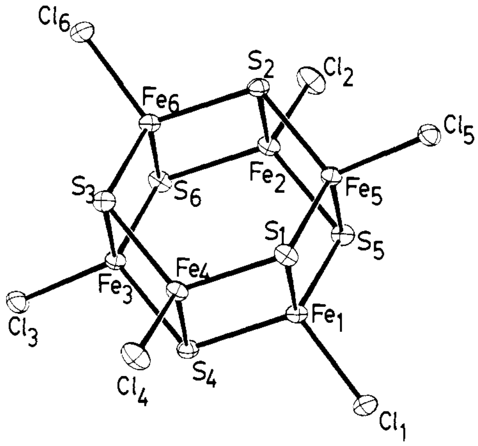

Figure 1. Structure and labeling of the anion in III. Thermal ellipsoids as drawn by ORTEP (C. K. Johnson, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965) represent the 40% probability surfaces.

Recently we reported[8] on the synthesis, structural characterization, and electronic properties of the new, apparently metastable, $(Fe_6S_6Cl_6)^{3-}$ "prismane" cluster (I). At approximately the same time the structural characterization of the analogous I^- cluster in a higher oxidation level, $(Fe_6S_6I_6)^{2-}$ (II), was reported.[9] In both of these clusters the Fe_6S_6 cores contain two Fe_3S_3 puckered ring units with long (~3.8 Å) distances and large (~114°) Fe–S–Fe angles. The core in II represents the first example of a Fe/S cluster with a Fe/S ratio of 1 and a formal Fe oxidation state of 2.67. With the anticipation that appropriate cleavage of the $(Fe_6S_6)^{4+}$ core may result in possible synthetic analogues for the reduced form of the 3Fe centers, we proceeded with studies on the reactivity of the $(Fe_6S_6L_6)^{2-}$ dianions.

As suggested by cyclic voltammetric measurements on CH_2Cl_2 solutions of I,[10] the chemical oxidation of the trianion should be readily accomplished in nonpolar solvents. Indeed, the reaction of CH_2Cl_2 solutions of I with a stoichiometric amount of ferrocenium hexafluorophosphate resulted in the clean quantitative oxidation of I as evidenced by characteristic spectral changes.[11] Unfortunately, this synthetic procedure predicates the use of the $(Fe_6S_6Cl_6)^{3-}$ trianion, which is metastable and is obtained in crystalline form only as the Et_4N^+ salt.[8]

In search of a general procedure[12] for the synthesis of the $(Fe_6S_6X_6)^{2-}$ dianions from readily available reagents, the oxidation of the $(Fe_4S_4X_4)^{2-}$ clusters was attempted in CH_2Cl_2 according to the reaction

$$3(Fe_4S_4X_4)^{2-} + 2(Fe(C_5H_5)_2)^+ \rightarrow 2(Fe_6S_6X_6)^{2-} + 2Fe(C_5H_5)_2 \quad (1)$$

The reaction proceeds cleanly at ambient temperature and for X = Cl and Br (eq 1) the oxidative transformation of the $(Fe_4S_4X_4)^{2-}$ clusters to the $(Fe_6S_6X_6)^{2-}$ "prismanes" is quantitative. Crystalline Ph_4P^+ or R_4N^+ salts can be isolated in excellent yields; however, solutions of these compounds in polar solvents (CH_3CN,

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[1] Beinert, H.; Thomson, A. J. *Arch. Biochem. Biophys.* **1983**, *222*, 333–361.

[2] Emptage, M. H.; Kent, T. A.; Huynh, B. H.; Rawlings, J.; Orme-Johnson, W. H.; Munck, E. *J. Biol. Chem.* **1980**, *255*, 1793–1796.

[3] Johnson, M. K.; Robinson, A. E.; Thomson, A. J. In "Iron–Sulfur Proteins"; Spiro, T. G., Ed.; Wiley: New York, 1982; pp 367–406.

[4] Moura, J. J. G.; Moura, I.; Kent, T. A.; Lipscomb, J. D.; Huynh, B. H.; Legall, J.; Savier, A. V.; Munck, E. *J. Biol. Chem.* **1982**, *257*, 6259–6267.

[5] Antonio, M. R.; Averill, B. A.; Moura, I.; Moura, J. J. G.; Orme-Johnson, W. H.; Teo, B. K.; Savier, A. V. *J. Biol. Chem.* **1982**, *257*, 6646–6649.

[6] Beinert, H.; Emptage, M. .; Dreyer, J. L.; Scott, R. A.; Hahn, J. E.; Hodgson, K. O.; Thomson, A. J., *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 393–396.

[7] Ghosh, D.; O'Donnell, S.; Furey, W., Jr.; Robbins, A. H.; Stout, C. D. *J. Mol. Biol.* **1982**, *158*, 73–109.

[8] Kanatzidis, M. G.; Dunham, W. R.; Hagen, W. R.; Coucouvanis, D. *J. Chem. Soc., Chem. Commun.* **1984**, 356–358.

[9] Saak, W.; Henkel, G.; Pohl, S. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 151.

[10] On a Pt electrode, 10^{-3} M, with Bu_4NClO_4 as the supporting electrolyte; $E_{1/2} = +0.300$ V.

[11] In CH_2Cl_2 solution the $(Fe_6S_6X_6)^{3-}$ (X = Cl, Br) anions show electronic transitions at 270 and 306 nm, respectively. The oxidized $(Fe_6S_6X_6)^{2-}$ show transitions at 287 and 326 nm, respectively.

[12] We have been unable to repeat the reported synthesis[9] of the $(Fe_6S_6I_6)^{2-}$ cluster in our laboratory. The synthetic procedure as outlined in ref 9 in our hands afforded $(FeI_4)^-$ salts in excellent yields. We suspect that the $[Fe_6S_6I_6]^{2-}$ cluster that allegedly is obtained by the published[9] procedure is only a minor reaction byproduct.