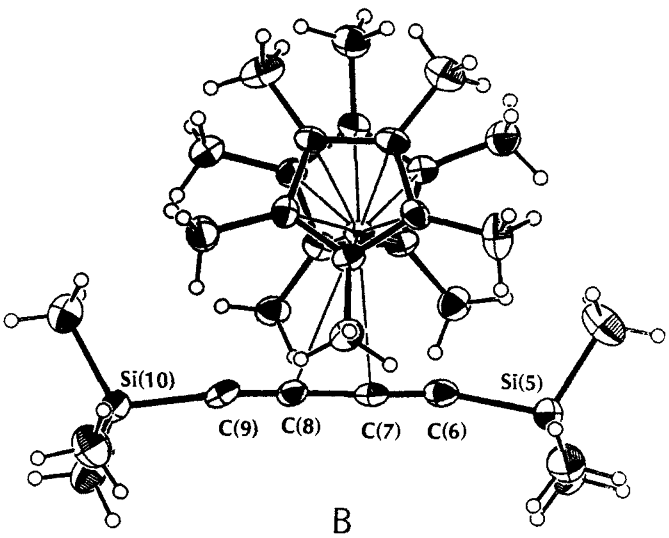

Figure 2. ORTEP view of adduct "B" of $(Me_5C_5)_2Ca(Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3)$. The two shortest Ca–C(methyne) contacts are represented by lines from the Ca to the diyne. Relative to adduct "A", the diyne has moved 0.81 Å to the side of the ring centroid–Ca–ring centroid plane.

average Ca–C distances are 2.64 (2) Å in one molecule ("A") and 2.66 (2) Å in the other ("B"); ring centroid–Ca–ring centroid angles are 143.4° and 145.4°, respectively (Figures 1 and 2). Although the average Ca–C distances are the same as those observed in $Cp^*{}_2Ca$ (2.64 (2) Å),[15] the ring centroid–metal–ring centroid angles are slightly less than in the free metallocene (147.0°).

The distances within the butadiynes are typical for an uncomplexed alkyne, with C≡C, C–C, and C(methyne)–$SiMe_3$ distances averaging 1.21 (1), 1.38 (1), and 1.87 (1) Å, respectively. The terminal $SiMe_3$ groups are nearly eclipsed, with a torsion angle of 3.1° in "A" and 4.3° in "B". The $SiMe_3$ groups are bent away from the metal centers, the maximum deviation being 167.5 (4)° in "A" (C(8)–C(9)–Si(10)) and 167.4 (5)° in "B" (C(7)–C(6)–Si(5)).

The major difference between the conformers is the manner in which the butadiyne is associated with the metal center. In the "A" adduct (Figure 1), the diyne is symmetrically disposed around the ring centroid–Ca–ring centroid plane, with the two center methyne carbons at distances of 3.024 (5) Å (Ca–C(7)) and 2.991 (5) Å (Ca–C(8)), whereas the outer methyne carbons are substantially farther away (3.60 Å (Ca–C(6)) and 3.53 Å (Ca–C(9)). In the "B" adduct (Figure 2), the diyne has slipped ca. 0.81 Å to one side of the plane, so that the distances from the calcium to the center methyne carbons now differ by 0.23 Å (Ca–C(7), 2.878 (5); Ca–C(8), 3.104 (5) Å), and C(6) is brought to within 3.173 (5) Å of the metal center.

The significance of these Ca–diyne contacts is difficult to assess. The Ca–center methyne distances are considerably longer (by 0.24–0.46 Å) than the average Ca–Cp* distances, but the shorter ones are not far from the values observed for the f-element alkyne complex $Cp^*{}_2Yb(\eta^2\text{-}MeC{\equiv}CMe)$ (2.829 (5), 2.871 (5) Å)[13] (the radius of Yb^{2+} differs by 0.02 Å from Ca^{2+}).[18] The Ca–C(8) distance of 3.104 Å is paralleled by a long Ca–(η^1-Cp) interaction at 3.100 (2) Å in the structure of Cp_2Ca.[19] Whether the 3.17 Å Ca–C(6) distance in "B" represents a significant bonding interaction, however, is not readily apparent.

The full extent of the interaction of group II organometallics with unsaturated hydrocarbons is under investigation.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Supplementary Material Available: Tables of crystal data, fractional coordinates, bond distances and angles, and anisotropic thermal parameters (15 pages); table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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New μ_2-S^{2-}-Coupled, Singly Bridged Double Cubane with the $[(Fe_4S_4Cl_3)_2S]^{4-}$ Core. The Stepwise Synthesis and Structural Characterization of $(n\text{-}Bu_4N)_2(Ph_4P)_2[(Fe_4S_4Cl_3)_2S]$

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Received October 16, 1989

Synthetic analogues for the Fe/S sites in certain non-heme iron proteins, which contain cores such as $[Fe_2S_2]^{2+}$ and $[Fe_4S_4]^{2+}$, can be prepared conveniently by "spontaneous self-assembly", SSA, reactions from mixtures of appropriate reagents.[1] A drawback inherent in SSA reactions is the lack of predictability in situations where the target clusters are not necessarily the most thermodynamically stable species. An example of such a case has been encountered in attempts[2] to obtain Fe/Mo/S clusters, as analogues for the active site in nitrogenase.[2] The employment of SSA procedures thus far has not yielded clusters with the desired[2] Fe:Mo:S ratio of 7 ± 1:1:9 ± 1. Instead, single or double cubanes are obtained[3] with a Fe:Mo:S ratio of 3:1:4.

The Fe/M proteins in Mo nitrogenase[2] and in the recently discovered V[4] and Fe[5] variants (M = V, Fe) appear to contain structurally and stoichiometrically similar Fe/M/S centers. Recently we suggested[6] a general structural model for the Fe/M/S centers in the nitrogenases, with a site (M) capable of accommodating Mo, V, or Fe. This model (Figure 1) is a composite octanuclear cluster that contains the well-known Fe_4S_4[7] and MFe_3S_4 structural subunits (M = Mo,[3] V[8]) coupled by a single Fe–μ_2-S–Fe bridge. This cluster cannot be obtained by SSA reactions and must be synthesized by carefully controlled coupling reactions.

While this work was in progress, the solution NMR spectrum and electrochemical properties of a sulfide-bridged Fe_4S_4 double-cubane cluster were reported.[9] This compound was obtained by the sulfide coupling of a "site-differentiated" cubane.[10] In this communication, we demonstrate the feasibility of coupling

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[10] The "site-differentiated" cubanes contain a tripodal ligand that blocks reactivity at three of the four iron sites and contains a substitutionally labile ligand at the fourth iron site.

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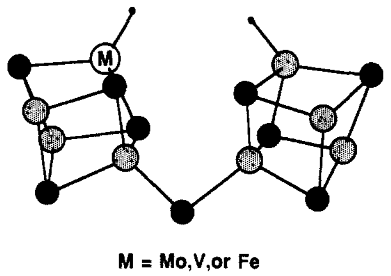

Figure 1. A proposed structural model for the Fe/M/S core in the Mo, V, or Fe nitrogenases.

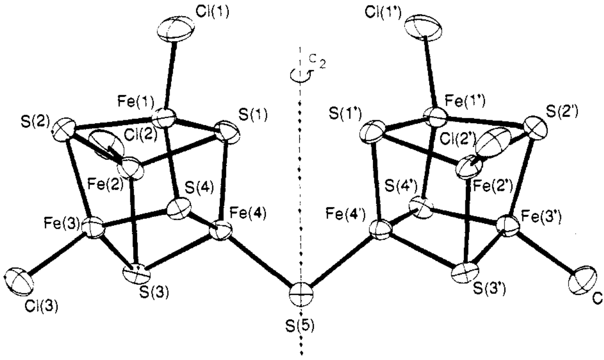

Figure 2. Structure and labeling of the $[(Fe_4S_4Cl_3)_2S]^{4-}$ anion (III). Thermal ellipsoids as drawn by ORTEP[17] represent the 40% probability surfaces.

two simple, *unfunctionalized*, $[Fe_4S_4Cl_4]^{2-}$ cubanes into a singly bridged double cubane and report on the structure determination of this cluster, which contains a new Fe/S core similar to that shown in Figure 1.

The reaction of either the Et_4N^+ or the n-Bu_4N^+ salts of the $[Fe_4S_4Cl_4]^{2-}$ anion, in CH_3CN solution, with Li_2S (Aldrich, no. 21324-1) in a 2:1 molar ratio results in the formation of the $[(Fe_4S_4Cl_3)_2S]^{4-}$ tetraanions. From the dark brown CH_3CN solutions, the $(Et_4N)_4[(Fe_4S_4Cl_3)_2S]$ (I) and $(n\text{-}Bu_4N)_4[(Fe_4S_4Cl_3)_2S]$ (II) salts can be isolated in crude form by addition of diethyl ether. Recrystallization from CH_3CN/benzene and acetone/ether of I and II, respectively, afforded crystalline solids[11] in >60% yields. Repeated attempts to obtain crystals of high crystallographic quality for either I or II failed. Subsequently, the "mixed-cation" salt $(n\text{-}Bu_4N)_2(Ph_4P)_2[(Fe_4S_4Cl_3)_2S]$ (III) was obtained[11] by the addition of a CH_2Cl_2 solution of Ph_4PCl to an acetone solution of II. The resulting solution, after filtration, afforded single crystals of III upon the slow diffusion of ether.

A crystal structure determination[12] of III shows the tetraanion (Figure 2) as a μ_2-S^{2-} singly bridged double cubane. The anion is located on a crystallographic 2-fold axis that passes through the μ_2-S^{2-} ligand. Intercluster S–S repulsions involving S(1), S(4), S(1′), and S(4′) in III are relieved by a twist of one cubane subunit relative to the other. This twist is reflected in an Fe(1)Fe(4)S(5)/Fe(1′)Fe(4′)S(5) dihedral angle of 38.3°. The $\overline{\text{Fe–Fe}}$, $\overline{\text{Fe–S}}$, and $\overline{\text{Fe–Cl}}$ bond lengths[13] at 2.787 (11), 2.293 (5), and 2.227 (5) Å, respectively, are unexceptional and similar to those reported[14] for the $[Fe_4S_4Cl_4]^{2-}$ cluster at 2.766 (5), 2.295 (3), and 2.216 (2) Å. The Fe–S bridge bonds in III at 2.206 (4) Å are similar to those found[14] in $[Fe_2S_2Cl_4]^{2-}$ (2.200 (1) Å) and in the Fe–μ_2-S–Fe bridges of the doubly bridged double cubanes $\{[Fe_3S_4Cl_2Mo(Cl_4cat)]_2(S)_2\}^{6-}$ (IV) and $\{[MoFe_3S_4Cl_2(Cl_4cat)]_2(S)(OH)\}^{5-}$ (V) at 2.20 (2) and 2.22 (2) Å, respectively.[6] The Fe–Fe distance across the Fe–μ_2-S–Fe bridge in III, at 3.433 (4) Å, is significantly longer than the corresponding distances in IV and V of 3.33 (2) and 3.35 (1) Å. With the Fe–S bridge bonds in III, IV, and V being of similar length, the long Fe–Fe interbridge distance in III, when compared to the corresponding distance in IV and V, can be attributed to the oblique Fe–μ_2-S–Fe angle of 102.2°. The latter is somewhat larger than the corresponding angles in IV and V of 98.7 (8) and 97.8 (8)°, respectively. The Fe–μ_2-S–Fe angles in III, IV, and V are considerably more acute than the calculated Fe–μ_2-S-Fe angle in the coupled, "site-differentiated" cubane[9] of 145°. The latter value is calculated with an associated Fe–Fe interbridge distance of 4.20 Å and may reflect steric constraints imposed by the considerable bulk of the tripodal ligands present in the "site-differentiated" cubanes.

The electronic spectra of I, II, and III are similar to those of the $[Fe_4S_4Cl_4]^{2-}$ anion and display absorptions at 670 ($\epsilon = \sim 10\,700$), ~480 (sh, $\epsilon = \sim 17\,700$), and 240 nm ($\epsilon = \sim 57\,500$). The Mossbauer spectra for each of these compounds show broad, asymmetric quadrupole doublets with average values of isomer shift and quadrupole splitting of 0.48 and 0.98 mm/s for I and 0.48 and 0.64 mm/s for III. The cyclic voltammograms of I, II, and III obtained in CH_3CN solution[15] are virtually identical and show two quasi-reversible waves at −0.80 and −1.10 V. Perhaps the most useful diagnostic features that differentiate I, II, and III from $[Fe_4S_4Cl_4]^{2-}$ are found in the far-infrared spectra of these compounds. The skeletal vibrations of the clusters result in absorption bands with distinct energies and profiles that make it possible to distinguish I, II, or III, with vibrations at 394, 376, 361, 346, and 331 cm^{-1}, from $[Fe_4S_4Cl_4]^{2-}$, with vibrations at 383 and 352 cm^{-1}. The 400–300-cm^{-1} region of the spectrum is free from cation vibrations.

The coupling of unfunctionalized cubanes is not limited to the $[Fe_4S_4Cl_4]^{2-}$ clusters. Recent studies in our laboratory show that cubanes with thiolate terminal ligands also undergo μ_2-S^{2-} coupling reactions. In a manner resembling the synthesis of derivatives of IV and V,[16] the singly bridged double cubanes reported herein might very well undergo additional intracluster bridging reactions with bifunctional ligands such as N_2H_4, CN^-, N_3^-, etc. Studies of such reactions are currently in progress.[16]

Acknowledgment. This research was supported by a grant from the National Institutes of Health (GM-26671).

Supplementary Material Available: Tables S1–S3 containing listings of positional parameters, thermal parameters, and selected distances and angles of $(n\text{-}Bu_4N)_2(Ph_4P)_2[(Fe_4S_4Cl_3)_2S]$ (III) (8 pages); Table S4 listing structure factors of $(n\text{-}Bu_4N)_2(Ph_4P)_2[(Fe_4S_4Cl_3)_2S]$ (III) (12 pages). Ordering information is given on any current masthead page.

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(11) $(Et_4N)_4[(Fe_4S_4Cl_3)_2S]\text{-}C_6H_6$. Anal. Calcd for $Fe_8Cl_6S_9N_4C_{38}H_{86}$ (MW 1547): Cl, 13.76; S, 18.62; N, 3.62; C, 29.47; H, 5.56. Found: Cl, 14.4; S, 19.3; N, 3.5; C, 29.6; H, 5.4. $(n\text{-}Bu_4N)_4[(Fe_4S_4Cl_3)_2S]$. Anal. Calcd for $Fe_8Cl_6S_9N_4C_{64}H_{144}$ (MW 1917): Cl, 11.10; S, 15.03; N, 2.92; C, 40.07; H, 7.51. Found: Cl, 11.16; S, 14.39; N, 2.64; C, 39.39; H, 7.33. $(n\text{-}Bu_4N)_2(Ph_4P)_2[(Fe_4S_4Cl_3)_2S]$. Anal. Calcd for $Fe_8Cl_6S_9P_2N_2C_{80}H_{112}$ (MW 2111): Fe, 21.2; Cl, 10.1; P, 2.94; N, 1.26; C, 45.5; H, 5.31. Found: Fe, 20.2; Cl, 10.6; P, 2.76; N, 1.33; C, 45.9; H, 5.27. EPR: The anions in I, II, and III are EPR silent at temperatures >12 K. The spectra were not examined at lower temperatures.

(12) Crystal and refinement data: black crystals of $(n\text{-}Bu_4N)_2(Ph_4P)_2[(Fe_4S_4Cl_3)_2S]$ (III) are monoclinic, space group $C2/c$, with $a = 14.096$ (2) Å, $b = 18.943$ (7) Å, $c = 35.940$ (8) Å, $\beta = 94.55$ (1)°, and $Z = 4$. Single-crystal X-ray diffraction data for III were collected on a Nicolet P3F automated diffractometer using Mo Kα radiation. The solution of the structure was carried out by a combination of heavy-atom Patterson techniques, direct methods, and Fourier techniques. The refinement of the structures by full-matrix least-squares methods was based on 2889 unique reflections ($2\theta_{max} = 45°$, $I > 3\sigma(I)$). Anisotropic temperature factors were used for all non-hydrogen atoms except for one of the cation carbon atoms, which was refined isotropically. At the current stage of refinement on 478 parameters, $R = 0.049$.

(13) Mean values of chemically equivalent bond lengths. The standard deviations in parentheses represent the larger of (1) the standard deviations for an individual value estimated from the inverse matrix or (2) the standard deviation $\sigma = [\sum(x_i - x)^2/N(N-1)]^{1/2}$.

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(15) Cyclic voltammetry was carried out in CH_3CN solutions on a Pt electrode with n-Bu_4NClO_4 as a supporting electrolyte. The potentials are reported vs a saturated calomel electrode, SCE.

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