methylphosphine and are continuing to develop methods to convert our initial metallacycles to synthetically useful organic compounds.

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Supplementary Material Available: Experimental procedure for the preparation of **2b**, NMR and high-resolution mass spectral data for the compounds shown in Schemes II and III, and tables of final positional and thermal parameters and bond distances and angles (13 pages); tables of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

Subsite-Specific Functionalization of the $[4Fe-4S]^{2+}$ Analogue of Iron–Sulfur Protein Clusters

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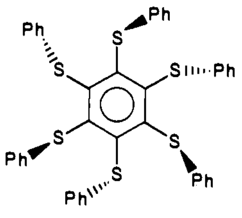
Structural and reactivity features are now known to be developed at specific iron subsites of protein-bound $Fe_4(\mu_3\text{-}S)_4(S\cdot Cys)_4$ clusters. Thus, siroheme in sulfite reductase is coupled to one cluster subsite by a bridging cysteinyl sulfur atom,[1] exogenous iron in the reconstitution $Fe_3S_4 \rightarrow Fe_4S_4$ is incorporated at one (at most two) subsite(s) of the product cluster,[2,3] substrate binds at this site in aconitase,[4,5] and a $CoFe_3S_4$ cluster has been produced by use of Co(II) in reconstitution.[6] One implication of these results is that the subsite voided in the oxidative transformation $Fe_4S_4 \rightarrow Fe_3S_4$ is that recovered in reconstitution. Analogue clusters $[Fe_4S_4L_4]^{2-}$ ($L = RS^-$, halide) exhibit statistical subsite reactions[7] and thus are unsuitable for probing subsite-specific features. We report here entry to clusters with one differentiated subsite and illustrative subsite-specific reactions thereof.



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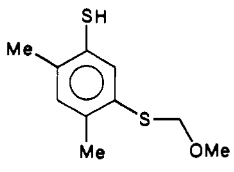

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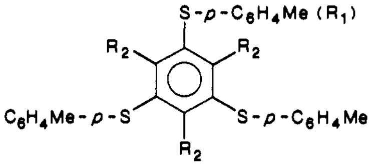
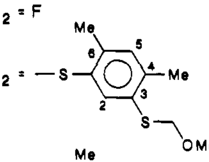
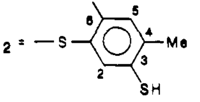


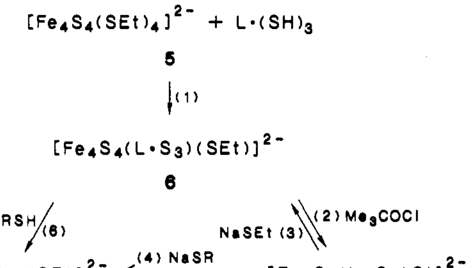
2, R_2 = F

4, R_2 =



5, R_2 =





The cavitand concept[8] and the alternating up–down stereochemistry of the "legs" of crystalline hexasubstituted benzenes such as **1**[9,10] (notation,[11] *ababab*) have been combined in the synthesis of a new type of semirigid tridentate ligand.[12] Reaction of 1,3,5-tribromo-2,4,6-trifluorobenzene[13] and *p*-tolyl thiocuprate[10b] (DMF, 140 °C, 36 h) gave **2** (56%). The sodium salt of thiol **3** [from 1,3-dimercapto-4,6-dimethylbenzene[14] + 2 equiv of NaH + 2 equiv of $ClCH_2OMe$ (DMF, 25 °C) followed by 1 equiv of NaSEt[15] (DMF, 160 °C, 60%)] combined with template **2** under conditions similar to those of MacNicol et al.[16] (DMEU, 70 °C, 5 days) gave bright yellow **4** (41%). Deprotection [$Hg(OAc)_2$, H_2S] afforded yellow, air-sensitive trithiol **5** (97%, 17% based on $1,3,5\text{-}C_6H_3F_3$). Equimolar ligand substitution reaction 1 in situ[12a] gave the ethanethiolate *mono*substituted cluster **6** (identified by ^{1}H NMR), which in reaction 2 afforded $(Ph_4P)_2[Fe_4S_4(L\cdot S_3)Cl]$ (**7**, 58%, from DMF/ether). The structure of anion **7**[12b] (Figure 1) proves formation of the desired cluster. The three R_2 legs of **7** lie on the same side of the planar central ring, with angles $C_{ring}\text{–}S\text{–}C = 103.1\ (1)\text{–}106.2\ (1)°$, binding three irons atoms; the remaining iron subsite is bound to chloride. Cluster atom S(4)

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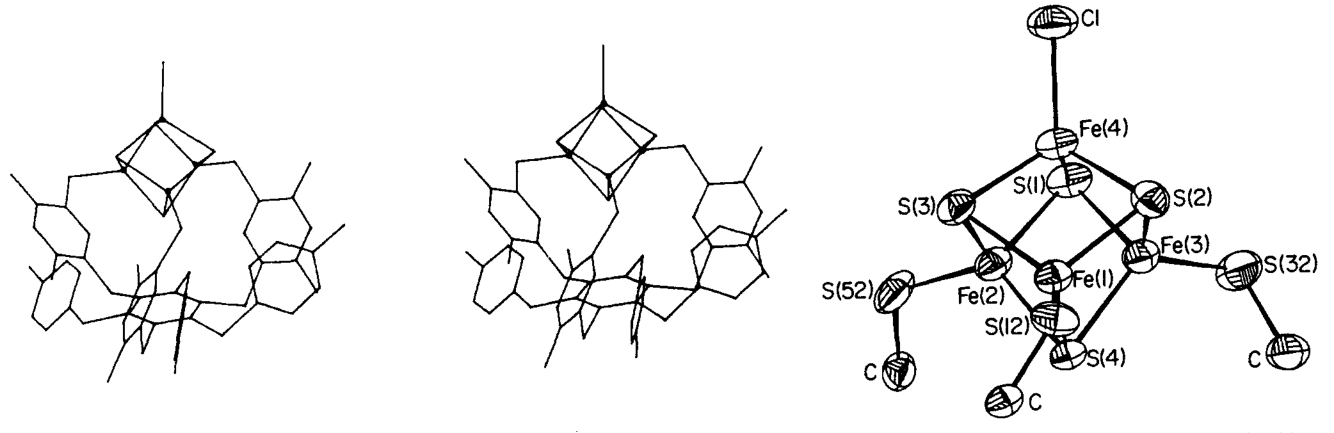

Figure 1. Left: Stereoview representation of the structure of 7, showing binding of the cluster and the *aaaaab* conformation of legs (• = Fe). Right: Structure of the cluster portion of 7. Mean values (Å, deg) of selected structural parameters: Fe–Cl, 2.226 (2); Fe ··· Fe, 2.766 (1); Fe–S, 2.287 (2); Fe–S(C), 2.261 (2); S–C, 1.772 (6); S–Fe–S, 103.64 (9); Fe–S–Fe, 74.41 (7).

is 3.74 Å from the centroid of the central ring, ~0.3 Å beyond van der Waals contact. Cluster dimensions are normal, and the only apparent ligand structural effect is suppression of the usual core tetragonal distortion of $[Fe_4S_4L_4]^{2-}$.[7] The ligand has the unprecedented *aaaaab* conformation.

In DMF solution cluster 7 exhibits λ_{max} (ϵ_M) = 480 (sh, 10000) and two one-electron reductions at −1.03 (reversible) and −1.80 V (irreversible) vs. SCE. A potential separation $\Delta E \approx 0.75$ V assures the presence of a Fe_4S_4 cluster.[17] Further, 7 shows *one* set of ^1H and ^{13}C NMR signals[18] indicative of a single species with effective trigonal symmetry. In contrast, $(Ph_4P)_2[Fe_4S_4(SPh)_2Cl_2]$[19] displays four meta H signals in CD_3CN (8.1–8.4 ppm),[12a] consistent with statistical disproportionation to $[Fe_4S_4(SPh)_{4-n}Cl_n]^{2-}$ (n = 0–3). Reactions 1–6 (R = 2,6-$C_6H_3Cl_2$) in situ, conducted stoichiometrically and monitored by ^1H NMR,[12a] have been shown to proceed with conversions of >90%. Thiolate groups are readily detected by their characteristic shifts: 13.2 ppm (SCH_2) in 6 and 8.34 ppm (meta H) in 8. The spectra of 6 and 8 also consist of a single set of signals. Given the sensitivity of isotropically shifted cluster resonances to structural differences,[20] we conclude that in solution **6–8** possess trigonal symmetry. This requires a conformational change of two R_1 legs to generate *ababab*. Rotational barriers may be low inasmuch as C_6(S-2-$MeC_6H_4)_6$ (9, two conformers: *aabbab* + *aaabbb*) and 4 (*aabaab*), whose indicated conformations have been established by X-ray crystallography,[21] show ^1H and ^{13}C NMR spectra (CD_2Cl_2, 210–300 K) consistent with trigonal symmetry.

These results demonstrate that a Fe_4S_4 cluster can be mounted on the semirigid tridentate ligand 5 with cavity occupancy and that the differentiated subsite is susceptible to high-yield substitution reacitons. These are the first *subsite-specific* reactions of synthetic Fe_4S_4 clusters. Cluster 7 in particular appears to be a potentially suitable vehicle for expression of the protein structural and reactivity features noted at the outset. Ligand 5 should accommodate the Fe_3S_4 cubane fragment (conceivably obtainable by oxidative removal of the unique subsite) proposed for protein sites[22,23] and is designed so as not to stabilize the alternative linear $Fe_3(\mu_2\text{-}S)_4$ unit found in the synthetic clusters $[Fe_3S_4SR_4]^{3-}$[24] and the unfolded form of aconitase.[25] These matters will be the subjects of future reports.

Acknowledgment. This research was supported by National Institutes of Health Grant GM 28856. X-ray diffraction equipment was obtained by NSF Grant CHE 80-00670 and NIH Grant 1 S10 RR 02247 and NMR equipment by NSF Grant 84-10774.

Supplementary Material Available: Tables of atom coordinates and thermal parameters for $(Ph_4P)_2[Fe_4S_4(L\cdot S_3)Cl]$ (8 pages). Ordering information is given on any current masthead page.

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Et_3B-Induced Radical Addition of R_3SnH to Acetylenes and Its Application to Cyclization Reaction

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The cyclization of vinyl acetylene to methylene-substituted five-membered rings has been described by Stork and Mook.[1] We have studied this reaction further and report that trialkylborane mediates a facile addition of R_3SnH to an acetylenic bond to give vinylstannane regioselectively, and this new method is applied to vinyl radical cyclization reactions[2,3] effectively.

The hydrostannation of acetylenes[4] takes place readily either in the absence of a catalyst or in the presence of a catalytic amount of free radical initiator such as azobisisobutyronitrile (AIBN),[5] but these reaction conditions (without solvent, heat to 80–100 °C)

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