previously reported organocobalt(III) complexes of these ligands.[4,12]

The electronic spectra of the complexes reported in Table I are all very similar and strongly dominated by charge transfer absorptions arising from the completely conjugated ligand. The electronic spectrum of [Co(I)-CH_3] consists of the following absorptions (extinction coefficients in parentheses): 830 nm (1.52×10^3) 560 (3.50×10^3), 370 (8.60×10^3), 330 (8.72×10^3). The lowest energy absorption may be of d–d origin, arising from the very strong tetragonal distortions present in these five-coordinate cobalt(III) complexes. The complexes are photosensitive with the secondary alkyl complexes decomposing much more rapidly than those with primary alkyl groups.

We have also found that iron(III) complexes of II undergo a redox reaction similar to the above cobalt complexes with alkyl- or arylhydrazines. Thus the reaction of high spin $[Fe(C_{22}H_{22}N_4)(NCS)]$ with $RNHNH_2$, R = $-CH_3$, $-C_2H_5$, or $-C_6H_5$, in acetonitrile under nitrogen yields low spin iron(III) complexes, $[Fe(C_{22}H_{22}N_4)R]$ (μ = 2.21 BM for R = $-CH_3$). These were presumed to be five-coordinate organoiron(III) complexes from the results of analytical and mass spectroscopic data.

Unlike the organocobalt(III) complexes, where the nmr spectra serve as a diagnostic tool for confirmation of cobalt–alkyl or –aryl bonds, these paramagnetic iron complexes are less amenable to structural proof. The reports of iron(III) alkyls are rare[13,14] and those which appear to be well characterized differ in spin state[14b] from those which we have isolated. Also, an attack of the alkyl group on the ligand nitrogen might be possible since *N*-methylated porphyrins and their metal complexes are known.[15] Complexes of this type would not be differentiable from a five-coordinate organoiron complex on the basis of elemental analysis or mass spectroscopic data. For these reasons, the crystal structure of the iron(III) phenyl compound was determined to more fully characterize this unusual species.

Crystals of the complex $[Fe(C_{22}H_{22}N_4)(C_6H_5)]$ belong to space group $P\bar{1}$, with a = 9.645 (1) Å, b = 12.544 (1) Å, c = 9.969 (1) Å, α = 88.26 (1)°, β = 76.82 (1)°, γ = 72.22 (1)°, ρ_{calcd} = 1.408, and ρ_{found} = 1.39 g/cm^3 for which Z = 2. The structure was solved by the heavy-atom method and refined with full-matrix least-squares techniques to R_1 = 6.6 and R_2 = 4.7% using 4206 data with F's > 3σ.[16]

The molecular structure consists of five-coordinate iron(III) σ bonded to the carbon of phenyl ring and the four nitrogen atoms of a dianionic macrocyclic ligand. The structure and pertinent distances and angles are presented in Figure 1. The ligand is not flat but rather is saddle shaped due to steric interactions of the methyl groups with the hydrogen atoms of the benzenoid rings. The Fe–N distances are markedly shorter, 1.90–1.91 Å, than those observed in the low spin bis(imidazole)-

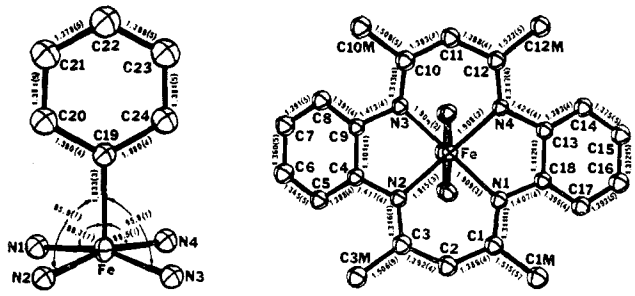

Figure 1. Two views, labeling scheme, and the important distances and angles in $[Fe(C_{22}H_{22}N_4)C_6H_5]$.

tetraphenylporphyriniron(III) species where the Fe–N(porphyrin) distances vary from 1.980 (4) to 1.999 (4) Å.[17] The Fe–C distance is shorter than that observed in Co(III)–C bonds and is indicative of a very strong σ bond. The orientation of the phenyl ring minimizes the steric interactions of the hydrogen atoms of C20 and C24 with the nitrogen atoms of the ligand. The iron atom is displaced significantly from the least-squares plane of the four nitrogen atoms, 0.23 Å. This is probably due to contractile forces of the macrocyclic ligand as well as the strong binding of the phenyl ligand in the fifth coordination site and the absence of any ligand in the sixth position.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health, Grant No. HL14827, for support of this work.

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Synthetic Analogs of the Active Sites of Iron–Sulfur Proteins. IV.[1] Ligand Substitution Reactions of the Tetranuclear Clusters $[Fe_4S_4(SR)_4]^{2-}$

Sir:

We have recently reported the synthesis and structural and partial electronic characterization of low molecular weight iron–sulfur complexes[1-3] which serve as close representations of the active sites of several classes of iron–sulfur proteins.[4] The tetranuclear cluster complexes $[Fe_4S_4(SR)_4]^{2-}$ (R = alkyl, aryl) possess the same total oxidation level as the $Fe_4S_4(S\text{-}cys)_4$ centers in reduced "high-potential" (HP_{red}) and oxidized bacterial ferredoxins[2,3] (Fd_{ox}), and the Fe_4S_4 core of the prototype species $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ has a distorted (D_{2d}) cubane stereochemistry.[2,3] Structures

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(13) D. A. Clarke, R. Grigg, and A. W. Johnson, *Chem. Commun.*, 208 (1966).
(14) (a) F. Calderazzo and C. Floriani, *Chem. Commun.*, 417 (1968); (b) C. Floriani and F. Calderazzo, *J. Chem. Soc. A*, 3665 (1971).
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(16) $R_1 = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$; $R_2 = \{\Sigma[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$.

(1) Part III: J. J. Mayerle, R. B. Frankel, R. H. Holm, J. A. Ibers, W. D. Phillips, and J. F. Weiher, *Proc. Nat. Acad. Sci. U. S.*, 70, 2429 (1973).
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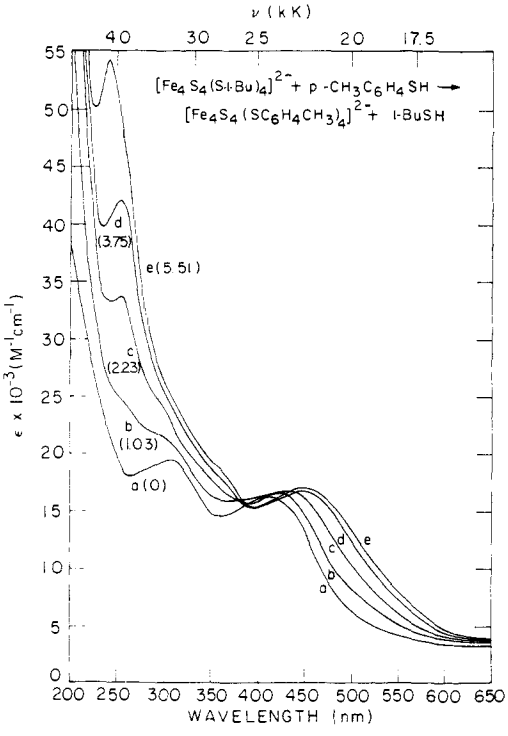

Figure 1. Spectral changes produced by the addition of various amounts of *p*-tolylthiol to an acetonitrile solution of $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$ *(initially* 3.0×10^{-3} *M)* at ~25°. The numerical values are the mole ratios of added thiol to original tetramer. Spectra were recorded under anaerobic conditions.

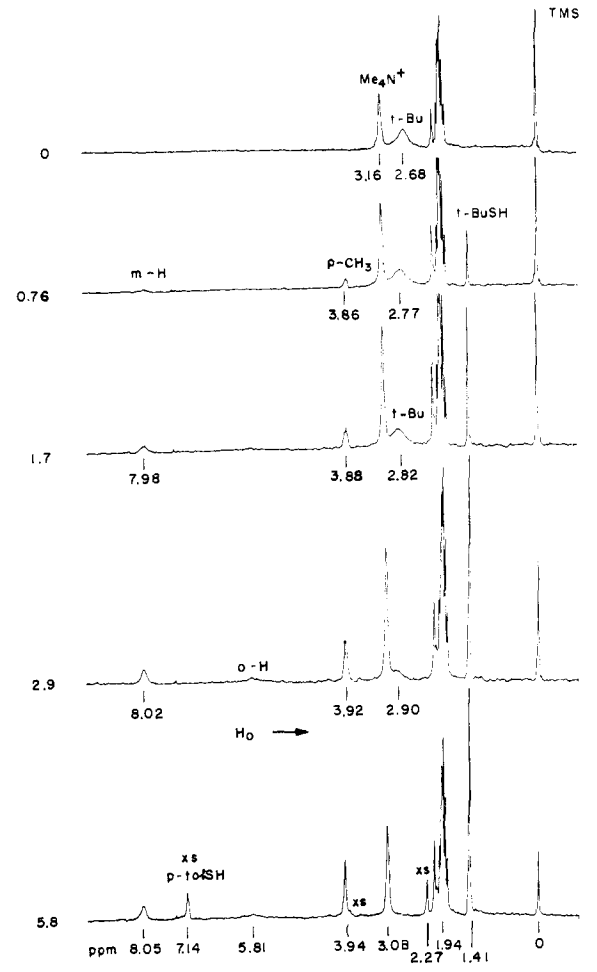

Figure 2. Fourier transform pmr spectra (60 MHz) of the system $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$–*p*-tolylthiol in CD_3CN solution at ~30°. The concentration of initial tetramer was 1.1×10^{-2} *M;* numerical values are the mole ratios of added thiol to original tetramer. The complex feature at 1.94 ppm is due to residual solvent protons and water. Spectra were recorded under anaerobic conditions.

of the active sites in HP_{red}[5] and Fd_{ox}[5,6] proteins are unquestionably closely similar to that of the synthetic analog. The paramagnetic nature of the latter[2] suggests lability of mercaptide coordinated to the approximately tetrahedral iron centers. We disclose here the occurrence of facile ligand exchange reactions (eq 1) which expand the fundamental chemistry and enhance the biological relevance of these systems.

$$[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-} + n\text{R}'\text{SH} \rightleftharpoons [Fe_4S_4(S\text{-}t\text{-}Bu)_{4-n}(\text{SR}')_n]^{2-} + n\text{t-BuSH} \quad (1)$$

Addition of *p*-tolylthiol to an acetonitrile solution of $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$ affords the spectral changes displayed in Figure 1. The spectrum of the initial tetramer (curve a, λ_{max} 413 nm, ϵ 16,900) is altered upon addition of 1 equiv of thiol (λ_{max} 422 nm). Further addition of thiol results in a progressive red shift until at a (R′SH)/(tetramer) mole ratio exceeding four (curve e) a spectrum essentially identical with that of $[Fe_4S_4(S\text{-}p\text{-}tol)_4]^{2-}$ measured separately (λ_{max} 453 nm, ϵ 17,200) is obtained. This system has been additionally examined by FT pmr spectroscopy (Figure 2). The spectrum of $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$ reveals a broad *t*-Bu methyl resonance at 2.68 ppm, which has been displaced 1.27 ppm downfield from that of *t*-BuSH by isotropic magnetic interactions.[7] Introduction of *p*-tolylthiol results in the emergence of three signals downfield of the Me_4N^+ resonance and a feature at 1.41 ppm due to *t*-BuSH, all of which increase in intensity as thiol is added. At (R′SH)/(tetramer) = 5.8 free *p*-tolylthiol signals are clearly evident (ring-H, 7.14; Me, 2.27; SH, ~3.84 ppm) and the coordinated *t*-Bu peak has disappeared. Only at ratios exceeding 4/1 are free thiol resonances observed, indicating nearly quantitative substitution, and under these conditions shifts of the three downfield peaks are identical with those of $[Fe_4S_4(S\text{-}p\text{-}tolyl)_4]^{2-}$ measured separately. Signals of mixed ligand tetramers are resolved at 100 MHz. At (R′SH)/(tetramer) = 2.0 four isotropically shifted resonances of the *p*-Me group are observed at 3.81, 3.84, 3.88, and 3.91 ppm. Spectra obtained at ratios in the range 0.3–5.0 indicate that these resonances arise from the n = 1, 2, 3, 4 species, respectively. No evidence of disruption of the Fe_4S_4 core has been found.[8]

Similar experiments reveal reactions of $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$ with aliphatic thiols; larger ratios are required to effect full substitution. Reaction of excess (~5/1) *N*-acetyl-L-cysteine-*N*-methylamide[9] with the tetramer in acetonitrile (1.5×10^{-3} *M*) produces a band (λ_{max}

(5) C. W. Carter, Jr., J. Kraut, S. T. Freer, R. A. Alden, L. C. Sieker, E. Adman, and L. H. Jensen, *Proc. Nat. Acad. Sci. U. S.*, **69**, 3526 (1972).

(6) E. T. Adman, L. C. Sieker, and L. H. Jensen, *J. Biol. Chem.*, **248**, 3987 (1973).

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(9) B. A. Averill, Ph.D. Thesis, M.I.T., 1973.

402 nm, $\epsilon \sim 15{,}400$) closely similar to that of *C. acidiurici* Fd_{ox}[10] (per active site). Pmr studies (FT, 60 MHz) in DMSO-d_6 further substantiate incorporation of Ac-L-cys-NHMe into the tetramer, resulting in formation of the Fe–S–CH_2–CH– unit in common with the proteins.[5,6] At, *e.g.*, a 7.7/1 ratio (initial tetramer 1.9×10^{-2} *M*), signal integration indicates complete substitution by added thiol, and isotropically shifted signals are observed at 13.0 ppm (CH_2, $\Delta\nu_{1/2}$ 160 Hz) and at 5.3 ppm (CH, $\Delta\nu_{1/2}$ 24 Hz) downfield of TMS. These data provide the first independent corroboration of β-CH_2 cysteinyl proton assignments in the pmr spectra of HP_{red} and Fd_{ox} proteins.[11] Pmr experiments also indicate the feasibility of forming tetramers linked by substitution reactions with dithiols. At (1,4-benzenedithiol)/(tetramer) ratios up to 1.3/1 in DMSO-d_6, *t*-BuSH but no free dithiol signals are observed. At a 0.5/1 ratio a broad feature at 5.9 ppm is evident and is tentatively assigned to dithiolate protons in $[(S\text{-}t\text{-}Bu)_3S_4\text{-}Fe_4\text{-}SC_6H_4S\text{-}Fe_4S_4\text{-}(S\text{-}t\text{-}Bu)_3]^{4-}$.

These results suggest the feasibility of several experiments which further explore the utility of $[Fe_4S_4(SR)_4]^{2-}$ as active site analogs. These include (i) protein reconstitution from the apoprotein and preformed cluster, (ii) extrusion of the intact Fe_4S_4 active site core from the holoprotein, and (iii) variable separation linkage of clusters thereby allowing examination of coupled redox and electronic interactions such as may exist between the two sites in 8-Fe ferredoxins. Further investigation of ligand substitution reactions is in progress.

Acknowledgment. This research was supported by NIH Grant GM-19256.

(10) J.-S. Hong and J. C. Rabinowitz, *J. Biol. Chem.*, **245**, 4982 (1970).

(11) These assignments refer to signals in the ~10–20 ppm downfield range: (a) W. D. Phillips, M. Poe, C. C. McDonald, and R. G. Bartsch, *Proc. Nat. Acad. Sci. U. S.*, **67**, 682 (1970); (b) M. Poe, W. D. Phillips, C. C. McDonald, and W. Lovenberg, *ibid.*, **65**, 797 (1970); (c) M. Poe, W. D. Phillips, C. C. McDonald, and W. H. Orme-Johnson, *Biochem. Biophys. Res. Commun.*, **42**, 705 (1971); (d) C. C. McDonald, W. D. Phillips, W. Lovenberg, and R. H. Holm, *Ann. N. Y. Acad. Sci.*, in press; (e) W. D. Phillips, C. C. McDonald, N. Stombaugh, and W. H. Orme-Johnson, *Proc. Nat. Acad. Sci. U. S.*, in press.

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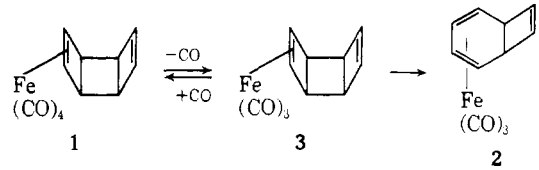
Disrotatory Ring Opening of Cyclobutene–Iron Carbonyl Complexes

Sir:

Several examples of facile transition metal catalyzed rearrangements of organic species, leading to products which would be "forbidden" by any concerted process in the absence of the metal, are now known. It is clearly of importance to determine whether the organic moiety, presumably now a ligand coordinated to the metal, is undergoing concerted rearrangement under these conditions. One such reaction is the facile disrotatory ring opening of strained cyclobutenes catalyzed, *inter alia*, by silver and cuprous ions.[1] Theoretical arguments have been produced indicating that the concerted disrotatory ring opening of a cyclobutene–Ag^+ olefin complex to a butadiene–Ag^+ complex is an "allowed" process;[1,2] however, the reality of this process has been brought into question.[3] We report now an analogous noncatalyzed reaction of cyclobutene–iron carbonyl complexes for which a concerted process is indicated.

Treatment of *syn*-tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene with $Fe_2(CO)_9$ affords *syn*-tricyclooctadiene–iron tetracarbonyl (**1**); the nmr spectrum of this complex clearly indicates that the organic ligand is attached to the metal by means of the standard olefin–metal interaction.[4]

In refluxing hexane, complex **1** is readily converted to bicyclooctatriene–iron tricarbonyl (**2**),[5] presumably



1 **3** **2**

having the anti configuration indicated. The rate of conversion of complex **1** to complex **2** is not significantly affected upon changing the solvent from hexane to methanol; hence, an ionic process is not indicated. The conversion is strongly inhibited by CO and added olefins such as dimethyl maleate and excess *syn*-tricyclooctadiene. Accordingly, we propose that the formation of **2** involves thermal loss of CO from complex **1** to yield the monoolefin–$Fe(CO)_3$ complex (**3**) in which the effective atomic number of iron is now two less than that of krypton. The organic ligand in **3** then undergoes concerted disrotatory ring opening of the coordinated ring to yield the butadiene–$Fe(CO)_3$ complex **2** in which the electronic inert gas structure about iron is regained. Added potential ligands such as CO and olefins would reduce the concentration of complex **3** and provide the observed inhibitory effect.

In an analogous manner *anti*-tricyclooctadiene and *syn*-tricyclooctene react with $Fe_2(CO)_9$ to produce the corresponding olefin–$Fe(CO)_4$ complexes **4** and **5**, respectively.[6] These latter complexes react in refluxing hexane giving *syn*-bicyclooctatriene–$Fe(CO)_3$ (**6**)[7] and *anti*-bicyclooctadiene–$Fe(CO)_3$ (**7**),[8] respectively. In refluxing hexane the extrapolated half-lives for the ring opening of the complexes **1** and **4** are 2.5 and 2 hr,[9] respectively, whereas for the free ligands, under

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(2) M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971).

(3) (a) L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 3515 (1970); F. D. Mango, *Tetrahedron Lett.*, 1509 (1973). (b) In accordance with a referee's suggestion we stress that the use of the term "concerted" in these processes is directed only to that part of the overall reaction pathway in which the carbon framework is undergoing rearrangement to that which is finally observed.

(4) The nmr spectrum (acetone-d_6) exhibits absorption at τ 3.57 (t, 2), 6.07 (d, 2), and 6.7–7.1 (m, 4).

(5) This compound as well as all new compounds gave satisfactory analyses. The nmr spectrum (acetone-d_6) exhibits absorption at τ 3.78 (s, 2), 4.35 (m, 2), 6.65 (m, 2), and 6.9 (m, 2).

(6) As in the case of *syn*-tricyclooctadiene a bisiron tetracarbonyl complex can also be obtained from *anti*-tricyclooctadiene. The nmr spectrum (acetone-d_6) of **4** exhibits absorption at τ 3.54 (t, 2), 5.8 (d, 2), 6.8 (m, 2), and 7.2 (m, 2).

(7) The nmr spectrum (acetone-d_6) of **6** possesses absorption at τ 3.95 (s, 2), 4.56 (m, 2), 6.5 (m, 2), and 7.4 (br s, 2).

(8) E. O. Fischer, C. Palm, and H. Fritz, *Chem. Ber.*, **92**, 2645 (1959).

(9) There also occurs some thermal degradation of the complexes **1** and **4** to liberate the free organic ligands which then inhibit the formation of the bicyclooctatriene complexes. The estimated half-lives of