was found to be ~65 kcal/mol in complete consistency with our conclusions.

In summary, measurement of the direct chemiluminescence from reaction 1 as a function of temperature allows us to conclude that neither formation of ^1A nor ^3A is activated beyond the activation required to achieve the transition state for disappearance of 1. This in turn implies that the latter TS possesses a higher energy content than ^1A or ^3A and that ϕ_*^T/ϕ_*^S is temperature independent.[11]

(11) Although we have confidence in the reliability of the data reported here, we should point out that in certain solvents an apparently catalyzed, nonchemiluminescence pathway may dominate the decomposition of dioxetane. An experimental clue to the occurrence of this complication is the observance of very low activation energies ($\Delta E < 20$ kcal/mol).[5b,c] We feel that the high activation energies, relative to previous reports and the demonstration of high yields of excited states, make the possibility of catalytic paths in our system very unlikely.

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A New Route to the Formation of Organocobalt(III) and Organoiron(III) Complexes. Alkylation via Oxidative Deamination of Organic Hydrazines

Sir:

Considerable attention has been focused on the formation of cobalt(III)-carbon bonds during the past 10 years.[1-5] The routes to organocobalt(III) complexes are contained in a recent comprehensive review.[6] We report herein a new route to the formation of stable organometallic complexes from organic hydrazines and cobalt or iron complexes of quadridentate or macrocyclic ligands, two of which are shown below.[7]

I   II
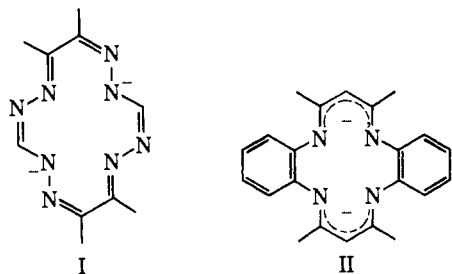
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(7) Bis(dimethylglyoximato), *N,N*-ethylenebissalicylideniminato, and 6,7,13,14-tetramethyl-1,2,4,5,8,9,11,12-octaazacyclotetradeca-5,7,12,14-tetraene complexes of cobalt undergo similar reactions with some organic hydrazines.

Organic hydrazines are usually not considered to be alkylating agents. However, they are easily oxidized, going through diazene intermediates.[8] These diazenes can be oxidized further or they can decompose spontaneously to molecular nitrogen and organic radicals.[9] The oxidation of organic hydrazines is catalyzed by transition metals,[10] and the possibility of trapping the resulting organic fragments by suitable transition metal complexes, especially of cobalt, appeared highly likely.[10a]

The organocobalt(III) complexes are formed simply by the addition of the appropriate organic hydrazine to a solution of the cobalt(II) complex, followed by the addition of 1 atm of oxygen. During the ensuing exothermic reaction, molecular nitrogen is evolved and the organocobalt(III) complexes are formed. The reactions are normally carried out in acetonitrile and the complexes are precipitated by the addition of water. Yields are generally high and nearly quantitative with the cobalt(II) complex of I. Five-coordinate complexes of the type Co(I)R have been isolated using hydrazines where R = $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2CH_3$, $-CH(CH_3)_2$, $-COCH_3$, $-COOC_2H_5$, $-C_6H_5$, and $-CH_2-C_6H_5$ (Table I).[11] Although the greatest variety of

Table I. Some of the New Complexes and Their Nmr Spectra

Compound[a]	Nmr (in CDCl₃)[b]
[Co(I)CH₃]	7.96(s, 2); 2.69(s, 6); 2.42(s, 6); 0.04(s, 3)
[Co(I)C₂H₅]	7.96(s, 2); 2.68(s, 6); 2.43(s, 6); 1.28(q, 2); −0.20(t, 3)
[Co(I)CH₂C₂H₅]	7.93(s, 2); 2.70(s, 6); 2.43(s, 6); 1.12 (t, 2); 0.8–1.8(m, 2); 0.55(t, 3)
[Co(I)CH(CH₃)₂]	7.97(s, 2); 2.69(s, 6); 2.43(s, 6); 1.6–2.2(m, 1); −0.03(d, 6)
[Co(I)CH(CH₃)(C₅H₅)]	7.97(s, 2); 2.68(s, 6); 2.43(s, 6); 1.0–2.4(m, 3); 0.62(t, 3); −0.18(d, 3)
[Co(I)C₆H₅]	8.25(s, 2); 2.82(s, 6); 2.52(s, 6); 5.6–6.1, 6.5–6.9, 7.3–7.4 (m, 5)
[Co(I)CH₂C₆H₅]	8.05(s, 2); 2.55(s, 6); 2.30(s, 6); 1.8–2.4(m, 2); 6.4–7.4 (m, 5)
[Co(I)COCH₃]	7.93(s, 2); 2.72(s, 6); 2.45(s, 6); 2.02 (s, 3)
[Co(I)CO₂C₂H₅]	8.17(s, 2); 2.83(s, 6); 2.52(s, 6); 3.18 (q, 2); 0.83(t, 3)

[a] (I) = $C_{10}H_{14}N_6$. [b] Numbers in parentheses refer to the integrated intensity of the absorptions. The meaning of the symbols is as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

organocobalt(III) complexes has been obtained with ligand I, we have been successful in obtaining at least methyl and ethyl derivatives with a variety of other ligands.[7] The new complexes of ligands I and II are five coordinate, whereas those of ref 7 are generally six coordinate and are identical in all respects with the

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(10a) Note Added in Proof. A reaction similar to that described here has recently been reported (P. Braunstein, *J. Chem. Soc., Chem. Commun.*, 851 (1973), in which aryl–gold(III) complexes are formed by the reaction of tetrachloro- or tetrabromoaurate(III) with phenylhydrazine hydrochloride.

(11) All compounds reported gave satisfactory elemental analyses and the parent peak for each was observed in high resolution mass spectrum.

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)-CH₃] consists of the following absorptions (extinction coefficients in parentheses): 830 nm (1.52 × 10³) 560 (3.50 × 10³), 370 (8.60 × 10³), 330 (8.72 × 10³). 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 RN-HNH₂, R = -CH₃, -C₂H₅, or -C₆H₅, in acetonitrile under nitrogen yields low spin iron(III) complexes, $[Fe(C_{22}H_{22}N_4)R]$ (μ = 2.21 BM for R = -CH₃). 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/cm³ 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)-
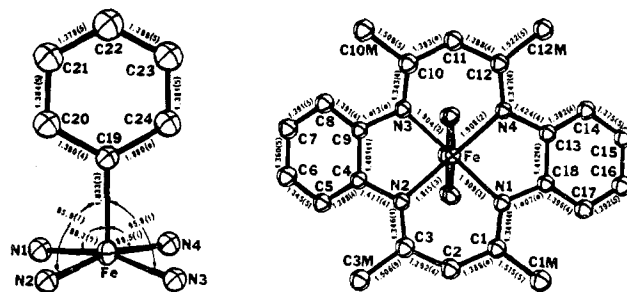

Figure 1. Two views, labeling scheme, and the important distances and angles in $[Fe(C_{22}H_{22}N_4)C_6H_5]$.

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.

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Synthetic Analogs of the Active Sites of Iron–Sulfur Proteins. IV.[1] Ligand Substitution Reactions of the Tetranuclear Clusters [Fe₄S₄(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 Fe₄S₄(S-cys)₄ centers in reduced "high-potential" (HP$_{red}$) and oxidized bacterial ferredoxins[2,3] (Fd$_{ox}$), and the Fe₄S₄ 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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(16) $R_1 = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$; $R_2 = \{\Sigma[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$.