(7) See Figures 2 and 3 in ref 6.
(8) Infrared spectra of isoelectronic D_{3h} M(CO)$_5^-$ (M = Mn, Tc, Re) and Fe(CO)$_5$ show E' and A$_2$'' modes at substantially higher energy. Sodium salts of M(CO)$_5^-$ in tetrahydrofuran absorb at 1898 (s), 1864 (s) (M = Mn), 1911 (s) and 1865 (s) (M = Tc) and 1910 (s) and 1864 (s) (M = Re).[9] Neutral Fe(CO)$_5$ in Nujol absorbs at 2024 (s) and 1984 (s).[10] All values are in cm^{-1}.
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(12) While Na$_2$Cr(CO)$_5$ shows sharp bands at 1760 and 1722 cm^{-1} in HMPA, it exhibits a sharp band at considerably higher frequency, 1819 cm^{-1}, and a broad absorption at ca. 1768 cm^{-1} in THF. Behrens, et al.,[2] suggest that the latter absorption consists of two bands (1772, 1738 cm^{-1}) and on this basis assign a symmetry of C_{4v} to Cr(CO)$_5^{2-}$ in THF. Edgell has established that ion pair formation in THF can effectively lower the symmetry of carbonylmetalate ions; e.g., that of Co(CO)$_4^-$ (counterion Na$^+$) is lowered from T_d to C_{3v} in THF.[13] It appears likely that Na$_2$Cr(CO)$_5$ exists in THF as tight ion pairs in view of Collman's evidence that constitutionally similar Na$_2$Fe(CO)$_4$ forms such ionic aggregates in this solvent. In contrast, ion pair formation in HMPA is relatively unimportant for Na$_2$Fe(CO)$_4$[14] and, by inference, for Na$_2$Cr(CO)$_5$.
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Received August 26, 1974

Carbon Monoxide and Methyl Groups as Symbiotic Trans Ligands in an Iron(II) Complex, [Fe(C$_{10}$H$_{19}$N$_8$)(CO)(CH$_3$)]

Sir:

The synthetic non-porphyrin macrocyclic complexes of iron have recently been shown to have a very diverse chemistry which complements the naturally occurring iron heme systems. Redox reactions have been observed in which iron assists in the oxidation of the planar macrocyclic ligand,[1] iron(III) alkyls have been formed by the oxidative deamination of alkyl hydrazines,[2] a number of iron(II) complexes have been shown to reversibly bind carbon monoxide,[3,4] and iron(I) complexes, including iron(I) hydrides, have been characterized.[5]

This report describes the preparation and structural characterization of a macrocyclic iron(II) complex which contains carbon monoxide and a methyl group in the axial positions. The results of this structural characterization are relevant to the study of the interaction of carbon monoxide with the isoelectronic cobalt(III)–alkyl complexes.[6] There has been intense interest in the reductive Co–C bond cleavage of alkylcorrins and other vitamin B$_{12}$ model compounds by carbon monoxide.[7] Evidence has been obtained for the existence of 1:1 carbon monoxide complexes of methylcobaloxime in solution,[8] but we are unaware of any successful attempts in which carbon monoxide adducts of cobalt(III)–alkyl complexes have been isolated. However, the analagous complexes of iron(II) should be more stable for the following reasons. First, low spin iron(II) forms stronger carbon monoxide complexes because it has better π-donor properties than cobalt(III). Stable carbon monoxide complexes of synthetic macrocyclic complexes of iron(II) have been well characterized.[3,4] Secondly, although iron(II)–alkyl complexes of tetraaza ligands are rare, alkyl complexes of bis-α,α'-dipyridyliron(II) are known.[9] Macrocyclic ligands containing α-diimine functions, such as I, might also stabilize iron(II)–alkyl bonds. Thirdly, a symbiotic relationship may exist between the bonding of carbon monoxide and alkyl groups whose trans effects are composed of

contrasting interactions, i.e., the strong π-acceptor properties of carbon monoxide vs. the strong σ-donor properties of alkyl groups.

The reaction of the bis-α-diimineiron(II) complex, I,[10] with carbon monoxide and CH$_3$NHNH$_2$ in trifluoroethanol results in the formation of a complex, [Fe(C$_{10}$H$_{20}$-N$_8$)(CO)(CH$_3$NHNH$_2$)]$^{2+}$, containing weakly bound carbon monoxide (ν = 2035 cm^{-1}). Dissolution of the complex in acetonitrile results in rapid loss of CO. However, if the complex is dissolved in acetonitrile under 1 atm of CO pressure, followed by the addition of potassium tert-butoxide with a slight excess of methylhydrazine, a complicated series of reactions takes place. The strongly basic alkoxide deprotonates the ligand. It may also result in some disproportionation of the iron to the univalent and trivalent states in a manner similar to that established for the disproportionation of cobaloximes under basic conditions.[11] Oxidative deamination of CH$_3$NHNH$_2$ also occurs with the methyl group being transferred to iron, as observed for some other cobalt and iron complexes,[2] yielding the desired complex, [Fe(C$_{10}$H$_{19}$N$_8$)(CO)(CH$_3$)] (II).[12]
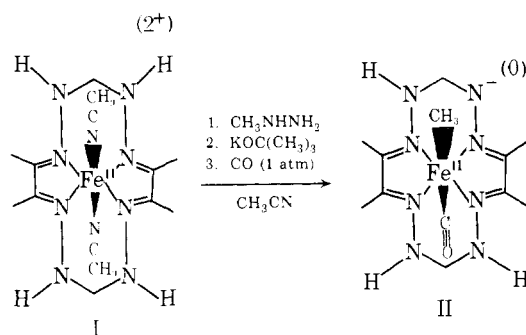
The compound is stable in wet or dry DMSO solutions for weeks when under a carbon monoxide atmosphere. It is not noticeably light sensitive, but does decompose rapidly when exposed to molecular oxygen. The carbon monoxide binding, which competes with the strong π-acceptor properties of the α-diimine functions of the macrocyclic ligand, is strengthened by the increased electron density placed on the iron by the methyl group. The carbon monoxide stretching frequency in [Fe(C$_{10}$H$_{19}$N$_8$)(CO)(CH$_3$)] (ν = 1925 cm^{-1}) is about 100 cm^{-1} lower than with CO complexes of iron(II) complexes with α-diimine ligands of I and the complexes described by Rose, et al.[3] The carbon monoxide in turn provides the iron(II) with an electronic environment conducive to forming a stable bond with the strong σ-donor properties of CH$_3^-$. The nmr spectrum (δ; solvent, DMSO-d; Fe–CH$_3$, 0.15 ppm; ligand CH$_3$'s, 2.05 and 2.20 ppm; ligand CH$_2$'s, 4.3 and 3.85 ppm) is similar to that expected for analogous Co(III) CH$_3$ complexes. The compound reacts with strong acids to give CH$_4$ and with Hg^{2+} in DMSO-d immediately (on mixing) to produce CH$_3$Hg$^+$ (nmr, 0.9 ppm).

The crystal structure of this complex was determined to examine the nature of the bonding of the coordination sphere and to establish whether the dominating trans effect is produced by the methyl group or carbon monoxide.

Crystals of the compound were found to belong to the space group Cmcm: a = 8.237 (2), b = 13.929 (4), c = 13.418 (4) Å; ρ_{calcd} = 1.51, ρ_{expl} = 1.49 g cm^{-1} for which Z = 4. A total of 1093 reflections were measured to sin θ/λ = 0.6497 on a Picker-FACS-1 diffractometer with Mo Kα radiation. The structure was solved by the heavy atom method and refined by conventional full-matrix least squares and Fourier techniques. Refinement of the positional and anisotropic thermal parameters for all non-hydrogen atoms converged to a final R = 4.2% (R_w = 3.4%) with 872 data with
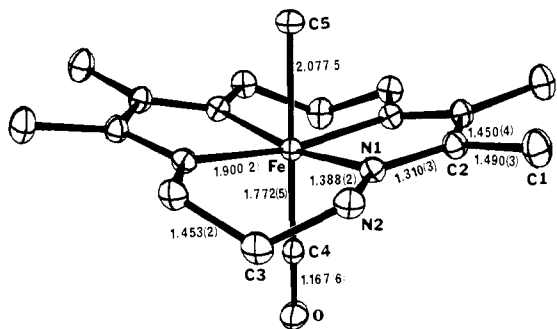
Figure 1. Structure, labeling scheme, and selected interatomic distances of $[Fe(C_{10}H_{19}N_8)(CO)(CH_3)]$.

F's $\geq 2\sigma$. All of the hydrogen atoms were located on a difference Fourier and then their positions were recalculated assuming normal geometry and a C–H distance of 0.95 Å. These were then included, but at fixed positions, in the final refinement. See paragraph at the end of the paper regarding supplementary material.

The structure consists of six-coordinate iron(II) coordinated to a macrocyclic ligand, a molecule of carbon monoxide, and a methyl group (Figure 1). The $CH_3FeC\equiv O$ axis is constrained to lie on the intersection of two perpendicular crystallographic mirror planes.[13]

The most significant aspect of the structure is that the Fe^{II}–CH_3 distance, 2.077 (5) Å, is markedly longer than might be predicted on the basis of known Co^{III}–C distances and the Fe–C distance, 1.933 (3) Å, of an iron(III)–aryl complex.[2] A similar lengthening of metal–carbon distance can be expected to occur on the interaction of carbon monoxide with alkyl corrins and could easily account for increased ease of cobalt–carbon bond rupture. The observed bond lengthening must be attributed to the weakening produced by the overriding trans effect of carbon monoxide. The remaining interatomic distances are normal. The Fe(II)–N distances, 1.900 (2) Å, are shorter than observed for most low-spin Fe(II)–N distances but are comparable to those found in the bisimidazole–bis(DMG) complex of Fe(II),[14] which also has "pure" α-diimine chelate moieties. The Fe(II) is displaced slightly, 0.187 Å, toward the carbon monoxide molecule from the least-square plane of the four nitrogen atoms.

Supplementary Material Available. A listing of atomic coordinates and structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D., C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-7826.

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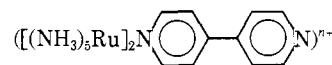
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Mixed Valence Complexes of Ruthenium Ammines with 4,4'-Bipyridine as Bridging Ligand

Sir:

Previous work on the complexes

($n = 4$, 5, and 6 to be denoted [2,2], [2,3], and [3,3] respectively) gave contradictory spectral and electrochemical results.[1-4] There did, however, seem to be agreement on the point that the stability of the mixed valence state when 4,4'-bipyridine bridges the ruthenium atoms is much less than for pyrazine as the bridging group.[5,6] In view of the current interest[7] in mixed valence complexes and of the fact that the nature of the ion
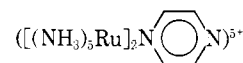
is not yet understood, we felt it worthwhile to investigate the 4,4'-bipyridine system further in the hope of illuminating the subject of mixed valence complexes.

The [2,2] species was formed by the reaction in acetone under argon of $(NH_3)_5RuOH_2(PF_6)_2$ and 4,4'-bipyridyl in 2:1 molar ratio. After 2 hr in the dark, the [2,2] complex

I
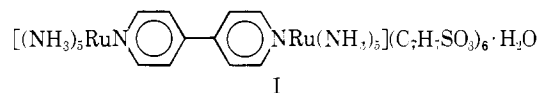
was precipitated by the addition of two volumes of ether. Oxidation of the [2,2] ion with Br_2 in 0.1 M HCl was followed by precipitation of the tosylate salt of the [3,3] ion. *Anal.* Calcd for I: C, 40.2; H, 4.1; N, 10.8; Ru, 13.0. Found: C, 37.9; H, 4.96; N, 10.4; Ru, 12.3.[8] The [3,3] perchlorate salt was formed by dissolving the tosylate complex in H_2O, passing the solution through Bio Rad AG1X2 resin in the perchlorate form, and evaporating to dryness.

Creutz[1] and Lavallee and Fleischer[2] had reported band maxima of the [2,2] ion in the visible at 513 and 542 nm, respectively. We observed λ_{max} for the [2,2] ion at 521 nm but noted that when the [2,2] complex is left in the presence of a strong reducing agent (*e.g.*, Eu^{2+}, Cr^{2+}, Zn(Hg)) for hours, λ_{max} shifts from 521 nm to shorter wavelengths with a decrease in intensity. The product is presumably the binu-