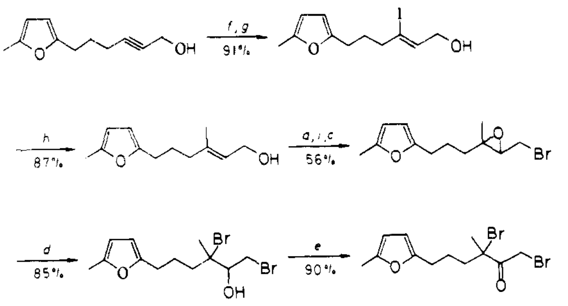

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Unexpected Reactions of Fe_2 and Fe in Low-Temperature Matrices

Sir:

The chemical reactions of metal atoms and small clusters in low-temperature matrices are being actively studied.[1] Such systems are models for both homogeneous and heterogeneous catalysis. Studies of metal vapors cocondensed with various substrates at 77 K are closely related.[2] Very little has been reported on the reactions of iron atoms. Iron vapors at 77 K react with cyclopentadiene to form ferrocene, and with 1,5-cyclooctadiene to give $Fe(COD)_2$.[2b]

The reaction of iron vapor condensed with nitrogen at 4-12 K showed that chemically bonded nitrogen was formed.[1b,3] Using a combination of Mössbauer and infrared spectroscopies, it was shown that the dimer, Fe_2, but not the monomer, Fe, reacted with nitrogen.[3] This is an unexpected result since Fe_2 is 30 kcal/mol more stable than 2Fe, owing to bond formation.[4]

In no case has a paraffin hydrocarbon been reported to react with metal atoms. Cr, V, and V_2 are inert in a number of hydrocarbon matrices, up to 80 K.[5] Ti is inert in cyclohexane, and Ni and Mg do not react with *n*-hexane. In fact, paraffin hydrocarbons are used as inert diluents in carrying out reactions at 77 K. Activated hydrocarbons, such as propylene, do react at 77 K. In some cases the reaction may be oxidative cleavage of the C-H bond.[2]

$$M + CH_3CH{=}CH_2 \rightarrow HMCH_2CH{=}CH_2 \qquad (1)$$

The Mössbauer spectrum of isolated iron atoms, Fe, in a methane matrix has been reported to have the same isomer shift as in an inert gas matrix.[6] We have confirmed this result, but, on increasing the iron concentration in the matrix to form the dimer, quite unexpected results were found. The isomer shift of the dimer (−0.11 mm/s with respect to iron metal) was not observed. Instead new lines at +0.58 mm/s and +1.42 mm/s were found. This is in the range of diamagnetic, covalent compounds of iron for the low value, and ionic compounds of iron(II) for the high value. Figure 1 shows the spectrum obtained.[7]

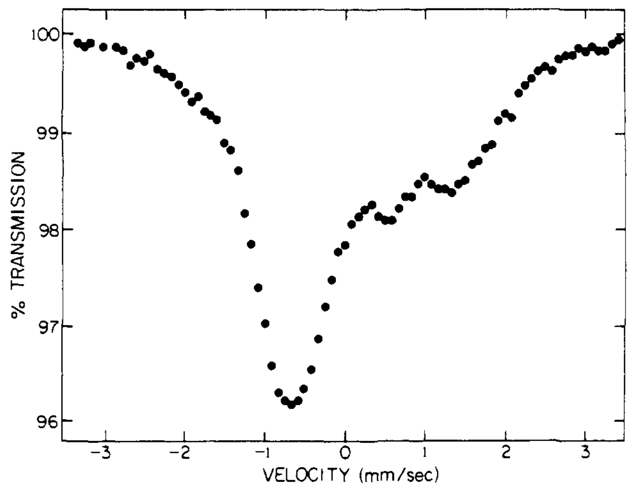
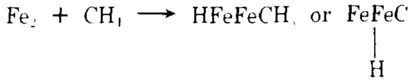


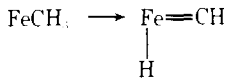
Figure 1. Mössbauer spectrum of solid methane matrix (20 K) with 2% ^{57}Fe (300 $\mu g/cm^2$ of iron). The matrix was deposited over a period of 20. The monomer absorbs at −0.75 mm/s.

The Mössbauer spectrum is strong evidence that chemical reaction between Fe_2 and CH_4 has occurred. The most plausible reaction is oxidative cleavage of the C-H bond, e.g.,



$$Fe_2 + CH_4 \longrightarrow HFeFeCH_3 \text{ or } \underset{\displaystyle H}{\overset{}{Fe}}{-}FeCH_3 \qquad (2)$$

As many as two CH_4 molecules could react per Fe_2 unit, based on the expected change in oxidation state from iron(0) to iron(II).[8] A subsequent reaction might be



$$FeCH_3 \longrightarrow \underset{\displaystyle H}{\underset{|}{Fe}}{=}CH_2 \qquad (3)$$

based on chemisorption studies of methane on iron films,[9] and on known reactions of transition metal alkyls.

A critical test of reactions 2 and 3 is the detection of Fe-H stretching vibrations in the 2000-cm^{-1} region of the infrared spectrum. Accordingly, the same matrix-producing system used for the Mössbauer studies was used to produce matrices of iron and methane on an aluminum foil at 12 K.[10]

Matrices with iron concentrations of 0.1 to 1.0% showed well-defined absorption bands at 2046, 2027, 2014, and 2019 cm^{-1}. In addition, there are weak lines at 2041, 2038, and 1981 cm^{-1}. A matrix of pure methane shows no absorption in this region. If, as the Mössbauer spectra indicate, the iron dimer is the initiating structure for the iron-methane reaction, then the infrared absorption should be proportional to the square of the iron concentration. For methane/iron ratios from 500 to 5000 the intensities of all the above lines vary as the square of the iron concentration. At higher concentrations this quadratic relationship breaks down, probably owing to the formation of higher multimers. In matrices in which the methane is progressively diluted with argon, the bands at 2046, 2014, and 2019 cm^{-1} decrease in intensity more rapidly than the band at 2027 cm^{-1}. This indicates that at least two products are formed with different Fe_2/CH_4 ratios.

When CD_4 is used as a matrix material instead of CH_4, the lines mentioned above all disappear. Presumably Fe-D stretching bonds could exist in the 1400-cm^{-1} region, which is just outside of our present range of measurement. New lines are found in the iron-CD_4 matrix at 2220 and 2195 cm^{-1}. We take these to be C-D stretches in either CD_3 or CD_2 groups bound to iron. The corresponding bands in Fe-CH_4 matrices should occur at ~3000 cm^{-1}. Unfortunately, this region is very heavily obscured by background, but one new band appears at 2899 cm^{-1}.

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We have also made Mössbauer studies using ammonia, isobutane, benzene, and hydrogen-argon as the matrix material for condensed iron vapor. In all these cases the normal spectrum of both Fe and Fe_2 disappears. New absorptions are found with positive isomer shifts characteristic of chemically bound iron. The nature of these products has not yet been completely probed by infrared spectroscopy. However, H_2 gives absorption bands in the metal-hydrogen stretching region, and NH_3 does not. If methane has indeed been oxidatively cleaved, then it is likely that i-C_4H_{10} and H_2 also have been cleaved. In chemisorption studies, both of these molecules are more reactive than is CH_4.[9] Benzene and NH_3 are also more reactive, but can form simple complexes on metal films. The enhanced reactivity of Fe_2 compared with Fe occurs with N_2 and with CH_4, the two most difficult molecules to chemisorb of those we have examined.

Very recently it has been shown that small nickel clusters, but not atoms, react with pentane between 77 and 143 K.[11] Organometallic species of unknown nature are formed.

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Structure and Electrochemistry of a Stable Enantiomeric Metalloflavin Complex

Sir:

Flavin coenzymes transfer electrons to and from heme, iron–sulfur, and molybdenum centers in proteins and serve as a required electron-pair splitting or -joining interface between metal one-electron donors or acceptors and organic two-electron oxidants or reductants.[1-3] Direct inner-sphere electron transfer has long been suspected between flavins and iron–sulfur or molybdenum sites,[1-11] but definitive evidence is lacking. Numerous model systems have been used to explain the nature of metal–flavin interactions,[5-19] but none have employed well-characterized metalloflavin complexes which maintain their integrity in both aqueous and nonaqueous solvents and incorporate a redox active metal ion with the same d-electron configuration as low-spin iron(II). We now report structural, spectroscopic, and electrochemical studies of stable ruthenium(II) isoalloxazine complexes which possess these properties and provide direct evidence for chirality and sequential one-electron reductions of the flavin due to metal coordination.

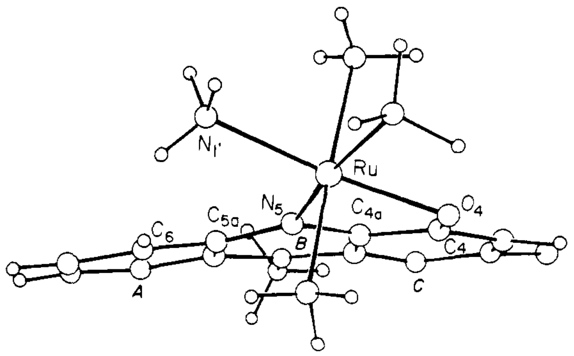

Figure 1. View of the $(10\text{-MeIAlo})(NH_3)_4Ru^{2+}$ complex ion.

The complexes were prepared by direct combination of $(H_2O)(NH_3)_5Ru^{2+}$, *cis*-$(H_2O)_2(NH_3)_4Ru^{2+}$, or *cis*-$(H_2O)_2(NH_3)_4Ru^{3+}$ with the isoalloxazine ligand and purified by ion-exchange chromatography. Crystallographic quality crystals of $[(10\text{-MeIAlo})(NH_3)_4Ru](PF_6)_2 \cdot 2H_2O$ (10-MeIAlo = 10-methylisoalloxazine) were grown by ethanol diffusion into saturated aqueous solutions of the complex seeded with small single crystals. These crystals belonged to the triclinic space group $P\bar{1}$ with unit cell dimensions of a = 9.631 (3), b = 10.618 (3), c = 13.216 (4) Å; α = 113.86 (2), β = 100.19 (2), γ = 94.12 (2)°.[20]

The structure of the $(10\text{-MeIAlo})(NH_3)_4Ru^{2+}$ ion is shown in Figure 1 and represents the first molecular structure determination of a 1:1 octahedral metalloflavin complex of the type postulated as an intermediate for inner-sphere electron transfer[16] and the first in which back-bonding and steric distortions of the heterocyclic ring are evident. The flavin ring chelates the metal ion via the N_5 and O_4 atoms with a N_5–Ru–O_4 angle of 80.9 (5)°. The four Ru–NH_3 bond lengths are a typical 2.12 Å,[21] while the Ru–N_5 distance is only 1.980 (6) Å. The latter bond length is significantly shorter than expected for a single bond to nitrogen for either Ru(II) or Ru(III)[21-23] and indicates some degree of multiple bonding. Back-bonding interactions were predicted for this series of metalloflavin complexes on the basis of their occurrence in a number of Ru(II) complexes with unsaturated heterocyclic molecules.[22-27] Remarkably, this bond length is shorter than the 1.991- and 2.058-Å distances reported for ammineruthenium(II) complexes with pyrazine[22] and isonicotinamide,[23] respectively, in which strong steric repulsion involving the heterocyclic ligand does not occur. The only shorter Ru(II)–N bond distance reported for a neutral nitrogen ligand is the 1.928-Å bond length for complexation by dinitrogen,[28] which is known to be a powerful π-acceptor ligand for this metal ion.

The Ru–O_4 bond distance of 2.088 (7) Å is similar to the 2.10-Å length expected for a Ru–O single bond.[27] The C_4–O_4 distance of 1.269 (10) Å is similar to those of other metalloflavin complexes which do not involve retrodative bonding,[15-19] so that back-bonding probably does not occur through the carbonyl group. Instead the metal back-donation of electron density appears to be localized in the N_5–C_{4a} bond via d–π^*-orbital overlap. This is evidenced by the fact that the N_5–C_{4a} bond distance of 1.351 (11) Å is ~0.05 Å longer than the corresponding bond lengths in either the free ligand[29] or other metalloflavin complexes,[15-19] whereas the N_1–C_{10a} bond distance of 1.309 (11) Å remains essentially unchanged.

Strong cooperative back-bonding and steric interactions induce significant departures from the coplanarity normally present between the benzene (A), bridging (B), and pyrimidine (C) rings of isoalloxazines.[29] The dihedral angles between the A and B rings and between the B and C rings are 6.2 and 3.7°,