produced a somewhat simplified spectrum. In the $-CH_3$ region, the decoupled spectrum consisted of at least four singlets at δ 1.68, 1.40, 1.25, and 1.10. Comparison with the normal nmr spectrum showed that the two peaks at δ 1.40 and 1.10 were each the center of a triplet, while the peaks at δ 1.68 and 1.25 were unaffected by decoupling the $-CH_2-$ protons. These decoupling experiments allowed the two peaks at δ 1.40 and 1.10 to be unambiguously assigned to the $-S_2CN(C_2H_5)_2$ groups, and the peak at δ 1.25, to the remaining $-SCH_3$ group. The chemical shifts of the two $-SCH_3$ groups of this dimer at δ 1.68 and 1.25 also compare favorably to those found for *anti*-$[Fe(CO)_3SCH_3]_2$ at δ 1.54 and 1.16. Several of the isomers in Figure 1 can be eliminated from consideration by these results. Isomers e, f, h, l, and m can be eliminated since their $-SCH_3$ groups are equivalent. However, the nmr spectrum gives insufficient information to distinguish among the remaining 10 isomers.

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The Carbonyl Insertion Reaction of Iron Pentacarbonyl with Nonaromatic Nitro Compounds

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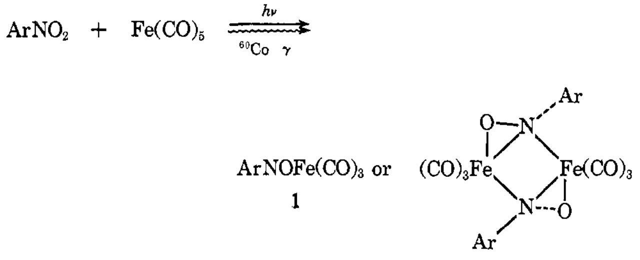
Aliphatic, cycloalkyl, and α,β-unsaturated nitro compounds were allowed to react with iron pentacarbonyl in dry diglyme. Carbonyl insertion products were obtained from nitroalkanes and nitrocycloalkanes, the product distribution being dependent on the size of the group attached to the nitro function. Treatment of 1-nitropropane and 2-methyl-2-nitropropane with diiron enneacarbonyl in benzene gave organoiron carbonyl complexes of the types $(RN)_2Fe_3(CO)_9$, $(RN)_2Fe_2(CO)_6$, $(RNH)_2Fe_2(CO)_6$, and $(RN)_2Fe_2(CO)_7$, identified by elemental and infrared and mass spectral analyses. The complexes were converted to formamide and/or ureas by heating in diglyme. A multistep reaction sequence involving these iron carbonyl complexes is proposed for the reductive carbonylation reaction. α,β-Unsaturated nitro compounds failed to react with iron pentacarbonyl in diglyme.

The reduction of aromatic nitro compounds by carbon monoxide and hydrogen in the presence of catalytic quantities of transition metal carbonyls has been investigated in considerable detail.[1,2] Amines, coupling, and carbonyl insertion products have been isolated from these reactions, the nature of the product(s) depending on the nitro compound, the type of catalyst, and the reaction conditions.

Few reports have appeared in the literature concerning the photochemical or thermal reactions of nitro compounds with metal carbonyls functioning as reagents. Irradiation of a mixture of iron pentacarbonyl and an aromatic nitro compound gives novel monomeric (1) or dimeric (2) nitrosobenzene complexes.[3] The crystal structure of one of the dimeric complexes, bis(tricarbonyl-2-methyl-3-chloronitrosobenzeneiron), has been determined by Barrow and Mills.[4] As part of a study of the utility of iron pentacarbonyl as a reagent for organic synthesis,[5] we have recently shown that the metal carbonyl is a useful reagent for thermally converting aromatic nitro compounds to azoxy or azo compounds, or amines, subject to reagent concentration and the nature of substitution on the benzene ring.[6] This paper describes the first results of the reactions of a number of aliphatic, cycloalkyl, and α,β-unsaturated nitro compounds with iron pentacarbonyl. The purpose of this investigation was to determine the products formed in these reactions and the pathways leading to their formation. A thorough understanding of the reaction mechanism may ultimately lead to a rationale for the catalytic reduction process, an important but not well-understood reaction.



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Results and Discussion

Primary, secondary, tertiary, and α,β-unsaturated nitro compounds were allowed to react with iron pentacarbonyl in dry diglyme at 120–132° for 15–17 hr. The results are recorded in Table I. Saturated nitro compounds gave the carbonyl insertion products, formamides (3) and ureas (4), in modest yields. It is

$$RNO_2 + Fe(CO)_5 \xrightarrow[120-132^\circ]{\text{diglyme}} \underset{\mathbf{3}}{RNHCHO} + \underset{\mathbf{4}}{(RNH)_2CO}$$

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TABLE I
PRODUCTS OBTAINED FROM REACTION OF NONAROMATIC NITRO COMPOUNDS (1.0 MOL) WITH IRON PENTACARBONYL (1.4 MOL) IN DIGLYME

Nitro compound	% yield of products[a] 3	4
1-Nitropropane	13.8	7.4
2-Nitropropane	5.8	14.8
Nitrocyclohexane	13.0	18.5
2-Methyl-2-nitropropane[b]	3.9	13.3
1-Nitroadamantane	Trace	9.2

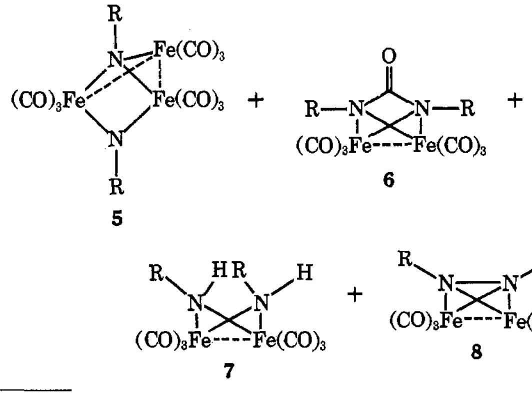
[a] Products were identified by comparison of melting or boiling points (see Expermental Section) and spectral properties (infrared, nuclear magnetic resonance) with those reported in the literature. Only starting material (2-nitro-1-ferrocenylethylene) or starting material and polymer (β-nitrostyrene) were obtained using α,β-unsaturated nitro compounds (see Experimental Section). [b] Use of a 3.8/1.0 mole ratio of metal carbonyl to nitro compound gave **3**, R = $C(CH_3)_3$, in 6.3% yield and **4**, R = $C(CH_3)_3$, in 19.3% yield.

noteworthy in these reactions that the formamide is the major product with relatively small alkyl groups (R = n-C_3H_7) and the urea predominates when bulky alkyl groups (R = *tert*-butyl, 1-adamantyl) are attached to the nitro function. This variation in product distribution is an apparent indication of the importance of steric effects in this reaction.

The reaction of two nitro compounds with diiron enneacarbonyl was undertaken. Diiron enneacarbonyl is a more reactive species than iron pentacarbonyl and hence the polynuclear carbonyl can effect reactions with a given reactant under milder conditions than required for the mononuclear metal carbonyl. It was anticipated that some, if not all, of the intermediates formed in the aliphatic and cycloalkyl nitro compounds–iron pentacarbonyl reaction at 120–132° could be isolated using diiron enneacarbonyl at room temperature. Treating the organometallic intermediates, obtained in this manner, under conditions used in the iron pentacarbonyl reaction could indicate the mechanism for the latter process. The pathway, outlined below, is a complex one.

In 1967, Dekker and Knox[7] reported the capture of nitrenes by iron carbonyls. They showed that reaction of nitromethane with diiron enneacarbonyl in benzene gave the trinuclear complex **5** (R = CH_3) as the major product and small amounts of the urea and methylamido complexes, **6** and **7** (R = CH_3), respectively. Use of methyl azide, instead of nitromethane, in reaction with diiron enneacarbonyl, gave similar products. Complexes **6**–**8** (R = C_6H_5) were obtained from reaction of phenyl azide with the enneacarbonyl.[7] Single-crystal X-ray analyses have confirmed the structures of complexes **5** (R = CH_3),[8] **6** (R = CH_3,[9] C_6H_5[10,11]), **7** (R = H),[12] and **8** (R = CH_3).[13] It seemed conceivable that a complex such as **6** could be the precursor to the urea and complexes of types **5**, **7**, and **8** could be intermediates in amine formation (the necessary hydrogen being abstracted from solvent). Aliphatic and heterocyclic amines react with iron pentacarbonyl to give formamides.[14,15] Doedens[9] has noted that complexes **7** and **8** may be precursors to **6**. Calderazzo and coworkers[1] have suggested the intermediacy of complexes analogous to **6** and **8** to account for the formation of N,N'-diphenylurea and aniline, respectively, from the ruthenium carbonyl catalyzed reduction of nitrobenzene.

$RNO_2 + Fe_2(CO)_9 \longrightarrow$



This author treated 1-nitropropane, which gave the formamide as the major product on iron pentacarbonyl treatment, and 2-methyl-2-nitropropane, which gave urea as the predominant product using $Fe(CO)_5$, with diiron enneacarbonyl in anhydrous benzene at room temperature. The red-black complex **5**, R = n-C_3H_7, was obtained as the major product from 1-nitropropane with **6** and **7** (R = n-C_3H_7) formed in low yield (Table II). Similar results were reported for the nitromethane–diiron enneacarbonyl reaction.[7] Complex **6** [R = $C(CH_3)_3$] was obtained as the major product [**5** and **8** (R = *tert*-butyl) as by-products] from treatment of 2-methyl-2-nitropropane with the enneacarbonyl.

When the trinuclear complex **5** (R = n-C_3H_7) was heated in diglyme at 120–130° for 1 hr, **8** was produced as well as traces of **3** and **4**. Complex **8** was converted to **7** (R = n-C_3H_7) by further heating in diglyme. Formamide was obtained from **7** by heating the latter in diglyme in the presence of iron pentacarbonyl. Heating the urea complex **6** (R = n-C_3H_7) in diglyme for 2 hr gave free urea along with small quantities of the decarbonylated product **8** (R = n-C_3H_7). Dekker and Knox[7,16] also observed this decarbonylation reaction. The reverse process, **8** → **6** [R = C_6H_5; free urea also produced], was reported[7] to occur "spontaneously" either in refluxing benzene or at ambient temperature.[16] N,N'-Di-*tert*-butylurea was obtained, along with traces of the formamide, by heating **6** [R = $C(CH_3)_3$] in diglyme for 10 hr. The complexes **5** and **8** [R = $C(CH_3)_3$], formed in minor quantities, gave formamide [*via* **7**] and small amounts of urea (*via* **6**) on heating in diglyme for 10 hr.

The following conclusions concerning the nonaromatic nitro compound–$Fe(CO)_5$ reaction can be drawn from the results described above: (a) the urea complex **6** does serve as the precursor to urea (and some formamide by decarbonylation of **6**); (b) complexes **5** and **8** give not only the predicted formamide but also some urea (probably *via* **6**); (c) formamides may result by the sequence

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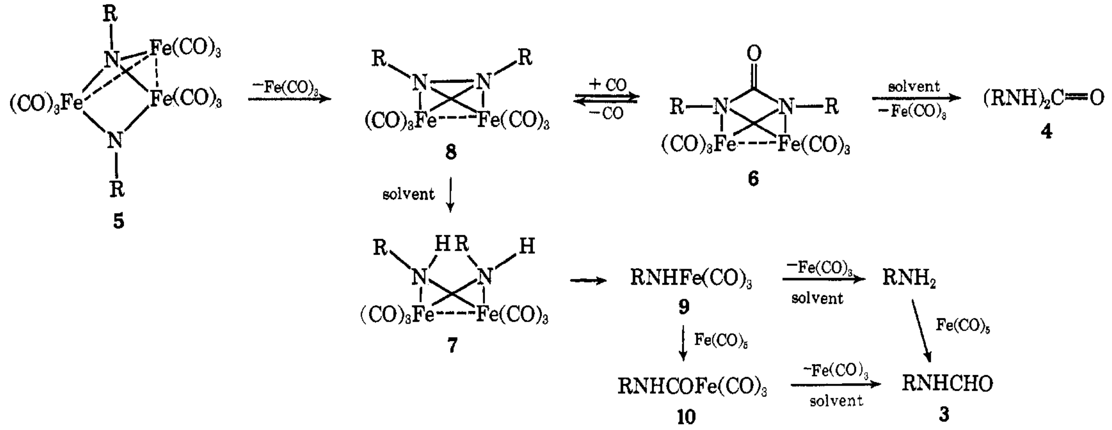
TABLE II

COMPLEXES OBTAINED BY REACTION OF NITRO COMPOUNDS WITH $Fe_2(CO)_9$[a]

Complex	Mp,[b] °C	Infrared carbonyl stretching bands, cm^{-1} $\nu_{C\equiv O}$	Infrared carbonyl stretching bands, cm^{-1} $\nu_{C=O}$	Molecular ion[c] *m/e*
5, R = *n*-C_3H_7	118.0–120.0	2082 m, 2044 s, 2002 s		534
6, R = *n*-C_3H_7	102.0–103.0	2082 m, 2046 s, 2002 vs, 1991 ms	1729 m	422
7, R = *n*-C_3H_7	84.0–85.0	2075 m, 2051 ms, 2034 s, 1998 s, 1992 s		396
8, R = *n*-C_3H_7	69.5–72.0	2072 m, 2032 s, 1999 s, 1991 s, 1972 sh		394
5, R = $C(CH_3)_3$	83.0–84.0	2084 m, 2042 s, 2005 s, 1993 s		562
6, R = $C(CH_3)_3$	163.0–165.0	2082 m, 2045 s, 1998 s	1716 m	450
7, R = $C(CH_3)_3$	96.0–97.0	2066 m, 2047 s, 2033 s, 1992 s		424
8, R = $C(CH_3)_3$	89.0–90.5	2060 m, 2022 s, 1994 s, 1972 sh		422

[a] Satisfactory (±0.4%) elemental analysis was obtained for all compounds and the analytical data were made available to the editors and referees. [b] Melting points were recorded in sealed tubes and are uncorrected. [c] Expected successive loss of carbon monoxide groups was observed in all instances.

SCHEME I



of steps outlined in Scheme I, *i.e.*, collapse of the trinuclear complex **5** to **8**, N–N bond cleavage and hydrogen abstraction from solvent to give **7** followed by conversion to **9**, **9** either abstracting hydrogen from solvent with loss of an iron tricarbonyl fragment to give amine or reacting with additional iron pentacarbonyl to form **10**, and formylation of the amine or hydrogen abstraction from solvent by **10** (accompanied by destruction of the complex) giving the formamide.

Rather unexpectedly, the *α,β*-unsaturated nitro compounds *β*-nitrostyrene and 2-nitro-1-ferrocenylethylene did not react with iron pentacarbonyl under the described conditions to give formamides or ureas. In addition, no olefin–iron tetracarbonyl complexes were isolated which would have been analogous to those obtained from reaction of olefins having other electronegative substituents (*e.g.*, ester, acid, halogen functionalities) with diiron enneacarbonyl or with iron pentacarbonyl under ultraviolet irradiation.[17,18]

In summary, this investigation has shown that iron pentacarbonyl can convert nitro compounds to formamides and ureas. More importantly, this paper has presented the first clear evidence for the pathway of reductive carbonylation and the results obtained herein may be applied to the general catalytic reduction process of nitro compounds by transition metal carbonyls. For example, it now appears likely that the ruthenium carbonyl catalyzed reduction of nitrobenzene proceeds *via* the ruthenium analogs of complexes **5–8**.[1]

Experimental Section

General Comments.—Melting points were determined on a Fisher-Johns or Gallenkamp apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer; the wavelength readings were calibrated with a polystyrene film.

Iron pentacarbonyl (Pressure Chemical Co. and Alfa Inorganics, Inc.) was used as received; distillation prior to use did not improve results. Diiron enneacarbonyl (Pressure Chemical Co.) was used as received. All reactions involving metal carbonyls were run under nitrogen. Solvents were dried and purfied by standard methods. 1-Nitropropane, 2-nitropropane, nitrocyclohexane, 2-methyl-2-nitropropane, and *β*-nitrostyrene were commercial products and were distilled or recrystallized prior to use. 2-Nitro-1-ferrocenylethylene (mp 138.0–139.5°) was prepared in 62% yield by reaction of a mixture of ferrocenecarboxaldehyde and nitromethane with sodium methoxide in methanol, as described by Shiga and coworkers.[19]

1-Nitroadamantane has been prepared in low yield by nitration of adamantane with concentrated nitric acid in glacial acetic acid at 140° and 500 psi.[20] Stretter and coworkers[21] oxidized 1-aminoadamantane to the nitro compound in unreported yield with potassium permanganate. Robinson, Milewich, and Hofer[22] have demonstrated the utility of *m*-chloroperbenzoic acid as a reagent for oxidizing steroidal amines to nitro steroids. The use of this peracid for the oxidation of 1-aminoadamantane provides a convenient preparation of the desired 1-nitroadamantane. The following procedure was employed.

A solution of 1-aminoadamantane (3.03 g, 20.0 mmol, Aldrich Chemical Co.) in chloroform (130 ml) was added dropwise over a 30-min period to a refluxing stirred solution of *m*-chloroperbenzoic acid (24.2 g, 140 mmol, Aldrich Chemical Co.) in chloroform (100 ml). The reaction mixture was refluxed for 10 min

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more, cooled, and then washed successively with four 200-ml portions of 10% aqueous sodium sulfite, two 200-ml portions of a saturated sodium bicarbonate solution and once with water. The chloroform extract was dried (Na_2SO_4) and then the solvent was evaporated *in vacuo* at room temperature to give 1-nitroadamantane. Sublimation of the product at 80° at 10 mm for 12 hr gave 2.75 g (76%) of colorless, waxy crystals of 1-nitroadamantane, mp 158.0–159.0° (lit. mp 158.5–159.0°).[20] The infrared spectrum (chloroform solution) of the compound exhibited bands due to asymmetric and symmetric $-NO_2$ stretching vibrations at 1527 and 1369 cm^{-1}, respectively.

Reactions of Iron Pentacarbonyl. (i) With 1-Nitropropane.—A mixture of 1-nitropropane (2.67 g, 30.0 mmol) and iron pentacarbonyl (5.67 ml, 42.0 mmol) in dry diglyme (30 ml) was heated with stirring at 125–130° for 17 hr. The reaction mixture was filtered hot through a sintered-glass funnel and the filtrate concentrated *in vacuo* to a small volume. Dry hydrogen chloride gas was bubbled into the evaporated filtrate in order to isolate any amine formed in the reaction—no *n*-propylamine hydrochloride was obtained (similar results were obtained in the other reactions). The residue from the evaporation was treated with pentane (100 ml) and filtered, and the filtrate was evaporated to give 0.300 g (11.5%) of *N*-propylformamide (**3**, R = $n\text{-}C_3H_7$), bp 75.0–77.0° (3 mm) (lit.[23] bp 99.0–101.0° (12 mm)). The diglyme- and pentane-insoluble materials were combined and then treated with pentane (250 ml) and filtered; evaporation of the filtrate gave 0.061 g (2.3%) of **3**, R = $n\text{-}C_3H_7$ (total yield 13.8%). The pentane-insoluble solid was now treated with ether–methylene chloride (1:1) and filtered, and the filtrate was evaporated to give an oily residue. The oil was dissolved in chloroform and chromatographed on Florisil. Elution with chloroform gave 0.02 g of an unidentified complex. The ether–methylene chloride insoluble solid was treated with methanol (75 ml) and filtered, and the fitrate was evaporated *in vacuo*. Pentane (100 ml) was added to the residual oil and crystallization of 1,3-di-*n*-propylurea (**4**, R = $n\text{-}C_3H_7$), mp 103.0–104.0° (lit.[24] mp 105°), slowly took place. Yield of urea was 0.160 g (7.4%).

(ii) **With 2-Nitropropane.**—A mixture of 2-nitropropane (2.67 g, 30.0 mmol) and iron pentacarbonyl (5.67 ml, 42.0 mmol) in dry diglyme (30 ml) was heated with stirring at 120–130° for 17 hr. The reaction mixture was cooled somewhat and filtered, and the filtrate was evaporated *in vacuo*. The residual oil was treated with pentane (100 ml) and filtered, and the filtrate was evaporated to give 0.15 g (5.8%) of *N*-isopropylformamide [**3**, R = $CH(CH_3)_2$], bp 223–225° (lit. bp 220°[25] and 70° at 1.5 mm[26]). The pentane-insoluble solid weighed 0.33 g and its infrared spectrum was very similar to that of 1,3-diisopropylurea. Treatment of the solid with hot chloroform, filtering, and evaporating the filtrate gave 0.16 g (7.4%) of 1,3-diisopropylurea [**4**, R = $(CH_3)_2CH$], mp 191.0–192.0° (lit.[27] mp 192°), as white needles. An additional 0.16 g of the urea was obtained by treating the diglyme-insoluble solid with chloroform in the described manner. Total yield of **4**, R = $(CH_3)_2CH$, was 0.32 g (14.8%).

(iii) **With Nitrocyclohexane.**—A mixture of nitrocyclohexane (2.52 g, 20.0 mmol) and iron pentacarbonyl (3.78 ml, 28.0 mmol) in diglyme (30 ml) was heated with stirring at 125–130° for 15 hr. The reaction mixture was filtered hot through a sintered-glass funnel and the filtrate was concentrated *in vacuo* to approximately one-third its volume. Pentane (100 ml) was added to the residue, and a brown solid precipitated out and was filtered. The precipitate was washed with 50 ml of pentane and the pentane washing was added to the filtrate. The solid was dissolved in absolute ethanol and percolated through a Florisil column to give 0.414 g (18.5%) of *N*,*N'*-dicyclohexylurea [**4**, R = C_6H_{11}], mp 236–238° (lit.[28] mp 238°). Evaporation of the pentane extracts gave 0.330 g (13.0%) of *N*-cyclohexylformamide [**3**, R = C_6H_{11}], bp 118–120° at 3.0 mm (lit.[29] bp 155–157° (22 mm)).[29]

(iv) **With 2-Methyl-2-nitropropane.**—A mixture of 2-methyl-2-nitropropane (3.09 g, 30.0 mmol) and iron pentacarbonyl (5.67 ml, 42.0 mmol) in diglyme (20 ml) was heated with stirring at 120–130° for 15 hr. The reaction mixture was filtered hot and the diglyme-insoluble solid was ignited. The filtrate was concentrated, *in vacuo*, to a small volume. Pentane (100 ml) was added to the residue, the solution was filtered, and the filtrate was evaporated to give 0.12 g (3.9%) of *N-tert*-butylformamide [**3**, R = $(CH_3)_3C$], bp 206–208° (lit. bp 202°[30] and 67° at 1.5 mm[26]). A white solid, on the walls of the reflux condenser, was recrystallized from chloroform to give 0.341 g (13.3%) of *N*,*N'*-di-*tert*-butylurea [**4**, R = $(CH_3)_3C$], mp 244–245° (sealed tube) [lit.[31] mp 242°, sealed tube]. Use of a 3.8:1.0 mole ratio of metal carbonyl to nitro compound gave **4**, R = $C(CH_3)_3$, in 19.3% yield and **3**, R = $(CH_3)_3C$, in 6.3% yield.

(v) **With 1-Nitroadamantane.**—A mixture of 1-nitroadamantane (1.09 g, 6.0 mmol) and iron pentacarbonyl (1.22 ml, 9.0 mmol) in diglyme (20 ml) was heated with stirring at 125–132° for 16 hr. The reaction mixture was filtered hot through a sintered-glass funnel and the filtrate evaporated *in vacuo*. Pentane (150 ml) was added to the residue and then the pentane solution was decanted from the oil. Evaporation of pentane gave 0.49 g of unreacted 1-nitroadamantane. The pentane-insoluble oil was dissolved in benzene and chromatographed on Florisil. Elution with benzene gave traces of diglyme. Elution with benzene–acetone (1:1) gave sufficient 1-formamidoadamantane [**3**, R = 1-adamantyl] to record an infrared spectrum and a melting point of 137.0–139.0° (lit.[32] mp 138.0–139.5°). The diglyme-insoluble solid was 1,3-di-1-adamantylurea [**4**, R = 1-adamantyl], mp 308°, sealed tube (lit.[33] mp 312°, sealed tube). Yield of urea was 0.050 g (9.2% based on unrecovered 1-nitroadamantane).

(vi) **With β-Nitrostyrene.**—A mixture of β-nitrostyrene (2.98 g, 20.0 mmol) and iron pentacarbonyl (3.78 ml, 28.0 mmol) in diglyme (27 ml) was heated with stirring at 120–130° for 22 hr. The reaction mixture was filtered hot through a sintered-glass funnel and the filtrate was evaporated *in vacuo*. Pentane (120 ml) was added to the residue, the solution was filtered, and the filtrate was evaporated to give recovered starting material. The pentane- and diglyme-insoluble solids were combined, treated with boiling methanol, and filtered; the filtrate was evaporated to give β-nitrostyrene (82%) and some polymer.

(vii) **With 2-Nitro-1-ferrocenylethylene.**—A mixture of 2-nitro-1-ferrocenylethylene (1.61 g, 6.26 mmol) and iron pentacarbonyl (1.20 ml, 8.93 mmol) in diglyme (20 ml) was heated at 120–130° for 23 hr. The solution was filtered hot and the filtrate was concentrated *in vacuo* to approximately one-fourth its original volume. Pentane (90 ml) was added to the residue. Filtration gave 1.46 g of recovered starting material. An additional 0.13 g of 2-nitro-1-ferrocenylethylene was obtained by treating the diglyme-insoluble solid with chloroform (40 ml), filtering, and evaporating the filtrate.

Reaction of Diiron Enneacarbonyl with 1-Nitropropane.—A mixture of 1-nitropropane (1.60 g, 18.0 mm) and diiron enneacarbonyl (7.26 g, 20.0 mm) in anhydrous benzene (50 ml) was stirred at room temperature for 27 hr. The solution was filtered, the filtrate was concentrated *in vacuo*, and the residue was chromatographed on Florisil. Elution with pentane gave 0.51 g (11%) of **5**, R = $n\text{-}C_3H_7$, as red-black needles. The orange-brown complex **7** (0.17 g, 0.48%) was isolated by elution with pentane or pentane–benzene (1:1). Elution with benzene gave the orange complex **6** (0.21 g, 5.5%). The melting point, analytical, and infrared and mass spectral data for these complexes are listed in Table II.

Reaction of Complexes 5–7 (R = $n\text{-}C_3H_7$) in Diglyme.—The trinuclear complex **5** [R = $n\text{-}C_3H_7$, 0.082 g] in diglyme (7 ml) was heated at 120–130° for 1 hr. The solution was cooled and filtered, and the filtrate was evaporated *in vacuo*. The residue was treated with pentane and filtered from trace amounts of **4**, R = $n\text{-}C_3H_7$; the filtrate chromatographed on Florisil. Elution with pentane gave 0.033 g (54%) of **8**, R = $n\text{-}C_3H_7$ (Table II), and traces of **3**, R = $n\text{-}C_3H_7$. Elution with pentane–acetone (1:3) gave traces of **4**, R = $n\text{-}C_3H_7$. Complex **7**, R = $n\text{-}C_3H_7$, was obtained from **8**, by heating the latter in diglyme for 5–8 hr. A mixture of **7** (0.029 g), iron pentacarbonyl (0.8 ml), and di-

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glyme (9 ml) was heated at 125–130° for 18 hr. Work-up as described above gave **3**, R = n-C_3H_7.

The urea complex **6** (0.18 g) in diglyme (5 ml) was heated at 125–130° for 2–5 hr. The reaction mixture was cooled somewhat and filtered, and the filtrate was evaporated *in vacuo*. The residue was treated with pentane (10 ml) and filtered, and the filtrate was evaporated to give 0.009 g (5.4%) of **8**, R = n-C_3H_7. The pentane-insoluble solid (0.049 g, 80%) was **4**, R = n-C_3H_7.

Reaction of Diiron Enneacarbonyl with 2-Methyl-2-nitropropane.—A mixture of 2-methyl-2-nitropropane (2.78 g, 27.0 mm) and diiron enneacarbonyl (10.9 g, 30.0 mm) in dry benzene (80 ml) was stirred at room temperature for 26 hr. The solution was filtered, the filtrate was concentrated *in vacuo*, and the residue was dissolved in pentane and chromatographed on Florisil. Elution with pentane gave 0.37 g (4.9%) of the red-orange complex **5**, R = $(CH_3)_3C$, and 0.036 g (0.63%) of **8**. Elution with benzene gave 0.59 g (10%) of **6**, R = $(CH_3)_3C$. See Table II for melting point, analytical, and infrared and mass spectral data concerning these complexes.

Reactions of Complexes 5, 6, and 8 [R = $(CH_3)_3C$] in Diglyme.—The urea complex **6** [R = $(CH_3)_3C$, 0.55 g] in diglyme (10 ml) was heated at 120–130° for 10 hr. Work-up as described for the 2-methyl-2-nitropropane–iron pentacarbonyl reaction gave 0.17 g (82%) of **4**, R = $(CH_3)_3C$, and traces of **3**, R = $(CH_3)_3C$.

The trinuclear complex **5** (0.30 g) in diglyme (7.5 ml) was heated at 120–130° for 5 hr. Work-up as for the corresponding reaction of **5**, R = n-C_3H_7, gave 0.19 g (84%) of **8** [R = $(CH_3)_3C$] and trace quantities of **3** and **4**. Heating **8** in diglyme gave **7** [see Table II]. A mixture of **7** (0.12 g), iron pentacarbonyl (1.1 ml), and diglyme (11 ml) was heated at 120–130° for 10 hr. Work-up as described earlier gave **3**, R = $(CH_3)_3C$.

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Cyclic Amine Complexes of Iron. Electrochemistry, Preparation, and Properties

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The electrochemistry, preparation, and properties of some iron complexes of a macrocyclic tetramine are reported. Compounds containing Fe(III), Fe(II), and a reduction product which appears to be an iron hydride were isolated and characterized. The dependence of the redox potentials of Cu, Ni, Co and Fe macrocyclic tetraamine complexes on electronic properties of the central metal ion is discussed.

Introduction

Transition metal complexes of tetradentate cyclic amines formed by condensing linear amines with ketones in the presence of certain metal salts were first discovered in 1960 by Curtis.[1] A growing interest in these complexes has led to a considerable amount of work on their preparation, properties, and chemistry. An excellent review article by Curtis[2] covering the work up to 1968 has appeared in the literature. More recently, electrochemical studies of a number of the cyclic amine complexes revealed the remarkable ability of these ligands to stabilize unusual oxidation states, *e.g.*, Ni(I) and Ni(III),[3] Co(I),[4] and Cu(III),[5] as well as Cu(I)[5,6] which is rarely found in a square-planar complex. Preparation and isolation of the M(I) and M(III) complexes as perchlorate or tetrafluoroborate salts demonstrated that most of them are surprisingly stable in the absence of oxidizing or reducing agents.

In an extension of our electrochemical investigation of cyclic amine complexes to other metals, we have carried out a study involving Fe. Some work on Fe complexes has already appeared in the literature. Thus, Fe(II) and Fe(III) complexes of the unsaturated cyclic ligand obtained by condensing acetone with ethylenediamine have been reported.[7] The Fe(II) complex of the corresponding saturated amine, L, shown in Figure 1, has also been isolated as the dichloride salt.[8] A recent electrochemical study of these complexes[8] indicated that Fe(II) cyclic amines exhibit a redox chemistry similar to the Cu, Ni, and Co compounds, but none of the oxidation or reduction products were isolated and characterized. We have prepared the new complexes $FeL(BF_4)_2$ and $(CH_3CN)_2FeL(BF_4)_2 \cdot 2CH_3CN$, containing Fe(II) in high- and low-spin states, respectively. Using electrochemical techniques, $(CH_3CN)_2Fe(BF_4)_3$ and what appears to be a hydride, $HFeL(solvent)(BF_4)$, have also been obtained. This report deals with the preparation, electrochemistry, and properties of these iron cyclic amines.

Experimental Section

Polarographic and Voltammetric Measurements.—The electrochemical instrumentation, cells, electrodes, and techniques have been previously described.[3,5,9] The purification of the solvent (acetonitrile) and of the supporting electrolyte (tetraethylammonium perchlorate) can be found in the above references. All measurements were carried out at 25.0 ± 0.05°.

Spectra.—The infrared spectra were measured, using a Beckman IR-5A. An IR-4 was used to locate the Fe–H stretch more accurately. The spectra were obtained in Nujol and Fluorolube mulls as well as KBr pellets.

The visible and ultraviolet spectra were obtained with a Cary 14 automatic spectrophotometer provided with an inert atmosphere. The cell length was varied between 0.1 mm and 1 cm in order to avoid the necessity for dilution of solutions.

Magnetic Measurements.—The magnetic measurements were made by the Gouy method using the solid samples. The balance was calibrated with diamagnetic and paramagnetic standards.

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