Organometallic Chemistry of Carbon-Nitrogen Multiple Bonds. 2. Reactions of Cyclopentadienyldicarbonyliron Anion with Iminium Salts; Chemistry of the Products

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Abstract: Reactions of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ with $[R_2C{=}NR'_2]X$ produce dialkylaminoalkyl complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CR_2NR'_2)]$ except when R is a primary or secondary alkyl group; in these cases an enamine and $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ are formed by an acid-base reaction. Unusual infrared and NMR spectra exhibited by a series of complexes of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2NR_2)]$ are interpreted as a result of detection of rotational isomers (about the Fe-CH_2 bond) in which there is an intramolecular iron-nitrogen interaction. $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}$ reacts, at nitrogen, with electrophiles; HCl and CH_3I give salts, which may be considered as derivatives of the nitrogen ylides $^-CH_2N^+(CH_3)_2H$ and $^-CH_2N^+(CH_3)_3$, whereas BF_3 and BH_3 give simple adducts. Reaction with CH_3COCl, $(CF_3CO)_2O$, or $(CF_3SO_2)_2O$ occurs with carbon-nitrogen bond cleavage to produce $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2Cl$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2OCOCF_3$, and $\{[(\eta^5\text{-}C_5H_5)Fe(CO)_2]N(CH_3)_2\}O_3SF_3$, respectively. Photolysis of the $\eta^1\text{-}CH_2N(CH_3)_2$ derivative produces $\{(\eta^5\text{-}C_5H_5)Fe(CO)[\eta^2\text{-}CH_2N(CH_3)_2]\}$, which reacts with phosphines (L) to produce $\{(\eta^5\text{-}C_5H_5)Fe(CO)(L)[\eta^1\text{-}CH_2N(CH_3)_2]\}$.

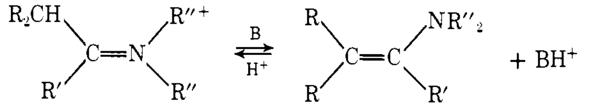
Introduction

As described in an earlier paper,[1] we have undertaken an investigation of the organometallic chemistry of a number of species containing carbon-nitrogen multiple bonds.[2] Our initial efforts have involved the preparation of complexes of iminium ions, $R_2C{=}NR'_2{}^+$. We have already described reactions of $(Ar_3P)_4Ni$ and $(Ar_3P)_2NiC_2H_4$ with $CH_2{=}NR_1R_2{}^+$, which yield products that contain the iminium ion bonded in a dihapto fashion.[2] One of these products, $\{Ph_3PNi(Cl)[\eta^2\text{-}CH_2N(CH_3)_2]\}$ was converted to $\{(\eta^5\text{-}C_5H_5)Ni[\eta^1\text{-}CH_2N(CH_3)_2]PPh_3\}$ by treatment with sodium cyclopentadienide. It seemed likely that complexes containing the iminium ion moiety bonded in monohapto form might be prepared directly by reaction of iminium salts with metal carbonyl anions since iminium ions are susceptible to nucleophilic attack at carbon.[3] Species containing the $>C\text{-}N<$ moiety in a dihapto configuration might then be obtained by intramolecular substitution of a carbonyl ligand by the amino group. We chose cyclopentadienyldicarbonyliron anion as the first nucleophile for study because of its ready availability and known nucleophilic properties. This paper reports the results of our work on the reactions of this nucleophile with a variety of iminium salts and novel aspects of the physical characterization and chemistry of the products obtained. While our studies on this system were in progress, Wilkinson and Fong reported reactions of some other metal carbonyl anions with dimethylmethyleneiminium iodide.[4a] Other somewhat related compounds that contain dihapto bonded C-N moieties have also been reported.[4b]

Results and Discussion

A summary of the preparative chemistry to be discussed in the following sections is given in Figure 1. The Experimental Section should be consulted for details of the individual reactions.

Reactions of Iminium Salts with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$. Reactions of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (hereafter $\eta^5\text{-}C_5H_5$ will be donated by Cp) with suspensions of iminium salts in THF occur rapidly, even at −78 °C, regardless of the extent of substitution of the iminium ion. The nature of the products obtained depends upon the type of substituent present in the iminium ion and to some extent upon the reaction temperature. Methylene iminium ions, $[CH_2{=}NR_2]^+$, invariably yield dark red complexes of the type $[CpFe(CO)_2(\eta^1\text{-}CH_2NR_2)]$ when reactions are conducted at −78 °C. Six complexes of this type were prepared (entries **1–6** in Table I). Information pertinent to their characterization is given in the following section. At room temperature only low yields of the aminoalkyl species are obtained; $[CpFe(CO)_2]_2$ is the principal iron containing product. The necessity of conducting these reactions at low temperature probably accounts for the failure of earlier workers to obtain the aminoalkyl product.[5] Likewise carbon-substituted iminium ions that do not have protons on the α carbon, such as $[(CH_3)_2C(CH_2C_6H_5)CH{=}N(CH_2CH_2)_2O]^+$, react at −78 °C to yield analogous products. However, C-substituted iminium salts that have one or more protons on the α carbon ultimately give $[CpFe(CO)_2]_2$ as the iron-containing product. The reaction of $[(CH_3)_2CHCH{=}N(CH_2CH_2)_2O]^+$ was studied in some detail. Salts of this ion reacted immediately with $CpFe(CO)_2^-$ at −78 °C to form a pale yellow solution. Upon warming to room temperature the solution darkened to the color of $[CpFe(CO)_2]_2$, which was subsequently isolated from the reaction mixture. In separate experiments enamine, $(CH_3)_2C{=}CHN(CH_2CH_2)_2O$, and $CpFe(CO)_2H$ were detected by NMR as products of the initial reaction. The interconversion of iminium ions and enamines by acid-base reactions, i.e.



$$\mathrm{R_2CH(R')C{=}N(R'')_2{}^+ \underset{H^+}{\overset{B}{\rightleftarrows}} (R)_2C{=}C(R')NR''_2 + BH^+}$$

is well documented[3] and it is likely that simple proton transfer to the carbonyl anion leads to the products observed. Although its p*K* value has not been determined, the carbonyl anion apparently behaves as a base in other reactions. For example, a standard preparation of $CpFe(CO)_2H$ involves the reaction of the carbonyl anion with *tert*-butyl chloride.[6] Although this is sometimes cited as an example of a β-hydride elimination reaction,[7] implying that nucleophilic displacement of chloride and formation of the alkyl compound precede the decomposition, recent work shows that $CpFe(CO)_2C(CH_3)_3$ prepared by an alternative route is quite stable.[8] The most likely pathway for hydride production is dehydrohalogenation (E2 elimination). In fact, Reger's work on the decomposition of $CpFe(CO)(PPh_3)CH_2CH_2R$, which does occur by a β-elimination process, shows that ligand dissociation is required prior

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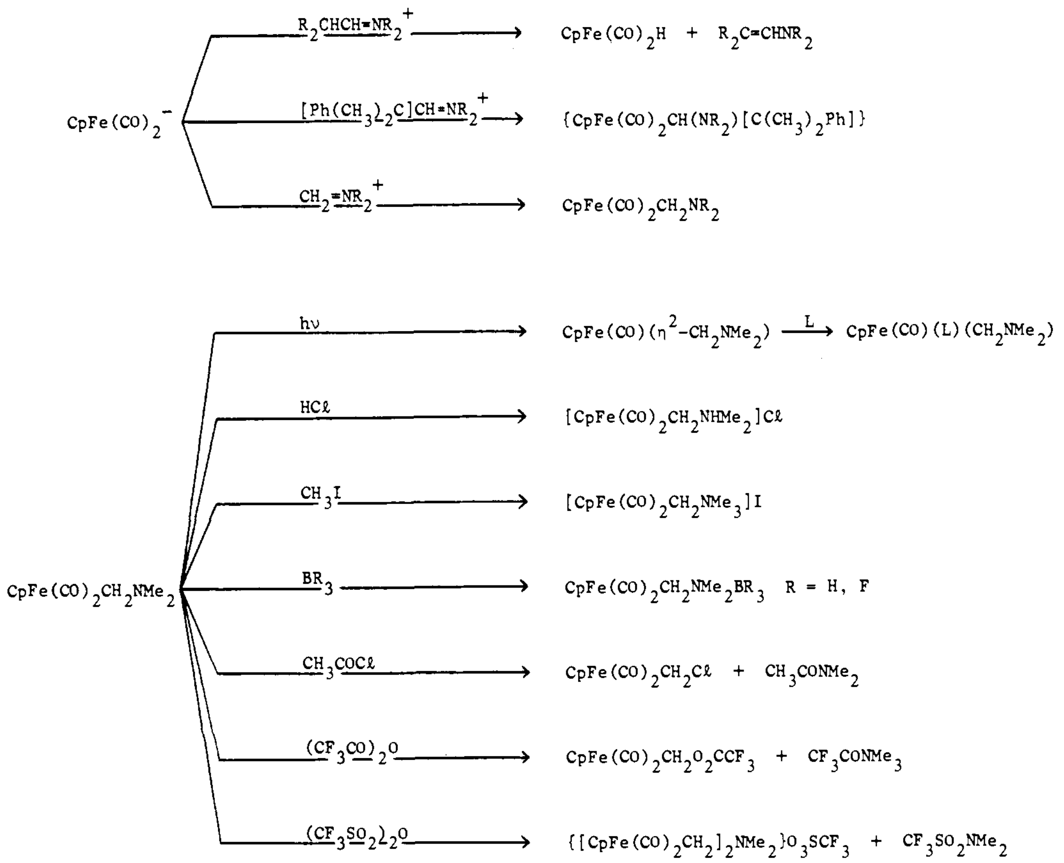


Figure 1. Summary of preparative chemistry involving $CpFe(CO)_2^-$ and iminium salts.

to the hydride transfer step.[9] Since thermal loss of CO is negligibly slow at room temperature in the $CpFe(CO)_2CH_2NR_2$ compounds, the β-hydride pathway can be eliminated as a possibility in the C-substituted iminium ion reactions.

The previously mentioned reduced yields of the aminoalkyl complexes obtained from reactions that were conducted at room temperature is puzzling since the aminoalkyl complexes are not especially thermally sensitive. It seems more likely that an alternative pathway for reaction, such as electron transfer, may compete with the nucleophilic path at the higher temperature. Production of 17 electron $CpFe(CO)_2$ would result in dimer formation and presumably $R_2NCH_2CH_2NR_2$ (or R_2NCH_3 depending upon the fate of the aminoalkyl radical). Both nucleophilic and electron transfer pathways have been suggested for reactions of organometallic anions with certain alkyl halides.[10] The effect of temperature on these reactions is not readily predicted but it should be noted that the nature of the carbonyl reagent is probably different at high and low temperatures since the ratio of solvent separated to contact ion pairs should be substantially different.[11] Whether or not this could affect the redox and/or nucleophilic properties of the anion remains to be determined.

All of the aminoalkyl complexes studied are viscous red oils that are air sensitive but are only moderately thermally sensitive. In fact, the lower molecular weight derivatives can be distilled at 50 °C in vacuo with little decomposition, although they do decompose when heated at higher temperatures. $[CpFe(CO)_2]_2$ forms in the thermal decomposition. Higher molecular weight derivatives are not distillable and could not be obtained in analytically pure form as the free amines. All of the aminoalkyl compounds could be obtained as crystallizable solids by complexation with Lewis bases, vide infra.

Several unsuccessful attempts were made to generate aminoalkyl complexes by other routes. $CpFe(CO)_2CH_2Cl$ was unreactive toward $LiN(C_2H_5)_2$, a result that is not surprising in view of the similarity of this complex to neopentyl systems. Green et al. found that the chloromethyl complex reacted with silver ion and on the basis of the product distribution suggested that unstable $[CpFe(CO)_2CH_2]^+$ was formed.[12] It seems reasonable that such a species would react readily with dialkylamines. Unfortunately, no conditions were found where Ag^+ would react with the chloromethyl complex in the presence of diethylamine.

IR and NMR Spectra of $[CpFe(CO)_2(\eta^1\text{-}CH_2NR_2)]$. As many as six carbonyl stretching absorptions are observed for $[CpFe(CO)_2(\eta^1\text{-}CH_2NR_2)]$ depending upon the nature of the substituents on nitrogen; the energies of certain of these absorptions are lower than expected for compounds with such alkyl substituents,[13] vide infra. In addition the NMR chemical shifts of the methylene group proton resonances are anomalously low for those complexes having low frequency infrared absorptions.

Carbonyl region infrared spectra of five derivatives are shown in Figure 2 (**6** has a spectrum identical with that of **4**). These five compounds can be classified into three categories based on their infrared spectral behavior: (a) **1**; ν_{CO} expected for an aminomethyl substituent, one pair of absorptions observed; (b) **5**; ν_{CO} at lower energy than expected, two pairs of absorptions observed;[14] (c) **2–4**; ν_{CO} at expected frequencies, one pair, and ν_{CO} at lower energy, two pairs, with relative intensities of high and low energy pairs of bands varying with the substituents on nitrogen. Infrared spectra of **3** obtained at several temperatures between +30 and −50 °C show that the intensities of the lower energy pairs of absorptions increase relative to those of the high energy pair as the temperature is lowered.

Room temperature NMR spectra of all of the aminoalkyl complexes (chemical shift data are tabulated in the table) are

Table I. Infrared and ^{1}H NMR Spectral Data for $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2NR_2$ and Derivatives

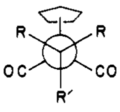
compound	IR^a		NMR^b		
			$\eta^5\text{-}C_5H_5$	Fe-CH_2	other
1 $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(C_6H_5)CH_3]\}$	2026	1966	5.65^c	7.43	NCH_3, 7.30, $-C_6H_5$, cm centered at τ 3.15
2 $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_2CH_2)_2O]\}$	2008 1993 sh 1988	1952 1937 sh 1933	5.75^c	6.13	NCH_2CH_2O, 6.42 ct; NCH_2CH_2O, 7.72 ct
3 $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_2CH_2)_2CH_2]\}$	2003 1991 sh 1985	1949 1933 sh 1927	5.73^c	5.78	NCH_2, 7.63 cm; $-(CH_2)_3-$, 8.52 cm
4 $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}$	2007 1992 sh 1987	1952 1935 sh 1930	5.76^c 5.26^d 5.40^e	5.76 5.69 5.77	7.90 7.89 7.90
5 $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_2CH(CH_3)_2)_2]\}$	1991 sh 1987	1930	5.77^c	5.60	NCH_2CH, 7.83 cm; NCH_2CH, 8.32 cm; $CH(CH_3)_2$, 9.08 d, $J = 6$ Hz
6 $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)CH_2CH_3]\}$	2005 1991 sh 1887	1950 1930	5.85^c	5.69	NCH_3, 7.87, $-CH_2CH_3$, 7.71 q; $-CH_2CH_3$, 8.01 t, $J = 7$ Hz
7 $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2NH(CH_3)_2]\}Cl$	2027	1969^d	4.73^d	6.71	7.30
8 $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_3]\}I$	2031	1972^d	4.79^d	6.00	6.93
9 $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2(BH_3)]\}$	2016	1963^d	5.80^c	6.43	7.58
10 $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2(BF_3)]\}$	2022	1962^d	6.02^c	6.50	7.78
11 $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2OC(O)CF_3]\}$	2032	1980	5.88^c	4.63	
12 $\{[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2)]_2N(CH_3)_2\}O_3SCF_3$	2025	1970	4.83^d	6.07	7.20
13 $\{(\eta^5\text{-}C_5H_5)Fe(CO)[\eta^2\text{-}CH_2N(CH_3)_2]\}$		1903	5.74^c 5.61^d	7.39, 8.02 7.15, 8.03	8.16, 8.21 7.63, 7.83
14 $\{(\eta^5\text{-}C_5H_5)Fe(CO)\text{-}[P(C_6H_5)(CH_3)_2]\text{-}[\eta^1\text{-}CH_2N(CH_3)_2]\}$		1912	5.86^c $J_P = 1.5$ Hz	6.49 d, 6.57 d $J_P = 3.2$ Hz	NCH_3, 7.67, PCH_3; 8.71 d, 8.79 d, $J_P = 3.9$ Hz; PC_6H_5, 2.55–2.97 cm
15 $\{(\eta^5\text{-}C_5H_5)Fe(CO)\text{-}[P(C_6H_5)_2CH_3][\eta^1\text{-}CH_2N(CH_3)_2]\}$		1914	5.72^c $J_P = 2$ Hz	6.33 d, 6.45 d $J_P = 3$ Hz	NCH_3, 7.72, PCH_3, 8.42 d, $J_P = 8$ Hz; PC_6H_5, 2.33–3.03 cm

[a] Spectra were taken on cyclohexane solutions unless otherwise indicated. Conditions are described in the Experimental Section. [b] Chemical shifts are τ values vs. Me_4Si as internal standard. Solvents are indicated by appropriate footnote letter. Abbreviations used to describe multiline patterns are: d, doublet; t, triplet; q, quartet; ct, complex triplet; cm, complex multiplet. [c] Benzene-d_6. [d] Acetonitrile-d_3 for NMR, acetonitrile for IR. [e] Carbon disulfide.

entirely consistent with their formulation and all contain only one resonance assignable to the methylene group; it is a singlet in each case. The spectrum of **4** was examined (as a toluene-d_8 solution) at −80 °C; again the methylene resonance consisted of one singlet. The chemical shifts of the methylene group singlets are anomalously low for compounds **2–6**, which also have unusual infrared spectra, whereas the shift of the resonance for **1** is as predicted.[15] The chemical shift of the methylene resonance increases as the relative intensity of the low frequency pairs of infrared bands increases.

Methylation, protonation, or adduct formation reactions of **4** yield compounds whose infrared spectra contain only one pair of carbonyl stretching absorptions vide infra. In each case, these occur at the higher frequencies expected for compounds with such electron-withdrawing substituents. The NMR chemical shifts of the methylene group proton resonances (singlets in each case) are *upfield of that of the parent compound.*

In general, complexes of the type $(Cp)Fe(CO)_2R$ exhibit two or more carbonyl stretching absorptions depending upon the symmetry and size of R and the frequencies of the absorptions increase as the electron-withdrawing power of R becomes greater.[15] More than two carbonyl absorptions *may be* observed when R has lower than threefold symmetry. For example, when R has only a plane of symmetry, two rotational isomers exist as a result of restricted rotation about the bond to iron, i.e.



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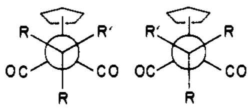
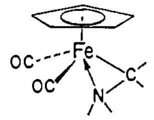


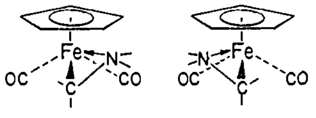
II

When the energies of the carbonyl stretching absorptions for these isomers are sufficiently different so that they can be resolved, four bands (two pairs) are observed.[16-21] This is the case when R is $SiHCl_2$,[16-18] $GeHCl_2$,[19] and CH_2Ph.[20]

The infrared and NMR spectral data are only consistent with the existence of a dynamic equilibrium between isomeric species in the case of **2–6**, whereas only a single species is detectable for **1**. At least three species are required for **2–4** and **6** and two of these, as well as the two detected for **5**,[14] have lower energy carbonyl infrared stretching absorptions than expected for such alkyl substituents. The low CO stretching frequencies and the existence of two similar species with low energy absorptions can be accounted for by species III and IV:



III



IV

in which there exits a net bonding interaction between the nitrogen atom and iron.[22] The increased electron density placed on iron as a result of this perturbation is transferred (in part) to the π^* orbitals of CO through the normal back-bonding interaction (which occurs here via the iron d_{xy}, $d_{x^2-y^2}$, and d_{z^2} orbitals)[25] resulting in a decrease in the C–O bond order and a reduction of the C–O stretching energy. Structures III and IV represent the same rotational isomers as I and II *with* the addition of the Fe–N interaction. The additional set of absorptions (highest energy peak) observed for **2–4** and **6** and the only set observed for **1** are in the energy range expected for such alkyls. We attribute these to a form in which there is no Fe–N interaction. In principle, rotational isomers exist for this species but their carbonyl absorptions are apparently not sufficiently different in energy to be resolved.

Consistent with the above interpretation, the increase in the ratio of interacting to noninteracting forms in going from **1** to **5** roughly parallels the increase in basicity of the secondary amine from which they are formally derived. The temperature dependence of the equilibrium is in the expected direction and the small enthalpy difference is consistent with the weak nature of the Fe–N interaction. The effect of complexation of the nitrogen by an external acid is also to be expected.

The chemical shifts observed for the methylene groups in **1–6** are obviously a mole fraction weighted average of the species participating in each equilibrium; the shifts of **1** and **5** should be close to the limits for noninteracting and interacting forms, respectively. The pronounced deshielding effect resulting from the Fe–N interaction is not readily explained. It does not seem reasonable that the inductive effect resulting from the interaction should be greater than that of a proton or methyl carbonium ion. Perhaps the precise location of the methylene protons relative to other parts of the molecule in the interacting form results in a deshielding effect.

Reactions of {$CpFe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]$} with Electrophiles. The aminoalkyl complexes react, at nitrogen, with a variety of electrophilic reagents including Brønsted acids, alkyl halides, Lewis acids, carboxylic and sulfonic acid halides, and anhydrides. Although it is probably safe to assume that these reagents react with the aminoalkyl compounds, regardless of the identity of the nitrogen substituents, not all combinations have been attempted and only reactions with the more extensively studied dimethylaminomethyl complex **4** will be described.

Complex **4** reacts immediately in petroleum ether with $HCl_{(g)}$ or CH_3I to give yellow precipitates (**7** and **8**, respectively). Both products are recrystallizable from polar solvents without change. Elemental analysis, IR, and ^1H NMR data are consistent with the formulation of these products as {$CpFe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2R]$}X: **7**, R = H, X = Cl; **8**, R = CH_3, X = I. The effects of introducing a strongly electron-withdrawing group into the molecule are readily apparent in the infrared and NMR spectra. In the former, the carbonyl stretching absorptions are shifted to higher energy compared with the parent molecule (Table I gives spectral data) consistent with electron density withdrawal from the metal and concomitant reduction in Fe–CO π-backbonding. Only two CO stretching absorptions are observed in both cases, rather than the six observed for the parent. Simpler spectra should be observed since the Fe–N interaction that results in stabilization of rotational isomers in the parent is blocked in the derivatives. Rotational isomers of the normal type are still possible but are not detected in the infrared spectra. The NMR spectra show downfield shifts of the cyclopentadienyl and methyl group resonances consistent with the deshielding that results from introduction of the positive charge. The methylene group resonances occur *upfield* of those in the parent. A satisfactory explanation for this phenomenon is not available but it must be associated with the unusual properties of the dimethylaminomethyl complex and not those of the quaternized forms. In fact, if the chemical shift of the methylphenylaminomethyl complex **1**, which shows "normal" behavior, is chosen as the reference (τ 7.43), then the shifts of both the protonated and methylated complexes are downfield (τ 6.71 and 6.0, respectively) as would normally be expected.

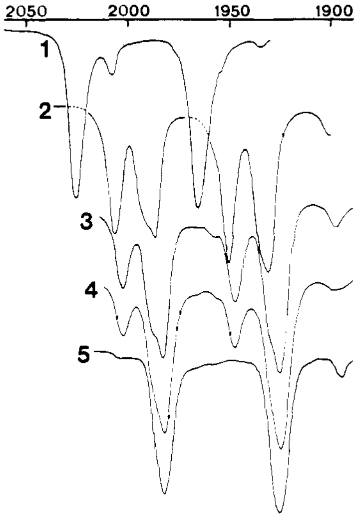


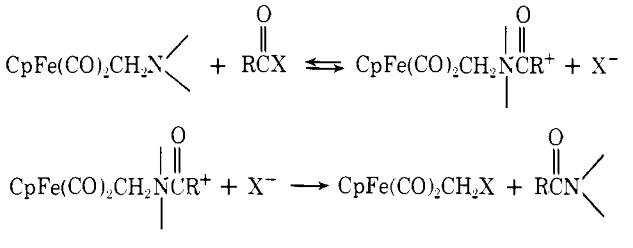
Figure 2. Carbonyl stretching absorptions of $[CpFe(CO)_2(\eta^1\text{-}CH_2NR_2)]$ (cyclohexane solutions): NR_2 = (**1**) $N(CH_3)Ph$, (**2**) $N(CH_2CH_2)_2O$, (**3**) $N(CH_2CH_2)_2CH_2$, (**4**) $N(CH_3)_2$, (**5**) $N[CH_2CH(CH_3)_2]_2$. Absorptions at ~1900 cm^{-1} in spectra **2–5** are due to $[CpFe(CO)(\eta^2\text{-}CH_2NR_2)]$ impurities. The absorption at 2007 cm^{-1} in **1** is from $[CpFe(CO)_2]_2$.

The quaternary salts are extremely resistant to hydrolysis, even in strong aqueous acid and they are unaffected by trifluoroacetic acid. Treatment of the protonated complex with K_2CO_3 in acetonitrile regenerates the starting material. The salts are also resistant to air oxidation both in solution and in the solid state.

$[CpFe(CO)_2CH_2N(CH_3)_3]^+$ and $[CpFe(CO)_2CH_2NH(CH_3)_2]^+$ may be considered as substitution products derived from reactions of $[CpFe(CO)_2L]^+$ with the ylides $^-CH_2N^+(CH_3)_3$ and $^-CH_2N^+(CH_3)_2H$, respectively. In fact, the related phosphorus derivative, $[CpFe(CO)_2CH_2PPh_3]BF_4$, has been prepared by reaction of $[CpFe(CO)_2(THF)]BF_4$[26a] or $CpFe(CO)_2I$,[26b] in the presence of $AgBF_4$, with the preformed ylide, $^-CH_2P^+Ph_3$. In contrast to phosphorus, simple nitrogen ylides are not isolable and can apparently only be generated as LiBr stabilized species.[27] Although a fair amount of organic chemistry has been done with these LiBr complexed species, transition metal complexes have not been generated from them. Of course, neither $^-CH_2N^+(CH_3)_2H$ nor $^-CH_2P^+(CH_3)_2H$ can be generated in the usual fashion from the quaternary salt so that protonation of substituted alkyl complexes represents a unique route to their complexes. Derivatization of substituted alkyl complexes could develop into a general method for generating ylide complexes, especially of those ylides that are inherently unstable. We earlier reported the preparation of $[CpNi(PPh_3)CH_2N(CH_3)_3]I$ by methylation of the aminoalkyl complex[1] and we have prepared the sulfur ylide complex, $[CpFe(CO)_2CH_2S(CH_3)CH_2CH_3]I$ by reaction of the thioether with $[(CH_3)_3O]BF_4$. Similar alkylations of $RSCH_2ML_n$ species have been performed by others.[27]

In view of the above results it is not surprising that the aminoalkyl complexes also react readily with Lewis acids. Both BF_3, **9**, and BH_3, **10**, complexes of $\{CpFe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}$ were prepared. These yellow complexes resemble closely the ylide complexes in their spectroscopic properties (Table I). Both show shifts of their carbonyl stretching absorptions to higher energy compared with the parent. The spectra are simplified (two bands for each adduct) for the same reasons described for the quaternary derivatives. The methylene group chemical shifts are at *higher field* than that of the dimethylaminomethyl complex, although the chemical shifts of cyclopentadienyl and methyl proton resonances are somewhat less affected than in the quaternary derivatives.

Low-temperature reaction of $\{CpFe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}$ with CH_3COCl, $[CF_3CO]_2O$, or $[CF_3SO_2]_2O$ results in cleavage of the methylene carbon–nitrogen bond. Products of these reactions are $CpFe(CO)_2CH_2Cl$, $CpFe(CO)_2CH_2OC(O)CF_3$ (**11**), and $\{[CpFe(CO)_2CH_2]_2N(CH_3)_2\}O_3SCF_3$ (**12**), respectively, and the appropriate dimethylamides. The first two reactions probably proceed in the following fashion:



$$CpFe(CO)_2CH_2N(CH_3)_2 + RC(O)X \rightleftharpoons CpFe(CO)_2CH_2N(CH_3)_2C(O)R^+ + X^-$$

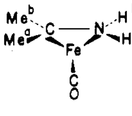
$$CpFe(CO)_2CH_2N(CH_3)_2C(O)R^+ + X^- \longrightarrow CpFe(CO)_2CH_2X + RC(O)N(CH_3)_2$$

Whether the second step proceeds by S_N2 displacement of the amide by the counterion or a dissociative (S_N1) reaction is not known. Other work suggests that the carbenoid species $[CpFe(CO)_2CH_2]^+$ is not stable[29] so that a purely dissociative reaction either does not occur or occurs in a tight ion pair where the counterion traps the carbene species before disproportionation takes place. The ultimate disproportionation products should be $[CpFe(CO)_2(C_2H_4)]X$ and/or $CpFe(CO)_2X$. Neither of these was observed.

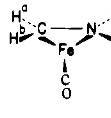
The reaction with $(CF_3SO_2)_2O$ probably proceeds through an ionic intermediate analogous to that above but excess $CpFe(CO)_2CH_2N(CH_3)_2$ (the anhydride was added to the aminomethyliron complex) either reacts with the ionic species or with the trifluorosulfonate which could form as an intermediate product. The dinuclear product is similar to products derived from the deprotonated phosphorus ylide $[(CH_3)_2P(CH_2)_2]^-$.[30]

Preparation and Reactions of $\{CpFe(CO)[\eta^2\text{-}CH_2N(CH_3)_2]\}$. Photolysis of $\{CpFe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}$ results in smooth evolution of CO with the formation of the η^2-iminium ion complex **13**, a low melting solid which is readily sublimed in vacuo. As expected this complex shows a single carbonyl stretching absorption (1903 cm^{-1} in cyclohexane). Its NMR spectrum (Table I) consists of a singlet for the cyclopentadienyl protons and *doublets* for the methylene and methyl group protons. As shown by A below, a fixed orientation of the dihapto iminium ion would result in nonequivalent methylene protons and methyl groups. The NMR spectrum confirms this structure and indicates that interconversion between A and A′ is slow at room temperature. In fact, the NMR spectrum is unchanged to ~100 °C (toluene solution) where the complex begins to decompose. This behavior is in contrast to that described by Wilkinson and Fong for $\{CpMo(CO)_2[\eta^2\text{-}CH_2N(CH_3)_2]\}$.[4a] The room temperature ^1H NMR spectrum of this complex consists of three singlets at τ 4.64, 7.31, 7.48 in the ratio 5:6:2, respectively. As shown by structure B, this complex should also have nonequivalent methylene protons and methyl groups and the observed NMR spectrum suggests that the complex is undergoing a rapid intramolecular rearrangement (B ↔ B′). We have confirmed that this is the case through variable temperature NMR measurements on $CDCl_3$ solutions of the complex. The two higher field resonances broaden as the temperature is lowered so that at −60 °C two doublets are clearly present consistent with static structures B and B′. The different behavior of the iron and molybdenum complexes of the $\eta^2\text{-}CH_2N(CH_3)_2$ ligand resembles that of the corresponding η^3-allyl complexes. $CpFe(CO)_2$(allyl) complexes rearrange (endo → exo) at moderate rates at room temperature. $\Delta G^{\ddagger}$ is 24.1 kcal/mol for the methallyl complex.[31] The comparable rate of conversion of anti ↔ syn groups to endo ↔ exo isomerization suggests that an η^3-η^1-η^3 process is responsible. In contrast, $CpMo(CO)_2$(allyl) complexes undergo rapid interconversion (endo ↔ exo) at room temperature with static forms observed (by ^1H NMR) at temperatures below 0 °C. $\Delta G^{\ddagger}$ for the intramolecular process in the methallyl complex is about 16 kcal/mol.[32] Anti-syn interconversion does not accompany the endo ↔ exo process leading to the conclusion that "... a rotation of the planar allyl about an axis between the metal and the center of gravity of the allyl appears most reasonable".[32] Although activation parameters and mechanistic details are not presently available for the iminium ion complexes, it is apparent that the relative stereochemical rigidities of iron and molybdenum compounds are the same as that of the allyl complexes. This observation suggests that the similarity between the η^3-allyl and η^2-iminium ligands is more than operational; they seem to impart much the same electronic effect to the metal.

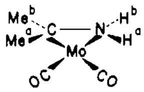
A



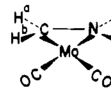
A′



B



B′



$\{CpFe(CO)[\eta^2\text{-}CH_2N(CH_3)_2]\}$ undergoes facile ring opening reactions with phosphines as evidenced by NMR and infrared spectra of reaction mixtures containing $PhP(CH_3)_2$ and Ph_2PCH_3. The monophosphine complexes $\{CpFe(CO)L[\eta^1\text{-}CH_2N(CH_3)_2]\}$, **14** and **15**, are asymmetric and their NMR spectra (Table I) contain multiplets consistent with the diasterotopic nature of the methylene protons and the methyl groups in the $PhP(CH_3)_2$ compound. Infrared spectra of the phosphine complexes contain a single symmetrical carbonyl stretching absorption (see Table I). The absence of any complexity to these spectra indicates that only one rotational isomer is present or, perhaps more likely, that the carbonyl stretching absorptions of the rotational isomers present (three are possible) are not sufficiently different in energy to be resolved and are contained in the absorption envelope. (The half-widths of the carbonyl bands are ~20 cm^{-1}, which is about twice the half-width of absorptions for the $CpFe(CO)_2(\eta^1\text{-}CH_2NR_2)$ derivatives.) Neither of the phosphine complexes could be crystallized; however, complexation of the amino nitrogen in

$\{CpFe(CO)(PPh_2CH_3)[\eta^1\text{-}CH_2N(CH_3)_2]\}$ by BF_3 produced a solid derivative **16** whose elemental analysis and spectroscopic properties are consistent with the desired compound and confirm the authenticity of the precursor complex.

Conclusion

This work and that of Wilkinson[4a] show that, subject to a few constraints, aminoalkyl complexes are readily obtained from reactions of iminium salts and metal carbonyl anions. The aminoalkyliron products undergo a number of reactions to produce novel compounds not readily available by other routes. Several of these reactions should be applicable to aminoalkyl complexes of most metals. Of special interest is C–N bond cleavage by electrophilic reagents which may provide a route to carbene complexes that do not have heteroatom substituents. Work in this area is underway.

The iron–nitrogen interaction proposed to occur in $CpFe(CO)_2(\eta^1\text{-}CH_2NR_2)$ species on the basis of infrared and NMR measurements is unusual and more definitive evidence would be desirable. Unfortunately, all of the compounds believed to have this interaction are liquids at ambient temperature so that X-ray data are not obtainable with our equipment. Neither of the phosphine complexes appear to have iron–nitrogen interactions. This could be because of unfavorable steric effects or because of the decrease in π-bonding capability of the phosphorus donor.

Experimental Section

All synthetic operations and manipulations of samples of organometallics were conducted in a nitrogen filled glovebox or under a nitrogen atmosphere in suitable glassware by using syringe techniques for sample transfer. Solvents were purified by distillation from drying agents under a nitrogen atmosphere. Iminium salts were prepared by literature methods and each was characterized by its NMR spectral properties and by elemental analysis before use.

$\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}$, 4. A solution of $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$, 75 mmol obtained by stirring 13.35 g of $[Fe(CO)_2(C_5H_5)]_2$ with an excess of 1% sodium amalgam in THF for several hours and decanted into a dropping funnel, was added over 1 h to 7.50 g (80 mmol) of $[(CH_3)_2NCH_2]Cl$ suspended in 75 mL of THF at −78 °C. After stirring for an additional 1.5 h at −78 °C, the reaction mixture was warmed to room temperature and the solvent evaporated. The residue was extracted four times with 35-mL portions of medium petroleum ether. After the extracts were filtered through a pad of Celite, the solvent was evaporated to yield 14.8 g (84%) of a dark, air-sensitive red-brown oil. Subsequent distillation in a molecular still at 50–55 °C (10^{-3} mm) gave pure $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[CH_2N(CH_3)_2]\}$. Anal. Calcd for $C_{10}H_{13}NFeO_2$: C, 51.10; H, 5.57; N, 5.96; Fe, 23.76. Found: C, 51.00; H, 5.40; N, 6.00; Fe, 23.26.

$\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)C_6H_5]\}$, 1. A solution of 13 mmol of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ in 40 mL of THF, prepared as described above, was added to a suspension of 2.0 g (13 mmol) of $[CH_2N(CH_3)C_6H_5]Cl$ in 100 mL of THF at −78 °C over a 45-min period. After stirring at −78 °C for an additional 2 h, the reaction mixture was gradually warmed to room temperature and the solvent evaporated. The residue was extracted four times with a 1:1 mixture of hexane/ether. The extracts were filtered through Celite, combined, and the solvent evaporated to yield 2.7 g (70%) of a red-brown oil. Chromatography of the product on silica gel, alumina, or charcoal/Celite resulted in decomposition. However, chromatography on a column of Celite with hexane yielded the product as a dark orange-red oil, contaminated with only a small amount of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2$ (by infrared spectroscopy). The compound decomposes extensively to $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and a colorless oil upon standing at 0 °C over a week.

$\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_2CH_2)_2O]\}$, 2. A solution of 20 mmol of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ in 40 mL of THF was added over 45 min to a suspension of 3.0 g (22 mmol) of $[CH_2N(CH_2CH_2)_2O]Cl$ in 85 mL of THF at −78 °C. After stirring an additional hour at −78 °C, the reaction flask was allowed to warm slowly to room temperature. Workup as described for **4** (extracted six times with a total of 100 mL of hexane) gave 5.2 g (94%) of the product as a dark red oil. Satisfactory analytical results for all elements could not be obtained on individual samples of **2** or **3**. However, their NMR spectra (Table I) were entirely consistent with their proposed structures and their infrared spectra did not vary with the particular preparation.

$\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_2CH_2)_2CH_2]\}$, 3. A solution of 25 mmol of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ in 50 mL of THF was added to a suspension of 4.0 g (30 mmol) of $[CH_2N(CH_2CH_2)_2CH_2]Cl$ in 75 mL of THF at −78 °C over a 1-h period. Workup of the reaction mixture as described above gave 5.3 g (77%) of the product as a red-brown oil. Distillation as above gave the product.

$(\eta^5\text{-}C_5H_5)Fe(CO)_2\{\eta^1\text{-}CH_2N[CH_2CH(CH_3)_2]_2\}$, 5. A solution of 20 mmol of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ in 40 mL of THF was added slowly to a suspension of 3.75 g (21 mmol) of $[CH_2N(CH_2CH(CH_3)_2)_2Cl$ in 75 mL of THF at −78 °C. Workup as above gave 5.2 g (82%) of the desired product. Distillation in high vacuum at 50 °C in a molecular still apparatus gave the product. Anal. Calcd for $C_{16}H_{25}FeNO_2$: C, 60.18; H, 7.90; N, 4.39. Found: C, 60.63; H, 8.43; N, 4.92.

$\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)(CH_2CH_3)]\}$, 6. Reaction of 10 mmol of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ and 1.1 g (10 mmol) of $[CH_2N(CH_3)(CH_2CH_3)]Cl$ and workup as above gave 1.1 g (44%) of $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[CH_2N(CH_3)(CH_2CH_3)]\}$. Anal. Calcd for $C_{11}H_{15}NFeO_2$: C, 53.04; H, 6.07; N, 5.62; Fe, 22.42. Found: C, 53.32; H, 6.04; N, 5.65; Fe, 21.22.

Reaction of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2)]$ with $[(CH_3)_2CHCH{=}N(CH_2CH_2)_2O]Cl$. A solution of 4.5 mmol of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ in 30 mL of THF was added dropwise over ca. 30 min to a suspension of 0.8 g (4.5 mmol) of the iminium salt in THF, which was maintained at −78 °C during the entire addition. Decolorization of the dark red-brown color of the carbonyl anion was rapid as each drop entered the iminium ion suspension. A pale yellow color persisted. After addition was complete the mixture was allowed to warm to room temperature with continuous stirring. After this time the mixture was a dark red-brown color. The solvent was removed under vacuum and the residue was extracted with 20 mL of pentane. After filtration the pentane was evaporated to leave a red-brown oily residue. An NMR spectrum obtained on this residue showed strong resonances for the enamine $(CH_3)_2C{=}CHN(CH_2CH_2)_2O$. In addition to resonances for the enamine, there were resonances attributable to the protons of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ as well as some unassigned resonances. The enamine constituted at least 60% of the sample.

In a second experiment, a solution of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (prepared from 0.89 g (2.5 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and excess Na(Hg) in about 10 mL of THF) was slowly added to a cooled (−96 °C toluene slush) flask that contained 0.90 g (5.0 mmol) of $[(CH_3)_2CHCH{=}N(CH_2CH_2)_2O]Cl$. The reactants were mixed by swirling and allowed to warm slightly by removal of the flask from the bath for short periods. The iminium salt gradually disappeared over about 30 min after which time a portion of solution was filtered into a cold NMR tube. A small quantity of toluene was added to the tube as a standard. The presence of a hydride was established by a singlet 18-ppm upfield from the phenyl proton resonance of toluene. A cyclopentadienyl proton resonance approximately five times as intense as the hydride resonance was also present and was assumed to be due to $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$.

$\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2NH(CH_3)_2]\}Cl$, 7. Two grams (8.5 mmol) of $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}$ was dissolved in 50 mL of medium petroleum ether in a three-necked flask fitted with a nitrogen bubbler system and a gas inlet. Gaseous HCl was bubbled into the solution for 5 min. Precipitation of a yellow solid occurred immediately. After stirring for 1 h, with occasional addition of HCl, the precipitate was collected, washed with ether, and dried to give a nearly quantitative yield of crude product. Recrystallization from hot acetonitrile/ether gave 1.60 g (70%) of $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2NH(CH_3)_2]\}Cl$ as fine, yellow crystals. Anal. Calcd for $C_{10}H_{14}NFeClO_2$: C, 44.24; H, 5.20; N, 5.16; Fe, 20.57; Cl, 13.06. Found: C, 44.47; H, 5.39; N, 5.28; Fe, 20.32; Cl, 12.77.

$\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_3]\}I$, 8. A 2.0-g portion of $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}$, 8.5 mmol, was dissolved in 25 mL of medium petroleum ether and 1.8 g (12.8 mmol) of methyl iodide was added. Precipitation of solid began immediately. After stirring for 5 h at room temperature, the product was collected and washed with ether. The crude salt was recrystallized from hot acetonitrile/ether to yield 2.20 g (69%) of bright yellow-orange crystals. Anal. Calcd for $C_{11}H_{16}NFeIO_2$: C, 35.05; H, 4.28; N, 3.71; Fe, 14.81;

I, 33.66. Found: C, 34.76; H, 4.28; N, 3.71; Fe, 14.75; I, 32.81.

$\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2(BH_3)]\}$, 9. A 1.50-g (6.4 mmol) portion of $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}$ was dissolved in 25 mL of THF in a three-necked flask connected to a nitrogen bubbler system. The flask was cooled to −78 °C and a stoichiometric amount of BH_3:THF in THF was added by syringe. The reaction mixture was stirred and allowed to warm slowly to room temperature. After an hour at room temperature, the solvent was evaporated under vacuum. The crude product was taken up in ether, petroleum ether was added, and solvent was evaporated to yield bright yellow crystals which were collected, washed with petroleum ether, and dried, yield 1.05 g (66%). Anal. Calcd for $C_{10}H_{16}FeNO_2B$: C, 48.26; H, 6.47; N, 5.63; Fe, 22.44. Found: C, 47.83, 48.22; H, 6.35, 6.22; N, 5.70, 5.98; Fe, 21.84, 21.46.

$\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2(BF_3)]\}$, 10. A three-necked flask equipped with a dropping funnel and a nitrogen inlet was charged with 1.0 g (4.25 mmol) of $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}$ in 25 mL of ether. A stoichiometric amount of boron trifluoride etherate, 0.60 g, was mixed with ether in the dropping funnel. After cooling the flask to −78 °C the boron trifluoride etherate solution was added over 25 min. Solid precipitated immediately. After warming to room temperature, the mixture was stirred for several hours. Petroleum ether was added to precipitate more of the product, which was then collected, washed, and dried. Recrystallization from hot THF/petroleum ether gave 0.58 g (45%) of a yellow orange solid. Anal. Calcd for $C_{10}H_{13}NFeO_2BF_3$: C, 39.65; H, 4.33; N, 4.62; Fe, 18.44. Found: C, 39.37; H, 4.44; N, 4.57; Fe, 18.15.

Reaction of $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}$ with CH_3COCl. Under nitrogen, a 2.00-g (8.5 mmol) portion of $(\eta^5\text{-}C_6H_5)\text{-}Fe(CO)_2(\eta^1\text{-}CH_2N(CH_3)_2)$ was dissolved in 50 mL of hexane in a 100-mL three-necked flask. A dropping funnel containing 20 mL of hexane and 0.70 mL (about 0.77 g, 9.00 mmol) of acetyl chloride (fractionally distilled from *N,N*-dimethylaniline) was attached to the third neck of the flask. The flask was cooled to −78 °C with a dry ice bath and the solution of acetyl chloride added over a 15-min period. A yellow solid formed in the cold reaction mixture. After maintaining the reaction mixture at −78 °C for an additional 45 min, it was allowed to warm slowly to room temperature. A small quantity (0.05 g) of insoluble grey-brown powder was removed by filtration; comparison of the infrared spectrum of the filtrate with that of the starting solution indicated complete consumption of the starting material. The solvent was evaporated from the filtrate to yield a dark brown-red gel, whose NMR spectrum showed it to consist of an equimolar mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2Cl)$ and *N,N*-dimethylacetamide. The product was kept at −10 °C for several days, which caused it to separate into an orange solid and a clear oil. The latter was removed by washing the solid twice with small amounts of cold hexane. After drying in vacuum, 1.40 g (73%) of a yellow orange solid, identified as $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2Cl)$ by comparison of its infrared and NMR spectra with that of an authentic sample, was obtained.

Reaction of $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}$ with Trifluoroacetic Anhydride. A three-necked flask containing a solution of 1.50 g (6.4 mmol) of $\{(\eta^5\text{-}C_5H_5Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}$ in 30 mL of hexane was placed under nitrogen and cooled at −78 °C. The cold solution was treated with 1.64 g (7.8 mmol) of trifluoroacetic anhydride, added slowly with a gas tight syringe. An immediate color change from yellow-orange to blood red was observed. The reaction mixture was stirred for 2 h at −78 °C. The infrared spectrum of the reaction mixture showed no absorptions from the starting material and the appearance of two new, terminal carbonyl absorptions as well as two new bands between 1710 and 1780 cm^{-1}. The flask was warmed slowly to room temperature and the solvent evaporated to yield an orange oil. The residue was chromatographed on a silica gel column with hexane. The leading orange band yielded 1.20 g (62%) of $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2OC(O)CF_3]\}$, **11**, as an orange oil. Elution with ether/hexane of the second red band yielded a small amount of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$. Anal. Calcd for $C_{10}H_7FeF_3O_4$: C, 39.51; H, 2.32. Found: C, 39.76; H, 2.29.

Reaction of $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}$ with Trifluoromethanesulfonic Anhydride. A solution of 1.50 g (6.4 mmol) of $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}$ in 40 mL of hexane contained in a three-necked flask was cooled to −78 °C, and 1.84 g (6.5 mmol) of trifluoromethanesulfonic anhydride was slowly added to the cold solution with a gas-tight syringe. Immediately upon addition, a yellow powdery solid formed. The reaction mixture was stirred at −78 °C for 1 h, then warmed to room temperature, filtered, and the filtered solid washed with ether. The yellow powdery product was recrystallized from acetonitrile/ether to give 1.65 g, 90% of bright yellow crystalline $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}SO_3CF_3$, **12**, identified on the basis of IR, NMR, and microanalytical data. Anal. Calcd for $C_{19}H_{20}Fe_2NSF_3O_7$: C, 39.68; H, 3.51; N, 2.44; S, 5.58. Found: C, 38.86; H, 3.45; N, 2.67; S, 6.11.

$\{(\eta^5\text{-}C_5H_5)Fe(CO)[\eta^2\text{-}CH_2N(CH_3)_2]\}$, 13. A solution of 3.0 g of $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}$ in 90 mL of ether was placed in a quartz tube equipped with a water-cooled cold finger and a nitrogen inlet. The tube was irradiated with light from a 200-W Hanovia mercury lamp. Infrared spectra of samples of the reaction mixture indicated rapid disappearance of the starting material, with complete reaction after about 3.5-h irradiation. The solution was transferred to a round-bottomed flask, the ether evaporated, and the residue extracted with several portions of medium petroleum ether. After filtration the solvent was evaporated, producing an oily material that sublimed in vacuo at 55 °C to yield 1.65 g (63%) of sublimed material as long, thin, dark red needles. Anal. Calcd for $C_9H_{13}NFeO$: C, 52.41; H, 6.30; N, 6.73; Fe, 26.85. Found: C, 52.40; H, 6.29; N, 6.36; Fe, 26.29.

$\{(\eta^5\text{-}C_5H_5Fe(CO)[(C_6H_5)P(CH_3)_2][\eta^1\text{-}CH_2N(CH_3)_2]\}$, 14. A 1.0-g (4.8 mmol) portion of $\{(\eta^5\text{-}C_5H_5)Fe(CO)[\eta^2\text{-}CH_2N(CH_3)_2]\}$ was dissolved in 25 mL of THF and 0.76 g (5.5 mmol) of $(C_5H_5)P(CH_3)_2$ was added. The solution was stirred overnight after which the solvent and excess phosphine were removed under vacuum. An NMR spectrum of the resulting brown oil indicated nearly complete reaction, with only traces of the starting materials detectable. Attempts at crystallization of the product from THF/petroleum ether or ether either at −78 °C or by evaporation cooling were not successful. The identity of the compound was confirmed by its NMR spectrum.

$\{(\eta^5\text{-}C_5H_5)Fe(CO)[(C_6H_5)_2P(CH_3)][\eta^1\text{-}CH_2N(CH_3)_2]\}$, 15. Reaction of 0.60 g (2.9 mmol) of $\{(\eta^5\text{-}C_5H_5)Fe(CO)[\eta^2\text{-}CH_2N(CH_3)_2]\}$ with 0.70 g (3.5 mmol) of $(C_6H_5)_2P(CH_3)$ as described above also gave the desired compound as brown oil. All attempts at crystallization failed. The identity of the compound was confirmed by its NMR spectrum.

$\{(\eta^5\text{-}C_5H_5)Fe(CO)[(C_6H_5)_2P(CH_3)][\eta^1\text{-}CH_2N(CH_3)_2\cdot BF_3]\}$, 16. A solution of 1.2 g (3.0 mmol) of $\{(\eta^5\text{-}C_5H_5)Fe(CO)\text{-}[(C_6H_5)_2P(CH_3)][\eta^1\text{-}CH_2N(CH_3)_2]\}$ in THF was treated with an excess of distilled boron trifluoride–etherate (0.60 g, 4.2 mmol) dissolved in 30 mL of 50:50 THF/ether. A solid formed after about 30 min. After the reaction mixture was stirred overnight, additional THF was added to dissolve the yellow solid and the solution was filtered. Part of the solvent was evaporated off and ether added. After further evaporation of solvent a yellow powdery solid was obtained. This solid was recrystallized by dissolution in acetonitrile, filtration of the solution, and evaporation of solvent until solid began to form. Crystallization was completed by cooling the mixture overnight at 0 °C. The supernatant was removed while cold and the well-formed orange crystals washed with ether and dried in vacuo: Yield 0.45 g (32%). A second crop was obtained by evaporation of the mother liquor. Anal. Calcd for $C_{22}H_{26}FeNOPBF_3$: C, 55.62; H, 5.52; N, 2.95; Fe, 11.76. Found: C, 55.18; H, 5.45; N, 2.92; Fe, 11.14.

Infrared measurements were made whenever possible on cyclohexane solutions by using 0.05- or 0.1-mm cells with NaCl windows and a Perkin-Elmer 521 or 621 spectrophotometer. Spectra shown in Figure 2 were obtained with a scan speed of 50 cm^{-1}/min and a linear 10× scale expansion. Calibration of each spectrum was made using indene. Compounds not soluble in cyclohexane were examined in THF or CH_3CN. Variable temperature spectra were obtained by using an Air Products Cryotip low-temperature cell[33] in conjunction with the Perkin-Elmer 621 spectrophotometer. The cell path length was about 0.2 mm. Temperature measurements were made with a thermistor mounted on the tail stock of the refrigerator. Both methylcyclohexane and hexane were used as solvents with identical results.

Routine NMR spectra were obtained with a Varian T-60 spectrometer operated at ~28 °C. The data given in Table I were obtained from such spectra. Low temperature spectra were obtained with Varian HA-100 or JEOL JNM-PS-100 spectrometers.

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(14) Close examination of the spectrum of **5** shows that the higher energy absorption is asymmetric. Although the lower energy band shows little asymmetry, it is assumed to also be a composite absorption.

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(21) If R has no plane of symmetry, then three rotational isomers exist. This could result in six infrared absorption bands (three pairs) if all were resolved. We are not aware of an example in which these have been resolved.

(22) By using representative bond distances and angles from X-ray structures on $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CO_2H$[23] and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)]$,[24] the Fe–N distance is 2.8–2.9 Å in the undistorted molecule. By using the same distances and angles, the *N*-carbonyl carbon distance is ~2.6 Å. Carbonyl ligands are, of course, susceptible to nucleophilic attack and the possibility that an interaction between nitrogen and CO exists cannot be totally excluded. However, we do not see how two different species involving N–CO interactions could occur.

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