Inorg. Chem. 1981, 20, 645-649 645

Contribution from the Department of Chemistry,
Miami University, Oxford, Ohio 45056

Synthesis and Decarbonylation of Fluorocarbon–Bis(acyl)tetracarbonyliron Complexes

DOUGLAS W. HENSLEY, WILLIAM L. WURSTER, and ROBERT P. STEWART, JR.*

Received July 17, 1980

The bis(acyl) complexes *cis*-$(R_FCO)_2Fe(CO)_4$ (R_F = CF_3, *n*-C_3F_7) have been prepared in good yield from the reaction of $(CF_3CO)_2O$ and *n*-C_3F_7COCl with $Na_2Fe(CO)_4 \cdot 1.5$(dioxane). These complexes readily undergo thermal decarbonylation to give the corresponding bis(alkyl) derivatives *cis*-$(R_F)_2Fe(CO)_4$. Evidence for the intermediacy of *cis*- and *trans*-$(R_FCO)(R_F)Fe(CO)_4$ was obtained from a ^{19}F NMR study of the decarbonylation of *cis*-$(CF_3CO)_2Fe(CO)_4$. Prolonged heating of *cis*-(*n*-$C_3F_7)_2Fe(CO)_4$ affords *trans*-(*n*-$C_3F_7)_2Fe(CO)_4$. Under the same conditions, *cis*-$(CF_3)_2Fe(CO)_4$ is stable with respect to isomerization. The infrared spectrum of *cis*-(*n*-$C_3F_7)_2Fe(CO)_4$ indicates the presence of two (or more) rotamers which differ in the relative conformations adopted by the *n*-C_3F_7 ligands.

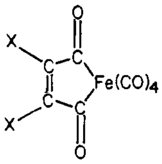
Introduction

The formation of iron–carbon σ bonds via the reaction of organic halides with $Na_2Fe(CO)_4$ is an area of much current interest.[1-5] In particular, Collman and co-workers[1-3] have carried out extensive studies involving the preparative and reaction chemistry of five-coordinate anionic $[RFe(CO)_4]^-$ and $[RCOFe(CO)_4]^-$ complexes. The further reactions of these species with alkyl and acyl halides to produce ketones are thought to proceed via six-coordinate neutral complexes of the type $(RCO)(R)Fe(CO)_4$ and $(RCO)_2Fe(CO)_4$, although direct evidence for these acylalkyl and bis(acyl) intermediates is apparently lacking.[1-3] Additional support for this contention comes from the much earlier synthesis[6] of the fluoroalkyl complexes $(R_F)_2Fe(CO)_4$ (R_F = C_2F_5, *n*-C_3F_7) from $Na_2Fe(CO)_4$ and the appropriate acid chloride (eq 1). By analogy

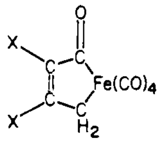
$$Na_2Fe(CO)_4 + 2R_FCOCl \rightarrow (R_F)_2Fe(CO)_4 + 2CO + 2NaCl \quad (1)$$

with closely related systems,[7-9] e.g., $R_FCOMn(CO)_5$ and $R_FCOCo(CO)_4$, these (fluoroalkyl)iron products were presumed to be formed by the decarbonylation of intermediate $(R_FCO)_2Fe(CO)_4$ and $(R_FCO)(R_F)Fe(CO)_4$ complexes. However, no attempt was made to isolate or identify such intermediates.

To date, *isolable* examples of bis(acyl)- and acylalkyltetracarbonyliron complexes are limited to *chelated* derivatives of types I[10-15] and II.[16] The lack of nonchelated $(RCO)_2Fe(CO)_4$ complexes is particularly surprising since electronically equivalent $[(RCO)_2M(CO)_4]^-$ anions have been prepared for manganese[17-20] and rhenium.[19,21,22] Rhenium analogues of $(RCO)(R)Fe(CO)_4$, e.g., $[(RCO)(R)Re(CO)_4]^-$, have also been characterized.[22]



I



II

In an attempt to obtain direct experimental evidence for nonchelated $(RCO)_2Fe(CO)_4$ and $(RCO)(R)Fe(CO)_4$ complexes, we have examined reaction 1 in more detail. This system was chosen for our initial studies since metal–*fluorocarbon* complexes are in general more kinetically robust than their metal–*hydrocarbon* analogues.[7-9] We report here the synthesis and characterization of *cis*-$(R_FCO)_2Fe(CO)_4$ (R_F = CF_3, *n*-C_3F_7), the first examples of nonchelated bis(acyl)tetracarbonyliron complexes. In addition, we report spectral evidence for the intermediacy of the acylalkyl complexes $(R_FCO)(R_F)Fe(CO)_4$ in the conversion of the bis(acyl) complexes to $(R_F)_2Fe(CO)_4$.

Experimental Section

General Procedures. All operations, including the purification of solvents, were carried out under an atmosphere of dry nitrogen. Schlenk-type apparatus was used for all reactions. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points were taken in capillaries sealed under nitrogen and are uncorrected.

Materials. The solvents (reagent grade) used in this work were dried by distillation from sodium/benzophenone (dioxane, ether), sodium (hexane, heptane), or P_4O_{10} (dichloromethane). The compounds $(CF_3CO)_2O$ (Aldrich) and *n*-C_3F_7COCl (PCR) were purchased from the indicated commercial source and were distilled under nitrogen immediately prior to use. Iron pentacarbonyl was purchased from Pressure Chemical Co. and was used without further purification.

The $Na_2Fe(CO)_4$ used in this work was prepared as the sesquidioxanate by the method of Finke and Sorrell.[23] The precipitated

---

(1) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342 and references cited therein.
(2) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 2515.
(3) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 4766.
(4) Cawse, J. N.; Fiato, R. A.; Pruett, R. L. *J. Organomet. Chem.* **1979**, *172*, 405.
(5) Mitsudo, T.; Watanabe, H.; Watanabe, Y.; Nitani, N.; Takegami, Y. *J. Chem. Soc., Dalton Trans.* **1979**, 395.
(6) King, R. B.; Stafford, S. L.: Treichel, P. M.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3604.
(7) McClellan, W. R. *J. Am. Chem. Soc.* **1961**, *83*, 1598.
(8) Treichel, P. M.; Stone, F. G. A. *Adv. Organomet. Chem.* **1964**, *1*, 143.
(9) Bruce, M. I.; Stone, F. G. A. *Prep. Inorg. React.* **1968**, *4*, 177.
(10) Brune, H. A.; Wolff, H. P.; Klein, W.; Zahurszky, U. I. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1972**, *27B*, 639.
(11) Pettersen, R. C.; Cihonsky, J. L.; Young, F. R., III; Levenson, R. A. *J. Chem. Soc., Chem. Commun.* **1975**, 370. Young, F. R., III; O'Brien, D. H.; Pettersen, R. C.; Levenson, R. A.; von Minden, D. L. *J. Organomet. Chem.* **1976**, *114*, 157.
(12) Grevels, F.-W.; Buchkremer, J.; Koerner von Gustorf, E. A. *J. Organomet. Chem.* **1976**, *111*, 235.
(13) Hoffman, E.; Weiss, E. *J. Organomet. Chem.* **1977**, *128*, 399.
(14) Victor, R.; Usielli, V.; Sarel, S. *J. Organomet. Chem.* **1977**, *129*, 387.
(15) Aime, S.; Milone, L.; Sappa, E.; Tiripicchio, A.; Manotti, Lanfredi, A. M. *J. Chem. Soc., Dalton Trans.* **1979**, 1664.
(16) Cotton, F. A.; Troup, J. M.; Billups, W. E.; Lin, L. P.; Smith, C. V. *J. Organomet. Chem.* **1975**, *102*, 345.
(17) Lukehart, C. M.; Torrence, G. P.; Zeile, J. V. *J. Am. Chem. Soc.* **1975**, *97*, 6903.
(18) Casey, C. P.; Bunnell, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 436.
(19) Lukehart, C. M.; Torrence, G. P.; Zeile, J. V. *Inorg. Chem.* **1976**, *15*, 2393.
(20) Casey, C. P.; Scheck, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 2728 and references cited therein.
(21) Lukehart, C. M.; Torrence, G. P. *Inorg. Chem.* **1979**, *18*, 3150 and references cited therein.
(22) Casey, C. P.; Scheck, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 2723.
(23) Finke, R. G.; Sorrell, T. N. *Org. Synth.* **1979**, *59*, 102.

0020-1669/81/1320-0645$01.00/0

Table I. Infrared and ^{19}F NMR Data

complex	ν(CO), cm^{-1} [a]	^{19}F NMR[b,c]			
		δ			
		α-CF$_2$	β-CF$_2$	CF$_3$	$^4J_{F_\alpha F_\gamma}$, Hz
cis-$(CF_3CO)_2Fe(CO)_4$	2139 m, 2087 s, 2075 vs, 2067 s			79.9 s	
cis-$(n\text{-}C_3F_7CO)_2Fe(CO)_4$	2139 m, 2088 s, 2077 vs, 2068 s	111.3 q	126.8 s	81.5 t	9.5
cis-$(CF_3)_2Fe(CO)_4$	2157 m, 2100 sh, 2098 vs, 2082 m			−2.9 s	
cis-$(n\text{-}C_3F_7)_2Fe(CO)_4$	2154 m, 2102 s, 2097 vs, 2084 m, 2079 m[d]	68.1 m	116.0 q	79.3 t	11.9[e]
trans-$(n\text{-}C_3F_7)_2Fe(CO)_4$	2155 vw, 2124 w, 2096 vs	65.0 q	116.0 t	79.2 t	11.5

[a] Heptane solution. [b] $CDCl_3$ solution; chemical shifts in ppm from $CFCl_3$. [c] Abbreviations: s, singlet; t, triplet; q, quartet; m, complex multiplet. [d] Reference 34 gives 2150, 2100, 2095, 2081, 2078 cm^{-1} (C_2Cl_4 solution). [e] Reference 30 gives 69.1, 115.3, 78.6 ppm; 11.1 Hz (THF solution).

product was washed with several portions of hexane, and the supernatant solvent was removed via syringe. The remaining solvent was removed in vacuo to afford white, *pyrophoric* $Na_2Fe(CO)_4\cdot1.5$(dioxane).

Spectra. Infrared spectra (Table I) were obtained on a Perkin-Elmer 180 spectrophotometer, which was calibrated with carbon monoxide and polystyrene. Solution spectra were run in NaCl cells with heptane as solvent.

The ^{19}F NMR spectra (Table I) were recorded at 84.6 MHz on a Bruker WH90-DS spectrometer operating in the FT mode. Chloroform-d_1 was used as the solvent. Hexafluorobenzene served as an internal reference, and chemical shifts are presented relative to $CFCl_3$ with use of the conversion[24] $\delta_{CFCl_3} = \delta_{C_6F_6} + 162.9$ ppm. Positive ^{19}F chemical shifts are *upfield* from $CFCl_3$.

The ^{13}C NMR spectra were obtained at 22.6 MHz on the same instrument. The spectra were referenced internally to the solvent (dichloromethane-d_2), and ^{13}C chemical shifts were converted to the Me_4Si scale by taking the chemical shift of CD_2Cl_2 as +53.8 ppm. Positive ^{13}C chemical shifts are *downfield* from Me_4Si. The shiftless relaxation reagent[25] $Cr(acac)_3$ (5–10 mg) was employed for all ^{13}C NMR measurements.

Preparation of *cis*-$(CF_3CO)_2Fe(CO)_4$. A slurry of $Na_2Fe(CO)_4\cdot1.5$(dioxane), prepared from $Fe(CO)_5$ (4.00 mL, 29.8 mmol) and Na (1.65 g, 71.7 mmol), in 150 mL of ether was cooled at −78 °C. An 11.1-mL (78.6 mmol) sample of cold (0 °C) $(CF_3CO)_2O$ was added dropwise via syringe, and the mixture was stirred at −78 °C for 12 h. Solvent was removed in vacuo at −10 °C, and the light tan solid residue was extracted with three 100-mL portions of cold (0 °C) CH_2Cl_2. The combined extracts were filtered, and the resulting yellow filtrate was concentrated in vacuo at 0 °C. Addition of hexane followed by further concentration in vacuo afforded a pale yellow microcrystalline product (yield 8.05 g, 74%), mp 43–44 °C. Anal. Calcd for $C_8F_6O_6Fe$: C, 26.55; F, 31.50. Found: C, 26.34; F, 31.34. ^{13}C NMR spectrum (CD_2Cl_2): 114.2 (CF_3, q, J_{FC} = 300 Hz), 196.6 (equatorial[26] CO, s), 197.5 (axial[26] CO, s), 228.5 (acyl CO, q, J_{FC} = 36.5 Hz).

Preparation of *cis*-$(n\text{-}C_3F_7CO)_2Fe(CO)_4$. This pale yellow microcrystalline complex was prepared in 53% yield by a similar method using $Na_2Fe(CO)_4\cdot1.5$(dioxane) and n-C_3F_7COCl; mp 58–59 °C. Anal. Calcd for $C_{12}F_{14}O_6Fe$: C, 25.65; F, 47.33. Found: C, 25.19; F, 47.64.

Preparation of *cis*-$(CF_3)_2Fe(CO)_4$. A slurry of *cis*-$(CF_3CO)_2Fe(CO)_4$ (2.03 g, 5.60 mmol) in 40 mL of heptane was heated under reflux for 2 h during which time the solid gradually dissolved. Off-white needles were deposited upon cooling the solution to 0 °C. The crude product (1.01 g) was separated by filtration. Recrystallization from CH_2Cl_2/hexane gave 939 mg (55%) of the very pale yellow crystalline product, mp 79–80 °C. Anal. Calcd for $C_6F_6O_4Fe$: C, 23.56; F, 37.26; Fe, 18.26. Found: C, 23.38; F, 37.10; Fe, 18.48. ^{13}C NMR spectrum (CD_2Cl_2): 143.6 (CF_3, q, J_{FC} = 365 Hz), 195.9 (equatorial CO, complex m), 197.8 (axial CO, septet, J_{FC} = 4.4 Hz).

Preparation of *cis*-$(n\text{-}C_3F_7)_2Fe(CO)_4$. Method a. A solution of *cis*-$(n\text{-}C_3F_7CO)_2Fe(CO)_4$ (1.68 g, 2.99 mmol) in 40 mL of benzene was heated at 50–60 °C for 8 h. Solvent was removed on a rotary evaporator, and the oily residue was crystallized from CH_2Cl_2/heptane at −15 °C to give a very pale yellow crystalline product (904 mg, 60%).

Method b. A flask containing solid *cis*-$(n\text{-}C_3F_7CO)_2Fe(CO)_4$ (9.02 g, 16.0 mmol) was heated under nitrogen at 40–45 °C for ~70 h. The solid residue was sublimed (40–45 °C, 0.01 torr) to afford very pale yellow crystals of the product (6.49 g, 80%), mp 91–92 °C (lit.[6] 88–90 °C). Anal. Calcd for $C_{10}F_{14}O_4Fe$: C, 23.74; F, 52.58. Found: C, 23.52; F, 52.13.

Preparation of *trans*-$(n\text{-}C_3F_7)_2Fe(CO)_4$. Method a. A solution of *cis*-$(n\text{-}C_3F_7CO)_2Fe(CO)_4$ (1.02 g, 1.81 mmol) in 20 mL of hexane was placed in a 100-mL Carius tube equipped with a threaded Teflon valve. The solution was degassed by several freeze–pump–thaw cycles, and the Carius tube was placed in an oil bath at 110 °C for 4 h. The cooled (25 °C) solution was transferred to a Schlenk tube via syringe, and solvent was removed in vacuo at −30 °C (bromobenzene slush bath). The solid residue was sublimed (40–50 °C, 0.01 torr) to afford very pale yellow crystals of the product (763 mg, 83%).

Method b. A Carius tube containing solid *cis*-$(n\text{-}C_3F_7)_2Fe(CO)_4$ (1.54 g, 3.05 mmol) was evacuated to 0.01 torr (−196 °C) and placed in an oil bath at 110 °C for 5 h. The tube was cooled to room temperature, and the solid residue was extracted with hexane. The combined hexane extracts were filtered, and solvent was removed from the filtrate in vacuo at −30 °C to give the very pale yellow crystalline product (1.41 g, 91%), mp 92–93 °C. Anal. Calcd for $C_{10}F_{14}O_4Fe$: C, 23.74; F, 52.58. Found: C, 23.69; F, 52.23.

Decarbonylation of *cis*-$(CF_3CO)_2Fe(CO)_4$—^{19}F NMR Study. A solution of *cis*-$(CF_3CO)_2Fe(CO)_4$ (55 mg) and C_6F_6 (~1 drop, internal reference) in toluene-d_8 (0.5 mL) was placed in a 5-mm NMR tube. The solution was degassed on a vacuum line by several freeze–pump–thaw cycles, and the tube was sealed under vacuum and placed in a constant-temperature bath at 60.0 ± 0.1 °C. The tube was periodically withdrawn from the temperature bath and quenched (0 °C) for ^{19}F NMR analysis. A series of representative ^{19}F NMR spectra is shown in Figure 3.

Results and Discussion

Synthesis of Bis(acyl) Complexes. The reaction of $Na_2Fe(CO)_4\cdot1.5$(dioxane) with $(CF_3CO)_2O$ or n-C_3F_7COCl in ether at −78 °C afforded the corresponding bis(acyl)tetracarbonyliron complexes *cis*-$(CF_3CO)_2Fe(CO)_4$ and *cis*-$(n\text{-}C_3F_7CO)_2Fe(CO)_4$, respectively, in good yield (50–75%). The acid anhydride was used for the synthesis of the trifluoroacetyl complex as a matter of convenience since CF_3COCl is a gas under ambient conditions. It is well-known[8,9,27] that acid anhydrides and acid chlorides can be used interchangeably in reactions with metal carbonyl anions. The pale yellow crystalline *cis*-$(R_FCO)_2Fe(CO)_4$ complexes can be handled in air for reasonable periods at room temperature, but noticeable decomposition occurs (even under a nitrogen atmosphere) within 1 day. The complexes are stable indefinitely at −10 °C.

The infrared spectra of the bis(acyl) complexes (Figure 1) exhibit four bands in the terminal ν(CO) region, consistent with a cis geometry. A single broad ($\Delta\nu_{1/2} \approx 50$ cm^{-1}) acyl

---

(24) Bruce, M. I. *J. Chem. Soc. A* **1968**, 1459.

(25) Gansow, O. A.; Burke, A. R.; LaMar, G. N. *J. Chem. Soc., Chem. Commun.* **1972**, 456.

(26) In accord with the usual convention for *cis*-$M(CO)_4X_2$ derivatives, the equatorial CO groups are defined as those which are trans to the X ligands.

(27) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1964**, *2*, 15.

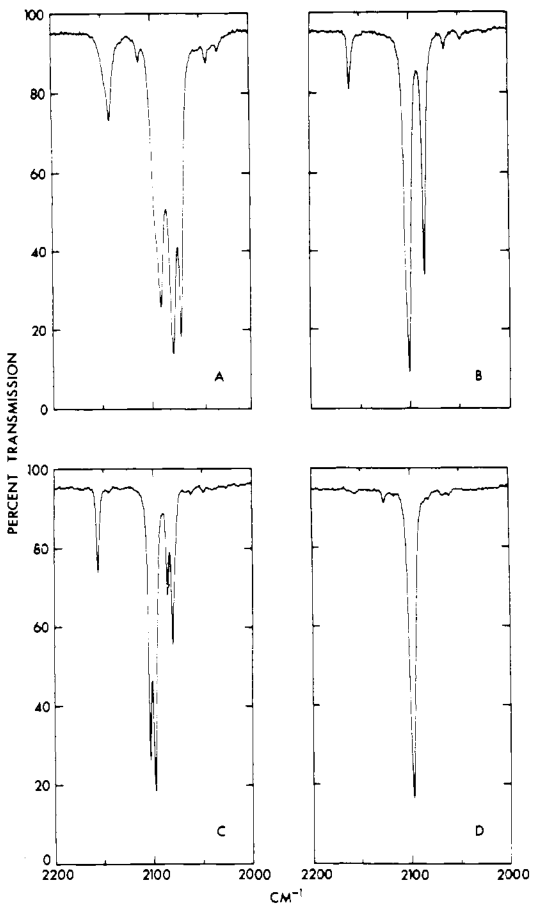


Figure 1. Infrared spectra in heptane solution of (A) *cis*-$(CF_3CO)_2Fe(CO)_4$, (B) *cis*-$(CF_3)_2Fe(CO)_4$, (C) *cis*-$(n\text{-}C_3F_7)_2Fe(CO)_4$, and (D) *trans*-$(n\text{-}C_3F_7)_2Fe(CO)_4$.

ν(CO) band was observed at 1695 cm^{-1}. Although two acyl ν(CO) bands are predicted from group theory, they are apparently not resolvable.[28] The ^{19}F NMR spectra of the *cis*-$(R_FCO)_2Fe(CO)_4$ complexes (Table I) are quite similar to the spectra of other trifluoroacetyl– and perfluorobutyryl–metal carbonyl complexes.[8,27,30] The ^{13}C NMR spectrum of *cis*-$(CF_3CO)_2Fe(CO)_4$ exhibited the expected two resonances of equal intensity in the metal–carbonyl region. Assignment of these signals to the axial[26] (197.5 ppm) and equatorial[26] (196.6 ppm) CO groups is made on the basis of Graham's empirical observations[31,32] for related *cis*-$M(CO)_4X_2$ systems (M = Fe, Ru, Os). Coupling of fluorine to the metal–CO carbons was not observed. Quartets at 228.5 ppm (J_{FC} = 36.5 Hz) and 114.2 ppm (J_{FC} = 300 Hz) are readily assigned to the fluorine-coupled acyl CO and CF_3 resonances, respectively. Satisfactory ^{13}C NMR spectra of *cis*-$(n\text{-}C_3F_7CO)_2Fe(CO)_4$ could not be obtained due to the lower solubility of this complex.

These *cis*-$(R_FCO)_2Fe(CO)_4$ complexes are the first isolable nonchelated bis(acyl)tetracarbonyliron derivatives. Although bis(acyl) complexes of other metals have been reported,[17-22,29,33] their occurrence is relatively limited. Known examples include *cis*-$(EtCO)_2Os(CO)_4$,[29] $[(MeCO)_2Os(CO)_2Br_2]^{2-}$,[33] and various *cis*-$[(RCO)_2M(CO)_4]^-$ anions of manganese[17-20] and rhenium.[19,21,22]

Decarbonylation of Bis(acyl) Complexes. Synthesis of Bis(alkyl) Complexes. The *cis*-$(R_FCO)_2Fe(CO)_4$ complexes undergo facile decarbonylation to give the corresponding bis(alkyl) $(R_F)_2Fe(CO)_4$ complexes when heated at 30–100 °C in hydrocarbon solvents such as hexane, heptane, or benzene. Reaction progress is conveniently monitored by infrared spectroscopy. Decarbonylation of *cis*-$(n\text{-}C_3F_7CO)_2Fe(CO)_4$ initially afforded *cis*-$(n\text{-}C_3F_7)_2Fe(CO)_4$, which on further heating underwent isomerization to the trans isomer. Both complexes are isolable in isomerically pure form. In contrast, decarbonylation of *cis*-$(CF_3CO)_2Fe(CO)_4$ under identical conditions afforded only *cis*-$(CF_3)_2Fe(CO)_4$. No evidence for the corresponding trans isomer was obtained. This difference must be steric in origin since the electronic properties of CF_3 and $n\text{-}C_3F_7$ ligands would be expected to be nearly identical.

Although appreciable decarbonylation was observed to occur within 1 h at room temperature, the reactions are more conveniently carried out at higher temperatures. For example, complete decarbonylation of *cis*-$(R_FCO)_2Fe(CO)_4$ is achieved in 2–4 h at 98 °C in heptane solution. In view of these observations and the rather vigorous conditions (refluxing THF) employed in the original[6] study of reaction 1, it is understandable why the intermediate bis(acyl) complexes were not previously observed.

Yields (55–90%) of the very pale yellow (almost white) air-stable bis(alkyl) complexes appear to be limited primarily by mechanical losses involved in separating these very volatile solids from the solvents used. Alternatively, decarbonylation was accomplished by heating the *solid* *cis*-$(R_FCO)_2Fe(CO)_4$ complexes in vacuo or under a nitrogen atmosphere. Vacuum sublimation of the residue afforded the bis(alkyl) complexes in excellent yield. For example, careful heating of *cis*-$(n\text{-}C_3F_7CO)_2Fe(CO)_4$ at 40–45 °C for ~70 h gave *cis*-$(n\text{-}C_3F_7)_2Fe(CO)_4$ in 80% yield.

The infrared spectrum of *cis*-$(CF_3)_2Fe(CO)_4$ (Figure 1) shows three well-resolved bands in the ν(CO) region. A fourth band (2100 cm^{-1}) is observed only on expanded scale as a high-frequency shoulder of the 2098-cm^{-1} band. In fact, the ν(CO) infrared spectrum is virtually superimposable with the infrared spectrum[34] of *cis*-$\overline{CF_2(CF_2)_2CF_2}Fe(CO)_4$. The ^{19}F NMR spectrum (Table I) exhibited a singlet 82.8 ppm *downfield* of the resonance in *cis*-$(CF_3CO)_2Fe(CO)_4$. This large downfield shift relative to the corresponding trifluoroacetyl–metal complex is characteristic of a variety of trifluoromethyl–metal complexes.[8,27,30]

The ^{13}C NMR spectrum of *cis*-$(CF_3)_2Fe(CO)_4$ showed two metal carbonyl resonances at 195.9 and 197.8 ppm which can be assigned on the basis of observable ^{19}F–^{13}C coupling. Since the two CF_3 groups are equivalent with respect to an axial CO ligand, axial carbon and the six fluorine atoms constitute an AX_6 spin system. Thus, the pattern for the axial carbon resonance is expected to be a septet. An equatorial CO is trans to one CF_3 group and cis to the other CF_3 group, resulting in an $AX_3X'_3$ spin system for equatorial carbon and the six fluorine atoms. The pattern for the equatorial carbon resonance is thus expected to be quite complicated. Accordingly, the septet (J_{FC} = 4.4 Hz) at 197.8 ppm and the complex multiplet at 195.9 ppm are assigned respectively to the axial and equatorial CO ligands. These assignments are consistent with the general observation[31,32] that for *cis*-$M(CO)_4X_2$ complexes (M = Fe, Ru, Os) the ^{13}C resonance of the equatorial CO is at higher field.

In view of the virtually identical ν(CO) infrared spectra of

---

(28) Similar observations have been noted for related bis(acyl)tetracarbonylmetal complexes; see ref 17 and 29.

(29) L'Eplattenier, F.; Pélichet, C. *Helv. Chim. Acta* **1970**, *53*, 1091.

(30) Pitcher, E.; Buckingham, A. D.; Stone, F. G. A. *J. Chem. Phys.* **1962**, *36*, 124.

(31) Vancea, L.; Pomeroy, R. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1976**, *98*, 1407.

(32) Pomeroy, R. K.; Vancea, L.; Calhoun, H. P.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1508.

(33) L'Eplattenier, F. *Inorg. Chem.* **1969**, *8*, 965.

(34) Pitcher, E.; Stone, F. G. A. *Spectrochim. Acta* **1962**, *18*, 585.

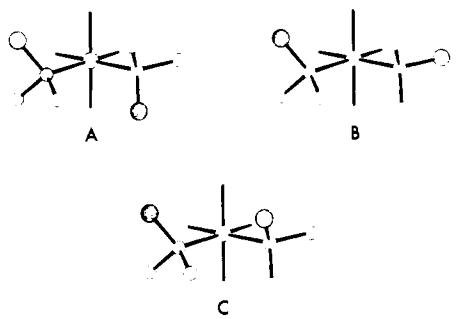


Figure 2. Some possible rotamers of *cis*-$(CF_2X)_2Fe(CO)_4$. The CO groups on iron have been omitted for clarity.

cis-$(CF_3)_2Fe(CO)_4$ and *cis*-$\overline{CF_2(CF_2)_2CF_2Fe}(CO)_4$, the infrared spectrum of *cis*-$(n\text{-}C_3F_7)_2Fe(CO)_4$ would be expected to show two medium-intensity bands at ~2155 and ~2080 cm^{-1} and a strong band at ~2098 cm^{-1}, having, perhaps, a barely discernible high-frequency shoulder. However, as originally reported by Pitcher and Stone,[34] the observed infrared spectrum of *cis*-$(n\text{-}C_3F_7)_2Fe(CO)_4$ (Figure 1) consists of *five well-resolved* ν(CO) bands. Two of these correspond to the bands expected at ~2155 and ~2098 cm^{-1}. In addition, a band at 2102 cm^{-1} and *two* bands (2084, 2079 cm^{-1}) in the vicinity of 2080 cm^{-1} are observed. Thus, the observed infrared spectrum of *cis*-$(n\text{-}C_3F_7)_2Fe(CO)_4$ has either one or two *extra* ν(CO) bands depending upon whether or not the well-resolved band at 2102 cm^{-1} is correlated with the poorly resolved shoulder at 2100 cm^{-1} in the spectrum of *cis*-$(CF_3)_2Fe(CO)_4$.

There are at least three potential origins of the anomalous infrared spectrum of *cis*-$(n\text{-}C_3F_7)_2Fe(CO)_4$. The first possibility—the presence of an impurity—can be ruled out on the basis that repeated purification of the complex by recrystallization and/or vacuum sublimation left the infrared spectral pattern unaltered. The possibility that the complex is in fact a cis–trans mixture must also be rejected. Assignment of the 2097-cm^{-1} band to the trans isomer (see below) would still leave *two* bands at ~2080 cm^{-1} in the spectrum of the cis isomer, contrary to what is observed for *cis*-$(CF_3)_2Fe(CO)_4$ and *cis*-$\overline{CF_2(CF_2)_2CF_2Fe}(CO)_4$. In addition, the ^{19}F NMR spectrum of *cis*-$(n\text{-}C_3F_7)_2Fe(CO)_4$ (Table I) shows a *single* α-CF_2 resonance, thus precluding the simultaneous presence of the trans isomer.

The most likely explanation is that the anomalous infrared spectrum of *cis*-$(n\text{-}C_3F_7)_2Fe(CO)_4$ arises from the presence of two (or more) rotamers. These rotamers would differ only in the relative conformations adopted by the mutually cis $n\text{-}C_3F_7$ groups. Several conformations are shown schematically in Figure 2; clearly many other conformations are also possible.[35] The occurrence of rotamers—and its resulting effect on terminal ν(CO) vibrations—is not unprecedented in metal–carbonyl chemistry.[31,36–38] Of particular relevance to the system at hand are the results obtained by Graham and coworkers[31] for a series of *cis*-$M(CO)_4(SiR_3)_2$ complexes (M = Fe, Ru, Os). In the case of an *axially symmetric* SiR_3 group (i.e., $SiMe_3$, $SiCl_3$), the infrared spectrum contains the expected number of ν(CO) bands. However, for SiR_3 groups which lack axial symmetry (i.e., $SiMe_2Cl$, $SiMeCl_2$), extra ν(CO) bands result due to the various possible conformations of the unsymmetrical silyl ligands.

The results obtained for *cis*-$(R_F)_2Fe(CO)_4$ complexes are in complete accord with these observations. Thus, the expected number of ν(CO) bands is seen only when the fluoroalkyl ligands are either axially symmetric, as in *cis*-$(CF_3)_2Fe(CO)_4$, or constrained to one conformation by a chelate ring, as in *cis*-$\overline{CF_2(CF_2)_2CF_2Fe}(CO)_4$. Extra ν(CO) bands appear when the lack of axial symmetry of the fluoroalkyl group leads to the occurrence of rotamers. This situation is apparently not restricted to the $n\text{-}C_3F_7$ ligand since the published[34] infrared spectrum of *cis*-$(C_2F_5)_2Fe(CO)_4$ is virtually identical with the infrared spectrum of *cis*-$(n\text{-}C_3F_7)_2Fe(CO)_4$.

The presence of a single rotamer in the case of the less bulky, axially symmetric CF_3 ligand can be attributed to essentially unhindered rotation about the iron–carbon bonds. Presumably, the main factor restricting the rotation about the iron–carbon bonds in these *cis*-$(R_F)_2Fe(CO)_4$ systems is the steric interaction between the mutually cis fluoroalkyl ligands. If steric interactions between a fluoroalkyl ligand and its cis-oriented CO groups were predominant, rotamers would be expected for *trans*-$(n\text{-}C_3F_7)_2Fe(CO)_4$, contrary to experimental observation (see below).

The ν(CO) infrared spectrum of *trans*-$(n\text{-}C_3F_7)_2Fe(CO)_4$ (Figure 1) exhibits a single strong band at 2096 cm^{-1}. This band is readily assigned to the infrared-active E_u mode under D_{4h} symmetry. As in the case of a variety of related $M(CO)_4X_2$ complexes,[31,39–41] the E_u mode of the trans isomer is essentially coincident with one of the ν(CO) bands of the cis isomer. An extremely weak band at 2155 cm^{-1} and a weak band at 2124 cm^{-1} are assigned to the normally only Raman-active A_{1g} and B_{1g} modes, respectively. These modes have gained a slight infrared intensity in the reduction of symmetry from strict D_{4h} due to the lack of axial symmetry of the $n\text{-}C_3F_7$ group.[42] The E-mode splitting[42] which often accompanies the appearance of formally Raman-active ν(CO) modes for *mono*(perfluoro-*n*-propyl)metal carbonyl complexes—e.g., *trans*-$(n\text{-}C_3F_7)(C_6F_5)Fe(CO)_4$,[43] *trans*-$(n\text{-}C_3F_7)Fe(CO)_4I$,[44] $n\text{-}C_3F_7Mn(CO)_5$[44]—is not observed for *trans*-$(n\text{-}C_3F_7)_2Fe(CO)_4$.

The ^{19}F NMR spectra of *cis*- and *trans*-$(n\text{-}C_3F_7)_2Fe(CO)_4$ (Table I) are quite similar to the spectra[8,27,30] of other (perfluoro-*n*-propyl)metal complexes. In particular, the large *downfield* shift (~45 ppm) of the α-CF_2 resonance in either isomer of $(n\text{-}C_3F_7)_2Fe(CO)_4$ relative to *cis*-$(n\text{-}C_3F_7CO)_2Fe(CO)_4$ is typical of a variety of related mono(perfluoro-*n*-propyl)metal systems.[8,27,30] The most noteworthy feature of the ^{19}F NMR spectra is that the α-CF_2 resonances of *cis*- and *trans*-$(n\text{-}C_3F_7)_2Fe(CO)_4$ differ by 3.1 ppm, an observation which allows the identification of one isomer in the presence of the other.[45]

It is not known at this time whether the complex multiplet patterns observed for the α-CF_2 and β-CF_2 resonances of *cis*-$(n\text{-}C_3F_7)_2Fe(CO)_4$ are due to the presence of rotamers. In principle, each rotamer would be expected to have slightly different ^{19}F chemical shifts and coupling constants. However, if the interconversion of the rotamers is rapid on the NMR time scale at room temperature, an averaged spectrum will result. Detailed variable-temperature ^{19}F NMR studies of *cis*-$(n\text{-}C_3F_7)_2Fe(CO)_4$ and the closely related perfluoroethyl analogue[6,34] are currently being carried out in order to pursue these ideas further.

---

(35) The closely related complex *cis*-$(CHF_2CF_2)_2Fe(CO)_4$ is known from X-ray diffraction to adopt conformation A in the *solid state*: Churchill, M. R. *Inorg. Chem.* **1967**, *6*, 185.
(36) Jetz, W.; Graham, W. A. G. *J. Am. Chem. Soc.* **1967**, *89*, 2773.
(37) Dalton, J. *Inorg. Chem.* **1971**, *10*, 1822; **1972**, *11*, 915.
(38) Evidence of rotamers in mono(perfluoroalkyl)metal complexes has been obtained by infrared and ^{19}F NMR spectroscopy: Stanley, K.; Zelonka, R. A.; Thomson, J.; Fiess, P.; Baird, M. C. *Can. J. Chem.* **1974**, *52*, 1781.
(39) Kummer, R.; Graham, W. A. G. *Inorg. Chem.* **1968**, *7*, 1208.
(40) Pankowski, M.; Bigorgne, M. *J. Organomet. Chem.* **1969**, *19*, 393.
(41) Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1978**, *17*, 2680.
(42) Wilford, J. B.; Stone, F. G. A. *Inorg. Chem.* **1965**, *4*, 389.
(43) Hensley, D. W.; Stewart, R. P., Jr. *Inorg. Chem.* **1978**, *17*, 905.
(44) Stewart, R. P., Jr.; Graham, W. A. G., unpublished observations.
(45) Note that infrared spectroscopy *cannot* distinguish between a pure cis isomer and a cis–trans mixture since the single ν(CO) band of the trans isomer is coincident with one of the ν(CO) bands of the cis isomer.

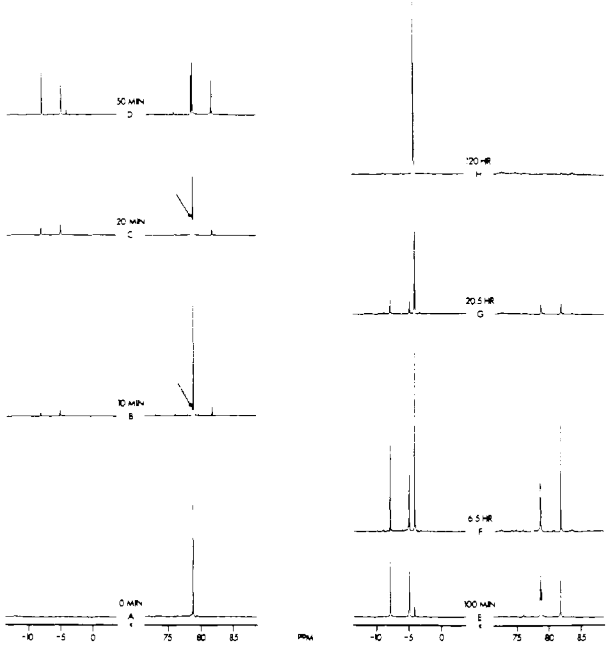


Figure 3. Selected time-dependent ^{19}F NMR spectra of the decarbonylation of *cis*-$(CF_3CO)_2Fe(CO)_4$ (60 °C, toluene-d_8 solution). Arrow denotes the partially obscured resonance at 78.6 ppm (see text).

Evidence for Acylalkyl Complexes as Intermediates. The decarbonylation of *cis*-$(CF_3CO)_2Fe(CO)_4$ in toluene-d_8 solution at 60 °C was monitored as a function of time by ^{19}F NMR spectroscopy. A series of representative ^{19}F NMR spectra is reproduced in Figure 3. Spectrum A is that of the initial solution of the bis(acyl) complex (78.8 ppm) prior to heating. Within 10 min of heating (spectrum B), a pair of resonances attributable to alkyl-CF_3 groups are observed at −7.9 and −4.9 ppm. Two additional resonances are seen in the acyl-CF_3 region at 78.6 and 81.8 ppm, the former occurring as a low-field shoulder on the resonance due to the bis(acyl) complex. These sets of resonances are more pronounced after 50 min in spectrum D. Here—and throughout the remainder of the reaction—it is apparent that each alkyl-CF_3 resonance can be associated with an acyl-CF_3 resonance of equal intensity. Thus, the four resonances can be grouped as follows into intensity-related pairs: (1) −7.9 and 81.8 ppm; (2) −4.9 and 78.6 ppm. We interpret these data as indicating the presence of both the cis and trans isomers of the acylalkyl complex $(CF_3CO)(CF_3)Fe(CO)_4$. The third alkyl-CF_3 resonance (−4.1 ppm) can be unambiguously assigned to *cis*-$(CF_3)_2Fe(CO)_4$ by comparison with an authentic sample.

Subsequent spectra (E–H) illustrate the further conversion of *cis*-$(CF_3CO)_2Fe(CO)_4$ into the isomeric acylalkyl complexes and the much more gradual conversion of these species into *cis*-$(CF_3)_2Fe(CO)_4$. The former process is complete within ~3 h, and by ~6 h (spectrum F) *cis*-$(CF_3)_2Fe(CO)_4$ is the predominant complex in solution. Very weak resonances due to *cis*- and *trans*-$(CF_3CO)(CF_3)Fe(CO)_4$ are still detectable after 72 h, but by ~120 h complete decarbonylation has been achieved (spectrum H).

Although the presence of both *cis*- and *trans*-$(CF_3CO)(CF_3)Fe(CO)_4$ is clearly indicated by the ^{19}F NMR data, unambiguous assignment of the resonances is not possible. We tentatively assign the pair of resonances at −4.9 and 78.6 ppm to *cis*-$(CF_3CO)(CF_3)Fe(CO)_4$ in view of their similarity to the chemical shifts of *cis*-$(CF_3)_2Fe(CO)_4$ (−4.1 ppm) and *cis*-$(CF_3CO)_2Fe(CO)_4$ (78.8 ppm), respectively. Regardless, there are a number of important conclusions which can be drawn from this ^{19}F NMR study.

First, there is no evidence for the formation of either *trans*-$(CF_3CO)_2Fe(CO)_4$ or *trans*-$(CF_3)_2Fe(CO)_4$ in spite of the intermediacy of *trans*-$(CF_3CO)(CF_3)Fe(CO)_4$. In addition, decarbonylation of the isomeric mixture of acylalkyl complexes is a stereospecific process. It is interesting to note that the decarbonylations of cis–trans mixtures of numerous $RCOMn(CO)_4L$ complexes likewise proceed stereospecifically to afford exclusively *cis*-$RMn(CO)_4L$ products.[46–48]

Second, the conversion of *cis*-$(CF_3CO)_2Fe(CO)_4$ into *cis*- and *trans*-$(CF_3CO)(CF_3)Fe(CO)_4$ is a significantly faster process than the subsequent conversion of these acylalkyl complexes into *cis*-$(CF_3)_2Fe(CO)_4$. Note that under the conditions used the former process requires only ~3 h of the total >72-h reaction time.

Third, the relative amounts of *cis*- and *trans*-$(CF_3CO)(CF_3)Fe(CO)_4$ change only during the first ~50 min of the reaction. This is most easily seen in the alkyl-CF_3 region of the spectra shown in Figure 3. Although *cis*-$(CF_3CO)(CF_3)Fe(CO)_4$ is the major isomer after 10 min (spectrum B), both isomers are present in approximately equal amounts after 20 min (spectrum C). After 50 min (spectrum D) *trans*-$(CF_3CO)(CF_3)Fe(CO)_4$ has become the major isomer and the trans:cis isomer ratio has attained a value (~3:2) which remains essentially constant throughout the rest of the reaction. Spectrum B indicates that the rate of formation of *trans*-$(CF_3CO)(CF_3)Fe(CO)_4$ is slower than the rate of formation of *cis*-$(CF_3CO)(CF_3)Fe(CO)_4$. Thus, the subsequent spectral changes clearly cannot be explained if decarbonylation of *cis*-$(CF_3CO)_2Fe(CO)_4$ is the *exclusive* route by which *trans*-$(CF_3CO)(CF_3)Fe(CO)_4$ is formed. It must therefore be concluded that *trans*-$(CF_3CO)(CF_3)Fe(CO)_4$ arises from the isomerization of *cis*-$(CF_3CO)(CF_3)Fe(CO)_4$ in addition to—or instead of—the decarbonylation of *cis*-$(CF_3CO)_2Fe(CO)_4$. The initial increase and eventual invariance of the trans:cis isomer ratio requires that the rate of cis → trans isomerization be comparable to the rate of formation of *cis*-$(CF_3CO)(CF_3)Fe(CO)_4$.[49]

Finally, it is significant to note that, in contrast to analogous hydrocarbon systems,[1–3] ketone formation does not appear to be an important side reaction[50] during the decarbonylation of *cis*-$(CF_3CO)_2Fe(CO)_4$. This difference is in accord with the generally accepted principle[8,9,49,53] that metal–fluorocarbon bonds are stronger than their hydrocarbon analogues.

Acknowledgment is made to the Research Corp. for the support of this research. We also thank the Faculty Research Committee, Miami University, for a Research Graduate Assistant award (D.W.H.). Discussions with Professors Gilbert Gordon, Anastas Karipides, and Richard T. Taylor are gratefully acknowledged.

Registry No. *cis*-$(CF_3CO)_2Fe(CO)_4$, 76136-68-0; *cis*-$(n\text{-}C_3F_7CO)_2F(CO)_4$, 76136-69-1; *cis*-$(CF_3)_2Fe(CO)_4$, 76136-70-4; *cis*-$(n\text{-}C_3F_7)_2Fe(CO)_4$, 76189-74-7; *trans*-$(n\text{-}C_3F_7)_2Fe(CO)_4$, 76136-71-5; $Na_2Fe(CO)_4$, 14878-31-0; $(CF_3CO)_2O$, 407-25-0; *n*-C_3F_7COCl, 375-16-6.

---

(46) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87.

(47) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299.

(48) Stewart, R. P., Jr. *Inorg. Chem.* **1979**, *18*, 2083 and references contained therein.

(49) Implicit in this discussion is the assumption that the decarbonylations are not appreciably reversible. At present there are no reported examples of the insertion of CO into a metal–fluorocarbon bond.[46]

(50) The ^{19}F chemical shift of $(CF_3)_2CO$ has been reported as 76.1 ppm[51] (acetonitrile solution) and 77.2 ppm[52] (solvent not given).

(51) Dungan, C. H.; Van Wazer, J. R. "Compilation of Reported ^{19}F NMR Chemical Shifts"; Wiley-Interscience: New York, 1970.

(52) Stone, F. G. A. *Pure Appl. Chem.* **1972**, *30*, 551.

(53) Blake, D. M.; Winkelman, A.; Chung, Y. L. *Inorg. Chem.* **1975**, *14*, 1326.