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Chemistry of the Metal Carbonyls. XVIII. Reactions between Perfluoropropyliron Carbonyls and Pyridine, 2,2′-Bipyridine, or Tertiary Phosphines[1,2]

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The reactions of perfluoropropyliron tetracarbonyl iodide and bis-(perfluoropropyl)-iron tetracarbonyl with pyridine, 2,2′-bipyridine, triphenylphosphine, and trimethylphosphite are described. Some new complexes were isolated and their properties are reported.

The isolation of fluorocarbon derivatives of metal carbonyls[5] and the discovery that these compounds are thermally more stable and less reactive than their alkyl analogs, where these are known, suggest that the fluorocarbon complexes could act as starting materials for the synthesis of many new transition metal compounds. On the other hand, the observation that fluorocarbon–manganese and –iron carbonyls release fluoroolefins on heating to about 100° or above, as well as the discovery that the fluorocarbon groups in these compounds are destroyed by aqueous base,[1] leads to the suspicion that the fluorocarbon–metal groups might not be preserved in many reactions. In this paper we describe work carried out to determine to what extent carbonyl groups in perfluoroalkyliron carbonyls can be replaced by certain other ligands and yet still afford definite complexes containing perfluoroalkyl groups.

Experimental

Infrared spectra were recorded using a Perkin-Elmer Model 21 double-beam spectrophotometer. Carbonyl stretching frequencies were determined from tetrachloroethylene solutions with the spectrophotometer fitted with a calcium fluoride prism. Other bands were measured using sodium chloride optics.

Perfluoropropyliron tetracarbonyl iodide and bis-(perfluoropropyl)-iron tetracarbonyl were prepared by the method described elsewhere.[6] Final purification was by sublimation.

1. **Perfluoropropyl-bis-(pyridine)-iron Dicarbonyl Iodide (I).**—Perfluoropropyliron tetracarbonyl iodide (930 mg., 2.0 mmoles) was added to pyridine (2 ml., ~25 mmoles) at room temperature. Vigorous evolution of carbon monoxide occurred with formation of a dark amber solution, from which brown crystals of I precipitated on cooling to 0°. Precipitation was completed by addition of 25 ml. of 37–51° petroleum ether. Filtration, followed by washing the crystals with petroleum ether, afforded I (1.13 g., 100% yield), m.p. 123° dec.

Anal. Calcd. for $C_{15}H_{10}F_7N_2O_2IFe$: C, 31.8; H, 1.78; N, 4.95; I, 22.4; Fe, 9.87; mol. wt., 566. Found: C, 32.1; H, 1.91; N, 4.77; I, 22.3; Fe, 9.89; mol. wt., 520.[7]

Compound I when obtained in the above manner is sufficiently pure for most purposes, but it can be recrystallized by solution in acetone or ethanol with reprecipitation by addition of a small quantity of water. It is moderately soluble in polar organic solvents, and is diamagnetic. The infrared spectrum shows the characteristic absorptions of a C_3F_7–Fe group,[8] and carbonyl stretching frequencies at 2051(s) and 2009(s) cm.$^{-1}$.

A 283-mg. (0.5 mmole) sample of I was heated in an evacuated bulb at 100° for 16 hr. On opening the bulb to the vacuum system, fractionation of the gaseous products gave 0.97 mmole of carbon monoxide (97% of theory) and 0.24 mmole (48% of theory) of heptafluoropropane containing a trace of perfluoropropene (both identified by their infrared spectra), and condensing at −78° gave a small quantity (0.12 mmole) of a non-identifiable gas, with a very complex infrared spectrum.

2. **Reaction between I and Pyridine.**—(a) A 930-mg. (2.0 mmoles) sample of perfluoropropyliron tetracarbonyl iodide was added to pyridine (3.0 ml., ~37 mmoles). When the vigorous evolution of carbon monoxide had ceased, the solution of I in pyridine was heated on a bath to about 70°. A steady evolution of carbon monoxide occurred, the solution darkened in color and slowly deposited yellow prismatic crystals of hexapyridine-iron(II) iodide (0.80 g., 1.0 mmole) which were filtered cold and washed with 37–51° petroleum ether.

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[1] Previous paper in this series, P. M. Treichel, E. Pitcher, and F. G. A. Stone, *Inorg. Chem.*, **1**, 511 (1962).

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[5] See ref. 1, and references cited therein, for a review of studies carried out to date on these substances.

[6] R. B. King, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3604 (1961).

[7] Microanalyses for C, H, and N reported in this paper were obtained by the Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Iron and iodine analyses, however, were made in our Laboratory.

[8] E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **18**, 585 (1962).

Anal. Calcd. for $C_{30}H_{30}N_6FeI_2$: Fe, 7.1; I, 32.4; Found: Fe, 7.5; I, 33.1.

On addition of excess petroleum ether to the dark amber filtrate a dark brown substance (~100 mg.) precipitated. This material, unstable and difficult to purify, was observed to form in several similar reactions. Analyses were somewhat variable, typical results being C, 35.7; H, 1.9; N, 4.5; Fe, 16.9.

(b) A 283-mg. (0.5 mmole) sample of I and pyridine (2 ml., ~25 mmoles) were heated to 100° in an evacuated Pyrex bulb. Fractionation of the gaseous products gave carbon monoxide (0.96 mmole, 96% of theory) and fluorocarbons (0.45 mmole) identified by their infrared spectra as perfluoropropene (about 15%) and heptafluoropropane (about 85%).

3. Perfluoropropyl-(bipyridyl)-iron Dicarbonyl Iodide (II).—Perfluoropropyliron tetracarbonyl iodide (930 mg., 2.0 mmoles), bipyridyl[9] (460 mg., 3.0 mmoles), and benzene (2 ml.) were heated to 70°. A vigorous evolution of carbon monoxide was observed and yellow-orange crystals of II (910 mg., 80% yield) precipitated. The diamagnetic crystals were washed with 37–51° petroleum ether and recrystallized by solution in absolute ethanol followed by precipitation with a small quantity of water. II (m.p. 195–200° dec.), less soluble in organic solvents than I, had carbonyl stretching bands at 2046(s) and 2004(s) $cm.^{-1}$. The infrared spectrum also showed bands characteristic of a C_3F_7–Fe group.[8]

Anal. Calcd. for $C_{15}H_8F_7N_2O_2IFe$: C, 31.9; H, 1.42; N, 4.96; I, 22.5; Fe, 9.85. Found: C, 32.0; H, 1.42; N, 5.04; I, 22.5; Fe, 9.93.

4. Reactions between Perfluoropropyliron Tetracarbonyl Iodide and Tertiary Phosphines.—(a) Trimethylphosphite (500 mg., 4 mmoles) reacted violently with perfluoropropyliron tetracarbonyl iodide (930 mg., 2 mmoles) in benzene (5 ml.) solution. Volatile material was removed at low pressure (1 mm., 25°) leaving a small quantity of a dark oil, which solidified when extracted with acetone–ether. The infrared spectrum of this material showed the absence of perfluoroalkyl groups and it was, therefore, not further investigated.

(b) Perfluoropropyliron tetracarbonyl iodide (930 mg., 2.0 mmoles) and triphenylphosphine (1.05 g., 4 mmoles) were refluxed in 37–51° petroleum ether for 2 hr. Large amber-brown crystals gradually precipitated which proved to be the mono-(triphenylphosphine) derivative $C_3F_7Fe[(C_6H_5)_3P](CO)_3I$ (III), 680 mg. (48% yield). III (m.p. 125° dec.) was diamagnetic, and was moderately soluble in organic solvents, but attempts to recrystallize it were unsuccessful. The infrared spectrum showed bands characteristic of a C_3F_7–Fe group,[8] and carbonyl stretching bands at 2103(w), 2051(s), and 2035(m, broad) $cm.^{-1}$.

Anal. Calcd. for $C_{24}H_{15}F_7O_3IPFe$: C, 41.3; H, 2.15; F, 19.1; P, 4.44; Fe, 8.02. Found: C, 41.46; H, 2.24; F, 18.6; P, 4.56; Fe, 7.75.

5. Bis-(perfluoropropyl)-bis-(pyridine)-iron Dicarbonyl (IV).—Bis-(perfluoropropyl)-iron tetracarbonyl (1.01 g., 2.0 mmoles) dissolved in pyridine (3 ml., ~37 mmoles) was heated on a bath at 90° for 15 min. Carbon monoxide was evolved and the color of the solution changed from pale yellow to dark amber. Yellow-brown diamagnetic crystals (800 mg., 65% yield) of IV were precipitated by cooling, and were washed with petroleum ether. The compound thus obtained was sufficiently pure for most purposes but could be purified further by recrystallization from pyridine at −40°.

Anal. Calcd. for $C_{18}H_{10}F_{14}O_2N_2Fe$: C, 35.5; H, 1.65; N, 4.60; Fe, 9.21; mol. wt., 608. Found: C, 35.8; H, 1.78; N, 4.34; Fe, 9.14; mol. wt., 563.

Compound IV (m.p. 138° dec.), moderately soluble in organic solvents, showed bands in its infrared spectrum corresponding to the presence of a C_3F_7–Fe group,[8] and carbonyl stretching bands at 2061(s) and 2008(s) $cm.^{-1}$.

6. Reaction between IV and Pyridine.—A 304-mg. (0.5 mmole) sample of IV and 3 ml. (~37 mmoles) of pyridine were heated at 90° in an evacuated bulb for 16 hr. On opening the bulb to the vacuum system 1.01 mmoles (101% of theory) of carbon monoxide was removed, and 0.87 mmole (87% of theory) of heptafluoropropane was recovered. The heptafluoropropane was identified by its infrared spectrum which showed that it contained a trace (<1%) of perfluoropropene. The residue in the bulb contained a compound which was soluble in pyridine to form a dark amber solution. This appeared identical with the pyridine-soluble material described in 2(a) above.

7. Bis-(perfluoropropyl)-(bipyridyl)-iron Dicarbonyl (V).—Bis-(perfluoropropyl)-iron tetracarbonyl (510 mg., 1 mmole) and bipyridyl (160 mg., 1 mmole) dissolved in heptane (5 ml.) were heated on a 70° bath until the slow evolution of carbon monoxide had ceased (~15 min.). Crude V was filtered from the hot solution, and then was recrystallized from ethanol by addition of a small amount of water. Light brown crystals (200 mg., 33% yield) of V (m.p. 195–200° dec.) were found to be diamagnetic, and to be moderately soluble in polar organic solvents.

Anal. Calcd. for $C_{18}H_8F_{14}N_2O_2Fe$: C, 35.6; H, 1.32; F, 43.9; N, 4.62; Fe, 9.24. Found: C, 35.8; H, 1.46; F, 44.1; N, 4.62; Fe, 9.17.

The infrared spectrum of V showed bands characteristic of the presence of a C_3F_7–Fe group, and carbonyl stretching bands at 2051(s) and 2003(s) $cm.^{-1}$.

8. Reactions between Bis-(perfluoropropyl)-iron Tetracarbonyl and Tertiary Phosphines.—Both trimethylphosphite and triphenylphosphine reacted violently with solutions of bis-(perfluoropropyl)-iron tetracarbonyl. Products containing perfluoropropyliron groups were not obtained from the reaction solutions.

9. Infrared Spectra.—As Kaydol mulls, the new compounds were observed to have infrared bands due to the C_3F_7 group as indicated below.

(a) I.—1325(m); 1190(s); 1024(m); 803(m); 665(m) $cm.^{-1}$

(b) II.—1320(s); 1178(s); 1020(m); 807(m); 661(m) $cm.^{-1}$

(c) III.—1315(s); 1190(s); 1025(m); 798(m); 662(m) $cm.^{-1}$

(d) IV.—1320(m); 1187(s); 1025(m); 796(m); 658(m) $cm.^{-1}$

(e) V.—1320(s); 1190(s); 1025(m); 800(s); 660(m) $cm.^{-1}$

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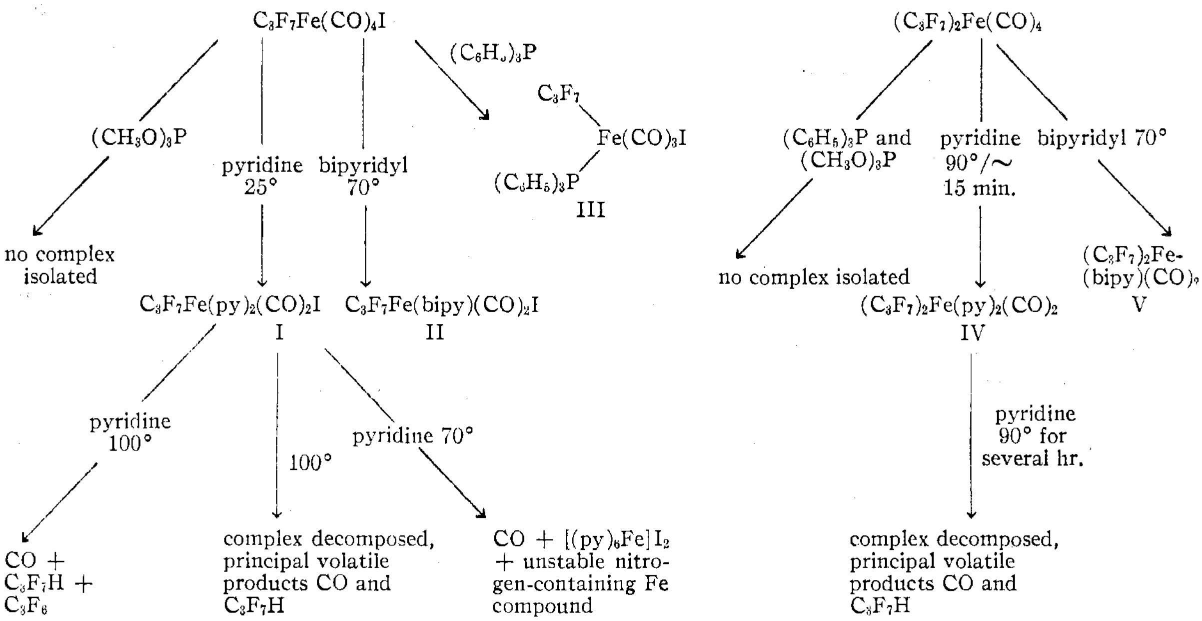
(9) 2,2-Bipyridine, abbreviated bipy throughout this paper.



Discussion

The chemical reactions described in the Experimental section are summarized in the chart. From this it is seen that it is possible to replace two carbonyl groups of perfluoropropyliron tetracarbonyl iodide with pyridine or bipyridyl, or one carbonyl group with triphenylphosphine. Reaction between trimethylphosphite and perfluoropropyliron tetracarbonyl iodide, however, is very vigorous and no perfluoropropyliron complex could be isolated. Toward the various ligands bis-(perfluoropropyl)-iron tetracarbonyl behaved in much the same way as perfluoropropyliron tetracarbonyl iodide, except that no complex was isolated with triphenylphosphine. It is apparent that whether a perfluoropropyliron carbonyl will undergo partial replacement of carbonyl groups by other ligands to give a complex containing R_F–Fe groups depends on the nature of the attacking ligand. In particular, tertiary phosphines tend to destroy perfluoropropyl–iron groups. Reaction of the perfluoropropyliron bis-pyridine complexes with excess of pyridine also results in removal of perfluoropropyl groups from iron. Thus as far as replacement of carbonyl groups by pyridine is concerned it appears that a minimum of two carbonyl groups must remain bonded to iron if the perfluoropropyl–iron bond is to be stable. Recent work has shown that σ-bonds between carbon atoms of alkyl groups and transition metals are in general likely to be more stable if the metal also is bonded to ligands able to π-bond with the d-electrons of the metal.[10] Carbon monoxide is believed to be able to π-bond with a metal more effectively than most other ligands (*e.g.*, pyridine). The results presented in this paper show that even when a carbon atom is part of a fluoroalkyl group the carbon–iron σ-bond decreases in stability when carbonyl groups are replaced by ligands which π-bond with iron less effectively. It thus would seem that the same factors which enhance the stability of alkyl derivatives of transition metals also enhance the stability of the fluorocarbon–metal compounds. However, the latter class of complex[5] appears capable of existing in greater number than the former; and since the work described here shows that fluorocarbon–metal groups can be preserved in certain substitution reactions, and probably would be preserved in many others, it is very likely that many new types of fluorocarbon–transition metal complexes are capable of existence.

It has been shown previously[6] that at temperatures of about 100° perfluoroalkyliron tetracarbonyl iodides and bis-(perfluoroalkyl)-iron tetracarbonyls release fluoroölefins. It is of interest to contrast this result with the formation of heptafluoropropane in some of the decomposition reactions summarized in the chart. Decomposition of the perfluoropropyliron–pyridine complexes presumably involves abstraction of hydrogen from the pyridine groups by perfluoropropyl

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(10) (a) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959); (b) J. Chatt, *Record Chem. Progr.* (Kresge-Hooker Science Library), **21**, 147 (1960); (c) G. E. Coates and F. Glockling, Am. Chem. Soc. Monograph (Ed., H. Zeiss), "Organometallic Chemistry," Reinhold Publ. Corp., New York, N. Y., 1960, chapter 9.

radicals formed by fission of C_3F_7–Fe bonds. Evidently the mode of decomposition is different from the shift of fluorine from fluoroalkyl groups to metals which occurs in the pyrolysis of fluoroalkylmetal carbonyls like $HCF_2CF_2Mn(CO)_5$, $CF_3Fe(CO)_4I$, or $(C_2F_5)_2Fe(CO)_4$.

The carbonyl stretching frequencies observed in the infrared spectra of the perfluoropropyliron–pyridine or –bipyridyl carbonyl complexes are about 60 cm.$^{-1}$ below those observed in perfluoropropyliron tetracarbonyl iodide and bis-(perfluoropropyl)-iron tetracarbonyl.[8] This drop in carbonyl stretching frequency can be understood in terms of a greater degree of π-bonding between iron and carbon atoms of the carbonyl groups in the pyridine or bipyridyl complexes. Such behavior is to be expected since in passing from the iron tetracarbonyl compounds to the iron dicarbonyl compounds carbonyl groups have been replaced by ligands believed to be less able to partake in π-bonding with iron. Consequently, the remaining carbonyl groups must accept more electron density from the iron atom to stabilize the complex, and in so doing the C–O bond acquires more double bond character and its absorption appears at a lower frequency.

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The Molecular and Crystal Structure of $Os_3(CO)_{12}$

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The crystal and molecular structure of $Os_3(CO)_{12}$ (previously formulated incorrectly as $Os_2(CO)_9$) has been determined by X-ray diffraction. Three-dimensional least-squares refinement of all atoms resulted in a final discrepancy factor, R_1, of 12.4%. The molecular unit of approximately D_{3h} symmetry consists of an equilateral triangular array of osmium atoms with four terminal carbonyls attached to each osmium; two of the carbonyls are approximately perpendicular to the plane of the osmium atoms while the other two are essentially in the plane. The three $Os(CO)_4$ fragments are linked to one another only by "bent" metal–metal bonds; the average Os–Os distance is 2.88 Å. The structure and bonding of $Os_3(CO)_{12}$ are discussed with respect to other metal carbonyl complexes, including $Fe_3(CO)_{12}$.

Introduction

Recent structural work[3] has shown that the dinuclear enneacarbonyls, $Ru_2(CO)_9$ and $Os_2(CO)_9$, were incorrectly formulated and are in fact trinuclear species with the formulas $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$. In this paper we wish to present the results of a complete structural determination of $Os_3(CO)_{12}$. This work is part of a systematic investigation of the second and third row transition metal carbonyls.

Experimental

Single crystals of yellow $Os_3(CO)_{12}$ were prepared by the high pressure reaction of carbon monoxide and osmium tetroxide.[4] The unit cell lengths were determined from *hk*0 and 0*kl* precession photographs, while β was obtained from *h*0*l* Weissenberg photographs. Multiple film equi-inclination Weissenberg photographs were obtained for reciprocal levels *h*0*l* through *h*12*l* from a crystal of length 0.21 mm. (along the rotation axis *b*) and of average width 0.12 mm. Since the crystal was somewhat irregularly shaped, no absorption correction was made; the resulting systematic error was minimized by the use of separate scale factors for each reciprocal layer which were determined by least-squares. Zr-filtered MoKα radiation (λ = 0.7107 Å.) was used to record 1873 independent diffraction maxima. The intensity of each reflection was estimated visually by comparison with a set of standard intensities. The raw intensities were corrected for Lorentz polarization effects. Timed-exposure *hk*0 and 0*kl* precession intensity data were used to scale the Weissenberg data and to calculate two-dimensional Patterson projections.

Results

Unit Cell and Space Group.—The parameters of the monoclinic unit cell are a = 8.10 ± 0.03 Å., b = 14.79 ± 0.04 Å., c = 14.64 ± 0.04 Å., β = 100° 27′ ± 20′. The angle and the axial ratios

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[3] E. R. Corey and L. F. Dahl, *J. Am. Chem. Soc.*, **83**, 2203 (1961).

[4] W. Hieber and H. Stallman, *Z. Elektrochem.*, **49**, 288 (1943).