Chemistry of the Metal Carbonyls. XVII. Addition of Manganese Pentacarbonyl Hydride to Some Fluoroolefins[1,2]

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This paper describes the preparation and some chemical properties of the compounds $HCF_2CF_2Mn(CO)_5$, HCF_2-$CF_2COMn(CO)_5$, $HCFClCF_2Mn(CO)_5$, $HCCl_2CF_2Mn(CO)_5$, and $CF_3CH=C(CF_3)Mn(CO)_5$. The infrared and ^{19}F and ^1H. n.m.r. spectra of the new manganese pentacarbonyl complexes are discussed.

We recently described a new class of compound wherein fluorocarbon groups are σ-bonded to transition metals. These substances were obtained from reactions between metal carbonyls or certain of their derivatives and perfluoroalkyl iodides or tetrafluoroethylene; or from reactions between sodium salts of metal carbonyls and perfluoroacyl or perfluoroallyl chlorides.[4] We now have found that transition metal carbonyl hydrides add to certain unsaturated fluorocarbons to give stable compounds of this type. In this paper we report the addition of manganese pentacarbonyl hydride to tetrafluoroethylene, chlorotrifluoroethylene, 1,1-dichloro-2,2-difluoroethylene, and hexafluoro-2-butyne.

It has been reported previously[5] that manganese pentacarbonyl hydride and ethylene do not react to give ethylmanganese pentacarbonyl, but form instead ethane and manganese carbonyl. Nevertheless, the recent work[4] on fluorocarbon–transition metal complexes establishes that the group $-CF_2-M$ (M = transition metal) is formed easily, and suggests that reactions between transition metal hydrides and appropriate fluoroölefins might afford stable compounds, provided the hydride did not readily decompose before addition could take place.

Experimental

Fluorine n.m.r. spectra were recorded at 40 and 56.4 Mc. with a Varian V-4300B high resolution spectrometer equipped with a flux stabilizer. A precision audio oscillator and associated frequency counter were used for measurements of line separations. Line positions were determined by means of superposition, or are the average of at least six calibrated traces. Proton n.m.r. spectra were recorded by means of a Varian A-60 spectrometer. The line positions were read from calibrated traces. Infrared spectra were recorded using a Perkin-Elmer Model 21 double-beam spectrophotometer.

Manganese pentacarbonyl hydride was obtained by acidification of the salt $NaMn(CO)_5$, prepared from sodium amalgam and manganese carbonyl in tetrahydrofuran.[6] Tetrafluoroethylene was obtained by pyrolysis of Teflon resin at 600°.[7] Hexafluoro-2-butyne was obtained by dechlorination of 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene.[8] Other reagents were commercial samples.

1. **Addition of Manganese Pentacarbonyl Hydride to Unsaturated Fluorocarbons.** (a) **Tetrafluoroethylene.—** A 150-ml. stainless steel Hoke bomb was attached to a high vacuum system, evacuated, and cooled to −196°. Pentane (20 ml.), manganese pentacarbonyl hydride (2.5 g., 12.8 mmoles), and tetrafluoroethylene (570 cc.,[9] 25.4 mmoles) were condensed into the bomb, which then was sealed and allowed to stand at ambient temperatures for 22 hr. After venting the bomb in a hood, its liquid contents were poured into a flask. The bomb was rinsed several times with pentane and the washings added to the flask. The pentane solution was slowly evaporated (20 mm.), and the resulting residue transferred to a sublimation apparatus. Sublimation (25°, 0.1 mm.) onto a 0° probe gave 2.6 g. (69% yield based on $HMn(CO)_5$ taken) of white crystalline $HCF_2CF_2Mn(CO)_5$ (I) (Table I).

Compound I was independently synthesized by the method previously described for preparing perfluoroalkylmanganese pentacarbonyls.[4a] The acyl compound II (Table I) was obtained (70% yield) as a white crystalline substance from the reaction between $NaMn(CO)_5$ and

(1) Previous paper in this series, D. W. McBride, S. L. Stafford, and F. G. A. Stone, *Inorg. Chem.*, **1**, 386 (1962).

(2) Presented in part at the 140th National Meeting of the Am. Chem. Soc., Chicago, 1961; see P. M. Treichel, E. Pitcher, and F. G. A. Stone, Abstracts of Meeting, p. 21-N.

(3) National Science Foundation Predoctoral Fellow.

(4) (a) H. D. Kaesz, R. B. King, and F. G. A. Stone, *Z. Naturforsch.*, **15b**, 763 (1960); (b) T. A. Manuel, S. L. Stafford, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 249 (1961); (c) R. B. King, P. M. Treichel, and F. G. A. Stone, *Proc. Chem. Soc.*, 69 (1961); (d) R. B. King, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3604 (1961); (e) T. D. Coyle, R. B. King, E. Pitcher, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **20**, 172 (1961); (f) R. B. King, E. Pitcher, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, ed., The Macmillan Co., New York, N.Y., 1961, p. 619.

(5) W. Hieber and G. Wagner, *Ann.*, **618**, 24 (1958).

(6) (a) W. Hieber and G. Wagner, *Z. Naturforsch.*, **13b**, 338 (1958); (b) R. B. King and F. G. A. Stone, *Inorg. Syn.*, **7**, in press.

(7) E. E. Lewis and M. A. Naylor, *J. Am. Chem. Soc.*, **69**, 1968 (1947).

(8) R. N. Haszeldine, *J. Chem. Soc.*, 2504 (1952).

(9) Throughout this paper the abbreviation "cc." refers to gases at standard conditions.

Table I

Some Fluorocarbon Derivatives of Manganese[a]

Compound	M.p., °C	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Fluorine, % Calcd.	Found	Manganese, % Calcd.	Found	Mol. wt.[b] Calcd.	Found
HCF₂CF₂Mn(CO)₅ (I)	30.5–31.5	28.4	28.3	0.34	0.41	25.6	25.4	18.6	18.9	296	297
HCF₂CF₂COMn(CO)₅ (II)	46.5–47.0	29.6	29.6	.31	.22	23.5	23.8	17.0	17.2	324	349
HCFClCF₂Mn(CO)₅ (III)[c]	43.0–44.0	26.9	27.0	.32	.47	18.2	18.1	17.6	17.8	312	322
HCCl₂CF₂Mn(CO)₅ (IV)	68.0–70.0	25.5	25.8	.30	.24	11.5	10.1	16.7	16.3	329	328
CF₃CH:C(CF₃)Mn(CO)₅ (V)	Yellow liquid	30.2	30.2	.28	.53	31.8	31.9	15.4	15.6	358	355

[a] Microanalyses were performed by Dr. A. Bernhardt, Max Planck Institut für Kohlenforschung, Mülheim, Germany, and by the Schwarzkopf Microanalytical Laboratories, Woodside, New York.   [b] Isopiestic method.   [c] Cl, calcd. 11.4%; found, 11.2%.

HCF₂CF₂COCl in tetrahydrofuran. Pyrolysis of II at 80° *in vacuo* for 18 hr. resulted in release of carbon monoxide and formation of I. (80% yield based on II taken.)

(b) **Chlorotrifluoroethylene.**—Using a similar technique to that described above, manganese pentacarbonyl hydride (2.4 g., 12.3 mmoles) in 20 ml. of pentane was treated with chlorotrifluoroethylene (750 cc., 33.5 mmoles). The product (III) (1.9 g., 49% yield based on manganese pentacarbonyl hydride taken) was a very volatile pale yellow solid (Table I).

(c) **1,1-Dichloro-2,2-difluoroethylene.**—From a reaction carried out in the Hoke bomb, IV (Table I) was isolated as pale yellow crystals (1.3 g., 39% yield) from manganese pentacarbonyl hydride (2.0 g., 10.2 mmoles) and 1,1-dichloro-2,2-difluoroethylene (665 cc., 29.7 mmoles).

(d) **Hexafluoro-2-butyne.**—From the reaction between manganese pentacarbonyl hydride (3.5 g., 17.8 mmoles) and hexafluoro-2-butyne (450 cc., 20 mmoles), under the conditions stated under (a) above, compound V (Table I) was obtained (0.8 g., 12.5% yield) as a pale yellow liquid.

2. Reaction of I, III, and IV with Bromine.—In the hope of obtaining evidence for the structure of the organo group bonded to manganese, especially in the case of compounds arising from unsymmetrical olefins when two products of addition might occur, these compounds were treated with bromine to cleave the organo group. Compound I (170.0 mg., 0.574 mmole) and a small glass tube containing bromine (1.0 g., 6.3 mmoles) were placed in a Pyrex reaction vessel of 300 ml. capacity. The reaction bulb was attached to the vacuum system, cooled, evacuated, and sealed. After heating for 14 hr. at 120° the bulb was cooled to −196° and opened to the vacuum system through an external trap containing an unsaturated hydrocarbon of low volatility, to absorb excess bromine. Fractionation of the volatile products gave 11.7 cc. (0.523 mmole, 91% of theory) of BrCF₂CF₂H (identified by its infrared spectrum[10]) and 64 cc. (2.86 mmoles, 100% of theory) of carbon monoxide.[11]

In a similar manner III (307.5 mg., 0.980 mmole) was treated with bromine (1.0 g., 6.3 mmoles) to give 10.3 cc. (0.46 mmole, 47% of theory) of BrCF₂CFClH (identified

by its infrared spectrum[10]) and 108.4 cc. (4.90 mmoles, 99% of theory) of carbon monoxide.

A sample (171.5 mg., 0.522 mmole) of IV on treatment with bromine (0.33 g., 2.1 mmoles) gave 3.1 cc. (0.138 mmole, 26% of theory) of BrCF₂CCl₂H (identified by its infrared spectrum[12]) and 58.6 cc. (2.6 mmoles, 100% of theory) of carbon monoxide. A less volatile liquid also was obtained which may have been a polybromoörganic compound, but it was not identified.

3. Pyrolysis of Compounds I and III.—A sample (654 mg., 2.21 mmoles) of I was placed in a 200-ml. Pyrex bulb, which then was evacuated, sealed off from the vacuum line, and heated for 18 hr. at 120°. On opening the bulb to the vacuum system the only observed product was a trace of non-condensable gas (carbon monoxide). Accordingly, the reaction vessel was resealed and heated at 150° for 3 days. After this treatment a white solid was observed and on opening the bulb to the vacuum line 206 cc. (9.24 mmoles, 84% of theory) of carbon monoxide and 20.9 cc. of a mixture (identified by its infrared spectrum) of trifluoroethylene and 1,1-difluoroethylene were recovered.

A 320.4-mg. (1.024 mmoles) sample of III was heated at 80° for 16 hr. in a 200-ml. Pyrex bulb. After this treatment yellow and red solids were observed in the bulb. On opening the bulb, 48.2 cc. (2.15 mmoles, 42% of theory) of carbon monoxide and 17.4 cc. (0.778 mmole, 76% of theory) of trifluoroethylene (identified by its infrared spectrum) were recovered. The yellow and red solids remaining in the reaction vessel were separated and shown by their infrared spectra[13] to be Mn(CO)₅Cl and [Mn(CO)₄Cl]₂.

4. Reactions of Fluorocarbon–Transition Metal Compounds with Bases.[14] (a) HCF₂CF₂Mn(CO)₅.—A small tube containing a 213-mg. (0.720 mmole) sample of I and 2 ml. of 20% sodium hydroxide solution was placed in a 250-ml. Pyrex bulb. This bulb then was attached to the vacuum line, evacuated, sealed off, and heated at 90° for 1 hr. The bulb then was reattached to the vacuum system and opened, carbon monoxide (0.72 mmole, 20% of theory) being removed. The material remaining in the bulb, which included a yellow solid, was filtered. The filtrate was brought to a pH of 5 with acetic acid, carbon dioxide being released. The solution was treated with

(10) R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 3747 (1954).

(11) Here and in other experiments described in this paper involving formation of carbon monoxide, the latter was measured and identified by the method described previously (P. M. Treichel, E. Pitcher, R. B. King, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 2593 (1961)).

(12) J. R. Lacher, J. J. McKinley, C. Walden, K. R. Lea, and J. D. Parks, *J. Am. Chem. Soc.*, **71**, 1334 (1949).

(13) E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

(14) We are indebted to Dr. R. A. Plowman for helping with the experimental work described in this and the following section, and for making many valuable suggestions.

calcium chloride. A white precipitate formed which was allowed to settle for one day, then filtered, ignited, and weighed as calcium fluoride (100 mg., representing 89% of the fluorine content of the sample of I taken for reaction). As a check on the result, the calcium fluoride was converted to calcium sulfate (177.0 mg., implying 90% of the fluorine in the sample of I taken).

The yellow solid produced by the base treatment proved to be insoluble in hydrocarbon solvents but soluble in acetone. On heating in air it explodes or burns. A 25.1-mg. sample was analyzed for manganese by treating it cautiously with nitric acid, followed by evaporation. The residue was converted to the oxide Mn_2O_3 by ignition in air at 800° and weighed (12.1 mg., implying Mn = 33.5% in the original solid). As a check, the oxide was treated with sulfuric acid and sugar, evaporated, and heated to about 500° to form manganese(II) sulfate (23.2 mg., implying Mn = 33.6% in the original solid). For a formulation $[HC{\equiv}CMn(CO)_3]_x$ for the yellow solid, Mn calcd. = 33.5%. The infrared spectrum of the solid (Nujol and hexachlorobutadiene mulls, NaCl prism) showed bands at 3610 (m), 2035 (s), 2015 (sh), 1958 (s), 1905 (s), 1600 (w, broad), 819 (m), 740 (m, broad), and 688 (m) cm.$^{-1}$. The band at 3610 cm.$^{-1}$ was very sharp, and was assigned to the C–H stretch of a ${\equiv}C$–H group.[15]

A number of experiments similar to the one described above were carried out. In one of these, a sample of I was heated at 80° for 30 min. with 20% sodium hydroxide. After removal of carbon monoxide the contents of the reaction bulb were acidified with acetic acid (liberation of carbon dioxide observed) before filtration. The filtrate contained F^- ion equivalent to 60% of the fluorine content of the sample of I taken for reaction. The yellow solid recovered was contaminated with Na_2SiF_6 (280 mg. $\equiv$ 32% of fluorine content of I). The yellow solid was removed from the fluorosilicate by washing with acetone.

(b) $(C_3F_7)_2Fe(CO)_4$.—In order to determine whether strong base has a similar effect to that described above on fluoroalkyl derivatives of transition metals other than manganese, a 186.4-mg. (0.368 mmole) sample of bis-(perfluoropropyl)-iron tetracarbonyl was treated with 20% sodium hydroxide (2 ml.) in a bulb for 2 hr. at room temperature. A black solid formed. On opening the bulb no carbon monoxide was detected. Filtration, followed by washing the precipitate with acetone, led to the recovery of 48 mg. of starting material. The black solid afforded carbon dioxide on treatment with acid, and was undoubtedly iron(II) carbonate. Carbon dioxide was released on acidification of the filtrate. The latter then was analyzed for F^- ion (see above). Found: CaF_2, 140.8 mg.; F = 81% of the amount of $(C_3F_7)_2Fe(CO)_4$ consumed.

Reactions between bis-(perfluoroalkyl)-iron tetracarbonyls and base at elevated temperatures afforded carbon monoxide, carbon dioxide, and fluorocarbons (5–20%), as well as fluoride ion in solution.

5. Reactions of Fluorocarbon–Transition Metal Compounds with Hydrogen Chloride. (a) $HCF_2CF_2Mn(CO)_5$. —A 197.5-mg. (0.668 mmole) sample of I was heated at 100° for 3 hr. with hydrogen chloride (86.5 cc.) in a Pyrex

bulb. A yellow solid appeared after 15 min., but subsequently disappeared. On opening the bulb to the vacuum line carbon monoxide (2.58 mmoles, 77% of theory) was removed. After treatment of the volatile components with triethylamine to remove excess hydrogen chloride, silicon tetrafluoride (6.9 cc., 46% of the fluorine content of the sample taken), identified by its infrared spectrum, was found as the only product. The solids in the bulb were extracted with cyclohexane, and, after filtering to remove the manganese(II) chloride, the solvent was evaporated and the residue sublimed giving a small amount of manganese carbonyl.

In other experiments it was observed that I and hydrogen chloride gas underwent little or no reaction below about 70°. At this temperature, however, trifluoroacetic acid and I afforded appreciable amounts of carbon monoxide and silicon tetrafluoride.

(b) $C_2F_5Mn(CO)_5$.—A 261.6-mg. (0.833 mmole) sample of perfluoroethylmanganese pentacarbonyl with hydrogen chloride gas (125.5 cc.) at 110° for 30 min. yielded carbon monoxide (4.06 mmoles, 97% of theory) and, after removal of the excess hydrogen chloride with triethylamine, silicon tetrafluoride (18.0 cc., 78% of the fluorine content of the $C_2F_5Mn(CO)_5$ taken), identified by its infrared spectrum.

(c) $(C_2F_5)_2Fe(CO)_4$.—A 208.3-mg. (0.514 mmole) sample of bis-(perfluoroethyl)-iron tetracarbonyl was observed not to react with hydrogen chloride gas (65.1 cc.) at room temperature over a period of 3 days. After heating (90°, 15 min.) some decomposition was observed and carbon monoxide (0.723 mmole, 35% of theory)[16] was obtained. After removal of excess hydrogen chloride with triethylamine, pentafluoroethane (2.4 cc., 10% of C_2F_5 groups present), identified by its infrared spectrum, was found. Starting material still was observed to be present in the reaction vessel, and no silicon tetrafluoride had been formed. Accordingly, the Pyrex bulb was resealed with 55.5 cc. of hydrogen chloride and heated (100° 1 hr.), thereby affording carbon monoxide (1.19 mmoles, 58% of theory),[16] and, after removal of hydrogen chloride with triethylamine, a mixture (11.9 cc.) of pentafluoroethane and silicon tetrafluoride. An examination of the infrared spectrum of this mixture suggested that its composition was approximately 30% C_2F_5H and 70% SiF_4.

6. Spectroscopic Studies.—The infrared absorptions of the various compounds are given in Table II. ^{19}F and ^1H chemical shifts and spin coupling constants for compounds I–IV are listed in Table III, along with, for comparison purposes, those of pentafluoroethane. The n.m.r. results for V are presented in Table IV, along with similar data for a *cis-trans* mixture of $CF_3ClC{=}CFCF_3$ studied in order to determine the structure of V.

Discussion

Formation of the compounds listed in Table I occurred under exceedingly mild conditions. In all cases room temperature and low olefin pressures (5 atm. or less) were sufficient to effect

(15) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen, London, 1956.

(16) The carbon monoxide, by ignition over copper oxide at 800° (see ref. 11), was shown to contain a trace (<1%) of hydrogen.

addition of the metal hydride to the fluoroölefin.[17]

Compounds I–IV are very volatile, white or pale yellow, crystalline solids, and V is a volatile yellow liquid. All the new manganese compounds are diamagnetic, and are stable to air and to moisture at ambient temperatures. As described above, treatment of I, III, or IV with bromine leads to release of carbon monoxide and cleavage of the fluorocarbon group. In this way I afforded HCF_2CF_2Br, and III and IV gave $HCFCl-CF_2Br$ and HCl_2CCF_2Br, respectively. The result for III and IV is of special importance, establishing that additions of manganese pentacarbonyl hydride to chlorotrifluoroethylene and to 1,1-dichloro-2,2-difluoroethylene occur so as to form in each case a single compound, in which the CF_2 group is bonded to manganese. As described below, n.m.r. studies on these compounds confirmed the structures indicated by the bromine cleavage studies.

In order to decompose I into fluoroethylenes and carbon monoxide, prolonged heating at temperatures above 120° was required. Compound III was significantly less stable, and furthermore decomposed in an entirely different manner. At 80° III undergoes a β-chloro-shift to manganese to afford $Mn(CO)_5Cl$ and $[Mn(CO)_4Cl]_2$.[19] Trifluoroethylene and carbon monoxide also were produced. Decomposition *via* a β-chloro- rather than a fluoro-shift is in contrast to certain other systems. Thus the silicon compound $HCFClCF_2-SiCl_3$ decomposes on heating to give trichlorofluorosilane and the carbene $HCFClCF:.$[20]

The thermal decomposition of I prompts brief comment on the relative thermal stability of metal–carbon bonds of $-CF_2-M$ and of $-CH_2-M$ groups (M = transition metal). The following comparisons may be made: $HCF_2CF_2Mn(CO)_5$ and $C_2F_5Mn(CO)_5$[4a] decompose above 120°, *vs.* $C_2H_5Mn(CO)_5$, the existence of which is doubtful[22a]; $CF_3Co(CO)_4$ does not decompose even when distilled at its normal boiling point of 91°[21]

(17) Addition of manganese pentacarbonyl hydride to the unsaturated fluorocarbons also was observed in the gas phase at 0°, even at pressures of less than an atmosphere. Other workers[18] have recently stated that manganese pentacarbonyl hydride and tetrafluoroethylene do not yield a product. That this reaction does indeed give a product was first indicated in reference 4c. Failure[18] to obtain I perhaps may have been due to its very high volatility. The compound sublimes away slowly even at atmospheric pressure.

(18) H. H. Hoehn, L. Pratt, K. F. Watterson, and G. Wilkinson, *J. Chem. Soc.*, 2738 (1961).

(19) Formation of the dimeric manganese tetracarbonyl chloride undoubtedly occurs through the decomposition of manganese pentacarbonyl chloride; see reference 13.

(20) W. I. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. Ind.* (London), 789 (1961).

(21) W. R. McClellan, *J. Am. Chem. Soc.*, **83**, 1598 (1961).

vs. $CH_3Co(CO)_4$, which decomposes above temperatures of $-35°$[22b]; $(C_2F_5)_2Fe(CO)_4$ decomposes appreciably at 100° whereas $(C_nH_{2n+1})_2Fe(CO)_4$ compounds are unknown, in spite of attempts at preparation.[4d] It is evident that the fluorocarbon metal compounds are thermally more stable than their alkyl analogs. Moreover, the mode of thermal decomposition for the two series of compounds is different. Thus from work described elsewhere[23] it appears that an equilibrium exists between an alkylmetal carbonyl (where the alkyl group is an ethyl group, or higher homolog) and a mixture of the metal carbonyl hydride and an olefin, which increasingly favors the latter mixture at higher temperatures. The fluorocarbon–metal compounds on the other hand afford unsaturated fluorocarbons, forming by way of shift of fluorine from the side chain to the metal. Thus $(CF_2)_4Fe(CO)_4$ yields perfluorocyclobutene after 15 hr. at 150°,[4b] and as described above fluorocarbon–manganese pentacarbonyls give fluoroölefins. Other examples of this kind of decomposition are mentioned elsewhere.[4] It is interesting that the first step in the decomposition of the fluorocarbon–metal compounds does not involve rupture of the metal–carbon bond.

The results described in the Experimental section concerning the effect of strong sodium hydroxide solution and hydrogen chloride gas on several of the fluorocarbon metal compounds are of considerable significance. Preliminary experiments previously reported[4b,d,f] showed that, unlike fluorocarbon derivatives of main group elements, fluorocarbon complexes of transition metals do not yield fluorocarbons quantitatively on treatment with bases, although at elevated temperatures small quantities are formed. With acids the fluorocarbon–transition metal carbonyl complexes also produce fluorocarbons but in small amounts. Because of this it was believed that the fluorocarbon–metal groups were being largely preserved in the various reactions, even though considerable quantities of carbon monoxide usually were produced. The more comprehensive studies reported in this paper show that in very strong basic solutions the fluoroalkyl metal groups are degraded with rupture of the C–F bonds forming fluoride ion in solution. Furthermore,

(22) (a) W. Hieber, G. Braun, and W. Beck, *Chem. Ber.*, **93**, 903 (1960); (b) W. Hieber, O. Vohler, and G. Braun, *Z. Naturforsch.*, **13b**, 192 (1958).

(23) R. F. Heck and D. S. Breslow, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, ed., the Macmillan Co., New York, N.Y., 1961, p. 282.

this process is not necessarily accompanied by quantitative cleavage of the metal–carbon bonds. Formation of carbonate ion also was observed. It is apparent that the products depend on many factors, including the nature of the fluorocarbon group and the metal with which it is associated. In the particular case of I, a yellow solid was recovered after the base treatment. The solid was perhaps a polymeric material [HC≡CMn-(CO)₃]ₓ,[24] stable to the reaction conditions, although additional work is necessary to establish the true nature of this compound.

It is evident that hydrogen fluoride must be an intermediate in those reactions of the fluorocarbon–metal complexes with hydrogen chloride which yield silicon tetrafluoride when carried out in glass bulbs. In the hydrogen chloride degradation of I a yellow solid sometimes was observed as an intermediate, but could not be isolated. It is possible that this transitory yellow solid was the same as the one obtained by base treatment, and referred to above. Some support for this idea comes from the observation that a sample of the solid [HC≡CMn(CO)₃]ₓ was decomposed with hydrogen chloride to afford manganese chloride, carbon monoxide, traces of an organic material not identified, and manganese carbonyl. The latter substance also is produced in small quantities from reactions between I and hydrogen chloride. Whatever the mechanisms of the degradation reactions which result in formation of fluoride and carbonate ions, or silicon tetrafluoride, cleavage of metal–carbon bonds of the M–CF₂ groups is not the first step. If this were the case, fluorocarbons would be produced, and the major products would have to be accounted for in terms of decomposition of the fluorocarbons to fluoride ion or silicon tetrafluoride under the reaction conditions, a process which is known not to occur. As mentioned in this paper and elsewhere,[4b,d,f] fluorocarbons were observed as reaction products in many instances but they were produced in relatively small amount showing that direct cleavage of the fluorocarbon group from the metal is not the chief route for decomposition. Further studies on reactions between fluorocarbon–metal complexes and aqueous bases and acids are continuing.

Attempts were made to add manganese penta-

carbonyl hydride to 1,1-difluoroethylene, 1-chloro-2,2-difluoroethylene, perfluoropropene, and perfluorobutene-2 under conditions under which the hydride adds readily to tetrafluoroethylene. In all cases no fluorocarbon–manganese pentacarbonyl compounds were obtained. From each of these reactions some manganese carbonyl was recovered. These negative results suggest that olefins in which hydrogen atoms or CF₃ groups are bonded to a carbon atom of the double bond are inert to manganese pentacarbonyl hydride, but further studies are needed to determine whether addition would occur under more vigorous conditions.

The infrared spectra of all the complexes listed in Table I show three terminal carbonyl stretching frequencies, in accord with an octahedral structure of C₄ᵥ symmetry (Table II). In addition, II shows a ketonic carbonyl stretch at 1644 (s) cm.⁻¹. Compounds I–IV each have a single C–H stretching band in the region 2950–2900 cm.⁻¹, and bands in the C–F region similar to those observed in other fluorocarbon–transition metal complexes.[25]

As an aid to assigning structure, and also to add to our knowledge of chemical shifts and spin coupling constants, the ¹H and ¹⁹F n.m.r. spectra of the compounds were studied (Tables III and IV).

The ¹⁹F n.m.r. spectrum of I consists of two doublets of equal intensity centered at 59.8 and 121.5 p.p.m., relative to trichlorofluoromethane as standard. The upfield doublet separation is 58 c.p.s., and the downfield doublet separation is 5.3 c.p.s. (Table III). Consistent with the ¹⁹F results, the proton resonance is split into three triplets centered at τ = 4.68, and separated by 58 c.p.s., with splittings in each triplet of 5.3 c.p.s. The 58 and 5.3 c.p.s. splittings in these spectra are of the magnitude expected for $J_{\text{H-F}}$ values where the hydrogen and the fluorine atoms are separated by one and two carbon atoms, respectively. The fluorine resonance at 59.8 p.p.m. in I may be assigned to the fluorine atoms of the CF₂ group bonded to the manganese atom (e.g., for C₂F₅Mn(CO)₅, δ(α-CF₂) = 68.8 p.p.m.),[26] while the resonance at 121.5 p.p.m. is characteristic of fluorine atoms of a CF₂H group[27] (e.g.,

(24) Polymerization could occur through donation of electrons from the triple bonds to adjacent manganese atoms, in a manner similar to that which is believed to operate in some other acetylenic-metal complexes; see G. E. Coates, "Organometallic Compounds," Methuen, London, 1960, p. 354.

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

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

(27) Yu. S. Konstantinov, *Dokl. Akad. Nauk SSSR*, **134**, 868 (1960).

Table II

Infrared Spectral Bands of Hydromanganation Products (cm.$^{-1}$)

Compound	Carbonyl stretching frequencies[a]	Other bands[b]
HCF$_2$CF$_2$Mn(CO)$_5$ (I)	2132 (m), 2045 (vs), 2014 (s)	2932 (w), 1353 (m), 1171 (w), 1094 (s), 1082 (m), 1012 (s), 991 (s), 930 (s), 781 (w), 656 (s,b)
HCF$_2$CF$_2$COMn(CO)$_5$ (II)[c]	2128 (m), 2040 (vs), 2023 (s), 1644 (s)	2947 (w), 1389 (w), 1236 (m), 1157 (m), 1114 (s), 1087 (m), 838 (m), 743 (s,b), 679 (m,b), 652 (m,b)
HCFClCF$_2$Mn(CO)$_5$ (III)	2132 (m), 2045 (vs), 2014 (s)	2947 (w), 1340 (w), 1312 (m), 1250 (m), 1147 (w), 1127 (m), 1081 (m), 1056 (s), 1002 (s), 963 (s,b), 937 (w), 825 (s,b), 792 (m), 691 (m), 652 (m,b)
HCCl$_2$CF$_2$Mn(CO)$_5$ (IV)	2133 (w), 2055 (vs), 2000 (s)	2905 (w), 1337 (w), 1230 (m), 1212 (w), 1131 (w), 1090 (s), 1079 (m), 1065 (w), 1039 (w), 972 (s), 922 (w), 809 (s), 789 (m), 747 (w), 768 (sh), 675 (w), 651 (m)
CF$_3$CH:C(CF$_3$)Mn(CO)$_5$ (V)[d]	2130 (m), 2045 (vs), 2012 (s)	3021 (w), 2427 (m), 1621 (sh), 1613 (s), 1341 (m), 1285 (s), 1256 (w), 1222 (vs), 1193 (w), 1141 (vs), 1129 (vs), 1110 (s), 1019 (w), 926 (w), 898 (m), 840 (s), 716 (m), 654 (vs,b)

[a] Tetrachloroethylene solution, CaF$_2$ prism. [b] Carbon disulfide solution, NaCl prism. [c] In cyclohexane solution terminal carbonyl stretches are at 2128, 2039, and 2023 cm.$^{-1}$. [d] In tetrachloroethylene solution V shows a C=C double bond stretch at 1613 cm.$^{-1}$.

Table III

Some ^{19}F and ^{1}H Chemical Shifts and Coupling Constants

Compound	$\delta(\alpha\text{-CF}_2)^a$	$\delta(\beta\text{-CF}_2)^a$	$\delta(\text{H})^b$	$J_{F\alpha-F\beta}$ c.p.s.	$J_{F\alpha-H}$ c.p.s.	$J_{F\beta-H}$ c.p.s.
HCF$_2$CF$_2$Mn(CO)$_5$ (I)	59.8	121.5	4.68[c]	<1	5.3	58
HCF$_2$CF$_2$COMn(CO)$_5$ (II)	117.5	139.8	4.14[c]	9.2	6.7	52
HCFClCF$_2$Mn(CO)$_5$ (III)	53.1	138.4[d]	4.17[c]	16.4, 12.4	12.4, 5.7	52
HCCl$_2$CF$_2$Mn(CO)$_5$ (IV)	45.8	..	4.30[e]	..	10.5	..
HCF$_2$CF$_3$	86.8	138.5	4.45[e]	3.0	3.0	53

[a] Chemical shifts in p.p.m. relative to CCl$_3$F (0.0 p.p.m.), increasing to high field. [b] Chemical shifts expressed in τ units. [c] Hexamethyldisiloxane internal standard. [d] Refers to F of β-CFClH group. [e] Tetramethylsilane external standard.

for HCF$_2$CF$_3$, δ(CF$_2$) = 138.5 p.p.m., Table III).

Both the ^{19}F and ^{1}H n.m.r. spectra of III and IV were relatively simple, indicating that only *one* of the two possible isomeric species was present. The ^{19}F spectrum of IV consists of a doublet (splitting 10.5 c.p.s.) at 45.8 p.p.m. The proton absorption is a triplet, with line separations of 10.5 c.p.s. The low position of the fluorine resonance[26] and the small J_{H-F} value show that the structure of IV is HCCl$_2$CF$_2$Mn-(CO)$_5$ and not HCF$_2$CCl$_2$Mn(CO)$_5$, thereby confirming the result of the bromine cleavage study.

The ^{19}F spectrum of III consists of two multiplets of intensity ratio 2:1, centered at 53.1 and 138.4 p.p.m., respectively. The relatively low position of the former resonance again confirms that the CF$_2$ group is adjacent to manganese.[26] Because the HCClF group has three different atoms bonded to the carbon atom the two fluorine atoms of the adjacent CF$_2$ group cannot be structurally equivalent.[28] Consequently, the CF$_2$

(28) J. A. Pople, *Mol. Phys.*, 1, 1 (1958).

multiplet centered at 53.1 p.p.m. has an AB rather than an A$_2$ pattern. Since the fluorine atoms of the α-CF$_2$ group are not equivalent the two $J_{F\alpha-F\beta}$ coupling constants are unequal, as are the two $J_{F\alpha-H}$ values. Thus the absorption of one of the fluorine atoms of the CF$_2$ group occurs as two quartets (intensity ratio 1:1:1:1 within each quartet, with separations 5.7, 10.7, and 5.7 c.p.s.), and the other occurs downfield as two triplets (intensity ratio 1:2:1 within each triplet, with separations 12.4 c.p.s.) resulting from overlap of two doublets.[29] The multiplet due to the fluorine atom of the CF group centered at 138.4 p.p.m. consists of two identical quartets (intensity ratio 1:1:1:1) separated by 52 c.p.s. ($J_{F\beta-H}$). Separations between lines in the quartets are 12.4, 4.0, and

(29) From the observed line separations at 56.4 Mc., the chemical shift between the two fluorine atoms of the CF$_2$ group was determined, by simple AB theory, to be 874 c.p.s. (15.5 p.p.m.) with $J_{F\alpha-F\alpha}$ = 276 c.p.s. From the 40 Mc. spectrum the corresponding results were δ = 617 c.p.s. (15.4 p.p.m.) and $J_{F\alpha-F\alpha}$ = 274 c.p.s., in excellent agreement with the proposed AB type spectrum.

TABLE IV

^{19}F CHEMICAL SHIFTS AND SPIN COUPLING CONSTANTS FOR COMPOUNDS OF THE TYPE

$$X_{(1)} \quad X_{(3)}$$
$$\diagdown \quad \diagup$$
$$C{=}C$$
$$\diagup \quad \diagdown$$
$$X_{(2)} \quad X_{(4)}$$

Compound	X_1	X_2	X_3	X_4	Chemical shift[a]				Spin coupling constants (c.p.s.)					
					δ_1	δ_2	δ_3	δ_4	$J_{1,2}$	$J_{1,3}$	$J_{1,4}$	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$
$CF_3CH{=}C(CF_3)Mn(CO)_5$	CF_3	Mn	H	CF_3	57.0	...	...[b]	58.8	...	9.6	2.3	...	...	2.3
trans-$CF_3ClC{=}CFCF_3$	CF_3	Cl	F	CF_3	64.9	...	113.9	68.4	...	24.9	1.1	...	...	5.2
cis-$CF_3ClC{=}CFCF_3$	CF_3	Cl	CF_3	F	62.3	...	66.4	106.8	...	11.5	8.9	...	...	7.2

[a] In p.p.m. relative to CCl_3F (0.0 p.p.m.) increasing to high field. [b] Proton n.m.r. spectrum shows four quartets centered at 3.02 τ units, with J_{CF_3-H} values of 9.6 and 2.3 c.p.s.

12.4 c.p.s., arising from $J_{F\alpha-F\beta}$ couplings of 12.4 and 16.4 c.p.s.

The proton n.m.r. spectrum of III shows two quartets separated by 52 c.p.s. The separations between lines in the quartets are 5.7, 6.7, and 5.7 c.p.s., representing $J_{F\alpha-H}$ couplings of 5.7 and 12.4 c.p.s.

The infrared and n.m.r. spectra of V are in accord with the formulation $CF_3CH{=}C(CF_3)$-$Mn(CO)_5$. The complex has a strong infrared absorption in the carbon–carbon double bond stretching region (Table II). The ^{19}F n.m.r. spectrum consists of two multiplets of equal intensity centered at 57.0 and 58.8 p.p.m. (Table IV), in the region expected for fluorine atoms of CF_3 groups adjacent to a carbon–carbon double bond.[30,31] The multiplet at 57.0 p.p.m. consists of two quartets, each set of quartets arising from spin coupling with the proton (J_{CF_3-H} = 9.6 c.p.s.) to give a doublet, and with the other CF_3 group ($J_{CF_3-CF_3}$ = 2.3 c.p.s.) to give quartets. The multiplet at 58.8 p.p.m. occurs as five peaks (intensity ratio 1:4:6:4:1) arising from two overlapping quartets: in this case $J_{CF_3-CF_3}$ = J_{CF_3-H} (Table IV). As expected, the proton spectrum of V shows four quartets with coupling constants as listed in Table IV.

The relative simplicity of the ^{19}F n.m.r. spectrum of V indicates that formation of the compound occurs so as to give predominantly (if not only) one geometrical isomer. In order to determine whether in V the two CF_3 groups are *cis* or *trans* to one another, the ^{19}F n.m.r. spectrum of a mixture of *cis*- and *trans*-$CF_3CF{=}CClCF_3$ was studied. In this mixture one isomer predominated so that two equally intense CF_3 absorptions (δ = 64.9 and 68.4 p.p.m.) and two other equally but less intense CF_3 absorptions (δ = 62.3 and 66.4 p.p.m.) were observed. In addition, two absorptions of unequal intensity were observed at 113.9 and 106.8 p.p.m., the latter being the weaker, corresponding to the fluorine atoms of the $=CF-$ groups. The appearance of the CF_3 multiplets was qualitatively similar to the CF_3 multiplets of V, consisting of pairs of quartets. The measured spin coupling constants are summarized in Table IV. The assignment to specific interactions was made on the basis of the fact that where CF_2 groups are *trans* to an F atom, J values are known to vary between 8 and 12 c.p.s., whereas when CF_3 groups are *cis* to an F atom, J values are known to vary from 20–25 c.p.s.[30-32] The observed coupling constant ($J_{1,4}$) between fluorine atoms of CF_3 groups in *trans*-$CF_3CF{=}CClCF_3$ is only 1.1 c.p.s., whereas in *cis*-$CF_3CF{=}CClCF_3$ the observed coupling constant ($J_{1,3}$) between fluorine atoms of the CF_3 groups is 11.5 c.p.s. Since the coupling constant between fluorine atoms of the CF_2 groups in V is very small ($J_{1,4}$ = 2.3 c.p.s.), the complex has been assigned a *trans*-configuration.[33]

(30) E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **17**, 1244 (1961).

(31) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **34**, 2122 (1961).

(32) H. M. McConnell, C. A. Reilly, and A. D. McLean, *ibid.*, **24**, 479 (1956).

(33) Cleavage of V with trifluoroacetic acid affords *trans*-$CF_3CH{=}$ $CHCF_3$ in 96% yield, in confirmation of the n.m.r. prediction that V has a *trans* configuration.