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THE FORMATION OF 3,3,4,4-TETRAFLUORO-1,2-DICHLOROCYCLOBUTENE AND ITS REACTIONS WITH METAL CARBONYL ANIONS*

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SUMMARY

The reported preparation of 1,2,3,4-tetrafluoro-3,4-dichlorocyclobutene from commercial 1,2-dichloro-1,2-difluoroethylene when carried out in stainless steel reaction vessels also yields some 3,3,4,4-tetrafluoro-1,2-dichlorocyclobutene. Reactions of the 3,3,4,4-tetrafluoro-1,2-dichlorocyclobutene with the sodium salts of the metal carbonyl anions $[C_5H_5Fe(CO)_2]^-$ and $Mn(CO)_5^-$ results in replacement of a vinylic chlorine atom with a metal atom to give yellow-orange $C_4F_4ClFe(CO)_2C_5H_5$ and white $C_4F_4ClMn(CO)_5$, respectively. Reaction of $C_4F_4ClFe(CO)_2C_5H_5$ with triphenylphosphine, preferably in the presence of ultraviolet irradiation, gives the triphenylphosphine derivative $C_4F_4ClFe(CO)[P(C_6H_5)_3](C_5H_5)$. The mass spectra of the new metal fluorocarbon complexes are discussed.

INTRODUCTION

During the last decade numerous stable transition metal derivatives of cyclobutadiene and substituted cyclobutadienes have been synthesized[1]. However, no transition metal complexes of tetrafluorocyclobutadiene (I) are known.

RESULTS AND DISCUSSION

In an attempt to prepare transition metal complexes of tetrafluorocyclobutadiene (I), we have studied the dehalogenation of 1,2,3,4-tetrafluoro-3,4-dichlorocyclobutene[2] (II) with various metal carbonyls.

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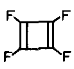
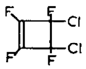


(I)



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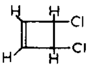
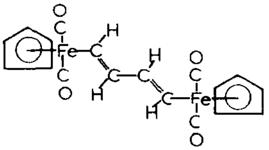


(III)

However, no metal complexes of tetrafluorocyclobutadiene were obtained by this preparative method. Even the reaction of $Fe_2(CO)_9$ with 1,2,3,4-tetrafluoro-3,4-dichlorocyclobutene (II) at room temperature failed to give any tetrafluorocyclobutadienetricarbonyliron, $C_4F_4Fe(CO)_3$, despite the fact that the analogous reaction of $Fe_2(CO)_9$ with 3,4-dichlorocyclobutene (III) gives a good yield of cyclobutadienetricarbonyliron, $C_4H_4Fe(CO)_3$[3].

We next investigated reactions of 1,2,3,4-tetrafluoro-3,4-dichlorocyclobutene (II) with various metal carbonyl anions. The reaction between 1,2,3,4-tetrafluoro-3,4-dichlorocyclobutene (II) and $NaFe(CO)_2C_5H_5$ was found to give a yellow crystalline product of stoichiometry $C_4F_4ClFe(CO)_2C_5H_5$. This reaction is clearly not analogous to the reported[4] reaction of the hydrogen analogue 3,4-dichlorocyclobutene (III) with $NaFe(CO)_2C_5H_5$ to give a product of stoichiometry $C_4H_4[Fe(CO)_2C_5H_5]_2$, shown by X-ray crystallography[5] to be the butadiene derivative (IV).



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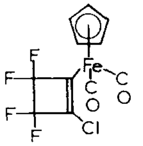

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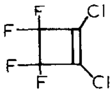


(VI)

In an attempt to elucidate the nature of the $C_4F_4ClFe(CO)_2C_5H_5$ obtained, its ^{19}F NMR spectrum was investigated (Table 1). Two apparent singlet resonances of equal relative intensities were observed thereby indicating that the four fluorine atoms in $C_4F_4ClFe(CO)_2C_5H_5$ were present in two equivalent pairs. This is clearly inconsistent with the compound $C_4F_4ClFe(CO)_2C_5H_5$ being a simple substitution product of the 1,2,3,4-tetrafluoro-3,4-dichlorocyclobutene (II) apparent starting material with one chlorine atom having been replaced by a $C_5H_5Fe(CO)_2$ group.

The number of possible formulations of a compound of stoichiometry $C_4F_4ClFe(CO)_2C_5H_5$ with two non-equivalent pairs of equivalent fluorine atoms is clearly limited. The most obvious structure of this kind for $C_4F_4ClFe(CO)_2C_5H_5$ is (V). A compound of structure (V) should be formed by replacement of one chlorine atom in 3,3,4,4-tetrafluoro-1,2-dichlorocyclobutene (VI) with a $C_5H_5Fe(CO)_2$ group. The reaction of an authentic sample of 3,3,4,4-tetrafluoro-1,2-dichlorocyclobutene (VI) with $NaFe(CO)_2C_5H_5$ was found to give a compound $C_4F_4ClFe(CO)_2C_5H_5$ which was identical in melting point, infrared spectrum, and NMR spectra (proton and fluorine) to the $C_4F_4ClFe(CO)_2C_5H_5$ obtained from our 1,2,3,4-tetrafluoro-3,4-dichlorocyclobutene (II) and $NaFe(CO)_2C_5H_5$.

TABLE 1

NMR SPECTRA OF 3,3,4,4-TETRAFLUORO-1,2-DICHLOROCYCLOBUTENE AND DERIVED METAL COMPLEXES

		^{19}F NMR spectrum, $\varphi^{b,c}$		^{1}H NMR spectrum, $\tau^{c,g}$	
Compound	Structure[a]	$CF_2(A)^{d,f}$	$CF_2(B)^{e,f}$	π-C_5H_5	C_6H_5
$C_4F_4Cl_2$	(VI)	118.7(s)	118.7(s)	—	—
$C_4F_4ClFe(CO)_2C_5H_5$	(V)	115.0(s)	110.9(s)	4.91(s)	—
$C_4F_4ClMn(CO)_5$	(IX)	115.2(s)	110.3(s)	—	—
$C_4F_4ClFe(CO)(PPh_3)(C_5H_5)$	(X)	116.2(d:15)	107.1(s)	5.39(s)	2.6–2.8(m)

[a] See the text for these structures.

[b] These ^{19}F NMR spectra were taken in dichloromethane solution and recorded on a Perkin–Elmer Hitachi R-20 spectrometer at 56.465 Mcps. The φ scale used here is the one proposed by G. FILIPOVICH AND G. V. D. TIERS, *J. Phys. Chem.*, *63* (1959) 761. Freon 112 ($CFCl_2CFCl_2$: φ 67.8) was used as an internal standard.

[c] The following abbreviations are used: s = singlet, m = asymmetric multiplet, d = doublet (coupling constants in cps). The fine structure described in the ^{19}F spectra is that observed on spectra run at 100 ppm sweep width.

[d] This refers to the CF_2 group closest to the metal atom (see structure (X) in the text).

[e] This refers to the CF_2 group furthest from the metal atom (see structure (X) in the text).

[f] These assignments are based on the ^{19}F NMR spectrum of $C_4F_4Fe(CO)[P(C_6H_5)_3](C_5H_5)$(X) as discussed in the text. They must be regarded as somewhat tentative.

[g] These proton NMR spectra were taken in $CDCl_3$ solution and recorded on a Varian HA-100 spectrometer at 100 Mcps. Tetramethylsilane was used as an internal standard.

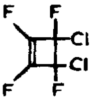
Two alternative explanations are available for the formation of a $C_4F_4ClFe(CO)_2C_5H_5$ compound of structure (V) from 1,2,3,4-tetrafluoro-3,4-dichlorocyclobutene and $NaFe(CO)_2C_5H_5$: (a) the 1,2,3,4-tetrafluoro-3,4-dichlorocyclobutene (II) undergoes a halogen shift upon reaction with $NaFe(CO)_2C_5H_5$ similar to the halogen shift undergone by perfluoroallyl chloride ($CF_2{=}CFCF_2Cl$) in its reported[6] reaction with $NaFe(CO)_2C_5H_5$ to give the perfluoropropenyl derivative $CF_3CF{=}CFFe(CO)_2C_5H_5$, or (b) the 1,2,3,4-tetrafluoro-3,4-dichlorocyclobutene (II) used in this work was contaminated by the isomeric 3,3,4,4-tetrafluoro-1,2-dichlorocyclobutene (VI).

The 1,2,3,4-tetrafluoro-3,4-dichlorocyclobutene (II) used in this work was prepared from 1,2-dichloro-1,2-difluoroethylene by the following three-step procedure developed by Haszeldine and Osborne[2]:

$$2ClFC{=}CFCl \xrightarrow[24\ h]{250^\circ} ClFC{=}CF{-}CFCl{-}CFCl_2 \qquad (1)$$

$$ClFC{=}CF{-}CFCl{-}CFCl_2 + Zn \xrightarrow{dioxane/100^\circ} ClFC{=}CF{-}CF{=}CFCl + ZnCl_2 \qquad (2)$$

$$ClFC{=}CF{-}CF{=}CFCl \xrightarrow{250^\circ/24\ h} \qquad (3)$$



(II)

Both pyrolysis reactions (steps (1) and (3)) were carried out in closed stainless steel cylinders ("Hoke bombs") rather than in the less convenient sealed silica tubes recommended by Haszeldine and Osborne[2]. Each intermediate product was purified by distillation before proceeding to the next step. However, the ^{19}F NMR spectra of both the ClFC=CF—CF=CFCl and the 1,2,3,4-tetrafluoro-3,4-dichlorocyclobutene (II) obtained from each of several preparations by the above method always exhibited a sharp singlet at φ 117.5 ± 0.2 characteristic of the four equivalent fluorine atoms in 3,3,4,4-tetrafluoro-1,2-dichlorocyclobutene (VI), as shown by comparison with a pure authentic sample of (VI) purchased commercially. Integration of these fluorine NMR spectra indicated that the 3,3,4,4-tetrafluoro-1,2-dichlorocyclobutene (VI) consisted of 50 to 60% of these mixtures of $C_4F_4Cl_2$ isomers. The presence of some 1,1-dichloro-2,2-difluoroethylene impurity in the commercial 1,2-dichloro-1,2-difluoroethylene used for the synthesis of 1,2,3,4-tetrafluoro-3,4-dichlorocyclobutene (II) is sufficient to account for this contamination with 3,3,4,4-tetrafluoro-1,2-dichlorocyclobutene (VI). In this connection the fluorine NMR spectra of the commercial samples of 1,2-dichloro-1,2-difluoroethylene used in this work indicated the presence of approximately equal quantities of *cis*-1,2-dichloro-1,2-difluoroethylene (φ 104.8), *trans*-1,2-dichloro-1,2-difluoroethylene (φ 119.4) and 1,1-dichloro-2,2-difluoroethylene (φ 87.6).

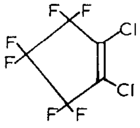
The reaction of 3,3,4,4-tetrafluoro-1,2-dichlorocyclobutene (VI) with $NaFe(CO)_2C_5H_5$ to give $C_4F_4ClFe(CO)_2C_5H_5$ (V) is another example of the nucleophilic displacement by a reactive metal carbonyl anion of a vinylic halogen in a highly fluorinated olefin[7]. There are two points of interest concerning this reaction:

(a) 3,3,4,4-Tetrafluoro-1,2-dichlorocyclobutene (VI) gives a fairly good yield (~60%) of $C_4F_4ClFe(CO)_2C_5H_5$ (V) when treated with $NaFe(CO)_2C_5H_5$, whereas 3,3,4,4,5,5-hexafluoro-1,2-dichlorocyclopentene (VII) gives only a low yield (10%) of the corresponding $C_5F_6ClFe(CO)_2C_5H_5$ (VIII) when reacted with $NaFe(CO)_2C_5H_5$[8]. Apparently side reactions occur more readily in the fluorinated cyclopentene system (VII) than in the fluorinated cyclobutene system (VI).

(b) In a mixture of 3,3,4,4-tetrafluoro-1,2-dichlorocyclobutene (VI) and 1,2,3,4-tetrafluoro-3,4-dichlorocyclobutene (II), only the former compound (VI) forms an isolable product with $NaFe(CO)_2C_5H_5$. This is in accord both with the expected greater reactivity of a vinylic chlorine atom than a vinylic fluorine atom toward nucleophilic substitution in a fluorinated olefin and with the greater potential susceptibility of an allylic chlorine atom than an allylic fluorine atom to destructive side reactions.

Sodium pentacarbonylmanganate, $NaMn(CO)_5$, although less nucleophilic[9] than $NaFe(CO)_2C_5H_5$, reacts with some, but not all, highly fluorinated olefins to form the corresponding pentacarbonylmanganese derivatives[7]. Reaction of $NaMn(CO)_5$ with 3,3,4,4-tetrafluoro-1,2-dichlorocyclobutene (VI) gave white crystals of composition $C_4F_4ClMn(CO)_5$. The ^{19}F NMR spectrum of this

$C_4F_4ClMn(CO)_5$ exhibits two singlets of similar chemical shifts to those found in $C_4F_4ClFe(CO)_2C_5H_5$ (V). Accordingly, $C_4F_4ClMn(CO)_5$ is formulated analogously as (IX). The infrared spectrum of $C_4F_4ClMn(CO)_5$ (IX) in the ν (CO) region in cyclohexane solution exhibited the expected two A_1 modes and single E mode at similar frequencies and of similar relative intensities to those observed[10] for other $R_fMn(CO)_5$ derivatives. Neither the splitting of the E mode nor the appearance of an infrared active B_1 mode was observed.



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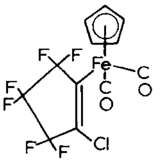
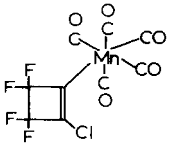


(VIII)



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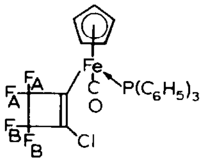

(X)

Compounds of the type $R_fFe(CO)_2C_5H_5$ have been shown[11] to react with tertiary phosphines to give substitution products of the type $R_fFe(CO)(PR_3)(C_5H_5)$. The compound $C_4F_4ClFe(CO)_2C_5H_5$ (V) was likewise found to react with triphenylphosphine to give $C_4F_4ClFe(CO)[P(C_6H_3](C_5H_5)$ (X). The best yields of (X) (~45%) were obtained by ultraviolet irradiation of (V) with triphenylphosphine in benzene, but a small yield of (IX) (~3.5%) could even be obtained by heating (V) with triphenylphosphine in boiling methylcyclohexane in the absence of ultraviolet irradiation. Structure (X) for $C_4F_4ClFe(CO)[P(C_6H_5)_3](C_5H_5)$ was confirmed by its ^{19}F NMR spectrum which exhibited two resonances of equal relative intensities and similar chemical shifts to the two resonances found in $C_4F_4ClFe(CO)_2C_5H_5$ (V) and $C_4F_4ClMn(CO)_5$ (IX). However, the higher field ^{19}F NMR resonance in the triphenylphosphine derivative $C_4F_4ClFe(CO)[P(C_6H_5)_3](C_5H_5)$ (X) was a distinct doublet (J = 15 cps) apparently arising from coupling of the phosphorus nucleus of the triphenylphosphine ligand with the fluorines of one of the CF_2 groups. If the CF_2 group exhibiting splitting of the ^{19}F resonance by the phosphorus of the triphenylphosphine ligand is assumed to be the one closest to the metal atom (F_A in (X)), then the higher field ^{19}F NMR resonances in the three transition metal–C_4F_4Cl derivatives (V), (IX) and (X) may be assigned to the CF_2 group closest to the metal atom (*e.g.* F_A in (X)) and the lower field ^{19}F NMR resonances in these complexes may be assigned to the CF_2 group closest to the chlorine atom (*e.g.* F_B in (X)). This is in accord with the expectation of greater shielding by a transition metal atom than by a halogen atom.

The presence of only two ^{19}F NMR resonances in the transition metal–C_4F_4Cl derivatives (V), (IX) and (X) requires an effective plane of symmetry bisecting all four carbon atoms of the cyclobutene ring. This implies free rotation around the transition metal–carbon σ-bond to the C_4F_4Cl group at least in the case of (V) and (X). This rotation around the metal–carbon σ-bond could not be slowed down to the NMR time scale by cooling to −80° in $C_4F_4ClFe(CO)_2C_5H_5$ (V) as indicated by the essential equivalence of the ^{19}F NMR spectrum of this compound at −80° and at ambient temperature (~30°).

The mass spectra of the complexes $C_4F_4ClFe(CO)_2C_5H_5$ (V), $C_4F_4ClFe(CO)[P(C_6H_5)_3](C_5H_5)$ (X) and $C_4F_4ClMn(CO)_5$ (IX) have been investigated. The presence of pyrolysis products such as $(C_5H_5)_2Fe^+$ (*m*/*e* 186) and $C_5H_5FeC_5H_4$-$C_4F_4Cl^+$ (*m*/*e* 344) complicated the mass spectrum of $C_4F_4ClFe(CO)_2C_5H_5$ (V) even when the sample inlet temperature was held to 85°. At more elevated temperatures (~100°), an ion at *m*/*e* 467 corresponding to $(C_4F_4C_5H_4)Fe(C_5H_4C_4F_4Cl)^+$ was even observed. The tendency for compounds of the type $RFe(CO)_2C_5H_5$ to give ions of the type $RC_5H_4FeC_5H_5^+$ and $(RC_5H_4)_2Fe^+$ by pyrolysis reactions in the mass spectrometer has been previously reported[12]. Other processes observed in the mass spectrum of $C_4F_4ClFe(CO)_2C_5H_5$ (V) include apparent losses of carbonyl groups, fluorine atoms and hydrogen fluoride similar to those reported[13,14] in the mass spectra of related $R_fFe(CO)_2C_5H_5$ derivatives.

The mass spectrum of the triphenylphosphine complex $C_4F_4ClFe(CO)[P(C_6H_5)_3](C_5H_5)$ (X) is of interest because of the occurrence of a loss of a neutral FeClF fragment according to the following process supported by an appropriate metastable ion*:

$$\underset{(m/e\ 542)}{C_4F_4ClFe[P(C_6H_5)_3](C_5H_5)^+} \xrightarrow{m^*\ 344} \underset{(m/e\ 433)}{C_4F_3C_5H_5P(C_6H_5)_3^+} + FeClF$$

Such losses of neutral metal chloride fluoride fragments are relatively rare. However, a similar process has been observed in the mass spectrum of the closely-related complex $C_5F_6ClFe(CO)_2C_5H_5$ (VIII) obtained from 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene and $NaFe(CO)_2C_5H_5$[14]. Other processes observed in the mass spectrum of $C_4F_4ClFe(CO)[P(C_6H_5)_3](C_5H_5)$ (X) are typical ones for either polyfluoroalkyl metal carbonyls[13,14,15] or phenylated tertiary phosphines[16,17] and their metal complexes[18].

An attempt to run the mass spectrum of $C_4F_4ClMn(CO)_5$ (IX) with the usual chamber temperature of 220° led to complete decomposition even when the sample was kept at room temperature. However, when the chamber temperature was reduced to 110° a good mass spectrum of $C_4F_4ClMn(CO)_5$ (IX) could be obtained. The principal features of this mass spectrum corresponded closely to those of the mass spectrum of the related compound $C_5F_6ClMn(CO)_5$ ((XI): M = Mn) as reported by Bruce[19]. The families of ions $C_4F_4ClMn(CO)_n^+$ ($n = 5, 4, 3, 2, 1$ and 0), $C_4F_3ClMn(CO)_n^+$ ($n = 5, 4, 3, 2, 1$ and 0), $Mn(CO)_n^+$ ($n = 5, 4, 3, 2, 1$ and 0), and $C_4F_4Mn(CO)_n^+$ ($n = 2, 1$ and 0) are observed with the last series having by far the lowest relative intensities. This suggests that in this type of system a bond

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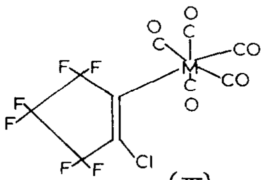
* This metastable ion was too broad to be resolved into the expected doublet corresponding to processes involving the ^{35}Cl and ^{37}Cl ions.

between carbon and an allylic fluorine atom is broken much more easily than a bond between carbon and a vinylic chlorine atom.

Metastable ions were observed in the mass spectrum of $C_4F_4ClMn(CO)_5$ (IX) which correspond to carbonyl losses involving some of the more abundant metal carbonyl ions. These metastable ions were doublets of relative intensities corresponding to processes involving ions containing each of the two chlorine isotopes ^{35}Cl and ^{37}Cl. A metastable ion doublet at m/e 251 and 253 corresponding to loss of two carbonyl groups from the molecular ion in one step was also observed. An additional metastable ion doublet at m/e 68.2 and 70.0 corresponds to a loss of a neutral essentially mono-isotopic m/e 93 fragment from the very abundant ion $C_4F_4ClMn^+$ (calculated for this doublet: m/e 68.3 and 70.1). This neutral essentially mono-isotopic m/e 93 fragment could either be C_3F_3 or MnF_2, but the latter possibility seems much more likely in view of the well-established eliminations of neutral metal fluoride fragments[13,14,15] including MnF_2 in fluorocarbon transition metal derivatives as contrasted with the absence of reported examples of eliminations of neutral C_3F_3 fragments even in the related compounds $C_5F_6ClM(CO)_5$ ((XI): M = Mn or Re)[19].



(XI)

The remaining observed metastable ion doublet occurs at m/e 44.3 and 45.2 corresponding to the elimination of a neutral CCl fragment (calculated m/e values for the metastable ion doublet: m/e 44.6 and 45.3) from the ion doublet at m/e 123 and 121 which is assigned to $C_4F_2Cl^+$. Similar metastable supported eliminations of neutral CF fragments are observed in the mass spectrum of the related $C_5F_6ClMn(CO)_5$ ((XI): M = Mn)[19].

EXPERIMENTAL

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, or Meade Microanalytical Laboratory, Amherst, Massachusetts. Infrared spectra were run in potassium bromide pellets using a Perkin–Elmer Model 621 spectrometer with grating optics and calibrated against the known 1601.4 cm^{-1} band of polystyrene. In addition, the $\nu(CO)$ frequencies of the metal carbonyl derivatives were measured in cyclohexane or pentane solution. Melting points were obtained on samples in capillaries and are uncorrected.

A nitrogen atmosphere was routinely provided for the following operations: (a) carrying out reactions, (b) handling filtered solutions of organometallic compounds and (c) admitting to evacuated vessels.

The 1,2-dichloro-1,2-difluoroethylene was purchased from Columbia Organic Chemicals, Inc., Columbia, S.C. The 1,2,3,4-tetrafluoro-3,4-dichlorocyclobutene was prepared from the 1,2-dichloro-1,2-difluoroethylene by the Haszeldine–Osborne procedure[2] with the modifications discussed above. The 3,3,4,4-tetrafluoro-1,2-dichlorocyclobutene was purchased from Peninsular Chem Research, Inc., Gainesville, Fla. The metal carbonyl derivatives $[C_5H_5Fe(CO)_2]_2$[20] and $Mn_2(CO)_{10}$[21] were prepared by published procedures. Tetrahydrofuran was always freshly distilled over lithium aluminium hydride.

Preparation of $C_4F_4ClFe(CO)_2C_5H_5$ (V)

A solution of $NaFe(CO)_2C_5H_5$ was prepared by stirring 2.5 g (7 mmoles) of $[C_5H_5Fe(CO)_2]_2$ with excess 3% sodium amalgam in 125 ml of tetrahydrofuran for 90 min at room temperature. Excess amalgam was removed and this solution cooled to −78°. A 2.0 g (10.2 mmoles) sample of either commercial 3,3,4,4-tetrafluoro-1,2-dichlorocyclobutene (VI) or the samples of 1,2,3,4-tetrafluoro-3,4-dichlorocyclobutene (II) or ClF=CF—CF=CFCl prepared[2] in this work was added drop-wise. The reaction mixture was stirred for 4 h at −78° and for an additional 12 h at ambient temperature. Solvent was then removed from the reaction mixture at 40°/30 mm. The residue was extracted with 250 ml of hot hexane. The hexane solution was concentrated to 50 ml and then chromatographed on a 2×75 cm Florisil column. The product was eluted from the yellow band with a 1:10 mixture of dichloromethane and hexane. The eluate was evaporated at 25°/40 mm. The residue was recrystallized from pentane and then sublimed at 50°/0.05 mm to give up to a 60% yield of $C_4F_4ClFe(CO)_2C_5H_5$ (V), m.p. 73–74°. Anal.: Calcd. for $C_{11}H_5ClF_4FeO_2$: C, 39.3; H, 1.5; Cl, 10.5; F, 22.7; Fe, 16.6; mol. wt., 336. Found: C, 39.3, 39.5, 39.3; H, 1.5, 1.6, 1.4; Cl, 11.6, 10.7; F, 22.6; Fe, 16.6, 16.6, 16.6; mol. wt., 324 (osmometer in benzene). Infrared spectrum (KBr pellet unless otherwise indicated): ν(CH) frequency at 3128 (w) cm^{-1}; ν(CO) frequencies at 2037 (s), 1996 (s) and 1982 cm^{-1} in a KBr pellet or at 2056 (s), 2007 (s) and 1997 (s, sh) cm^{-1} in cyclohexane solution; ν(CF) frequencies at 1312 (s), 1237 (s), 1234 (s), 1131 (s), 1106 (w) and 1078 (s) cm^{-1}; other bands at 1435 (w), 1421 (m), 1400 (vw), 1363 (vw), 1017 (vw), 1004 (vw), 954 (w), 946 (vw, sh), 883 (vw), 857 (m), 846 (m), 837 (m), 792 (s), 723 (m), 714 (vw), 669 (m), 662 (vw), 615 (m), 601 (m) and 587 (s) cm^{-1}.

Preparation of $C_4F_4ClMn(CO)_5$ (IX)

A solution of $NaMn(CO)_5$ was prepared by stirring 4.0 g (10.2 mmoles) of $Mn_2(CO)_{10}$ with excess ~3% sodium amalgam in 125 ml of tetrahydrofuran for 2 h. Excess amalgam was then removed and the solution cooled to −78°. A 4.0 g (20.5 mmoles) sample of 3,3,4,4-tetrafluoro-1,2-dichlorocyclobutene (VI) was added drop-wise. The reaction mixture was then stirred for 2 h at −78° and then for an additional 12 h at ambient temperature. Solvent was then removed at

25°/35 mm. The residue was extracted with 300 ml of pentane. The filtered pentane extracts were concentrated to 30 ml and then cooled to −78° for 2 h. The resulting white crystals were removed by filtration and purified further by sublimation at 50°/35 mm for 24 h on to a probe cooled with running water to give 4.6 g (64% yield) of white $C_4F_4ClMn(CO)_5$ (IX), m.p. 30–32°. Anal.: Calcd. for $C_9ClF_4MnO_5$: C, 30.4; Cl, 10.0; F, 21.4; Mn, 15.4; O, 22.5; mol. wt. 354. Found: C, 30.3; Cl, 10.0; F, 21.4; Mn, 15.4; O, 22.5; mol. wt. 352. Infrared spectrum (neat liquid unless otherwise indicated: No ν(CH) frequencies; ν(CO) frequencies at 2134 (s), 2084 (s) and 2070–2015 (vs, br) cm^{-1} in the neat liquid or at 2138 (m: A_1 mode), 2050 (s: E mode) and 2028 (s: A_1 mode) cm^{-1} in cyclohexane solution; ν(CF) frequencies at 1364 (w), 1334 (s), 1322 (s), 1259 (w), 1243 (s), 1144 (w), 1125 (m, sh) and 1093 (s) cm^{-1}; other bands at 1534 (w), 849 (s), 793 (s), 725 (s), 679 (s), 665 (s) and 645 (s) cm^{-1}.

The same $C_4F_4ClMn(CO)_5$ (IX), as shown by its elemental analyses and ^{19}F NMR spectrum, could be similarly obtained from $NaMn(CO)_5$ and the 1,2,3,4-tetrafluoro-3,4-dichlorocyclobutene (II) prepared in this work. However, it was obtained as a red liquid which could not be separated from a persistent impurity and hence could not be readily crystallized.

Preparation of $C_4F_4ClFe(CO)[P(C_6H_5)_3](C_5H_5)$ *(X)*

A mixture of 0.80 g (2.4 mmoles) of $C_4F_4ClFe(CO)_2C_5H_5$ (V), 2.5 g (9.6 mmoles) of triphenylphosphine and 125 ml of benzene were exposed for 12 h to the ultraviolet irradiation from a 125 W Nester–Faust mercury vapor ultra-violet lamp placed 7 cm from the Pyrex flask. During this period the heat from the ultraviolet lamp caused the solvent to boil. After the irradiation period was over, the reaction mixture was filtered. The filtrate was concentrated to 10 ml at 40°/40 mm and then chromatographed on a 2×40 cm Florisil column. The excess triphenylphosphine was eluted from the column with hexane. The yellow-orange band of product was then eluted with a 1:5 mixture of dichloromethane and hexane. Evaporation of the eluate at 25°/40 mm gave a crystalline residue. Recrystallization of this residue several times from mixtures of dichloromethane and hexane gave 0.630 g (45% yield) of orange crystalline $C_4F_4ClFe(CO)[P(C_6H_5)_3]$-$(C_5H_5)$ (X), m.p. 198–199° (dec.). Anal.: Calcd. for $C_{28}H_{20}ClF_4FeOP$: C, 57.4; H, 3.5; Cl, 6.0; F, 12.9; Fe, 9.5; P, 5.3; Found: C, 57.4; H, 3.4; Cl, 7.2; F, 13.1; Fe, 9.5; P, 5.3. Infrared spectrum (KBr pellet unless otherwise indicated): ν(CH) frequencies at 3123 (vvw), 3080 (vw), 3065 (vw) and 3053 (vw, sh); ν(CO) frequencies at 1970–1945 (vvs, br) cm^{-1} in a KBr pellet or at 1965 (s, sh) and 1961 (s) cm^{-1} in cyclohexane solution; ν(CF) frequencies at 1312 (vs), 1293 (m, sh), 1241 (s), 1125 (m), 1094 (s) and 1067 (s) cm^{-1}; other bands at 1598 (w), 1586 (vw), 1481 (m), 1434 (s), 1422 (w), 1397 (w), 1355 (m), 1203 (m), 1186 (w), 1030 (w), 1015 (w), 1001 (m), 975 (m), 940 (w), 860 (m), 845 (m, sh), 840 (s), 785 (s), 777 (m), 752 (m), 745 (m), 717 (m), 704 (s), 693 (s) and 664 (m) cm^{-1}.

The same product (X) was obtained in 3.5% yield by heating $C_4F_4ClFe(CO)_2C_5H_5$ (V) with an ~80% excess of triphenylphosphine in boiling methylcyclohexane for 25 h without added ultraviolet irradiation. In this latter reaction, essentially the same product isolation procedure was used as described above.

Attempts to prepare tetrafluorocyclobutadiene metal complexes

The following reactions of 1,2,3,4-tetrafluoro-3,4-dichlorocyclobutene (II) with metal carbonyls failed to give any tractable products under the indicated conditions:

(1) Reaction of (II) with $Fe_2(CO)_9$ either in pentane solution at room temperature for 20 h or in tetrahydrofuran solution at the boiling point for 12 h.

(2) Reaction of (II) with $Fe_3(CO)_{12}$ in boiling benzene for 12 h.

(3) Reaction of (II) with $Ni(CO)_4$ either in tetrahydrofuran at room temperature or at the boiling point for 12 h.

(4) Reaction of (II) with $Co_2(CO)_8$ in tetrahydrofuran at room temperature for 12 h.

(5) Reaction of (II) with $[(C_6H_5)_3PNP(C_6H_5)_3][Co(CO)_4]$ in tetrahydrofuran at room temperature or at the boiling point for 12 h.

(6) Reaction of (II) with $Na_2Fe(CO)_4$ (from $Fe_3(CO)_{12}$ and sodium amalgam) in tetrahydrofuran at room temperature for 12 h.

Mass spectra:

The mass spectra listed below were obtained at 70 eV electron energies, 220° chamber temperature (unless otherwise specified) and the indicated sample temperatures on a Perkin–Elmer Hitachi RMU-6 mass spectrometer. Relative intensities are given in parentheses.

$C_4F_4ClFe(CO)_2C_5H_5$ (sample temperature 85°)

$C_5H_5FeC_5H_4C_4F_4Cl^+$ (13), $C_4F_4ClFe(CO)_2C_5H_5^+$ (50), $C_4F_3ClFe(CO)_2C_5H_5^+$ (5), $C_4F_4ClFe(CO)C_5H_5^+$ (50), $C_4F_3ClFe(CO)C_5H_5^+$ (6), $C_4F_4ClFeC_5H_5^+$ (100), $C_4F_3ClFeC_5H_5^+$ (5), $C_5H_5C_4F_4Cl^+$ (110), $C_5H_5C_4F_3Cl^+$ (40), $C_5H_5C_4F_4^+$ (175), $(C_5H_5)_2Fe^+$ (265), $C_5H_5C_4F_3^+$ (110), $C_5H_4C_4F_3^+$ (190), $C_4F_4ClH^+$ (55), $C_5H_5FeCl^+$ (50), $C_5H_5C_4F_2^+$ (180), $C_5H_5FeF^+$ (240), $C_5H_5Fe^+$ (185), $C_4F_3^+$ (29), FeF^+ (135), $FeCl^+$ (50), $C_5H_5^+$ (70), $C_5H_3^+$ (48), Fe^+ (70) and $C_3H_3^+$ (95).

$C_4F_4ClFe(CO)[P(C_6H_5)_3](C_5H_5)$ (sample temperature 210°)

$C_4F_4ClFe(CO)[P(C_6H_5)_3](C_5H_5)^+$ (21), $C_4F_4ClFe[P(C_6H_5)_3](C_5H_5)^+$ (100), $C_4F_3ClFeP(C_6H_5)_3C_5H_5^+$ (5), $C_4F_4FeP(C_6H_5)_3C_5H_5^+$ (9), $C_4F_4ClFeP(C_6H_5)_3^+$ (8), $C_4F_3ClFeP(C_6H_5)_2C_5H_5^+$ (2), $C_4F_3C_5H_5P(C_6H_5)_3^+$ (96), $C_5H_5FeP(C_6H_5)_3^+$ (15), $C_4F_3P(C_6H_5)_3^+$ (19), $(C_6H_5)_3PFeCl^+$ (30), $(C_6H_5)_3PFeF^+$ (24), $(C_6H_5)_3PFe^+$ (61), $(C_6H_5)_3PCl^+$ (6), $(C_6H_5)_3P^+$ (940), $C_{12}H_9PFe^+$ (17), $(C_6H_5)_2P^+$ (113), $C_{12}H_8P^+$ (480), $C_5H_5C_4F_3^+$ (24), $C_5H_4C_4F_3^+$ (13), *m/e* 164 (11), *m/e* 157 (20),

$C_{12}H_8^+$ and/or $C_6H_5FeF^+$ (42), *m/e* 141 (16), $C_5H_5FeF^+$ (11), *m/e* 139 (10), $C_6H_5Fe^+$ (18), *m/e* 131 (13), $C_5H_5Fe^+$ (24), *m/e* 115 (18), $C_6H_5P^+$ (220), $C_6H_4P^+$ (60), $C_6H_5^+$ (13), $C_6H_3^+$ (22), $C_5H_6^+$ (19) and $C_5H_5^+$ (40). Metastable ions at *m/e* 516 (m) ($C_4F_4ClFe(CO)[P(C_6H_5)_3](C_5H_5)^+ \rightarrow C_4F_4ClFe[P(C_6H_5)_3]C_5H_5^+ + CO$), *m/e* 344 (m) ($C_4F_4ClFe[P(C_6H_5)_3]C_5H_5^+ \rightarrow C_4F_3C_5H_5P(C_6H_5)_3^+ + FeClF$), *m/e* 181 (m) ($(C_6H_5)_2P^+ \rightarrow C_{12}H_8P^+ + H_2$), *m/e* 129 (m) ($(C_6H_5)_3P^+ \rightarrow C_{12}H_8P^+ + C_6H_5 + H_2$) and *m/e* 44.5 (w) ($(C_6H_5)_3P^+ \rightarrow C_6H_5P^+ + C_{12}H_{10}$).

$C_4F_4ClMn(CO)_5$ (chamber temperature 110°, sample at room temperature)

$C_4F_4ClMn(CO)_5^+$ (37), $C_4F_3ClMn(CO)_5^+$ (3), $C_4F_4ClMn(CO)_4^+$ (0.4), $C_4F_3ClMn(CO)_4^+$ (6), $C_4F_4ClMn(CO)_3^+$ (18), $C_4F_3ClMn(CO)_3^+$ (1.5), $C_4F_4ClMn(CO)_2^+$ (33), $C_4F_3ClMn(CO)_2^+$ (2), $C_4F_4ClMnCO^+$ (13), $C_4F_4Mn(CO)_2^+$ (0.2), $C_4F_3ClMnCO^+$ (0.7), $C_4F_4ClMn^+$ (100), $C_4F_4MnCO^+$ (0.3), $C_4F_3ClMn^+$ (3), $Mn(CO)_5^+$ (6), $C_4F_4Mn^+$ (3), $Mn(CO)_4^+$ (4), $C_3F_2ClMn^+$ (4), $C_4F_4ClH^+$ (4), $C_3F_3Mn^+$ (1), $Mn(CO)_3^+$ (5), $C_4F_4ClMn(CO)_2^+$ (1.5), $C_3F_2Mn^+$ (5), $C_4F_2Cl^+$ (240), *m/e* 118 (5), MnC_2Cl^+ (6), $Mn(CO)_2^{2+}$ (4), C_3FMn^+ (2), $C_3F_2Cl^+$ (1), $C_4F_4ClMn^{2+}$ (2), $C_4F_3^+$ (31), C_4FCl^+ (11), $C_2F_4^+$ (1), *m/e* 98 (1.5), $MnCl^+$ (26), $C_4F_2^+$ (22), $MnCO^+$ (6), MnC_2^+ (9), $C_3F_2^+$ and possibly MnF^+ (52), *m/e* 71 (9), CF_3^+ (6.5), MnC^+ and/or C_4F^+ (3), $C_3F_2Mn^{2+}$ (6.5), Mn^+ (46), C_3Mn^{2+} (0.2) and $MnCO^{2+}$ (7). Metastable ions at *m/e* 281 and 283 (w) ($C_4F_3ClMn(CO)_5^+ \rightarrow C_4F_3ClMn(CO)_4^+ + CO$), *m/e* 251 and 253 (w) ($C_4F_4ClMn(CO)_5^+ \rightarrow C_4F_4ClMn(CO)_3^+ + 2CO$), *m/e* 244.5 and 246.5 (m) ($C_4F_4ClMn(CO)_3^+ \rightarrow C_4F_4ClMn(CO)_2^+ + CO$), *m/e* 216.2 and 218.2 (m) ($C_4F_4ClMn(CO)_2^+ \rightarrow C_4F_4ClMnCO^+ + CO$), *m/e* 189 and 191 (m) ($C_4F_4ClMnCO^+ \rightarrow C_4F_4ClMn^+ + CO$), *m/e* 68.2 and 70.0 (s) ($C_4F_4ClMn^+ \rightarrow C_4F_2Cl^+ + MnF_2$) and *m/e* 44.3 and 45.2 (w), ($C_4F_2Cl^+ \rightarrow C_3F_2^+ + CCl$).

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