# CHEMISTRY OF THE METAL CARBONYLS

## XXVI[a]. ADDITION OF ORGANOMANGANESE PENTACARBONYLS TO FLUORO-OLEFINS

J. B. WILFORD[b], P. M. TREICHEL[c] AND F. G. A. STONE[b],
*Department of Chemistry, Queen Mary College, University of London, London (Great Britain)*

(Received January 15th, 1964)

The work described in this paper extends the scope of the previously reported[2] hydromanganation reaction, and continues our studies on organometallic compounds having a fluorocarbon group $\sigma$-bonded to a transition metal[3]. In this paper we report the addition of methylmanganese pentacarbonyl to tetrafluoroethylene and to chlorotrifluoroethylene, of phenylmanganese pentacarbonyl to tetrafluoroethylene, and a further investigation of the addition of manganese pentacarbonyl hydride to chlorotrifluoroethylene.

A new synthetic method using ultra-violet irradiation to bring about the addition reactions is described. At the time of writing this affords products expected from thermal additions, but avoids the use of high reaction temperatures which sometimes lead to decomposition of the desired product.

### EXPERIMENTAL

Methyl- and phenylmanganese pentacarbonyls were prepared by the method of Closson *et al.*[4]. Manganese pentacarbonyl hydride was prepared as described elsewhere[2,5]. Tetrafluoroethylene was obtained by pyrolysis[6] of Teflon resin at 600°, and chlorotrifluoroethylene by dechlorination of 1,1,2-trichloro-1,2,2-trifluoroethylene[7]. Experiments were carried out with the aid of a conventional type of high vacuum system[8,9].

Fluorine NMR spectra were recorded at 56.4 Mc. with a Varian V-4300B high resolution spectrometer equipped with a flux stabilizer and precision audio oscillator. Line positions were determined by the side-band technique, and were the average of several calibrated traces. Proton NMR spectra were recorded by means of a Varian A-60 spectrometer, line positions being read from calibrated traces. Infrared spectra were recorded using a Unicam SP 100 prism-grating spectrophotometer.

### *1. Addition of methylmanganese pentacarbonyl to tetrafluoroethylene*[d]

Methylmanganese pentacarbonyl (624 mg, 2.97 mmole) was introduced via a side-arm into a 250 ml Pyrex reaction bulb. The latter was attached to the vacuum system and

---

[a] For Part XXV see ref. 1.

[b] Present address: Department of Inorganic Chemistry, The University, Bristol 8, Great Britain.

[c] Present address: Department of Chemistry, University of Wisconsin, Madison, Wisconsin, U.S.A.

[d] Ref. 10 gives a preliminary report of some of the work described in this paper.

evacuated, after the side-arm had been sealed. Tetrafluoroethylene (578 cc, 25.8 mmole) was condensed into the bulb, which was then sealed off. The reaction vessel was heated at 95° C for two hours. It was then allowed to cool and was attached to the vacuum system through a side-arm and tube opener[8,9]. In this manner 512 cc (22.9 mmole) of tetrafluoroethylene (identified by its infrared spectrum) were recovered. The solid contents of the bulb were extracted with two 20 ml portions of pentane. The resulting solution was slowly evaporated (—23° C, 10 mm) and the residue sublimed (20° C, 0.1 mm) affording 500 mg (56% yield based on methylmanganese pentacarbonyl taken) of the new white crystalline compound $CH_3CF_2CF_2Mn(CO)_5$ (I), (Table 1).

TABLE I

FLUOROCARBON DERIVATIVES OF MANGANESE[a]

| Compound | M.p. °C | Carbon, % | | Hydrogen, % | | Fluorine, % | | Manganese, % | | Chlorine, % | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| $CH_3CF_2CF_2Mn(CO)_5$ (I) | 41–42 | 31.0 | 30.6 | 0.98 | 0.79 | 24.5 | 24.7 | 17.7 | 17.3 | — | — |
| $C_6H_5CF_2CF_2Mn(CO)_5$ (II)[b] | 36–37 | 41.9 | 41.5 | 1.36 | 1.43 | 20.4 | 20.6 | 14.8 | 14.6 | — | — |
| $CH_3CF_2CFClMn(CO)_5$ (III) | 53–54 | 29.4 | 29.9 | 0.93 | 0.93 | 17.5 | — | 16.8 | 16.5 | 10.9 | 11.1 |
| $HCFClCF_2Mn(CO)_5$ (IV) | 41–42 | 26.9 | 26.6 | 0.32 | 0.31 | 18.2 | 17.8 | 17.6 | 17.4 | 11.4 | 11.0 |
| $HCF_2CFClMn(CO)_5$ (V) | 51–52 | 26.9 | 27.2 | 0.32 | 0.22 | 18.2 | 18.1 | 17.6 | 17.4 | 11.4 | 11.3 |

[a] Microanalyses for C, H, F, and Cl were performed by the Alfred Bernhardt Mikroanalytisches Laboratorium, Max-Planck-Institut für Kohlenforschung, Mülheim (Ruhr) West Germany. Manganese analyses were determined in our laboratory by oxidation of samples to $MnO_4^-$ which was estimated spectrophotometrically.

[b] Mol.Wt. (Mechrolab vapour pressure Osmometer) 368 (Theory 372).

*2. Addition of phenylmanganese pentacarbonyl to tetrafluoroethylene*

(*a*) *Ultra-violet light induced addition.* Phenylmanganese pentacarbonyl (680 mg, 2.5 mmole), tetrafluoroethylene (504 cc, 22.5 mmole) and pentane (30 ml) were sealed up in a 250 ml bulb made of glass transparent to UV radiation. The reaction vessel was irradiated for 14 h with light from a 250 watt mercury lamp. The bulb was opened and the pentane solution was evaporated at —23° C. The resulting solid (500 mg) was dissolved in pentane (2 ml) and chromatographed on a 1 × 50 cm Florisil column. A series of fractions (10 ml) were taken, the pentane evaporated (—23° C, 5 mm) and the resulting solid, if any, sublimed (30° C, 0.1 mm). The extent of the separation was followed by examining the infrared spectra of the fractions. Ether was used to remove the last traces of $C_6H_5CF_2CF_2Mn(CO)_5$ (II) from the column. In this way phenylmanganese pentacarbonyl (30 mg) and 425 mg (46% yield) of white crystalline (II) (Table 1) were obtained.

(*b*) *Thermal addition.* Phenylmanganese pentacarbonyl (650 mg, 2.4 mmole) and tetrafluoroethylene (244 cc, 10.9 mmole) were sealed into a 250 ml Pyrex reaction vessel and heated at 115° C for 2½ h, after which the bulb contained a yellow viscous liquid and an orange-red solid. On opening the bulb to the vacuum system, however, most of the tetrafluoroethylene (215 cc, 9.6 mmole) was recovered. Accordingly, the bulb was re-sealed with the tetrafluoroethylene and heated at 115° C for a further 4 h. On re-opening the bulb the uptake of the fluoro-olefin was an additional 0.5 mmole.

The solid material from the reaction vessel was extracted with pentane and chromatographed on Florisil, as described in (*a*) above. In this way dimanganese decacarbonyl, unreacted phenylmanganese pentacarbonyl and a trace of (II) (identified by its infrared spectrum) were recovered.

### 3. *Addition of methylmanganese pentacarbonyl to chlorotrifluoroethylene*

(*a*) *Ultra-violet light induced reaction.* Using a procedure similar to that described in 2(*a*), methylmanganese pentacarbonyl (519 mg, 2.47 mmole), chlorotrifluoroethylene (307 cc, 13.7 mmole) and pentane (50 ml) were irradiated for 8 h. The resulting solution was evaporated at —23° C, and chromatographed affording 160 mg (20 % yield based on methylmanganese pentacarbonyl taken for reaction) of the very volatile white crystalline complex (III) (Table 1).

(*b*) *Thermal reaction.* Following the procedure in 2(*b*), methylmanganese pentacarbonyl (232.5 mg, 11.7 mmole) and chlorotrifluoroethylene (497 cc, 22.2 mmole) were heated at 98° C for 14 h. The solid obtained after pentane extraction amounted to only 22 mg. It was shown by infrared spectroscopy to be a mixture of methylmanganese pentacarbonyl and the complex (III) obtained by method 3(*a*). Considerable decomposition took place during the reaction with formation of much intractable material.

In both procedures 3(*a*) and 3(*b*) careful spectroscopic examination of the products failed to detect the presence of the isomer $CH_3CFClCF_2Mn(CO)_5$.

### 4. *Addition of manganese pentacarbonyl hydride to chlorotrifluoroethylene*

(*a*) *Ultra-violet light induced addition.* Following the procedure described in 2(*a*), a mixture of manganese pentacarbonyl hydride (2.30 g, 11.74 mmole), chlorotrifluoroethylene (358 cc, 16.0 mmole) and pentane (20 ml) were irradiated for 2 h. Removal of solvent (—23° C, 10 mm) followed by sublimation (20° C, 0.1 mm) afforded 1.1 g (30 % yield) of pale yellow crystals (m.p. 42–43° C). The infrared spectra of these crystals, identical with that of the material obtained from reaction 4(*b*)(*i*) described below, showed them to be a mixture of the two isomers, $HCFClCF_2Mn(CO)_5$ (IV) and $HCF_2CFClMn(CO)_5$ (V), contaminated by a trace of dimanganese decacarbonyl. Separation of these isomers is described later.

(*b*) *Thermal reactions.* A series of reactions between chlorotrifluoroethylene and manganese pentacarbonyl hydride were carried out at ambient temperatures in the absence of ultra-violet light.

(*i*) Manganese pentacarbonyl hydride (1.04 g, 5.3 mmole) and chlorotrifluoroethylene (470 cc, 21.0 mmole) were condensed into a 250 ml Pyrex reaction bulb which was sealed off and left at ambient temperatures for 20 h. On re-opening to the vacuum system, 358 cc (16.0 mmole) of chlorotrifluoroethylene (identified by its infrared spectrum) were recovered. Residual yellow solids in the bulb were extracted with pentane (25 ml) which was then evaporated (—23° C, 5 mm). Sublimation (20° C, 0.1 mm) afforded 590 mg (36 % yield based on hydride taken for reaction) of pale yellow crystals (m.p. 43.5–44.6° C). The $^{19}F$ NMR spectrum (Fig. 1) of these crystals dissolved in trichlorofluoromethane, showed them to be a mixture of (IV) and (V), as discussed below. The infrared spectrum of the crystals was recorded in the 7–11 micron region (Fig. 2a).

(*ii*) A stainless steel Hoke bomb (150 ml) was charged with manganese pentacarbonyl hydride (453 mg, 2.32 mmole), chlorotrifluoroethylene (717 cc, 32.0 mmole) and pentane (20 ml). After standing at room temperature for 25 h the bomb was attached to the vacuum system, opened and unreacted chlorotrifluoroethylene (493 cc, 22.0 mmole) recovered. After removal of pentane, the usual procedure afforded 250 mg (35 % yield) of pale yellow crystals (m.p. 42–43° C). The $^{19}$F NMR spectrum of the product showed only the presence of (IV), but the infrared spectrum (7–11 μ) showed the presence of (V) as well, (Fig. 2b).

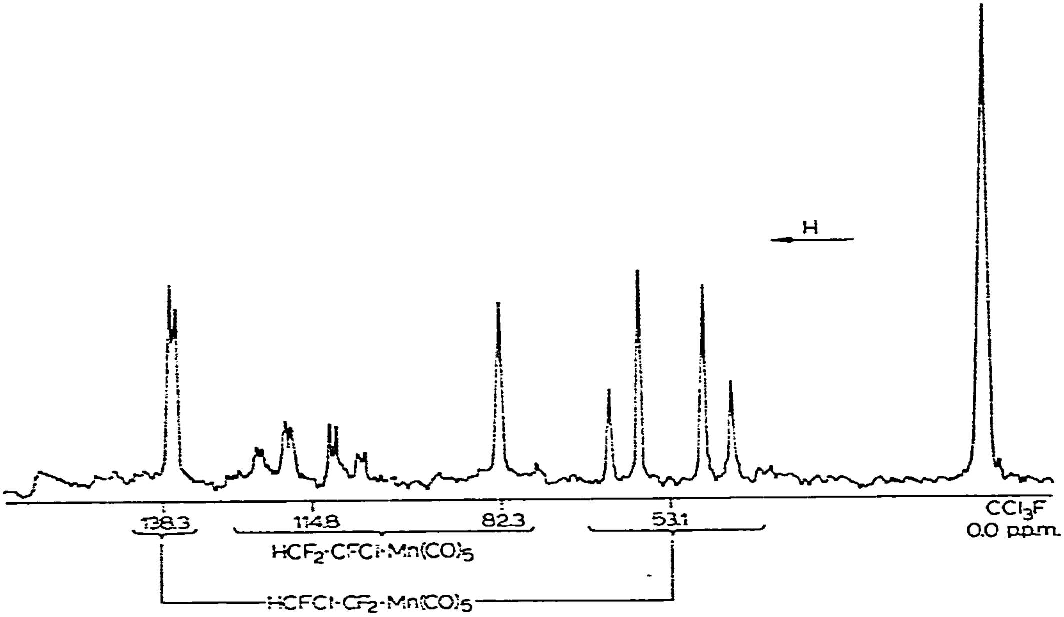

Fig. 1. $^{19}$F nuclear magnetic resonance spectra of a mixture of HCFCl–CF$_2$–Mn(CO)$_5$ and HCF$_2$–CFCl–Mn(CO)$_5$ from manganese pentacarbonyl hydride and chlorotrifluoroethylene at 2 atm.

(*iii*) In an experiment similar to (*ii*), manganese pentacarbonyl hydride (605 mg, 3.1 mmole), chlorotrifluoroethylene (856 cc, 38.2 mmole) and pentane (25 ml) afforded 226 mg of crystals (24 % yield). The infrared spectrum in the 7–11 μ region was very similar to that of the crystals obtained in (*ii*).

(*iv*) In an experiment similar to (*ii*), manganese pentacarbonyl hydride (922 mg, 4.71 mmole), chlorotrifluoroethylene (1444 cc, 64.5 mmole) and pentane (20 ml) yielded, after recovery of the fluoro-olefin (1355 cc, 60.5 mmole), 550 mg (37 % yield) of yellow product. The infrared spectrum showed it to be largely isomer (IV) (Fig. 2c).

### *5. Separation of the isomers IV and V*

The crystalline products from reactions 4(*a*) and 4(*b*)(*i*) were dissolved in pentane (2 ml) and chromatographed on Florisil. A pale yellow band subsequently shown to be dimanganese decacarbonyl appeared on the column. Elution with pentane afforded a series of fractions (10 ml). The pentane was evaporated (—23° C, 5 mm) and the resulting solid, if any, sublimed (20° C, 0.1 mm). A trace (less than 10 mg) of dimanganese decacarbonyl (identified from its infrared spectrum) was recovered from

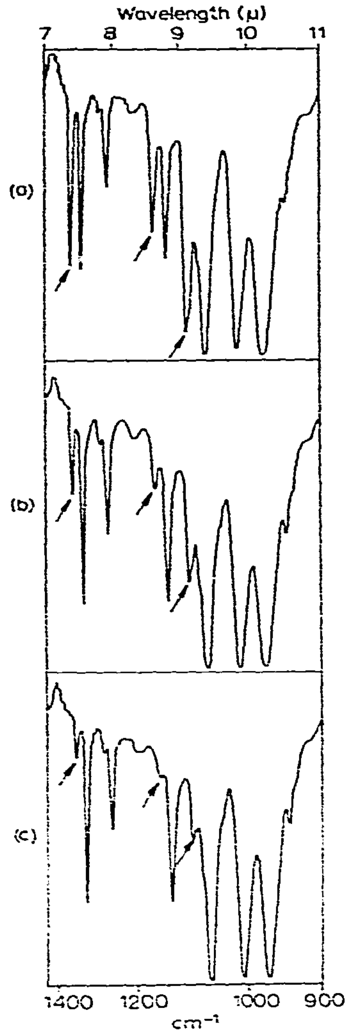

Fig. 2. Infrared spectra of mixtures of $HCFCl–CF_2–Mn(CO)_5$ and $HCF_2–CFCl–Mn(CO)_5$ prepared from $HMn(CO)_5$ and $CF_2{=}CFCl$.

an early fraction. Isomer (V) eluted next, and was recovered as colourless crystals (Table 1). Intermediate fractions afforded mixtures of (IV) and (V). To facilitate elution, diethyl ether was added to the column and in this way from final fractions complex (IV) was obtained also as colourless crystals.

## DISCUSSION

It was not found possible to add methylmanganese pentacarbonyl to tetrafluoroethylene below 80° even in the presence of a solvent. However, at 95° a rapid reaction afforded (I) in high yield. It is interesting to contrast these results with the observation[2] that manganese pentacarbonyl hydride adds to tetrafluoroethylene at room temperature to give $HCF_2CF_2Mn(CO)_5$.

Under conditions similar to those which yielded (I), phenylmanganese pentacarbonyl and tetrafluoroethylene gave only a trace of the desired product (II). Similarly, reactions between methylmanganese pentacarbonyl and chlorotrifluoroethylene carried out at 100° C or above, afforded (III) in only low yield. On the other hand, below 100° C only unchanged starting materials were recovered. These results led to a study of the effect of ultraviolet light on mixtures of the fluoro-olefins and the organomanganese pentacarbonyls dissolved in pentane. At room temperature the addition reactions:

$$C_6H_5Mn(CO)_5 + CF_2{=}CF_2 \longrightarrow \underset{\text{(II)}}{C_6H_5CF_2CF_2Mn(CO)_5}$$

$$CH_3Mn(CO)_5 + CF_2{=}CFCl \longrightarrow \underset{\text{(III)}}{CH_3CF_2CFClMn(CO)_5}$$

occurred to give the desired complexes in reasonable yield.

Lack of success in isolating the complexes from thermal reactions at about 100° C and above is understandable. Phenylmanganese pentacarbonyl was observed by us to decompose *in vacuo* at 100° C, and it has previously been reported[3] that the complex $HCFClCF_2Mn(CO)_5$ affords manganese carbonyl chlorides above 80° C.

Addition of methylmanganese pentacarbonyl across the double bond of chlorotrifluoroethylene could give either (III) or $CH_3CFClCF_2Mn(CO)_5$, or a mixture of both isomers. However, no conditions were found whereby the structural isomer $CH_3CFClCF_2Mn(CO)_5$ could be prepared in quantity sufficient to be detected spectroscopically. The NMR and infrared spectra of the products of several reactions were all found to be identical. Moreover, the spectra were relatively simple, indicating the presence of a single isomer. Furthermore, the $^{19}F$ and $^1H$ spectra of the material obtained from reaction 3(*a*) were in accord with structure (III), and could not be understood in terms of the presence of a complex containing the group $CH_3CFClCF_2Mn$. The $^{19}F$ spectrum consisted of three bands (intensity 1:1:1) centred at 78.2, 81.6 and 93.6 ppm (Table 2), corresponding to three magnetically non-equivalent fluorine

TABLE 2

SOME $^{19}F$ AND $^1H$ CHEMICAL SHIFTS AND COUPLING CONSTANTS

| *Compound* | $\delta(\alpha\text{-}CF_2)^a$ *ppm* | $\delta(\beta\text{-}CF_2)^a$ *ppm* | $\delta H^a$ $\tau$ | $J(F\alpha\text{-}F\beta)$ *cps* | $J(F\alpha\text{-}H)$ *cps* | $J(F\beta\text{-}H)$ *cps* |
|---|---|---|---|---|---|---|
| $CH_3CF_2CF_2Mn(CO)_5$ (I) | 58.3 | $93.4^b$ | $8.49^c$ | 4.2 | 2.5 | 18.9 |
| $C_6H_5CF_2CF_2Mn(CO)_5$ (II) | 58.9 | 99.5 | $2.57^d$ | < 1 | — | — |
| $CH_3CF_2CFClMn(CO)_5$ (III) | $78.2^e$ | 81.6, 93.6 | 8.17 | 13.0, < 1 | 2.0 | 18.5, 13.0 |
| $HCFClCF_2Mn(CO)_5$ (IV) | 48.1, 58.1 | $138.3^f$ | 4.10 | 16.4, 12.4 | 5.5, 12.5 | 52.0 |
| $HCF_2CFClMn(CO)_5$ (V) | $82.3^g$ | 108.3, 121.1 | 4.30 | 20.2, 10.0 | 5.3 | 61.3, 63.7 |

[a] $^{19}F$ chemical shifts relative to $CCl_3F$ (0.0 ppm) increasing to high field. $^1H$ chemical shifts in $\tau$ units. Solvent was $CCl_3F$ in all cases except $^1H$ spectrum of (I) for which $CS_2$ was used. [b] Observed as 4 triplets, intensity ratio 1:3:3:1. [c] Observed as 3 triplets. [d] Refers to phenyl group protons, unresolved. [e] Refers to F of α-CFCl group, observed as a doublet. [f] Refers to F of β-CFClH group, observed as a doublet. [g] Refers to F of α-CFCl group, observed as a singlet.

atoms. The resonance at 78.2 ppm was a doublet (splitting 13 cps). This resonance was at lowest field showing that it was due to the fluorine atom nearest to the manganese atom[11]. The doublet splitting represents coupling with an adjacent fluorine atom. The absence of further splitting shows that the methyl group is not bound to the same carbon atom[12]. The other two resonances (81.6 and 93.6 ppm), assigned to the $\beta$-$CF_2$ group, were in the form of an AB pattern, split into two sets of quartets by the expected coupling with the adjacent methyl groups. The pair of quartets centred at 81.6 ppm, were further split (13.0 cps) by coupling with the $\alpha$-fluorine atom. The non-equivalence of the fluorine atoms of the $CF_2$ group occurs because an adjacent carbon atom, that of the $CFClMn(CO)_5$ group, has three different groups bonded to it[2,13]. In agreement with the structure $H_3CCF_2CFClMn(CO)_5$, the proton spectrum (Table 2) consisted of a triplet [$J(H{-}F_\beta)$, 18.5 cps) with each line further split [$J(H{-}F_\alpha)$, 2 cps] into a doublet.

Both the stereospecific nature of the addition of methylmanganese pentacarbonyl to chlorotrifluoroethylene and formation of isomer (III) is surprising. According to the previous work[2], the addition of manganese pentacarbonyl hydride to chlorotrifluoroethylene afforded only the complex $HCFClCF_2Mn(CO)_5$ (IV), the CFCl group being in the $\beta$-position to the metal. In view of these differences in behaviour the addition of manganese pentacarbonyl hydride to chlorotrifluoroethylene was reinvestigated. Previous studies[2] had involved reaction in a bomb under conditions where the reactants would exert a pressure of about 4 atm. Accordingly, as described in the Experimental section, reactions were carried out using amounts of olefin both greater and smaller than in the earlier work, so that pressures in the reaction vessels ranged from approximately 2 to 5 atm. The upper limit on the pressure is determined by the vapour pressure of the olefin and of the pentane. That of the olefin is about 4 atm at ambient temperatures.

Under these conditions an appreciable concentration of chlorotrifluoroethylene must have been present in the liquid phase, especially in the experiment involving 64 mmole of olefin. The NMR and infrared spectra of the products of the various reactions were examined.

The $^{19}F$ spectrum of the material obtained from a reaction at about 2 atm is shown in Fig. 1. Chemical shifts and coupling constants are summarized in Table 2. Fig. 1 shows that the reaction product was a mixture of (IV) and (V). The presence of asymmetric carbon atoms in these isomers leads to non-equivalence of the fluorine atoms of the $CF_2$ groups in each complex. Bands due to these groups appear as an AB pattern[2,13]. That part of the spectrum (Fig. 1) due to (IV) is in excellent agreement with the spectrum observed in the earlier work[2,14]. Assignment (Table 2) of the peaks centred at 82.3, 108.3 and 121.3 ppm to the $\alpha$-CF and $\beta$-$CF_2$ groups of (V) follows both from arguments similar to those used above in the interpretation of the spectrum of (III), and from earlier discussions[2,12].

The infrared spectrum in the C–F absorption region[15] of the isomeric mixture ($CS_2$ solution) which afforded the $^{19}F$ NMR spectrum (Fig. 1) is shown in Fig. 2a. The three arrowed bands at 1342, 1149 and 1087 $cm^{-1}$ are due to (V). Figs. 2b and 2c show analogous spectra for reaction products in which 32 and 64.5 mmole of chlorotrifluoroethylene respectively, were taken for reaction with the hydride. The decrease in intensity of the three bands is obvious. Moreover, the $^{19}F$ and $^1H$ NMR spectra of products which gave infrared spectra corresponding to Figs. 2b and 2c showed resonance bands attributable only to the presence of (IV), confirming the predominant formation of this isomer under the reaction conditions.

Interestingly, in the previous work[2] the reaction conditions were fairly similar to those of the experiment in the present work which gave rise to the spectrum of Fig. 2b. Failure to detect (V) by previous NMR studies is thus understandable. However, it appears that trace amounts of this isomer were present, since weak infrared bands at 1340, 1147 and 1081 cm$^{-1}$ in the previously reported[2] spectrum of (IV) are in fact due to (V).

TABLE 3

INFRARED SPECTRAL BANDS OF THE FLUORO-ORGANOMANGANESE PENTACARBONYLS (cm$^{-1}$)

| *Compound* | *Carbonyl stretching*[a] *frequencies* | | *Other bands*[b] | | |
|---|---|---|---|---|---|
| $CH_3CF_2CF_2Mn(CO)_5$ (I) | 2136 (m) | 2041 (vs)<br>2012 (s) | 3000 (w)<br>1266 (s)<br>1093 (w)<br>980 (s)<br>837 (s) | 2941 (w)<br>1198 (s)<br>1075 (m)<br>940 (w)<br>645 (s, b) | 1380 (m)<br>1156 (s)<br>1031 (m)<br>870 (w) |
| $C_6H_5CF_2CF_2Mn(CO)_5$ (II) | 2130 (m) | 2039 (vs)<br>2010 (s) | 3093 (w)<br>2950 (w)<br>1186 (w)<br>1095 (w)<br>1026 (m)<br>917 (w)<br>695 (s)<br>619 (m) | 3061 (w)<br>2912 (w)<br>1143 (w)<br>1072 (w)<br>1009 (s)<br>901 (w)<br>662 (m, sh) | 3030 (vw)<br>1272 (m)<br>1117 (m)<br>1058 (s)<br>953 (m)<br>808 (s)<br>645 (s, b) |
| $CH_3CF_2CFClMn(CO)_5$ (III) | 2132 (m) | 2041 (vs)<br>2010 (s) | 3050 (w)<br>1387 (m)<br>1143 (s)<br>962 (s)<br>758 (s) | 2980 (w)<br>1238 (s)<br>1053 (w, b)<br>930 (m)<br>637 (s, b) | 2410 (w)<br>1190 (s)<br>990 (m)<br>833 (s) |
| $HCFClCF_2Mn(CO)_5$ (IV) | 2137 (m) | 2041 (vs)<br>2013 (s) | 2963 (vw)<br>1316 (s)<br>1124 (s)<br>1005 (vs)<br>820 (s)<br>699 (m) | 2915 (w)<br>1274 (w)<br>1093 (w)<br>962 (vs)<br>784 (m)<br>645 (s, b) | 2856 (vw)<br>1257 (m)<br>1057 (vs)<br>935 (w, sh)<br>752 (w) |
| $HCF_2CFClMn(CO)_5$ (V) | 2137 (m) | 2058 (vs)<br>2016 (s) | 2973 (w)<br>1087 (vs)<br>905 (w)<br>645 (s, b) | 1342 (s)<br>1053 (m)<br>791 (s)<br>597 (m) | 1149 (m)<br>962 (s)<br>770 (s) |

[a] Cyclohexane solution. [b] Carbon disulphide solution.

The fluorocarbon-manganese compounds described in this paper are stable in air. Their infrared spectra show three carbonyl stretching absorptions, as expected for an octahedral structure of $C_{4v}$ symmetry. These and other bands are listed in Table 3. As mentioned in the experimental section, separation of the isomers (IV) and (V) was accomplished by chromatography. Because of the demonstrated importance of infrared spectroscopy as a tool for establishing the presence of isomeric mixtures the individual spectra of the two isomers are reproduced in Fig. 3.

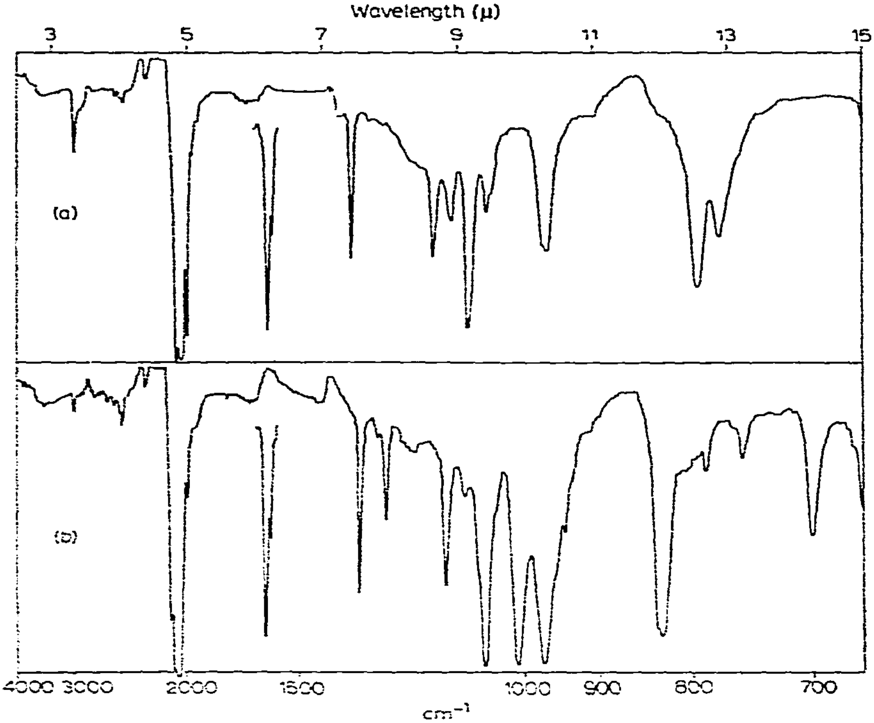

Fig. 3. Infrared spectra of (a) $HCF_2$-CFCl-Mn$(CO)_5$, m.p. 51–52°, and (b) HCFCl-$CF_2$-Mn$(CO)_5$, m.p. 41–42°.

## ACKNOWLEDGEMENTS

The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank D. SHAW for recording the proton NMR spectra and A. J. R. BOURN for measuring the fluorine NMR spectra.

One of us (J. B. W.) thanks the Department of Scientific and Industrial Research for the award of a Research Studentship, and P. M. T. thanks the National Science Foundation for the award of a Postdoctoral Fellowship.

## SUMMARY

At 90–100° methylmanganese pentacarbonyl adds across the double bond of tetrafluoroethylene to give $CH_3CF_2CF_2Mn(CO)_5$. Under the same conditions reactions between phenylmanganese pentacarbonyl and tetrafluoroethylene, and between methylmanganese pentacarbonyl and chlorotrifluoroethylene failed to give desired complexes in reasonable yield. By using ultra-violet irradiation however, it was possible to obtain $C_6H_5CF_2CF_2Mn(CO)_5$ and $CH_3CF_2CFClMn(CO)_5$ in good yield.

Reinvestigation of the addition of manganese pentacarbonyl hydride to chlorotrifluoroethylene led to the formation and characterisation of the two isomers $HCFClCF_2Mn(CO)_5$ and $HCF_2CFClMn(CO)_5$.

## REFERENCES

1 D. W. McBride, E. Dudek and F. G. A. Stone, *J. Chem. Soc.*, (1964) in press.
2 P. M. Treichel, E. Pitcher and F. G. A. Stone, *Inorg. Chem.*, 1 (1962) 511.
3 P. M. Treichel and F. G. A. Stone, *Advances in Organometallic Chemistry*, Vol. I, Academic Press, New York, 1964, 143–220.
4 R. D. Closson, J. Kozikowski and T. H. Coffield, *J. Org. Chem.*, 22 (1957) 598.
5 R. B. King and F. G. A. Stone, *Inorg. Syn.*, 7 (1963) 198.
6 E. E. Lewis and M. A. Naylor, *J. Am. Chem. Soc.*, 69 (1947) 1968.
7 M. W. Buxton, D. W. Ingram, F. Smith, M. Stacey and J. C. Tatlow, *J. Chem. Soc.*, (1952) 3830.
8 W. L. Jolly, *Synthetic Inorganic Chemistry*, Prentice-Hall, Englewood Cliffs, New Jersey, 1960.
9 R. T. Sanderson, *Vacuum Manipulation of Volatile Compounds*, Wiley, New York, 1948.
10 J. B. Wilford, P. M. Treichel and F. G. A. Stone, *Proc. Chem. Soc.*, (1963) 218.
11 E. Pitcher, A. D. Buckingham and F. G. A. Stone, *J. Chem. Phys.*, 36 (1962) 124.
12 J. A. Pople, W. G. Schneider and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance*, Mc-Graw-Hill, New York, 1959.
13 J. A. Pople, *Mol. Phys.*, 1 (1958) 1.
14 E. Pitcher, Ph. D. Thesis, Harvard University 1962.
15 E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, 18 (1962) 585.

*J. Organometal. Chem.*, 2 (1964) 119–128