1096. *Chemistry of the Metal Carbonyls. Part XXXI.*[1] *Reactions Between Some Fluoro-olefins and Carbonylmetal Anions*

By P. W. Jolly, M. I. Bruce, and F. G. A. Stone

By treating perfluoro-cyclohexene, -cyclobutene, -propene, or -ethylene with certain carbonylmetal anions new metal complexes have been obtained with structures in which the metal has replaced one of the fluorine atoms attached to a carbon of the double bond. In these reactions the anion $[Re(CO)_5]^-$ was shown to be comparable in nucleophilic power with $[\pi\text{-}C_5H_5\cdot Fe(CO)_2]^-$ and, moreover, will replace fluorine in perfluorobenzene to afford $C_6F_5\cdot Re(CO)_5$. The latter compound was also prepared by decarbonylating $C_6F_5\cdot CO\cdot Re(CO)_5$. Some properties of the new compounds are reported.

In contrast to their hydrocarbon analogues, perfluoro-olefins are highly susceptible to nucleophilic attack. The nature of the product depends on whether the intermediate carbanion eliminates fluoride ion or abstracts a proton from the solvent. Moreover, where possible, allylic rearrangements occur. These reactions have been well reviewed.[2-5] Perfluorobenzene also readily undergoes nucleophilic attack.[6-8]

Little attention has been given to the nucleophilic properties of carbonylmetal anions in reactions of the above type. Three such anions $[Mn(CO)_5]^-$, $[\pi\text{-}C_5H_5\cdot Fe(CO)_2]^-$, and

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[1] Part XXX, P. W. Jolly and F. G. A. Stone, *J.*, 1965, 5259.
[2] D. R. Sayers, R. Stephens, and J. C. Tatlow, *J.*, 1964, 3035.
[3] D. C. England, L. R. Melby, M. A. Dietrich, and R. V. Lindsey, *J. Amer. Chem. Soc.*, 1960, **82**, 5116.
[4] W. T. Miller, J. H. Fried, and H. Goldwhite, *J. Amer. Chem. Soc.*, 1960, **82**, 3091.
[5] J. D. Park and R. Fontanelli, *J. Org. Chem.*, 1963, **28**, 258.
[6] J. A. Godsell, M. Stacey, and J. C. Tatlow, *Nature*, 1956, **178**, 199.
[7] J. C. Tatlow, *Endeavour*, 1963, **22**, 89.
[8] R. J. Harper, E. J. Soloski, and C. Tamborski, *J. Org. Chem.*, 1964, **29**, 2385.

[π-C_5H_5·Ni(CO)]$^-$, have been reported[9] to react with perfluoroallyl chloride, but this is the only fluoro-olefin so far treated in this way. In these reactions rearrangements readily occur. Thus, the products from [π-C_5H_5·Fe(CO)$_2$]$^-$ and [Mn(CO)$_5$]$^-$ are predominantly, if not only, complexes containing the *trans*-CF_3·CF:CF–metal group, although in the case of manganese an intermediate pentacarbonyl-σ-perfluoroallylmanganese compound can be detected spectroscopically. With the anion [π-C_5H_5·Ni(CO)]$^-$ a mixture of the two complexes π-C_5H_5·Ni(CO)CF_2·CF:CF_2 and π-C_5H_5·Ni(CO)CF:CF·CF_3 is obtained. It has recently been reported[10] that perfluorobenzene undergoes nucleophilic attack by the anion [π-C_5H_5·Fe(CO)$_2$]$^-$ to afford π-C_5H_5·Fe(CO)$_2C_6F_5$. Certain substituted perfluorophenyl dicarbonyl-π-cyclopentadienyliron complexes have been made in the same manner. However, as a route to perfluorophenyl complexes in general, this type of reaction appears to be of limited use since several other carbonylmetal anions were observed not to react with perfluorobenzene.

In this Paper we describe reactions between several fluoro-olefins and carbonylmetal anions, as well as some analogous studies with perfluorobenzene.

EXPERIMENTAL

Fluorine-19 nuclear magnetic resonance spectra were recorded at 56·4 Mc./sec. with a Perkin-Elmer R10 spectrometer. Infrared spectra were obtained using a Perkin-Elmer model 237 grating spectrophotometer. For the carbonyl region of the spectrum the spectrophotometer was connected to a scale expander having 9-in. chart paper. Measurements of the carbonyl frequencies were calibrated against the two benzene absorptions at 2326 and 2211 cm.$^{-1}$. Molecular weights were obtained in benzene using a Mechrolab vapour-pressure osmometer, and melting points are corrected. Chromatography was performed using Florisil-packed columns. The sodium salts of the appropriate metal carbonyls were prepared in tetrahydrofuran by techniques described elsewhere.[11] With vigorous stirring formation of these salts is complete in 1½—2 hr. All operations were carried out under nitrogen. Light petroleum was a fraction of b. p. 60—80°.

Pentacarbonyl-σ-perfluorocyclohexenylrhenium.—A mixture of sodium amalgam (0·18 g. sodium in 100 g. of mercury) and decacarbonyldirhenium (2 g., 31 mmoles) in tetrahydrofuran (50 ml.) was stirred vigorously for 2 hr. After removal of excess of amalgam through a stopcock attached to the bottom of the flask, the reactants were briefly stirred with more mercury (100 g.). Following removal of the latter, the solution was added (1 hr.) to a flask fitted with a condenser and containing perfluorocyclohexene (2 g., 7·6 mmoles) in tetrahydrofuran (20 ml.), cooled to 0° and magnetically stirred. The reaction mixture was kept at 0° for 2 hr., and then stirred at room temperature for 15 hr. Solvent was removed at 0°/30 mm., and the residue sublimed at 40°/0·05 mm. on to a probe cooled by solid carbon dioxide. In this manner, white *pentacarbonyl-σ-perfluorocyclohexenylrhenium* (2·3 g., 65%) was obtained and recrystallised from light petroleum (Table 1).

The following compounds were similarly prepared by first forming the sodium salt of the metal carbonyl and adding it to the fluoro-olefin. In the reactions using perfluorocyclobutene, perfluoropropene, and tetrafluoroethylene a −78° condenser was employed and the mixture was held at 0° for 6 hr., before stirring at room temperature overnight. Microanalytical data and melting points for the various new compounds are recorded in Table 1.

Pentacarbonyl-σ-perfluorocyclohexenylmanganese (3·7 g., 85%), a white crystalline solid, was obtained from decacarbonyldimanganese (1·95 g., 5·0 mmoles) and perfluorocyclohexene (3 g., 11·1 mmoles).

Dicarbonyl-π-cyclopentadienyl-σ-perfluorocyclohexenyliron was obtained from the sodium salt from dicarbonyl-π-cyclopentadienyliron dimer (5 g., 14·0 mmoles) and perfluorocyclohexene (7·3 g., 28·1 mmoles) as an orange crystalline *solid* (4·1 g., 36%).

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[9] (*a*) H. D. Kaesz, R. B. King, and F. G. A. Stone, *Z. Naturforsch.*, 1960, **15**b, 763; (*b*) W. R. McClellan, *J. Amer. Chem. Soc.*, 1961, **83**, 1598; (*c*) R. B. King, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *ibid.*, p. 3604; (*d*) E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, 1961, **17**, 1244; (*e*) D. W. McBride, E. Dudek, and F. G. A. Stone, *J.*, 1964, 1752.

[10] R. B. King and M. B. Bisnette, *J. Organometallic Chem.*, 1964, **2**, 38.

[11] R. B. King and F. G. A. Stone, *Inorg. Synth.*, 1963, **7**, 110.

trans-*Tetracarbonyl-σ-perfluorocyclohexenyl(triphenylphosphine)manganese*, obtained after chromatography, using diethyl ether as eluant, formed white crystals (1·6 g., 47%) from tetracarbonyl(triphenylphosphine)manganese dimer (2·15 g., 2·5 mmoles) and perfluorocyclohexene (1·5 g., 5·6 mmoles). The geometry of the product was established from the infrared spectrum (see Discussion section).

Pentacarbonyl-σ-perfluorocyclobutenylrhenium, white crystals (1·9 g., 65%), was prepared from decacarbonyldirhenium (2 g., 3·1 mmoles) and perfluorocyclobutene (2·5 g., 15·5 mmoles).

TABLE 1

Fluorocarbon–metal complexes

Compound	M. p.	Found (%)			Required (%)		
		C	H	F	C	H	F
$CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF{:}C{\cdot}Re(CO)_5$	69—70°	23·2	0·0	29·8	23·2	0	30·0
$CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF{:}C{\cdot}Fe(CO)_2(\pi\text{-}C_5H_5)$ *	97—98	37·2	1·2	40·6	37·2	1·2	40·7
$CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF{:}C{\cdot}Mn(CO)_5$ †	35	30·1	0·0	39·2	30·2	0	39·0
$CF_2CF_2CF{:}C{\cdot}Re(CO)_5$	55—56	23·2	0·0	20·2	23·0	0	20·2
$CF_2{\cdot}CF_2CF{:}C{\cdot}Fe(\pi\text{-}C_5H_5)(CO)_2$ ‡	50—51	41·7	1·6	29·2	41·3	1·6	29·7
$CF_2{\cdot}CF_2{\cdot}CF{:}C{\cdot}Mn(CO)_5$	33	32·2	0·1	27·9	32·0	0	28·1
trans-$CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF{:}C{\cdot}Mn(CO)_4PPh_3$ §	159—160	50·2	2·3	25·6	50·0	2·2	25·4
cis-$CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF{:}C{\cdot}Mn(CO)_4PPh_3$ ¶	132—133	50·2	2·6	25·4	50·0	2·2	25·4
$CF_3{\cdot}CF{:}CF{\cdot}Re(CO)_5$	88—89	20·9	0·0	20·7	21·0	0	20·8
$CF_3{\cdot}CF{:}CF{\cdot}Fe(CO)_2(\pi\text{-}C_5H_5)$	70—71 ‖	39·1	1·5	—	39·0	1·6	—
$CF_2{:}CF{\cdot}Re(CO)_5$	45	20·7	0·0	13·8	20·6	0	13·9
$CF_2{:}CF{\cdot}Fe(CO)_2(\pi\text{-}C_5H_5)$	27	42·0	2·2	—	41·9	2·0	—
$C_6F_5{\cdot}CO{\cdot}Re(CO)_5$	114	27·7	0·0	18·3	27·6	0	18·2
$C_6F_5{\cdot}Re(CO)_5$	152	27·0	0·0	19·2	26·8	0	19·2

* Found: Fe, 13·2%; *M*, 444. Required: Fe, 13·3%; *M*, 420. † Found: Mn, 11·8. Required: Mn, 12·5%. ‡ Found: Fe, 17·0%; *M*, 315. Required: Fe, 17·5%; *M*, 320. § Found: Mn, 8·0; P, 4·8%; *M*, 650. Required: Mn, 8·0; P, 4·6%; *M*, 674. ¶ Found: P, 4·6%; *M*, 710. Required P, 4·6%; *M*, 674. ‖ Compound previously known (lit.,[9c] m. p. 69·5—70·5°).

Pentacarbonyl-σ-perfluorocyclobutenylmanganese was obtained as an extremely volatile white solid (2·1 g., 80%) from decacarbonyldimanganese (1·5 g., 3·8 mmoles) and perfluorocyclobutene (1·4 g., 8·6 mmoles).

Dicarbonyl-π-cyclopentadienyl-σ-perfluorocyclobutenyliron, orange crystals (3·7 g., 35%), was prepared from dicarbonyl-π-cyclopentadienyliron dimer (5·9 g., 17 mmoles) and perfluorocyclobutene (6·4 g., 40 mmoles).

Pentacarbonyl-σ-perfluoropropenylrhenium, white needles (1·7 g., 61%), was prepared from decacarbonyldirhenium (2 g., 3·1 mmoles) and perfluoropropene (2·5 g., 16·7 mmoles).

Pentacarbonyl-σ-perfluoropropenylmanganese formed white crystals (identified by their infrared spectrum [9d]) in low yield, from decacarbonyldimanganese (2 g., 5·0 mmoles) and perfluoropropene (3 g., 20·0 mmoles).

Dicarbonyl-π-cyclopentadienyl-σ-perfluoropropenyliron, orange crystals (8·7 g., 56%), identified spectroscopically [9d] and by analysis (Table 1), from dicarbonyl-π-cyclopentadienyliron dimer (8·9 g., 25·0 mmoles) and perfluoropropene (6·0 g., 40 mmoles).

Decacarbonyldirhenium (1·1 g., 1·6 mmoles) was converted into the sodium salt and the latter run into a flask cooled to −78°. Tetrafluoroethylene (0·47 g., 4·7 mmoles) was slowly bubbled into the solution, with a nitrogen stream, from a storage vessel at −78°. The product, *pentacarbonyl-σ-perfluorovinylrhenium* (0·9 g., 63%), was an extremely volatile white solid.

The sodium salt from dicarbonyl-π-cyclopentadienyliron (1·8 g., 5·1 mmoles) was added to a flask cooled in liquid nitrogen and containing tetrafluoroethylene (5 g., 50 mmoles) in tetrahydrofuran (20 ml.). The mixture was warmed to −78° and after 4 hr. allowed to reach room temperature overnight. Chromatography using 75% benzene–25% light petroleum as eluant afforded bright yellow-orange crystals of *dicarbonyl-π-cyclopentadienyl-σ-perfluorovinyliron* (0·5 g., 20%).

cis-*Tetracarbonyl-σ-perfluorocyclohexenyl(triphenylphosphine)manganese.*—Pentacarbonyl-σ-perfluorocyclohexenylmanganese (0·22 g., 0·50 mmole) and triphenylphosphine (0·15 g., 0·57 mmole) were refluxed in cyclohexane (50 ml.). The reaction, monitored by observing the infrared spectra of samples in the carbonyl region, was complete in 10 hr. After removal of solvent (30 mm., 0°) the residue was chromatographed. Elution with 10% diethyl ether–90% light petroleum afforded the pale yellow crystalline cis-*compound* (0·24 g., 77%), whilst elution with diethyl ether gave a small quantity (55 mg., 23%) of the white *trans*-compound. As described later, the two isomers were distinguished by their infrared spectra.

Pentacarbonyl-σ-perfluorophenylrhenium.—Decacarbonyldirhenium (1·1 g., 1·6 mmoles) was converted into its sodium salt and the latter added to perfluorobenzene (0·8 g., 4·3 mmoles) and the mixture refluxed for 15 hr. Solvent was removed at 0°/30 mm. and the residue sublimed at 100°/0·05 mm., giving solid (400 mg.) the spectrum of which showed peaks attributable to decacarbonyldirhenium. Chromatography afforded white *crystals* (0·25 g., 16%) (Table 1).

Pentacarbonyl-σ-perfluorobenzoylrhenium.—Obtained as cream coloured *crystals* (100 mg., 3%) by first subliming and then chromatographing the product obtained by adding pentacarbonylrhenate anion, from decacarbonyldirhenium (2·0 g., 3·1 mmoles), to perfluorobenzoyl chloride (1·4 g., 6·2 mmoles) in tetrahydrofuran (100 ml.).

When pentacarbonyl-σ-perfluorobenzoylrhenium is heated at 130° for 30 min. it is converted into pentacarbonyl-σ-perfluorophenylrhenium with release of carbon monoxide.

DISCUSSION

The anions $[\pi\text{-C}_5\text{H}_5\cdot\text{Fe(CO)}_2]^-$, $[\text{Re(CO)}_5]^-$, and $[\text{Mn(CO)}_5]^-$ displace fluoride ion from the two cyclic fluoro-olefins perfluorocyclohexene and perfluorocyclobutene, and from perfluoropropene. In contrast to the other two anions, however, $[\text{Mn(CO)}_5]^-$ does not react readily with perfluoropropene. A nucleophilic substitution reaction also occurs between perfluorocyclohexene and the anion $[\text{Mn(CO)}_4\text{PPh}_3]^-$. Whereas $[\pi\text{-C}_5\text{H}_5\cdot\text{Fe(CO)}_2]^-$ and $[\text{Re(CO)}_5]^-$ both afforded σ-bonded perfluorovinyl complexes when treated with tetrafluoroethylene, under similar conditions $[\text{Mn(CO)}_5)]^-$ did not displace fluoride from this olefin. During the course of the study, reactions between perfluorocyclohexene and the anions $[\text{Co(CO)}_4]^-$ and $[\text{Fe(CO)}_4]^{2-}$ were investigated but no fluorine-containing metal complexes were produced. Moreover, we prepared tetracarbonyl(triphenylphosphine)-rhenium dimer in order to investigate the nucleophilicity of the anion $[\text{Re(CO)}_4\text{PPh}_3]^-$. However, we were not able to form the sodium salt, even after heating the complex under reflux in tetrahydrofuran for 48 hr. Consequently the effect of the anion $[\text{Re(CO)}_4\text{PPh}_3]^-$ on the various fluoro-olefins could not be investigated.

Reference was made previously to King and Bisnette's[10] discovery that the reaction between the anion $[\pi\text{-C}_5\text{H}_5\text{Fe(CO)}_2]^-$ and perfluorobenzene afforded dicarbonyl-π-cyclopentadienyl-σ-perfluorophenyliron. These workers also found that the anions $[\text{Co(CO)}_4]^-$, $[\text{Fe(CO)}_4]^{2-}$, and $[\text{Mn(CO)}_5]^-$ did not react with perfluorobenzene. We have confirmed these observations and, moreover, have found that the anion $[\text{Mn(CO)}_4\text{PPh}_3]^-$ is also an insufficiently strong nucleophile to replace a fluorine atom in perfluorobenzene. However, the observation that the pentacarbonylrhenate anion was as powerful a nucleophile as $[\pi\text{-C}_5\text{H}_5\cdot\text{Fe(CO)}_2]^-$ towards the various perfluoro-olefins, prompted experiments to determine whether the rhenium anion would displace a fluoride ion from perfluorobenzene. As described in the Experimental section, pentacarbonyl-σ-perfluorophenylrhenium can be prepared in this way. This complex was also synthesised by the more classical route[12] involving the decarbonylation of the new complex $\text{C}_6\text{F}_5\cdot\text{CO}\cdot\text{Re(CO)}_5$.

An increase in the Lewis basicity of the carbonyl metal anions in passing down the subgroup from manganese to rhenium is probably a characteristic property of the transition metals. In addition to the studies reported here, some recent work of Parshall[13] on borane adducts of carbonylmetal anions supports this idea. Thus, salts of the anion $[\text{H}_3\text{B}\cdot\text{Mn(CO)}_5]^-$ were less stable towards dissociation than salts of the anion $[\text{H}_3\text{B}\cdot\text{Re(CO)}_5]^-$. Moreover, $[\text{H}_3\text{B}\cdot\text{Mn(CO)}_4\text{PPh}_3]^-$ was found to be more stable than $[\text{H}_3\text{B}\cdot\text{Mn(CO)}_5]^-$.

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[12] P. M. Treichel and F. G. A. Stone, *Adv. Organometallic Chem.*, 1964, **1**, 143.

[13] G. W. Parshall, *J. Amer. Chem. Soc.*, 1964, **86**, 361.

On the basis of our results and those of Parshall[13] it is possible to establish a sequence of increasing nucleophilicity for the carbonylmetal anions examined: $[Fe(CO)_4]^{2-} \sim [Co(CO)_4]^- < [Mn(CO)_5]^- \leqslant [Mn(CO)_4PPh_3]^- < [Re(CO)_5]^- \leqslant [\pi\text{-}C_5H_5\cdot Fe(CO)_2]^-$.

Of these, the anion $[Re(CO)_5]^-$ is the most efficient nucleophile giving clean reactions and high yields of pentacarbonylrhenium complexes. The reactions of $[\pi\text{-}C_5H_5\cdot Fe(CO)_2]^-$ are more complex. Thus, if a large excess of the sodium salt is added to perfluorocyclohexene, or if the perfluoro-olefin is added to the sodium salt, a mixture of products is produced, the infrared spectrum of which shows four peaks in the range 1640—1600 cm.$^{-1}$. However, the single band at 1635 cm.$^{-1}$ shown by dicarbonyl-π-cyclopentadienyl-σ-perfluorocyclohexenyliron in this double-bond absorption region predominates. We attempted to separate the additional products, which may contain no iron, by chromatography on alumina, but were unsuccessful.

The new compounds (Table 1) appear to be indefinitely stable on exposure to air. In solution the iron complexes decompose more rapidly than the manganese compounds, whilst the rhenium complexes can be recovered essentially quantitatively from solutions in organic solvents after several hours. In common with most σ-bonded fluorocarbon derivatives of the transition metals, they are not decomposed by water, and indeed some of the iron derivatives may be recrystallised from hot ethanol. All the compounds sublime very easily, and the lower-melting manganese and rhenium complexes will even sublime at room temperature under atmospheric pressure.

In an attempt to replace an olefinic fluorine atom in pentacarbonyl-σ-perfluorocyclohexenylrhenium with a methyl group, this complex was treated with methyl-lithium. However, decomposition occurred, even at —40°.

Reference was made earlier to the reactions of perfluoroallyl chloride and carbonylmetal anions which yield perfluoropropenylmetal compounds. As described in the Experimental section, the previously reported complexes $CF_3\cdot CF{:}CF\cdot Mn(CO)_5$ and $CF_3\cdot CF{:}CF\cdot Fe(CO)_2(\pi\text{-}C_5H_5)$ were obtained when perfluoropropene was treated with $[Mn(CO)_5]^-$ or $[\pi\text{-}C_5H_5\cdot Fe(CO)_2]^-$. These results make it likely that the new complexes obtained from perfluorocyclohexene or from perfluorocyclobutene have structures in which the metal is attached to one of the carbon atoms of the double bond of the rings. This is confirmed by the infrared spectra, and also by the fluorine-19 nuclear magnetic resonance studies described below.

Infrared-spectral bands are listed in Table 2. The absorptions in the various complexes in the range 1705—1620 cm.$^{-1}$ may be assigned to the double-bond stretching frequency. The frequency of this band in the perfluorocyclo-hexenyl and -butenyl complexes is in accord with structures in which the metal is attached directly to the double bond rather than to a carbon atom in the α-position to the double bond.[14] In the latter eventuality the absorption would occur above 1700 cm.$^{-1}$, as it does in perfluorocyclohexene (1738 cm.$^{-1}$), perfluorocyclobutene (1798 cm.$^{-1}$), and perfluoroallyl chloride (1792 cm.$^{-1}$). Below 1900 cm.$^{-1}$ the spectra of the perfluorovinyl–transition-metal compounds are simple, being very similar to the well known perfluorovinyl derivatives of main-group metals. The spectra have four main bands in this region, attributable to the C=C stretch, the $=CF_2$ asymmetric stretch, the =CF stretch, and the $=CF_2$ symmetrical stretch.[14]

The spectra of the complexes in the metal-carbonyl stretching region are of interest. Eight of the compounds are mono-substituted octahedral pentacarbonylmetal complexes. This class of octahedral complex often shows three infrared active carbonyl stretching modes as predicted for C_{4v} symmetry,[15] or for C_{2v} symmetry in the case of pentacarbonyl-σ-perfluorophenylrhenium (Table 2) and its manganese analogue.[16] However, if the mono-substituent is a non-axially symmetric fluorocarbon group, the overall molecular symmetry is reduced to pseudo-C_{4v}, or more strictly to C_s or even C_1 symmetry. In this event,

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[14] S. L. Stafford and F. G. A. Stone, *Spectrochim. Acta*, 1961, **17**, 412.
[15] L. E. Orgel, *Inorg. Chem.*, 1962, **1**, 25.
[16] J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, 1965, **4**, 389.

additional bands would be expected to appear and this has been experimentally confirmed.[16] Several of the new pentacarbonyl derivatives show more than three carbonyl bands (Table 2) in accord with their formal C_s symmetry. The appearance of four bands rather than five probably arises through accidental degeneracy of the expected two strong A″ modes as a consequence of the very small degree of axial symmetry introduced by the fluorocarbon group concerned. In accord with this, the A′ mode near 2070 cm.$^{-1}$ is of very weak intensity compared with the other two A′ modes near 2140 and 2015 cm.$^{-1}$. Interestingly, the weak band near 2070 cm.$^{-1}$ in the σ-perfluorocyclohexenyl- and σ-perfluorobutenyl-manganese complexes is not present in the spectra of their rhenium analogues. Similar results involving other analogous manganese and rhenium complexes have been previously described.[16] These systems can all be very fruitfully treated as C_{4v} for force-constant calculations.[16,17]

TABLE 2

Infrared-spectral bands (cm.$^{-1}$)

Compound	Fundamental carbonyl stretching frequencies *	Other bands †
$\overline{CF_2\cdot(CF_2)_3\cdot CF{:}C}\cdot Mn(CO)_5$	2137w, 2075vw, 2047vs, 2020s	1633w, 1332w, 1278m, 1247m, 1210m, 1185s, 1158m, 1118m, 1087m, 1014s, 951s, 800w, 736w, 754s, 639s
$\overline{CF_2\cdot CF_2\cdot CF{:}C}\cdot Mn(CO)_5$	2134w, 2070vw, 2048vs, 2022s	1623w, 1373m, 1362s, 1262s, 1171w, 1111m, 1098s, 934s, 786s, 775w, 675w, 650s, 631s
trans-$\overline{CF_2\cdot(CF_2)_3\cdot CF{:}C}\cdot Mn(CO)_4PPh_3$	2085w, 2038w, 1996s	1620vw, 1273m, 1245m, 1206m, 1190m, 1178s, 1152m, 1104m, 1082m, 1009s, 947s, 796w, 740m, 688m, 646s, 626m
cis-$\overline{CF_2\cdot(CF_2)_3\cdot CF{:}C}\cdot Mn(CO)_4PPh_3$	2088s, 2015s, 2010s, 1970s	1625vw, 1330w, 1274m, 1241m, 1204m, 1188m, 1176s, 1154m, 1102m, 1081m, 1011s, 948s, 796w, 744m, 694m, 664m, 636m
$\overline{CF_2\cdot(CF_2)_3\cdot CF{:}C}\cdot Re(CO)_5$	2150w, 2042vs, 2018s	1635m, 1330w, 1280m, 1250m, 1211m, 1186s, 1159s, 1116m, 1085m, 1015s, 950s, 800w, 746w, 605s, ‡ 587s ‡
$\overline{CF_2\cdot CF_2\cdot CF{:}C}\cdot Re(CO)_5$	2145w, 2041vs, 2018s	1633w, 1379m, 1367s, 1263s, 1179w, 1122m, 1106m, 1096s, 936s, 795s, 780w
trans-$CF_3\cdot CF{:}CF\cdot Re(CO)_5$	2143w, 2065vw, 2045vs, 2015s	1678w, 1643m, 1322s, 1189s, 1154m, 1124s, 1055m, 969w, 808w, 668m
$CF_2{:}CF\cdot Re(CO)_5$	2145w, 2065vw, 2040vs, 2002s	1705m, 1242s, 1050m, 970s
$C_6H_5CO\cdot Re(CO)_5$	2140w, 2073w, 2033vs, 2030vs, 2012s	1615m, 1505m, 1485m, 1380w, 1295m, 1097s, 987m, 976s, 935w, 700m
$C_6F_5\cdot Re(CO)_5$	2145w, 2046vs, 2006s	1061m, 1055m, 1045m, 956s, 845s, 776m
$\overline{CF_2\cdot(CF_2)_3CF{:}C}\cdot Fe(CO)_2(\pi\text{-}C_5H_5)$	2055s, 2012s	1635w, 1330w, 1277m, 1247m, 1208m, 1191m, 1183s, 1154s, 1105m, 1089m, 1014s, 950s, 840w, 798w, 750w
$\overline{CF_2\cdot CF_2\cdot CF{:}C}\cdot Fe(CO)_2(\pi\text{-}C_5H_5)$	2053 2008s	1632w, 1373m, 1360s, 1260s, 1174w, 1101m, 1090s, 934s, 838w, 794w, 776w, 634w,
$CF_2{:}CF\cdot Fe(CO)_2(\pi\text{-}C_5H_5)$	2050s 2000s	1710m 1235s, 1040m, 960s, 827w

* Cyclohexane solutions. † Carbon disulphide solutions. ‡ KBr disc.

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[17] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.

TABLE 3

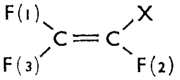
Fluorine-19 chemical shifts

Formula (I)	X	p.p.m.* $\delta_{(1)}$	$\delta_{(2)}$	$\delta_{(3)}$	c./sec. $J_{1,2}$	$J_{1,3}$	$J_{2,3}$
$CF_2{:}CFCl$	Cl	121	145	105	115	78	58
$CF_2{:}CF{\cdot}Re(CO)_5$	$Re(CO)_5$	131·7	154·3	96·1	120·0	98·0	36·6
$CF_2{:}CF{\cdot}Fe(CO)_2(\pi\text{-}C_5H_5)$	$\pi\text{-}C_5H_5{\cdot}Fe(CO)_2$	139·6	147·3	89·5	122·4	107·1	46·8
Formula (II)		$\delta_{(1)}$	$\delta_{(2)}$	$\delta_{(CF_3)}$	$J_{1,2}$	J_{1,CF_3}	J_{2,CF_3}
$CF_3{\cdot}CF{:}CF_2$	F ‡	192	107	72	120	13	21
trans-$CF_3{\cdot}CF{:}CF{\cdot}Mn(CO)_5$ †	$Mn(CO)_5$	165	95	67	127	12	23
trans-$CF_3{\cdot}CF{:}CF{\cdot}Re(CO)_5$	$Re(CO)_5$	160·5	93·8	58	141	13	24

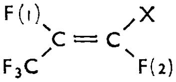
Formula (III)		$\delta_{(1)}$	$\delta_{(2)}$	$\delta_{(3)}$	$\delta_{(4)}$	$\delta_{(5)}$	$\delta_{(6)}$	Integrated intensities in order of increasing field
$CF{:}CF{\cdot}(CF_2)_3{\cdot}CF_2$	F	126·6	126·6	142·6	162·7	162·7	142·6	4 : 4 : 2
$CF_2{\cdot}(CF_3)_3{\cdot}CF{:}C{\cdot}Fe(CO)_2(\pi\text{-}C_5H_5)$	$\pi\text{-}C_5H_5Fe(CO)_2$	—	104·5	124·1	143·5	141·0	99·0	2 : 1 : 2 : 2 : 2
$CF_2{\cdot}(CF_2)_3{\cdot}CF{:}C{\cdot}Mn(CO)_5$	$Mn(CO)_5$	—	97·7	124·9	143·5	141·6	96·4	2 : 1 : 2 : 2 : 2
$CF_2{\cdot}(CF_2)_3{\cdot}CF{:}C{\cdot}Re(CO)_5$	$Re(CO)_5$	—	97·0	124·8	143·5	141·3	97·0	3 : 2 : 2 : 2
Formula (IV)								
$CF{:}CF{\cdot}CF_2{\cdot}CF_2$	F	122·5	122·5	117·6	117·6	—	—	4 : 2
$CF_2{\cdot}CF_2{\cdot}CF{:}C{\cdot}Fe(CO)_2(\pi\text{-}C_5H_5)$	$\pi\text{-}C_5H_5Fe(CO)_2$	—	124·1	123·4	119·1	—	—	2 : 3
$CF_2{\cdot}CF_2{\cdot}CF{:}C{\cdot}Mn(CO)_5$	$Mn(CO)_5$	—	118·6	123·7	117·7	—	—	3 : 2
$CF_2{\cdot}CF_2{\cdot}CF{:}C{\cdot}Re(CO)_5$	$Re(CO)_5$	—	118·1	122·0	118·6	—	—	3 : 2

* Carbon disulphide solutions, relative to CCl_3F as internal standard increasing to high field. † Ref. 9*d*. ‡ δ 93 p.p.m.

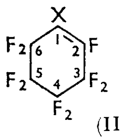
Assignment of the structures of the *cis*- and *trans*-isomers of the compound $CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF{:}C{\cdot}Mn(CO)_4PPh_3$ is based upon their carbonyl stretching frequencies. Both isomers have C_s symmetry. The spectrum of the *trans*-isomer would be expected to show two anti-symmetrical stretching frequencies of high intensity and two symmetrical stretching frequencies of lower intensity. However, the perfluorocyclohexene group is not sufficiently asymmetric to enable the two anti-symmetrical bands to be resolved. The observed spectrum has two weak bands and one strong band. The *cis*-isomer shows the predicted four bands.



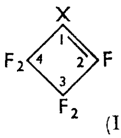
(I)



(II)



(III)



(IV)

The differences in spectra of the two isomers in the carbonyl region were used to follow the formation of these complexes. Thus, as described in the Experimental section, when pentacarbonyl-σ-perfluorocyclohexenylmanganese was treated with triphenylphosphine a mixture of *cis*- and *trans*-isomers of tetracarbonyl-σ-perfluorocyclohexenyl(triphenylphosphine)manganese was obtained, and separated by chromatography. Treatment of $CH_3{\cdot}CF_2{\cdot}CF_2{\cdot}Mn(CO)_5$ with triphenylphosphine, on the other hand, affords *trans*-$CH_3{\cdot}CF_2CF_2{\cdot}Mn(CO)_4PPh_3$ exclusively,[18] perhaps because of differing steric requirements of the fluorocarbon groups concerned.

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[18] J. B. Wilford and F. G. A. Stone, unpublished results.

On heating either the pure *cis*- or the pure *trans*-form of tetracarbonyl-σ-perfluorocyclohexenyl(triphenylphosphine)manganese in cyclohexane for 12 hours, the same equilibrium mixture, 77% *cis*–23% *trans*, was obtained. A similar effect has been observed with the *cis*- or *trans*-isomers of $Mo(CO)_4(PEt_3)_2$ which upon warming in solution to 45° afford a mixture containing 80% of the *trans*-structure.[19] It has been suggested that isomerisations of this kind involve dissociation of the ligand.[20]

The reaction between the anion $[Mn(CO)_4PPh_3]^-$ and perfluorocyclohexene afforded exclusively *trans*-tetracarbonyl-σ-perfluorocyclohexenyl(triphenylphosphine)manganese. This is of interest because treatment of $[Mn(CO)_4PPh_3]^-$ with methyl iodide is reported[21] to give *cis*-$CH_3{\cdot}Mn(CO)_4PPh_3$.

The F^{19} n.m.r. studies made on the various compounds are summarised in Table 3. The perfluorovinyl compounds show the characteristic pattern of three quartets with $J_{cis} < J_{gem} < J_{trans}$.[22] The spectrum of the compound obtained by treating perfluoropropene with pentacarbonylrhenate is virtually identical with that of *trans*-pentacarbonyl-σ-perfluoropropenylmanganese,[9d] confirming that the fluorocarbon ligand has the *trans*-configuration. The spectra obtained for the σ-perfluorocyclohexenyl- and σ-perfluorocyclobutenyl-metal complexes demonstrate unambiguously that they have structures in which metal atoms are attached to one of the double-bonded carbon atoms of the rings. Under high resolution the spectra of these compounds are complex and an analysis of the fine structure was not attempted. However, under lower resolution the spectra are particularly revealing. The spectrum of dicarbonyl-π-cyclopentadienyl-σ-perfluorocyclohexenyliron, for example, shows five well-separated bands with integrated intensities 2 : 1 : 2 : 2 : 2 which may be assigned to the fluorine atoms bonded to C-6, C-2, C-3, C-5, and C-4, respectively.[9d,23] A different intensity pattern would be predicted for a structure in which the metal atom had replaced one of the fluorine atoms of a ring CF_2 group. Moreover, in this event it would be anticipated that a band due to a single fluorine atom bonded to a tertiary carbon atom would be observed at high field. In pentacarbonyl-σ-perfluoroisopropylmanganese such an absorption occurs at 160 p.p.m.[9b,24] No absorption occurs in the spectrum of the perfluorocyclohexenylmetal complexes above 143 p.p.m. As might be expected, in the perfluorocyclohexenyl and in the perfluorocyclobutenyl compounds the chemical shift of the olefinic fluorine atom at C-2 is more dependent upon the metal atom next to it than are the shifts of the flurorine atoms in the remainder of the molecule. In the spectrum of pentacarbonyl-σ-perfluorocyclohexenylrhenium the shift of the fluorine at C-2 is coincident with that of the fluorine atoms at C-6, while in the manganese analogue the respective shifts have become very close. In the perfluorocyclobutenylmetal derivatives the chemical shifts of all the fluorine atoms fall within a smaller range. The shift of the fluorine atom at C-2 coincides with the absorption due to the fluorine atoms at C-4 in the case of the manganese and rhenium compounds and with that of the fluorine atoms bonded to C-3 in the iron compound.

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