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METAL CARBONYL CHEMISTRY
XVII*. σ-(PERFLUORO-1-CYCLOPENTENYL)METAL COMPLEXES

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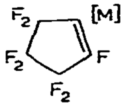
SUMMARY

Perfluorocyclopentene reacts with sodium pentacarbonylmanganate(−1) to give the σ-(perfluoro-1-cyclopentenyl)manganese complex $C_5F_7Mn(CO)_5$, and the reactions of this new complex with triphenylphosphine and with sulphuric acid are reported. Similar complexes are obtained when perfluorocyclopentene is treated with the anions $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ and $[Mn(CO)_4PPh_3]^-$.

INTRODUCTION

Perfluoroolefins are characteristically susceptible to nucleophilic attack[2], and their reaction with alkali-metal derivatives of metal carbonyls provides a convenient synthetic route to σ-bonded fluorocarbon complexes of transition metals[3-5]. Since the only cyclic perfluorinated monoenes used in such reactions so far are perfluorocyclobutene and perfluorocyclohexene[4], it was of interest to examine the reactions of carbonylmetal anions with perfluorocyclopentene. This work yielded several new σ-(perfluoro-1-cycloalkenyl)metal complexes [(Ia)–(Ic)], produced by reaction of the anions $[Mn(CO)_5]^-$, $[\pi\text{-}C_5H_5Fe(CO)_2]^-$, and $[Mn(CO)_4PPh_3]^-$ with the cyclopentene.



(I)

(Ia) ; M = $Mn(CO)_5$
(Ib) ; M = $\pi\text{-}C_5H_5Fe(CO)_2$
(Ic) ; M = $Mn(CO)_4PPh_3$ (*trans* isomer)
(Id) ; M = $Mn(CO)_4PPh_3$ (*cis* isomer)

EXPERIMENTAL

Products were identified by elemental analysis, IR [Perkin–Elmer spectrophotometer model 21 with rock salt optics (with calcium fluoride optics and a scale expander for measurement of carbonyl stretching frequencies)], NMR (Perkin–

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* For part XVI see ref. 1.

Elmer permanent magnet instrument model R10 operating at 56.46 MHz and 35°), and mass spectrometry (AEI spectrometer model MS/2H).

Perfluorocyclopentene was obtained by fluorination of perchlorocyclopentene with anhydrous potassium fluoride in *N*-methyl-2-pyrrolidone[6]. Sodium salts of the metal carbonyl anions were prepared by treating the appropriate metal carbonyl in tetrahydrofuran solution with sodium amalgam[7]. Reactions between perfluorocyclopentene and metal carbonyl anions were carried out in tetrahydrofuran; the reaction mixture was stirred at 0° overnight and finally for a short period (ca. 1 h) at 50°. Chromatography was performed using alumina-packed columns.

Reactions of perfluorocyclopentene

(*a*). *With* $[Mn(CO)_5]^-$

The product obtained by treating perfluorocyclopentene (4.0 g, 18.9 mmole) with the sodium salt from $Mn_2(CO)_{10}$ (1.7 g, 4.4 mmole) was chromatographed on alumina. Elution with light petroleum (b.p. 40–60°) gave $Mn_2(CO)_{10}$ (0.3 g, 0.8 mmole) and pentacarbonyl-σ-(perfluoro-1-cyclopentenyl)manganese, (Ia) (1.4 g, 3.6 mmole, 40%), m.p. 73–74°. (Found: C, 31.3; H, 0.0. $C_{10}F_7MnO_5$ calcd.: C, 30.9; H, 0.0%.)

The principal peaks in the mass spectrum of this complex had *m/e* values of 388 [$C_5F_7Mn(CO)_5^+$, 6%], 304 [$C_5F_7Mn(CO)_2^+$, 6%], 276 ($C_5F_7MnCO^+$, 5%), 248 ($C_5F_7Mn^+$, 35%), 155 ($C_2F_4Mn^+$, 100%), 117 ($C_2F_2Mn^+$, 9%), 105 (CF_2Mn^+, 15%), 74 (FMn^+, 37%), 69 (CF_3^+, 20%), and 55 (Mn^+, 20%). A metastable peak was observed at *m/e* 250 corresponding to the transition $C_5F_7Mn(CO)_2^+ \rightarrow C_5F_7MnCO^+ + CO$.

(*b*). *With* $[\pi\text{-}C_5H_5Fe(CO)_2]^-$

The product from treatment of perfluorocyclopentene (4.7 g, 22.2 mmole) with the sodium salt from $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (2.5 g, 7.1 mmole) was chromatographed on alumina to yield dicarbonyl-σ-(perfluoro-1-cyclopentenyl)(π-cyclopentadienyl)iron (Ib) (0.75 g, 2.0 mmole, 14%), m.p. 87°. (Found: C, 38.9; H, 1.3. $C_{12}H_5F_7FeO_2$ calcd.: C, 38.9; H, 1.4%.) The principal peaks (rel. intensity ≥10%) in the mass spectrum of this complex had *m/e* values of 370 [$CpFe(CO)_2C_5F_7^+$, 18%], 342 [$CpFe(CO)C_5F_7^+$, 20%], 314 ($CpFeC_5F_7^+$, 26%), 220 ($CpFeC_5F_2H^+$, 100%), 202 ($CpFeC_2F_3^+$, 11%), 155 ($C_5F_5^+$, 72%), 151 ($C_3HF_6^+$, 20%), 140 ($CpFeF^+$, 97%), 75 ($C_3HF_2^+$, 24%), 65 ($C_5H_5^+$, 21%), 56 (Fe^+, 17%), and 39 ($C_3H_3^+$, 25%); metastable peaks were observed at *m/e* 288 and 270 corresponding to the transitions $CpFe(CO)C_5F_7^+ \rightarrow CpFeC_5F_7^+ + CO$ and $CpFe(CO)C_5F_6^+ \rightarrow CpFeC_5F_6^+ + CO$ [the peak at *m/e* 323 corresponding to $CpFe(CO)C_5F_6^+$ had a relative intensity of 7%, and that at *m/e* 295 ($CpFeC_5F_6^+$) 4%].

(*c*). *With* $[Mn(CO)_4PPh_3]^-$

Similarly, treatment of perfluorocyclopentene (2.4 g, 11.3 mmole) with the sodium salt of $Mn(CO)_4PPh_3$ (2.5 g, 5.5 mmole) gave *trans*-tetracarbonyl(triphenylphosphine)-σ-(perfluoro-1-cyclopentenyl)manganese (Ic) (1.5 g, 2.4 mmole, 45%), m.p. 135–136°. (Found: C, 53.0; H, 2.0; P, 4.6. $C_{27}H_{15}F_7MnO_4P$ calcd. C, 52.1; H, 2.4; P, 5.0%.)

Reactions of pentacarbonyl-σ-(perfluoro-1-cyclopentenyl)manganese (Ia)

(*a*). *With* H_2SO_4

The complex (0.6 g, 1.5 mmole) was treated with 80% sulphuric acid (20 ml) at 110° for 14 h in a Pyrex ampoule. The volatile product was identified[8] by GLC (2 m silicone MS550/Celite column; an authentic sample was available), IR [bands at 3120, (C–H str.) and 1695 cm^{-1} (CF=CH str.)] and molecular weight determination (Regnault's method. Found: mol.wt., 192. C_5HF_7 calcd.: mol.wt., 194.) as 1*H*-heptafluorocyclopentene (0.13 g, 0.67 mmole, 47%).

(*b*). *With triphenylphosphine*

Treatment of the complex (1.0 g, 2.6 mmole) with a solution of triphenylphosphine (3 g, 11.5 mmole) in light petroleum (20 ml) at 110° during 24 h gave a solid product that was chromatographed on alumina; elution with light petroleum gave pale yellow *cis*-tetracarbonyl(triphenylphosphine)-σ-(perfluoro-1-cyclopentenyl)-manganese (Id) (1.0 g, 1.6 mmole, 65%), m.p. 84°, (Found: C, 52.3; H, 2.5; P, 5.2. $C_{27}H_{15}F_7MnO_4P$ calcd.: C, 52.1; H, 2.4; P, 5.0%.), and *trans*-tetracarbonyl-σ-(perfluoro-1-cyclopentenyl)manganese (Ic) (0.12 g, 0.2 mmole, 8%), m.p. and mixed m.p. 135–136°.

(*c*). *With* $[Mn(CO)_5]^-$

(*i*). Complex (Ia) (1.7 g, 4.4 mmole) was treated with the sodium salt of $Mn_2(CO)_{10}$ (1.4 g, 3.6 mmole) in tetrahydrofuran. Chromatography of the solid product gave $Mn_2(CO)_{10}$ (0.25 g, 0.6 mmole) and unchanged starting material (Ia) (0.3 g, 0.8 mmole, 18% recovery).

(*ii*). In a similar experiment, the solid product was treated with 80% sulphuric acid at 110° for 15 h. The volatile product was shown by GLC and IR analysis to be 1*H*-heptafluorocyclopentene. No hexafluorocyclopentene, which might have arisen by hydrolysis of a disubstituted product, was detected.

RESULTS AND DISCUSSION

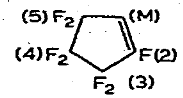
Reaction of perfluorocyclopentene with the anions $[Mn(CO)_5]^-$, $[\pi\text{-}C_5H_5Fe(CO)_2]^-$, and $[Mn(CO)_4PPh_3]^-$ gave the complexes (Ia)–(Ic). In each case the sole product isolated was a compound in which a vinylic fluorine atom had been replaced. Careful chromatography of the reaction mixture gave no other fluorocarbon derivative.

In an attempt to replace more than one fluorine atom in perfluorocyclopentene by a metal carbonyl group, complex (Ia) was treated with $[Mn(CO)_5]^-$ in tetrahydrofuran, but careful chromatographic separation of the product gave only unchanged (Ia) and some $Mn_2(CO)_{10}$. The product from one experiment was treated with sulphuric acid in an attempt to obtain evidence for the presence of a disubstituted product, but the only volatile product was 1-hydroheptafluorocyclopentene, arising from unchanged (Ia) (see below); formation of a hexafluorocyclopentene would have indicated the presence of a disubstituted complex $C_5F_6[Mn(CO)_5]_2$. A similar failure to observe disubstituted products in reactions between aromatic fluorocarbons and metal carbonyl anions has been ascribed to the deactivating effect of the metal on the aromatic nucleus[3].

Treatment of pentacarbonyl-σ-(perfluoro-1-cyclopentenyl)manganese (Ia) with triphenylphosphine gave a mixture of complexes (Ic) and (Id), the *cis*- and *trans*-isomers of $C_5F_7Mn(CO)_4PPh_3$. Interestingly, treatment of perfluorocyclopentene with $[Mn(CO)_4PPh_3]^-$ gave exclusively the *trans*-isomer (Ic); a similar observation has been made for (perfluoro-1-cyclohexenyl)manganese complexes[3]. Treatment of

TABLE 1

^{19}F NMR SPECTRA



Compound		Chemical shifts (ppm)[a]			
		δ(2)	δ(3)	δ(4)	δ(5)
$C_5F_7Mn(CO)_5$	(Ia)	43.4	41.6	52.6	21.4
π-$C_5H_5Fe(CO)_2C_5F_7$	(Ib)	47.0	40.2	51.8	22.0
trans-$C_5F_7Mn(CO)_4PPh_3$	(Ic)	41.6	41.6	53.4	22.0
cis-$C_5F_7Mn(CO)_4PPh_3$	(Id)	41.8	41.8	53.2	20.0

[a] Acetone solution. Chemical shifts relative to CF_3CO_2H as external reference. All the bands are multiplets but no attempt was made to derive coupling constants because of their complexity.

TABLE 2

IR SPECTRA

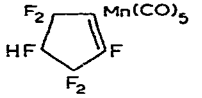
Compound		Metal carbonyl bands (cm^{-1})[a]	Other bands (cm^{-1})[b]
$C_5F_7Mn(CO)_5$	(Ia)	2135 w, 2079 vw, 2070 vw, 2047 s, 2020 s, 2010 w, 1976 vw	2439 vw, 1754 vw, 1701 vw, 1631 m[c], 1613 w, 1321 m, 1220 s, 1190 s, 1136 s, 1096 s, 957 s, 806 m, 763 s, 685 m, 657 s
π-$C_5H_5Fe(CO)_2C_5F_7$	(Ib)	2050 s, 2006 s, 1998 vw, 1972 vw	1629 m[c], 1608 vw, 1316 s, 1220 s, 1183 s, 1151 w, 1126 s, 1094 s, 971 m, 954 s, 833 m, 804 m, 783 m, 772 s, 680 w
trans-$C_5F_7Mn(CO)_4PPh_3$	(Ic)	2088 w, 2031 w, 1993 s, 1963 w	3080 w, 1620 vw[c], 1480 m, 1440 m, 1340 s, 1320 m, 1260 w, 1220 w, 1180 m 1120 m, 1090 m, 1020 m, 1000 vw, 952 s, 800 w, 763 m, 746 m, 741 m, 699 m, 690 s, 622 s
cis-$C_5F_7Mn(CO)_4PPh_3$	(Id)	2089 m, 2019 s, 2008 s, 1969 s, 1929 vw	3070 w, 1630 w[c], 1480 m, 1440 m, 1340 m, 1320 m, 1260 w, 1210 m, 1180 m, 1110 m, 1090 m, 1080 w, 1030 m, 1000 w, 952 s, 800 w, 752 m, 746 m, 741 m, 704 m, 694 s, 685 m, 658 s

[a] Pentane solution, CaF_2 optics. [b] Pentane solution [(Ia) and (Ib)] or Nujol mull [(Ic) and (Id)]. [c] ν(MnC=CF)

(Ia) with sulphuric acid gave 1-hydroheptafluorocyclopentene, confirming that the complex has a structure in which the manganese atom is attached to one of the olefinic carbons.

Further evidence for the proposed structure of the complexes comes from their ^{19}F NMR spectra. Thus, complexes (Ia) and (Ib) show four regions of absorption (40.2–41.8, 51.8–53.4, 20.0–22.0, and 41.6–47.0 ppm upfield from external CF_3CO_2H; see Table 1), with integrated intensities 2/2/2/1, which may be assigned to the three difluoromethylene groups and the vinylic fluorine atom, respectively, of the perfluorocyclopentenyl group. In the spectrum of each of the triphenylphosphine derivatives of (Ia), the absorption of the vinylic fluorine is coincident with that ascribed to the fluorines of one of the difluoromethylene groups.

IR spectral bands for the complexes are summarised in Table 2. As expected for octahedral complexes of the type LM(CO)$_5$ having C_{4v} symmetry[9], the spectrum of (Ia) shows three major bands; the two A_1 modes (2020 and 2135 cm^{-1}) and the E mode (2047 cm^{-1}). The weak bands in the spectrum can be assigned to the B$_1$ mode (2079 cm^{-1}) and those due to ^{13}CO-substituted molecules in natural abundance (2010 and 1976 cm^{-1})[10]. Further support for the structure proposed may be deduced from the observation that the IR spectrum of the complex (Ia) in the carbonyl stretching region is almost identical in band position with the spectrum of the previously characterised[11] adduct of perfluorocyclopentadiene and manganese carbonyl hydride, namely pentacarbonyl-σ-(4*H*-hexafluoro-1-cyclopentenyl)manganese (II). Neither (Ia) nor (II) shows any splitting of its E carbonyl stretching mode implying axial symmetry (presumably by free rotation in solution) of the fluorocarbon residue, with respect to the metal atom[12].



(II)

Isomers (Ic) and (Id) were characterised by their IR absorptions in the carbonyl stretching region. Octahedral complexes of the type *trans*-L$_2$M(CO)$_4$ should show only one IR active absorption; (Ic) will have lower symmetry than this and consequently, in addition to the one major band (1993 cm^{-1}), three weak absorptions are observed. The *cis*-isomer (Id) shows the four strong bands expected[9].

All the complexes showed an absorption near 1630 cm^{-1} which is assigned to the double bond stretching frequency, [*e.g.*, ν(MnC=CF) for (Ia) 1631 cm^{-1}, which compares well with that (1629 cm^{-1}) for compound (II)].

The mass spectra of (Ia) and (IIb) showed peaks corresponding to the molecular ions at *m/e* 388 and 370, respectively. Both showed peaks corresponding to the loss of carbonyl groups and fluorine atoms with retention of the metal–carbon bond.

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