Journal of Organometallic Chemistry, 67 (1974) 87—92

THE PREPARATION AND PYROLYSIS OF SOME (POLYFLUORO-1,3-CYCLOHEPTADIENE)IRON TRICARBONYL COMPLEXES

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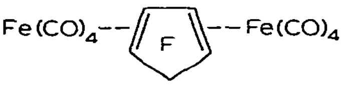
(Received July 11th, 1973)

Summary

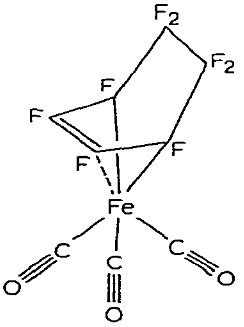
Some new (polyfluoro-1,3-cycloheptadiene)iron tricarbonyl complexes have been prepared by the reaction of triiron dodecacarbonyl with decafluoro-1,3-cycloheptadiene, 1*H*-nonafluoro-1,3-cycloheptadiene and 1*H*,4*H*-octafluoro-1,3-cycloheptadiene. Spectral data for the complexes are described. Pyrolysis of the complexes at 440° was found to give polyfluorobenzenes and a possible mechanism for this process is proposed.

Introduction

The formation of diene—iron carbonyl complexes is well-known [1] and (1,3-cycloheptadiene)iron tricarbonyl has been prepared [2,3]. Two examples involving the reaction of a cyclic perfluorodiene with an iron carbonyl have been reported. These are the reaction [4] of perfluorocyclopentadiene with iron pentacarbonyl to give complex (I) and, in contrast, the reaction [5] of perfluoro-1,3- or 1,4-cyclohexadienes with triiron dodecacarbonyl to give complex (II), the structure of which has been elucidated by an X-ray crystallographic examination [6,7].



(I)

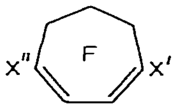


(II)

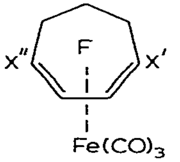
This study is concerned with the preparation of some (polyfluoro-1,3-cycloheptadiene)iron tricarbonyl complexes. The complexes were then pyrolysed in the hope that polyfluorocycloheptatrienes would be obtained, since the pyrolysis of (II) was found [8] to give hexafluorobenzene.

Results and discussion

The polyfluoro-1,3-cycloheptadienes used in this work, namely compounds (III), (IV) and (V) were obtained from the products of the fluorination of cycloheptane or 1,3,5-cycloheptatriene with cobalt trifluoride by routes which have been mentioned previously [9].



(III), X′, X″ = F
(IV), X′ = H, X″ = F
(V), X′, X″ = H



(VI), X′, X″ = F
(VII), X′ = H, X″ = F
(VIII), X′, X″ = H

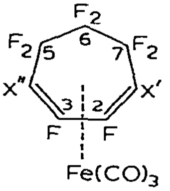
The (polyfluoro-1,3-cycloheptadiene)iron tricarbonyl complexes (VI), (VII) and (VIII) were prepared by heating the appropriate diene (III), (IV) or (V) with triiron dodecacarbonyl at 130° in a sealed tube, a similar method to that used for the preparation [5] of (II). Some iron pentacarbonyl and unreacted dienes were recovered from the reaction mixtures. An attempted reaction between decafluoro-1,4-cycloheptadiene and $Fe_3(CO)_{12}$ gave a trace amount of a solid which elemental analysis and mass spectral evidence indicated could be complex (VI). It is likely that the structures of the 1,3-heptadiene complexes are analogous to that of the 1,3-hexadiene complex (II), although a detailed X-ray examination of (VI) is being undertaken.

The infra-red spectra of (VI), (VII) and (VIII) showed the expected C—O stretching bands between 2010 and 2130 cm^{-1}. Absorptions at 1520 - 1530 cm^{-1} were assigned to the C=C stretch associated with the conjugated double bond system. This can be compared with C=C stretches in the uncomplexed dienes (III) [10], (IV) [11] and (V) [11] which occur at 1700 - 1730, 1690 - 1710 and 1670 - 1700 cm^{-1} respectively. Numerous absorptions in the range 650 - 1450 cm^{-1} were also observed.

Intelligible mass spectra of the complexes could only be obtained when a low source temperature (75°) was used. The observed cracking patterns reflected both stepwise loss of CO from the parent complexes and, to a greater extent, the formation of fragments $Fe(CO)_x$, where $x = 1 - 3$. Peaks corresponding to $[C_7F_6X'X'']^+$ and $[C_7F_5X'X'']^+$, i.e. the cyclic triene and tropylium molecular ions respectively, were particularly prominent. However, the largest peak in all spectra, apart from $[CO]^+$, was due to the polyfluorobenzenes $[C_6F_4X'X'']^+$. This compares with the mass spectrum [5] of complex (II) in which a prominent peak was due to $(C_6F_6)^+$, and Jenkins [12] has noted that the mass spectrum of perfluoro-1,3,5-cycloheptatriene shows a large peak due to the same molecular ion.

TABLE 1

NMR DATA[a] FOR (POLYFLUORO-1,3-CYCLOHEPTADIENE) IRON TRICARBONYLS



Complex	X′	X″	^{19}F Chemical shifts (φ* ppm)							^{1}H Shifts (δ ppm)	
			X′	F(2)	F(3)	X″	CF_2(5)	CF_2(6)	CF_2(7)	X′	X″
(VI)	F	F	179.6	171.7	171.7	179.6	104.9 116.4 (J_{AB} 263Hz)	114.4 144.4 (J_{AB} 281Hz)	104.9 116.4 (J_{AB} 263Hz)		
(VII)	H	F		148.6	168.9	177.2	104.7 115.9 (J_{AB} 259Hz)	114.5 141.5 (J_{AB} 276Hz)	93.5	3.51	
(VIII)	H	H		148.1	148.1		93.0	113.9 140.1 (J_{AB} 276Hz)	93.0	3.95	3.95

[a] Measured in acetone-d_6 using CCl_3F and $Si(Me)_4$ as internal references, ^{1}H at 60 MHz and ^{19}F at 56.4 MHz.

The ^{1}H and ^{19}F NMR data for the complexes (VI), (VII) and (VIII) are summarised in Table 1 and the assignments made are consistent with the spectra reported for (II) [5] and for $C_7H_{10}Fe(CO)_3$ [2]. It can be seen that when X′ or X″=F, the vicinal CF_2 group gives rise to an AB quartet [$J_{AB} \approx 260$ Hz] reflecting the differing magnetic environments of each fluorine atom of the CF_2. However, when X′ or X″=H the vicinal CF_2 group is observed as a singlet, indicating that each fluorine atom is now in a similar magnetic environment. In contrast, both CF_2 groups of (II) [5] and (1*H*-heptafluoro-1,3-cyclohexadiene)iron tricarbonyl [8] were found to appear as AB patterns. The remaining CF_2 group, namely CF_2(6), shows an AB quartet ($J_{AB} \approx 280$ Hz) in (VI), (VII) and (VIII).

The three complexes were pyrolysed at 440° by passage, in a stream of nitrogen, through a heated glass tube. This high temperature was used because previous work [8] has shown that (II) is not completely pyrolysed in such a flow system below 350° and, furthermore, (VI) was recovered unchanged from a sealed tube maintained at 200° for 8 h. Apart from a small amount of high volatiles, the major products from each pyrolysis were polyfluoroaromatics. Thus (VI) afforded hexafluorobenzene, (VII) gave pentafluorobenzene and (VIII) gave a mixture (≈2/3) of 1*H*, 3*H*- and 1*H*, 4*H*-tetrafluorobenzenes. In the last case a hydrogen shift clearly occurs but this is discussed later. The trace of highly volatile products (b.p. —186° to ambient temp.) from the pyrolysis of (VI) was shown to be a mixture of C_2F_4 and SiF_4.

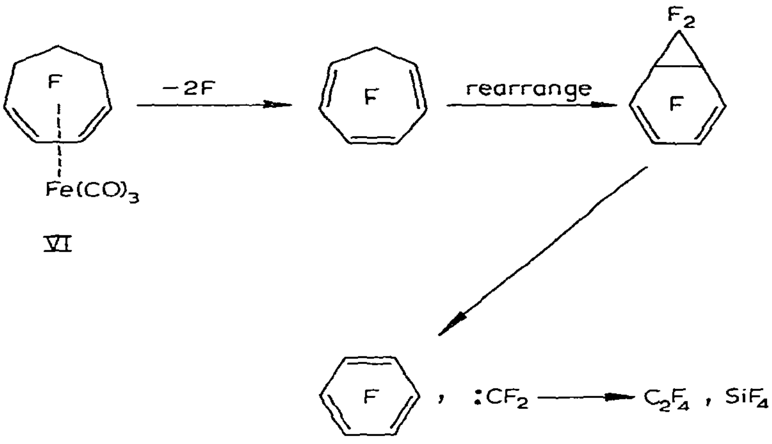


Fig. 1. A possible scheme for the pyrolysis of $C_7F_{10}Fe(CO)_3$.

A possible pathway for the pyrolyses is shown in Fig. 1, using complex (VI). Any scheme involving the liberation of the free diene is unlikely since perfluoro-1,3-cycloheptadiene was found [10] to give the bicyclo-[3.2.0]hept-6-ene (52%) on passage over iron gauze at 450° and was largely unchanged on passage over Fe_2O_3 at 300°. Neither of these compounds were detected in the present work. Thus the first step is probably the breakdown of the complex such that defluorination occurs, giving perfluoro-1,3,5-cycloheptatriene. [It is at this stage during the pyrolysis of (VIII) that the hydrogen shift could take place since thermally-induced skeletal rearrangements of cycloheptatrienes have been reported [13]]. Thermal rearrangement to the norcaradiene followed by thermal elimination of the relatively stable difluorocarbene could then give hexafluorobenzene.

In support of this sequence the elimination of "stable" carbenes from substituted cycloheptatrienes *via* the norcaradiene is known [14], although it should be noted that rearrangement to the toluene derivative occurs with cycloheptatriene [15] at 478° and perchlorocycloheptatriene [16] at 190°. Furthermore, the formation of difluorocarbene could give rise to C_2F_4 by dimerisation and SiF_4 by reaction with the SiO_2 in glass, as was suggested [17] in the pyrolysis of (octafluorotetramethylene)iron tetracarbonyl. Although inconclusive results were obtained from the pyrolyses [12] of perfluoro-1,3,5-cycloheptatriene and perfluorotropone, the pyrolyses [12] of 5*H*-nonafluoro-1,3-cycloheptadiene and 6*H*-nonafluoro-1,4-cycloheptadiene over sodium fluoride did afford hexafluorobenzene almost exclusively. It was suggested that the triene was an intermediate.

Experimental

$Fe_3(CO)_{12}$ was prepared by a literature method [18]. GLC analysis was performed on a Perkin—Elmer Fraktometer Model 154B fitted with 2 glass columns (1.0 m × 4.0 mm) containing diisodecyl phthalate on chromosorb P (1/2) and maintained at 72°.

Preparation of complexes

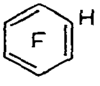
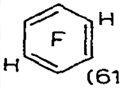
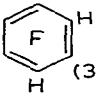
(i). (Decafluoro-1,3-cycloheptadiene)iron tricarbonyl (nc). $Fe_3(CO)_{12}$ (2.0 g) and decafluoro-1,3-cycloheptadiene [9] (3.5 g) were sealed under nitrogen in a hard glass tube (15 cm × 1.7 cm) and heated at 130° for 15 h. The tube was cooled, opened, and the volatile products (3.0 g) carefully distilled out *in vacuo*. IR and GLC examinations showed them to consist of $Fe(CO)_5$ and unchanged diene. The solid residue from the distillation was extracted with light petroleum (b.p. 40 - 60°) (150 ml) and the extract filtered before being cooled to −78°. The pale yellow solid (1.3 g) which crystallised out was filtered off and a portion (0.35 g) sublimed (50°/17 mmHg) to give yellow crystals of (decafluoro-1,3-cycloheptadiene)iron tricarbonyl (0.31 g) m.p. 90 - 91°. (Found: C, 29.3; H, 0.0. $C_{10}F_{10}FeO_3$ calcd.: C, 29.0; H, 0.0%.) Top mass peak 414 corresponding to M^+.

(ii). (1H-nonafluoro-1,3-cycloheptadiene)iron tricarbonyl (nc). 1*H*-nonafluoro-1,3-cycloheptadiene [9] (3.5 g) was reacted with $Fe_3(CO)_{12}$ (2.0 g) under the conditions described above. After work-up, a portion (0.35 g) of the crude complex (1.3 g) was sublimed (55°/17 mmHg) to give yellow crystals of (1*H*-nonafluoro-1,3-cycloheptadiene)iron tricarbonyl (0.32 g) m.p. 81 - 82°. (Found: C, 30.2; H, 0.4. $C_{10}HF_9FeO_3$ calcd.: C, 30.3; H, 0.3%.) Top mass peak 396 corresponding to M^+.

(iii). (1H, 4H-octafluoro-1,3-cycloheptadiene)iron tricarbonyl (nc). 1*H*, 4*H*-octafluoro-1,3-cycloheptadiene [9] (3.5 g) was reacted with $Fe_3(CO)_{12}$ under the usual conditions. Work-up in the normal way gave the crude complex (1.2 g), a portion (0.30 g) of which was sublimed (45°/17 mmHg) to give yellow crystals of (1*H*, 4*H*-octafluoro-1,3-cycloheptadiene)iron tricarbonyl (0.29 g) m.p. 86 - 87.5°. (Found: C, 31.7; H, 0.8. $C_{10}H_2F_8FeO_3$ calcd.: C, 31.8; H, 0.5%.) Top mass peak 378 corresponding to M^+.

TABLE 2

PYROLYSES OF THE COMPLEXES

Complex	Wt. in (g)	Wt. out[a] (g)	Product[a]
$C_7F_{10}Fe(CO)_3$	0.25	0.10[b]	
$C_7HF_9Fe(CO)_3$	0.30	0.14	
$C_7H_2F_8Fe(CO)_3$	0.25	0.09	 (61%)[c]  (39%)[c]

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[a] Refers to product with b.p. > ambient temp. [b] Vapour IR of product with b.p. < ambient temp. showed C_2F_4 and SiF_4. [c] Percentages estimated from ^{19}F NMR spectrum of mixture.

Pyrolysis of complexes

Pyrolyses were carried out using a flow system which consisted of a horizontal, electrically heated glass tube (40 cm × 2.5 cm) maintained at 440°. The complex under investigation was slowly sublimed into a stream of nitrogen (1.6 l/h) and passed through the tube, the products being condensed into a glass trap cooled in liquid air. In each case only trace amounts of products with b.p. < ambient temperature were observed. The major products (b.p. > ambient temperature) were identified by a comparison of their IR and NMR spectra and GLC retention times with those of authentic samples. Details of the pyrolyses are shown in Table 2.

Acknowledgements

The authors thank Dr. R. Stephens and Mr. M.E. Allen for the provision of a sample of perfluoro-1,3-cycloheptadiene.

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