Syntheses and Reactions of Bromotetrafluorophenyl(cyclopentadienyl)dicarbonyliron Derivatives

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The isomeric bromotetrafluorophenyl(cyclopentadienyl)dicarbonyliron compounds have been prepared by both the nucleophilic displacement of bromide ion from dibromotetrafluorobenzene by the (cyclopentadienyl)dicarbonyliron anion, in the form of its lithium salt, and by reaction between the corresponding lithiobromotetrafluorobenzene and (cyclopentadienyl)dicarbonyliron iodide. The resultant bromotetrafluorophenyliron derivatives undergo lithium–bromine exchange in preference to carbon–iron bond cleavage, to give the corresponding lithiotetrafluorophenyliron derivative. Reaction of the *m*- and *p*-isomers of the above with (cyclopentadienyl)dicarbonyliron iodide gave the 1,3- and 1,4-bis-[(cyclopentadienyl)dicarbonyliron]tetrafluorobenzenes.

ALTHOUGH numerous polyfluoroaryl(cyclopentadienyl)dicarbonyliron derivatives have been reported[1] since the initial formation of the pentafluorophenyl-compound, $C_6F_5Fe(CO)_2(C_5H_5)$,[2,3] halogenotetrafluorophenyliron derivatives have been limited to the observation[4] of a 2-iodotetrafluorophenyliron compound in a complex mixture.

The low yield[3] of the pentafluorophenyliron compound, obtained by the reaction of pentafluorophenylmagnesium bromide with (cyclopentadienyl)dicarbonyliron iodide, compared with the larger yields obtained by the use of the sodium salt of the (cyclopentadienyl)dicarbonyliron anion, $(C_5H_5)Fe(CO)_2^-Na^+$, has apparently led to the sole use of the latter reagent as a precursor for the organo-iron derivatives.

RESULTS AND DISCUSSION

The (cyclopentadienyl)dicarbonyliron anion was prepared as its lithium salt by reacting two equivalents of n-butyl-lithium with (cyclopentadienyl)dicarbonyliron–mercuric chloride in ether at room temperature. Addition of 1,3-dibromotetrafluorobenzene gave a 21% yield of 3-bromotetrafluorophenyl(cyclopentadienyl) dicarbonyliron. Similar reactions with 1,2- and 1,4-dibromo- and 1,3-dichloro-tetrafluorobenzenes, however, gave little or no product, but did produce high yields of (cyclopentadienyl)dicarbonyliron dimer. By cooling the anion to −78° using dry ice–acetone, before addition of the dihalogenotetrafluorobenzene, substantial increases in the yields of the resultant halogenotetrafluorophenyl(cyclopentadienyl)dicarbonyliron compounds were obtained, and are shown in the Table. The formation of (cyclopentadienyl)dicarbonyliron dimer as by-product has been previously observed in reactions involving the sodium salt of the (cyclopentadienyl)dicarbonyliron anion,[2,4] but, in these reactions, the lowering of temperature somehow inhibits its formation, allowing the nucleophilic substitution reaction to take place.

2,3,4,5-Tetrafluorophenyl(cyclopentadienyl)dicarbonyliron was obtained as a by-product in the above preparation of the bromotetrafluorophenyl derivative, and was itself prepared in 68% yield, by the nucleophilic replacement of bromide ion, from 1-bromo-2,3,4,5-tetrafluorobenzene,[5] by the (cyclopentadienyl)dicarbonyliron anion at −78°.

Reaction between the (cyclopentadienyl)dicarbonyliron anion and pentafluorobenzene gave a 63% yield of 2,3,5,6-tetrafluorophenyl(cyclopentadienyl)dicarbonyliron, identified by comparison of its m.p., i.r. and ^1H n.m.r. spectra with a sample previously prepared in 39% yield by use of the sodium salt of the above anion.[2]

The compounds described above were also prepared by utilizing the known halogenoaryl-lithium reagents,[1] reacting them with (cyclopentadienyl)dicarbonyliron iodide at −78°. The yield of the resultant 2-, 3-, and 4-bromo- and 3-chlorotetrafluorophenyliron derivatives range from 30—70% and are given in the Table. This method of synthesis was also found to be highly successful for the

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[1] S. C. Cohen and A. G. Massey, *Adv. Fluorine Chem.*, 1970, **6**, 83.

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

[3] M. D. Rausch, *Inorg. Chem.*, 1964, **3**, 300.

[4] M. I. Bruce and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1966, 1837.

[5] D. E. Fenton, A. J. Park, D. Shaw, and A. G. Massey, *J. Organometallic Chem.*, 1964, **2**, 437.

preparation of 2,4,5,6-tetrafluorophenyl(cyclopentadienyl)dicarbonyliron from 1-lithio-2,4,5,6-tetrafluorobenzene, but failed in the reaction between 1-lithio-3,4,5,6-tetrafluorobenzene and (cyclopentadienyl)dicarbonyliron iodide, although 3,4,5,6-tetrafluorophenyl-metal derivatives have been previously prepared[1] by this method.

In the preparation of 4-bromotetrafluorophenyl(cyclopentadienyl)dicarbonyliron, trace amounts of the corresponding 2,3,5,6-tetrafluorophenyl-derivative were obtained, possibly due to some dilithiation of the 1,4-dibromotetrafluorobenzene starting material. Intentional formation of the dilithio-derivative by use of two equivalents of n-butyl-lithium, followed by reaction with two equivalents of (cyclopentadienyl)dicarbonyliron iodide, gave 1,4-bis[(cyclopentadienyl)dicarbonyliron]tetrafluorobenzene, which precipitated out of the ether solvent. This same compound was also prepared by the reaction of one equivalent of n-butyl-lithium with 4-bromotetrafluorophenyl(cyclopentadienyl)dicarbonyliron to form the intermediate 4-lithiotetrafluorophenyl-derivative, followed by reaction with an equivalent of (cyclopentadienyl)dicarbonyliron iodide. The corresponding 1,3-bis[(cyclopentadienyl)dicarbonyliron]tetrafluorobenzene was prepared from 3-bromotetrafluorophenyl(cyclopentadienyl)dicarbonyliron in an analogous manner, but attempts to prepare the corresponding 1,2-bis derivative proved to be unsuccessful, probably due to steric crowding of the required product.

Analytical and other data for X-$C_6F_4Fe(CO)_2(C_5H_5)$, 1,3-, and 1,4-$[(C_5H_5)Fe(CO)_2]_2C_6F_4$

		Analysis								
		Calc.			Found			Yields		
X	M.p.	C	H	F	C	H	F	*a*	*b*	*c*
2-Br	135·5—136·5	38·6	1·2	18·8	38·9	1·4	18·5	0	61	36
2-H	135·5—136·5	47·9	1·9	23·3	47·9	2·1	21·1 [d]	68	—	0
3-Br	209—211 d.	38·6	1·2	18·8	38·8	1·4	18·5	21	68	32
3-H	87·5—88	47·9	1·9	23·3	48·1	2·1	23·2	—	—	82
4-Br	139·5—140·5	38·6	1·2	18·8	38·7	1·3	18·7	Trace	60	69
3-Cl	209—211	43·3	1·4	21·1	43·5	1·4	20·9	Trace	29	62
1,3-	164—165·5	47·85	2·0	15·1	47·6	2·0	14·8			
1,4-	248—250 d.	47·85	2·0	15·1	48·1	2·0	15·1			

[a] $(C_5H_5)Fe(CO)_2^-Li^+$ + RX at room temperature. [b] $(C_5H_5)Fe(CO)_2^-Li^+$ + RX at −78°. [c] $(C_5H_5)Fe(CO)_2I$ + RLi. [d] The mean of 3 determinations; 21·6, 21·1, 20·6; a low reading being due to incomplete removal of metal interference by cation exchange. This effect was not observed for the other compounds analysed.

The intermediate lithiotetrafluorophenyliron derivatives can be obtained from the corresponding halogenophenyl derivatives, and the carbon–iron bond remains intact at the expense of lithium–bromine or lithium–hydrogen exchange. When starting with the bromotetrafluorophenyl derivatives, reaction with a slight excess of n-butyl-lithium at −78°, followed by the addition of water, gives the corresponding tetrafluorophenyl derivatives. The yields obtained for the 3,4,5,6-, 2,4,5,6-, and 2,3,5,6-derivatives are 93, 82, and 87%, respectively. Reaction between 3-chlorotetrafluorophenyl(cyclopentadienyl)dicarbonyliron and n-butyl-lithium, however, resulted in incomplete lithium–chlorine exchange, the yield, after hydrolysis, of 2,4,5,6-tetrafluorophenyliron derivative being estimated at 65% from the ^1H n.m.r. spectrum of the mixture. Reaction of the tetrafluorophenyliron derivatives with a slight excess of n-butyl-lithium, followed by an excess of bromine, gave a mixture of bromo- and unchanged tetrafluorophenyliron derivatives, indicating incomplete lithium–hydrogen exchange.

The yield of pentafluorophenyl(cyclopentadienyl)dicarbonyliron has been substantially increased from previous observations[2,4] by the use of methods analogous to those utilised for the tetrafluorophenyl derivatives.

EXPERIMENTAL

Reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. ^1H N.m.r. spectra were obtained on a Varian A-60 spectrometer. Analyses were carried out by Micro-Analysis, Inc., Wilmington, Delaware, U.S.A. (Cyclopentadienyl)dicarbonyliron–mercuric chloride was prepared as previously described.[6]

Preparation of the (Cyclopentadienyl)dicarbonyliron Anion as its Lithium Salt, $(C_5H_5)Fe(CO)_2^-Li^+$.—A solution of n-butyl-lithium in hexane was slowly added to a stirred suspension of (cyclopentadienyl)dicarbonyliron–mercuric chloride, using a 2 : 1 reactant ratio, in ether at room temperature. A transient red colouration developed as the n-butyl-lithium was being added, and became permanent after *ca.* 75% had been added. This colouration disappeared as the addition continued, resulting in a yellow-brown solution (containing the required lithium salt) and an off-white solid (lithium chloride).

Reaction of (Cyclopentadienyl)dicarbonyliron Anion with Halogenotetrafluorobenzenes.—The above lithium salt was either maintained at room temperature or cooled at −78° using dry ice–acetone. A slight excess of the required halogenobenzene was added neat and the mixture stirred at room temperature for 12 h. An immediate darkening was observed as the halogenobenzene was added. The resultant dark brown solution was filtered, to remove lithium salts, and solvent removed. The residue was dissolved in the minimum volume of benzene and chromatographed on alumina, eluting with benzene. Two bands were clearly observable; the faster moving yellow band was collected as an orange-yellow solution, with the slower moving red-brown band [due to (cyclopentadienyl)dicarbonyliron dimer] remaining on the column. Removal of solvent gave a yellow-orange crystalline solid, which was recrystallized

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[6] J. C. Thomas, U.S.P. 2,849,471/1958 (*Chem. Abs.*, 1959, **53**, 4298h).

from pentane, hexane, or ethanol. The yields obtained by the reactions at both room temperature and −78° are given in the Table.

Reaction of (Cyclopentadienyl)dicarbonyliron Iodide with Tetrafluoroaryl-lithium Compounds.—n-Butyl-lithium was added to an equivalent amount of the halogenobenzene in ether at −78°. After stirring for 1 h, an equivalent amount of (cyclopentadienyl)dicarbonyliron iodide was added. The resultant mixture was allowed to warm to room temperature and stirred for several hours. After filtration and removal of solvent, the residue was dissolved in benzene and the above chromatographic procedure followed. The second band now observed was due to (cyclopentadienyl)dicarbonyliron iodide, and the required tetrafluoroaryliron derivatives were isolated in a similar manner to the above. The yields are given in the Table.

Preparation of Lithiotetrafluorophenyl(cyclopentadienyl)-dicarbonyliron.—(*a*) From bromotetrafluorophenyl(cyclopentadienyl)dicarbonyliron. n-Butyl-lithium was added to a solution of an equivalent amount of the iron compound in ether at −78°. After stirring for 2 h, water was added and the resultant mixture allowed to reach room temperature. The yellow organic layer was separated from the aqueous layer, dried over magnesium sulphate, then filtered. The solvent was removed. The resultant tetrafluorophenyl(cyclopentadienyl)dicarbonyliron compounds were identified by comparison of their i.r. spectra with samples prepared by the above methods. The yields of the 2,3,4,5-, 2,4,5,6-, and 2,3,5,6-tetrafluorophenyl-derivatives were 93, 87, and 89%, respectively.

(*b*) From tetrafluorophenyl(cyclopentadienyl)dicarbonyliron. n-Butyl-lithium was added to a solution of an equivalent amount of the iron compound in ether at −78°. After stirring for 2 h, an excess of bromine was added and the mixture allowed to reach room temperature. Sodium thiosulphate solution was added, and after stirring the mixture, the ether layer was removed, dried over magnesium sulphate, filtered and the solvent removed. The resultant orange-yellow solid was identified by i.r. and ^{1}H n.m.r. spectra to be a mixture of starting material and the corresponding bromotetrafluorophenyl(cyclopentadienyl)dicarbonyliron, with the latter in excess.

Preparation of 1,4-Bis[(cyclopentadienyl)dicarbonyliron]-tetrafluorobenzene.—(a) *From 1,4-dilithiotetrafluorobenzene*. Two equivalents of n-butyl-lithium were added to a solution of 1,4-dibromotetrafluorobenzene in ether at −78°. After stirring for about half an hour, two equivalents of (cyclopentadienyl)dicarbonyliron iodide were added. The mixture was allowed to attain room temperature and stirring continued for several hours. The amount of solid deposited was observed to be in excess of that possible for precipitation of lithium iodide only. The solid was filtered, washed with water to remove lithium iodide, and then extracted with hot benzene, in which it was partially soluble and from which it was recrystallized. Removal of ether from the original reaction solution did not yield additional product. The resultant 1,4-bis[(cyclopentadienyl)dicarbonyliron]tetrafluorobenzene was obtained in 58% yield as orange-yellow crystals. A sample for analysis was obtained by recrystallization from ethanol, in which the compound was only slightly soluble.

(b) *From 4-lithiotetrafluorophenyl(cyclopentadienyl)dicarbonyliron*. 4-Lithiotetrafluorophenyl(cyclopentadienyl)dicarbonyliron was prepared as above. An equivalent amount of (cyclopentadienyl)dicarbonyliron iodide was added at −78°, and the resultant mixture was stirred at room temperature for several hours. The extraction procedure described above was followed and the desired compound was obtained in 87% yield. The corresponding 1,3-bis[(cyclopentadienyl)dicarbonyliron]tetrafluorobenzene was prepared by an analogous method.

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