Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

The synthesis and reactions of 3-lithiotetrafluorophenylcyclopentadienyliron dicarbonyl

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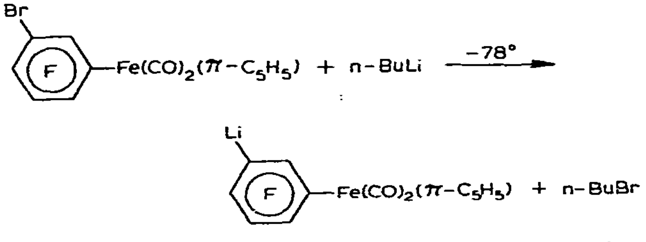
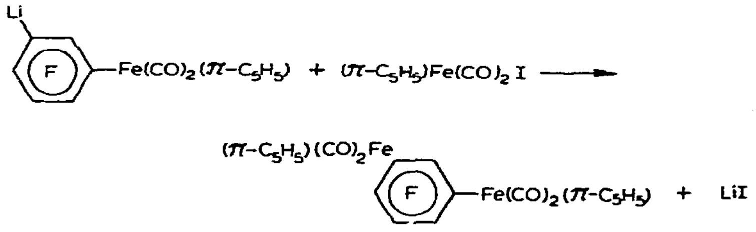
(Received March 29th, 1971)

It has been observed[1] that several bromotetrafluorophenyl derivatives of metals and metalloids undergo Li/Br exchange with n-butyllithium, whilst maintaining the carbon—metal bond. In view of the observed metal/lithium exchange reaction between dicyclopentadienylbis(pentafluorophenyl)titanium and methyllithium[2], and between polyfluoroarylmercurials and alkyllithium reagents[3,4], the reaction between 3-bromotetrafluorophenylcyclopentadienyliron dicarbonyl and n-butyllithium might be expected to proceed with Fe/Li exchange.

When, however, an equivalent amount of n-butyllithium was added to 3-bromotetrafluorophenylcyclopentadienyliron dicarbonyl at —78° and the resultant mixture hydrolyzed, an almost quantitative yield of 3-hydrotetrafluorophenylcyclopentadienyliron dicarbonyl (m.p. 87.5—88°) resulted. This indicates the preference of Li/Br exchange to Li/Fe exchange, the resistance of the iron—carbon bond to rupture, and the formation of the novel intermediate 3-lithiotetrafluorophenylcyclopentadienyliron dicarbonyl:



This lithium intermediate can similarly be obtained by Li/H exchange from 3-hydrotetrafluorophenylcyclopentadienyliron dicarbonyl and reacts with cyclopentadienyliron dicarbonyl iodide to give the unusual bis-iron compound, 1,3-bis(cyclopentadienyliron dicarbonyl) tetrafluorobenzene (m.p. 164—165.5° (dec)):



The 3-bromotetrafluorophenyliron derivative used in this study was prepared both by nucleophilic replacement of bromide ion from 1,3-dibromotetrafluorobenzene by the anion $[(\pi\text{-}C_5H_5Fe(CO)_2]^-$ and by reaction of 1-lithio-3-bromotetrafluorobenzene with cyclopentadienylirondicarbonyl iodide. During this study, it has been observed that reactions between polyfluoroaryllithium derivatives and cyclopentadienylirondicarbonyl iodide are cleaner and produce better yields than corresponding reactions involving the anion $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$.

All of the above new compounds were purified by column chromatography with benzene on alumina, and recrystallized from ligroin or ethanol. Correct analyses for C, H and F were obtained and the compounds gave the expected parent peaks and fragmentation patterns in their mass spectra. A complete mass spectral analysis will be reported at a later date.

This work is being extended to similar studies utilizing the 2- and 4-substituted tetrafluorophenyliron derivatives.

The author acknowledges the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

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