

## Preliminary communication

### Reactions of $\pi$ -cyclopentadienyliron dicarbonyl-mercurials with organolithium reagents

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An attempt to prepare pentafluorophenylmercury- $\pi$ -cyclopentadienyliron dicarbonyl,  $\text{feHgC}_6\text{F}_5$  ( $\text{fe} = \text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ ), for iron-Mössbauer studies, by treating pentafluorophenyllithium with  $\pi$ -cyclopentadienyliron dicarbonyl-mercuric chloride,  $\text{feHgCl}$ <sup>1</sup>, resulted in the formation of bis(pentafluorophenyl)mercury and bis( $\pi$ -cyclopentadienyliron dicarbonyl)mercury,  $\text{fe}_2\text{Hg}$ . Both compounds were readily separated by recrystallization and sublimation, and identified by infrared, <sup>1</sup>H NMR (for  $\text{fe}_2\text{Hg}$ ,  $\tau$  5.21 ppm relative to TMS; lit.<sup>2</sup> 5.23 ppm) and mass spectrometry. The formation of these mercurials can be explained by elimination of lithium chloride between  $\text{feHgCl}$  and  $\text{C}_6\text{F}_5\text{Li}$ , followed by disproportionation of the resultant unsymmetrical organomercurial:



This disproportionation reaction was initially unexpected, due to the observed<sup>2</sup> exchange reactions between  $\text{fe}_2\text{Hg}$  and mercuric halides at room temperature to form stable  $\text{feHgX}$ , and the position of the  $\text{C}_6\text{F}_5$  group in the electronegativity series<sup>3</sup>  $\text{Cl} > \text{C}_6\text{F}_5 > \text{Br}$ . However, attempts<sup>2</sup> to prepare methylmercury-molybdenum derivatives by an exchange reaction proved to be unsuccessful, indicating that for the reaction:



the position of equilibrium is far to the right for X = halogen, but far to the left for X = organo group\*\*\*.

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\*\*\*The unsymmetrical mercurial,  $\text{feHgC}_6\text{F}_5$ , was detected in the mass spectrum of the product, prior to separation. The parent ion  $\text{feHgC}_6\text{F}_5^+$  was of considerably lower intensity than the parent ions  $(\text{C}_6\text{F}_5)_2\text{Hg}^+$  and  $\text{fe}_2\text{Hg}^+$ . Since the expected volatility would be  $(\text{C}_6\text{F}_5)_2\text{Hg} \gg \text{feHgC}_6\text{F}_5 > \text{fe}_2\text{Hg}$ , this would indicate the presence of  $\text{feHgC}_6\text{F}_5$  in trace amounts only.

Previous reports<sup>4-7</sup> on the synthesis of  $\text{Fe}_2\text{Hg}$  have generally involved  $\text{Na}^+\text{Fe}^-$ ; utilization of the above reaction would appear to offer an alternative route, if the bis-organomercurial could be easily removed. The volatility of di-*n*-butylmercury suggested the use of *n*-butyllithium in lieu of pentafluorophenyllithium.

The addition of a hexane solution of *n*-butyllithium to an equimolar amount of  $\text{FeHgCl}$  in ether produced an immediate red coloration which quickly gave way to a yellow-brown solution and white precipitate (lithium chloride) on stirring. Filtration, followed by removal of solvent and  $\text{Bu}_2\text{Hg}$  under vacuum, gave  $\text{Fe}_2\text{Hg}$  in almost quantitative yield. These observations indicated that reactions analogous to (1) and (2) had occurred.

An interesting feature of the above reaction was the appearance of the transient red coloration. Reactions of *n*-butyllithium with  $\text{FeHgCl}$ , using a 1.5/1 molar ratio of reactants gave a permanent red coloration. Workup of this reaction mixture as above produced a much smaller yield of  $\text{Fe}_2\text{Hg}$ , indicating that the latter had been attacked by the excess *n*-butyllithium to produce another species. An increase in the *n*-BuLi/ $\text{FeHgCl}$  ratio to 2/1 resulted in loss of the red coloration and formation of an orange-brown solution and precipitate. In order to detect any formation of Li-Fe, hexafluorobenzene was added to reaction mixtures which contained 1/1, 1/1.5 and 1/2 ratios of  $\text{FeHgCl}$  to *n*-butyllithium. The resultant  $\text{FeC}_6\text{F}_5$ , formed by nucleophilic displacement of  $\text{F}^-$  from  $\text{C}_6\text{F}_6$  by  $\text{Fe}^-$ ,<sup>8</sup> was taken as a measure of the amount of Li-Fe formed. The 1/1 reaction afforded only  $\text{Fe}_2\text{Hg}$  and no  $\text{FeC}_6\text{F}_5$ , whereas the 1/2 reaction produced the latter quantitatively and none of the former. The 1/1.5 reaction yielded a mixture of these with  $\text{FeC}_6\text{F}_5$  in excess. These results strongly indicate formation of Li-Fe by attack of *n*-butyllithium on the mercurial  $\text{Fe}_2\text{Hg}$ .

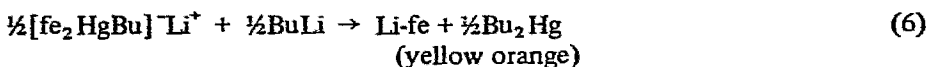
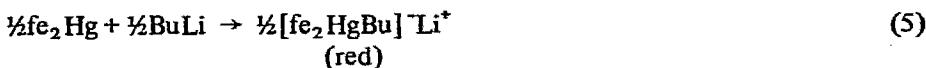
In order to obtain additional information about the identity of the red intermediate, the reaction of  $\text{Fe}_2\text{Hg}$  with *n*-butyllithium was carried out and monitored by infrared spectroscopy under an argon atmosphere. Using a 1/1 ratio of reactants in ether produced a red solution and light colored precipitate. The IR spectrum of the former indicated a substantial decrease in the amount of  $\text{Fe}_2\text{Hg}$ . Apparently the red intermediate was present in too low a concentration to be detected by IR. A 1/2 ratio of  $\text{Fe}_2\text{Hg}$  to *n*-BuLi, however, gave a light orange solution, which contained essentially no iron carbonyl species, and a large quantity of light, orange-yellow solid, subsequently identified as Li-Fe.

In tetrahydrofuran (THF), however, the above 1/1 ratio of reactants gave a very deep red solution but no precipitate. The IR spectrum indicated the loss of over 90% of the initial  $\text{Fe}_2\text{Hg}$  accompanied by the formation of a mixture of Li-Fe (minor) and a highly colored complex anion, probably  $\text{Li}^+[\text{Fe}_2\text{HgBu}]^-$  (major). The former ( $\nu(\text{CO})$  1878m, 1862m, 1806m, 1745m  $\text{cm}^{-1}$ ) was identified by comparison with an authentic sample prepared from  $\text{Fe}_2$  and Li/Hg, while the identity of the latter was inferred from its color and the similarity of its IR spectrum ( $\nu(\text{CO})$  1945m, 1913s, 1871ms (sh), 1868ms  $\text{cm}^{-1}$ ) to that of the deep red complex  $(\text{n-Bu}_4\text{N})^+[\text{HgFe}_3]^-$  ( $\nu(\text{CO})$  1944m, 1916vs, 1873s, 1860m (sh)  $\text{cm}^{-1}$ )<sup>9</sup>. It is also quite possible that the colored complex was  $\text{Li}^+[\text{Fe}_3\text{Hg}]^-$  but this is considered less likely\*. Use of a 1/2 reactant ratio gave a dark orange solution

\*A THF solution of  $\text{Li}^+[\text{Fe}_3\text{Hg}]^-$  prepared from Li-Fe and  $\text{Fe}_2\text{Hg}$  exhibited  $\nu(\text{CO})$  1953, 1918, 1875 and 1859 (sh)  $\text{cm}^{-1}$  in addition to moderately strong absorptions caused by  $\text{Fe}_2$ , a self-decomposition product characteristic of  $\text{Fe}_3\text{Hg}$ . The complex from the BuLi/ $\text{Fe}_2\text{Hg}$  reaction showed only a very weak band that could be attributed to  $\text{Fe}_2$ .

containing only  $\text{Li}^+\text{fe}^-$ . Addition of further n-butyllithium did not appreciably change the spectrum, and indicated lack of reaction between  $\text{Li}^+\text{fe}^-$  and the alkylolithium.

The above observations indicate that Li-fe is insoluble in ether but soluble in THF, and that the red coloration of the n-BuLi/feHgCl reaction mixture is due to formation of a complex ion, most likely  $\text{Li}^+[\text{fe}_2\text{HgBu}]^-$ . The latter reaction can then be represented by the following sequence.



The overall reaction scheme represents a convenient procedure for formation of  $\text{fe}^-$ , complementing the widely used  $\text{Na}^+\text{fe}^-$ <sup>10</sup>, and offers strong possibilities for its application in organometallic synthesis. The red coloration serves as a good indicator for the presence of  $\text{fe}_2\text{Hg}$  (in complexed form) which is completely removed when the coloration disappears. Subsequent addition of a reactive halide such as  $\text{Ph}_3\text{SnCl}$ , for example, gave  $\text{Ph}_3\text{Snfe}$ <sup>11</sup> in good yield.

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