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

Preliminary communication

Reactions of π-cyclopentadienylirondicarbonyl-mercurials with organolithium reagents

S.C. COHEN, S.H. SAGE★, W.A. BAKER, Jr.
Department of Chemistry, Syracuse University, Syracuse, New York 13210 (U.S.A.)
JAMES M. BURLITCH★★ and ROBERT B. PETERSEN
Department of Chemistry, Cornell University, Ithaca, New York 14850 (U.S.A.)

(Received January 26th, 1971)

An attempt to prepare pentafluorophenylmercury-π-cyclopentadienylirondicarbonyl, $\mathrm{feHgC_6F_5}$ ($\mathrm{fe = Fe(CO)_2C_5H_5}$), for iron–Mössbauer studies, by treating pentafluorophenyllithium with π-cyclopentadienylirondicarbonyl–mercuric chloride, feHgCl[1], resulted in the formation of bis(pentafluorophenyl)mercury and bis(π-cyclopentadienylirondicarbonyl)mercury, $\mathrm{fe_2Hg}$. Both compounds were readily separated by recrystallization and sublimation, and identified by infrared, ^{1}H NMR (for $\mathrm{fe_2Hg}$, τ 5.21 ppm relative to TMS; lit.[2] 5.23 ppm) and mass spectrometry. The formation of these mercurials can be explained by elimination of lithium chloride between feHgCl and $\mathrm{C_6F_5Li}$, followed by disproportionation of the resultant unsymmetrical organomercurial:

$$\mathrm{feHgCl + C_6F_5Li \rightarrow feHgC_6F_5 + LiCl} \tag{1}$$

$$\mathrm{2feHgC_6F_5 \rightarrow fe_2Hg + (C_6F_5)_2Hg} \tag{2}$$

This disproportionation reaction was initially unexpected, due to the observed[2] exchange reactions between $\mathrm{fe_2Hg}$ and mercuric halides at room temperature to form stable feHgX, and the position of the $\mathrm{C_6F_5}$ group in the electronegativity series[3] $\mathrm{Cl > C_6F_5 > Br}$. However, attempts[2] to prepare methylmercury–molybdenum derivatives by an exchange reaction proved to be unsuccessful, indicating that for the reaction:

$$\mathrm{fe_2Hg + HgX_2 \rightleftharpoons 2feHgX}$$

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

★Research Associate (1969–1970).
★★Fellow of the Alfred P. Sloan Foundation, 1970–1972.
★★★The unsymmetrical mercurial, $\mathrm{feHgC_6F_5}$, was detected in the mass spectrum of the product, prior to separation. The parent ion $\mathrm{feHgC_6F_5}^+$ was of considerably lower intensity than the parent ions $\mathrm{(C_6F_5)_2Hg^+}$ and $\mathrm{fe_2Hg^+}$. Since the expected volatility would be $\mathrm{(C_6F_5)_2Hg \gg feHgC_6F_5 > fe_2Hg}$, this would indicate the presence of $\mathrm{feHgC_6F_5}$ in trace amounts only.

Previous reports[4-7] on the synthesis of fe_2Hg have generally involved Na^+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 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 Bu_2Hg under vacuum, gave fe_2Hg 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 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 fe_2Hg, indicating that the latter had been attacked by the excess n-butyllithium to produce another species. An increase in the n-BuLi/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 feHgCl to n-butyllithium. The resultant feC_6F_5, formed by nucleophilic displacement of F^- from C_6F_6 by fe^-,[8] was taken as a measure of the amount of Li-fe formed. The 1/1 reaction afforded only fe_2Hg and no feC_6F_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 feC_6F_5 in excess. These results strongly indicate formation of Li-fe by attack of n-butyllithium on the mercurial fe_2Hg.

In order to obtain additional information about the identity of the red intermediate, the reaction of fe_2Hg 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 fe_2Hg. Apparently the red intermediate was present in too low a concentration to be detected by IR. A 1/2 ratio of fe_2Hg 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 fe_2Hg accompanied by the formation of a mixture of Li-fe (minor) and a highly colored complex anion, probably $Li^+[fe_2HgBu]^-$ (major). The former (ν(CO) 1878m, 1862m, 1806m, 1745m cm^{-1}) was identified by comparison with an authetic sample prepared from fe_2 and Li/Hg, while the identity of the latter was inferred from its color and the similarity of its IR spectrum (ν(CO) 1945m, 1913s, 1871ms (sh), 1868ms cm^{-1}) to that of the deep red complex $(n\text{-}Bu_4N)^+[Hgfe_3]^-$ (ν(CO) 1944m, 1916vs, 1873s, 1860m (sh) cm^{-1})[9]. It is also quite possible that the colored complex was $Li^+[fe_3Hg]^-$ but this is considered less likely★. Use of a 1/2 reactant ratio gave a dark orange solution

---

★A THF solution of $Li^+[fe_3Hg]^-$ prepared from Li-fe and fe_2Hg exhibuted ν(CO) 1953, 1918, 1875 and 1859 (sh) cm^{-1} in addition to moderately strong absorptions caused by fe_2, a self-decomposition product characteristic of fe_3Hg^-. The complex from the BuLi/fe_2Hg reaction showed only a very weak band that could be attributed to fe_2.

containing only Li^+fe^-. Addition of further n-butyllithium did not appreciably change the spectrum, and indicated lack of reaction between Li^+fe^- and the alkyllithium.

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 $Li^+[fe_2HgBu]^-$. The latter reaction can then be represented by the following sequence.

$$\text{feHgCl} + \text{BuLi} \rightarrow \text{feHgBu} + \text{LiCl (s)} \tag{3}$$

$$\text{feHgBu} \rightleftharpoons \tfrac{1}{2}\text{fe}_2\text{Hg} + \tfrac{1}{2}\text{Bu}_2\text{Hg} \tag{4}$$

$$\tfrac{1}{2}\text{fe}_2\text{Hg} + \tfrac{1}{2}\text{BuLi} \rightarrow \underset{\text{(red)}}{\tfrac{1}{2}[\text{fe}_2\text{HgBu}]^-\text{Li}^+} \tag{5}$$

$$\tfrac{1}{2}[\text{fe}_2\text{HgBu}]^-\text{Li}^+ + \tfrac{1}{2}\text{BuLi} \rightarrow \underset{\text{(yellow orange)}}{\text{Li-fe} + \tfrac{1}{2}\text{Bu}_2\text{Hg}} \tag{6}$$

$$\text{Overall: feHgCl} + 2\ \text{BuLi} \rightarrow \text{Li-fe} + \text{Bu}_2\text{Hg} + \text{LiCl(s)} \tag{7}$$

The overall reaction scheme represents a convenient procedure for formation of fe^-, complementing the widely used Na^+fe^- [10], and offers strong possibilities for its application in organometallic synthesis. The red coloration serves as a good indicator for the presence of fe_2Hg (in complexed form) which is completely removed when the coloration disappears. Subsequent addition of a reactive halide such as Ph_3SnCl, for example, gave Ph_3Snfe [11] in good yield.

We thank the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation, for partial support of this work.

REFERENCES

1 J.C. Thomas, *U.S. Patent 2,849,471* (1958); *Chem. Abstr.*, 53 (1959) 4298h.
2 M.J. Mays and J.D. Robb, *J. Chem. Soc. A*, (1968) 329.
3 S.C. Cohen and A.G. Massey, *Advan. Fluorine Chem.*, 6 (1970) 83.
4 E.O. Fischer and R. Böttcher, *Z. Naturforsch., B*, 10 (1955) 600.
5 M.L.H. Green and P.L.I. Nagy, *J. Chem. Soc.*, (1963) 189.
6 R.B. King, *J. Inorg. Nucl. Chem.*, 25 (1963) 1296.
7 J.M. Burlitch and A. Ferrari, *Inorg. Chem.*, 9 (1970) 563.
8 R.B. King and M.B. Bisnette, *J. Organometal. Chem.*, 2 (1964) 38.
9 (*a*) J.M. Burlitch and R.B. Petersen, *CIC/ACS Conference*, Toronto, Canada, May, 1970. *Abstr. Inorg.-25*; (*b*) J.M. Burlitch, R.B. Petersen, H.L. Conder and W.R. Robinson, *J. Amer. Chem. Soc.*, 92 (1970) 1783.
10 (*a*) R.B. King, *Accounts Chem. Res.*, 3 (1970) 417;
(*b*) R.B. King, *Advan. Organometal. Chem.*, 2 (1964) 229.
11 R.D. Gorsich, *J. Amer. Chem. Soc.*, 84 (1962) 2486.