The Direct Formation of Biferrocenyl and Polyferrocenyls from Ferrocenyllithium

By Kazuo Hata, Izumi Motoyama and Hamao Watanabe

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Although many synthetic methods of biferrocenyl have been proposed, all of these routes are circuitous and troublesome. Moreover, the formation of polyferrocenyls other than biferrocenyl has never been reported. The present authors wish to report on the direct formation of biferrocenyl and polyferrocenyls from ferrocenyllithium.

In a previous paper[1] the synthesis of glycidylferrocenes was reported. In the course of this synthesis, when chlorohydrin derivatives of ferrocene were derived from the products of the reaction between ferrocenyllithium and epichlorohydrin, a small amount of biferrocenyl was obtained as orange crystals. The yield was ca. 0.3% based on ferrocene. In order to determine the step of the formation of biferrocenyl, a mixture containing lithiated ferrocene was hydrolyzed by pouring it into ice water immediately after the reaction of ferrocene and *n*-butyllithium in ether. An organic solid mixture, obtained from the ethereal layer, was submitted to vacuum sublimation in order to collect the recovered ferrocene. Even in this reaction biferrocenyl was isolated from the sublimation residue in a 0.4% yield. On the other hand, the reaction between *n*-butyl bromide and ferrocene in an ethereal solution did not occur, and the formation of biferrocenyl could not be observed. From these facts, it is obvious that biferrocenyl was directly derived from ferrocenyllithium, and that the formation of biferrocenyl is attributable to the Wurtz-type reaction as follows:[2]

$$\mathrm{FcLi} \xrightarrow{n\text{-BuBr}^{*}} \mathrm{FcBr} \xrightarrow{\mathrm{FcLi}} \mathrm{Fc{-}Fc}$$

$$\mathrm{FcLi} \xrightarrow{\mathrm{FcBr}} 2\mathrm{Fc}\cdot \longrightarrow \mathrm{Fc{-}Fc}$$

$$\mathrm{FcLi} \longrightarrow \mathrm{Fc}\cdot \longrightarrow 1/2\ \mathrm{Fc{-}Fc}$$

$$(\mathrm{Fc}=\text{ferrocenyl})$$

Among these reactions, the radical species are considered on the basis of the results mentioned below to be mainly participated in the formation of biferrocenyl. The radical

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[1] K. Hata, I. Motoyama and H. Watanabe, This Bulletin, 36, 1698 (1963).

[2] D. Bryce-Smith, *J. Chem. Soc.*, 1956, 1603.

* *n*-Butyl bromide may remain after the reaction with lithium metal in the preparation of *n*-butyllithium.

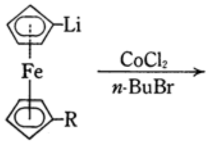
TABLE I. THE ANALYTICAL RESULTS OF THE PRODUCTS

Compound	Yield based on FcH %		Elemental analysis Found %	Elemental analysis Calcd. %	M. p. in sealed capillary °C	Mol. weight Found	Mol. weight Calcd.	Solubility in benzene
I	ca. 11	C	64.78	64.91	233.8～234.5	370*	370	Soluble
		H	5.05	4.90		330**		
II	ca. 5	C	64.89	65.03	226.5～227.2	554*	554	Sparingly soluble
		H	4.81	4.73				
III	ca. 6.5	C	67.61	67.64	68.2～ 70.2	446*	426	Very soluble
		H	5.95	6.19		400**		

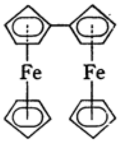
* Determined by the Rast method.
** Determined with a vapor pressure osmometer.

mechanism is also suitable for the explanation of the experimental results which Goldberg et al. have observed previously.[3)]

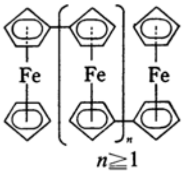
With a view to finding a possibility of the formation of any polyferrocenyls and one of the increase in the yield of biferrocenyl, a reaction of ferrocenyllithium and cobaltous chloride was carried out according to the method reported by Kharasch and his co-workers,[4)] and Wittig and Lehmann.[5)] A small amount of anhydrous cobaltous chloride was added to an anhydrous ethereal solution of lithiated ferrocene, in the presence of an equimolar amount of n-butyl bromide to the ferrocence used as the starting material. A considerably vigorous reaction occurred, with an evolution of gas as had been expected. After the reaction was over, the mixture was poured into ice water in order to hydrolyze the remained lithium compounds, and many solid products were separated from the organic mixture by means of an appropriate procedure. The products were found to be biferrocenyl, butylated biferrocenyl, terferrocenyl, many polyferrocenyls and butylated polyferrocenyls, some of which were not yet identified. The analytical results of the identified products are shown in Table I. The identification was also supported by their infrared spectra. Other polyferrocenyls and butylated polyferrocenyls were found to have a larger molecular weight than 600, and they are scarcely soluble in common organic solvents. As a whole, about 36% of the ferrocene used was converted into these reaction products. A detailed investigation of all these products is in progress and will be reported on later.



R=H and/or Li

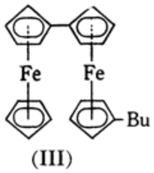


(I)



$n \geqq 1$

(II) $n=1$



(III)

Department of Chemistry
Faculty of Science
Tokyo Metropolitan University
Setagaya-ku, Tokyo

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3) S. I. Goldberg and D. W. Mayo, *Chem. & Ind.*, **1959**, 671; S. I. Goldberg, D. W. Mayo and J. A. Alford, *J. Org. Chem.*, **28**, 1708 (1963).

4) M. S. Kharasch, D. W. Lewis and W. B. Reynolds, *J. Am. Chem. Soc.*, **65**, 498 (1943).

5) G. Wittig and G. Lehmann, *Chem. Ber.*, **90**, 875 (1957).