

The Co-ordinating Effect of an Ether Oxygen in the 2-Metallation of Ferrocenes¹

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Summary Carbinol ethers of type (III) are obtained *via* 2-metallation of alkoxyethylferrocenes, followed by condensation with benzophenone.

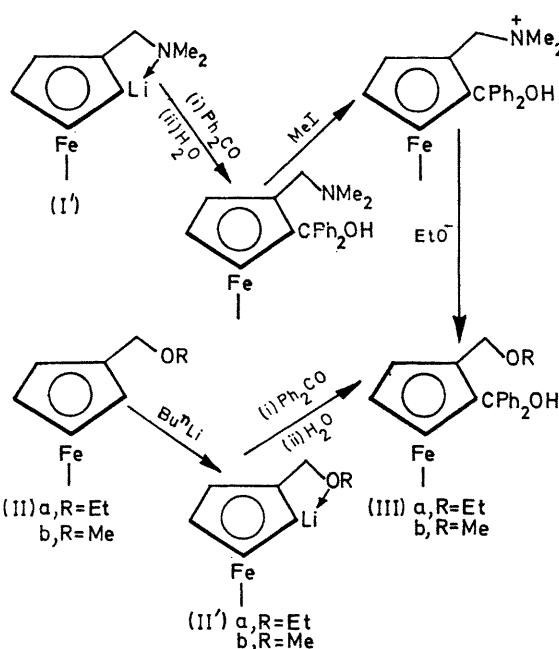
We have recently reported on the directed 2-metallation of dimethylaminomethylferrocene (I),² dimethylaminoethylferrocene,³ and *N*-alkylferrocenecarboxamides.⁴ Similar results had earlier been obtained for the corresponding derivatives of benzene, namely, dimethylbenzylamine,⁵ β -phenethyldimethylamine^{5b,6} and *N*-methylbenzamide.⁷ Interpretation of the 2-disposition of metallation involved

the postulation in the case of dimethylaminomethylferrocene (I) of lithio-intermediates such as (I')² where the nitrogen atom stabilized the 2-lithiated species by means of a co-ordinated ring structure.

Only scattered information is available on the direction of metallation by atoms other than nitrogen. For oxygen, early studies of lithiation of benzyl-type ethers led to reports of both Wittig rearrangement and 2-metallation products.⁸ The lithiation of certain benzyl ethers has recently been re-examined with the aid of modern techniques;⁹ no 2-metallation products were found but, where appropriate, the Wittig rearrangement was observed. Benzyl alcohol and related compounds are known to undergo 2-lithiation.^{8,10}

A successful demonstration of the co-ordinating ability of the oxygen atom in metallation (intermediate II') was demonstrated in the lithiation of ethoxymethylferrocene (IIa). The reaction of this compound with 1.5 equiv. of *n*-butyl-lithium and condensation with benzophenone yielded 62%[†] of 2-substituted product (IIIa). Its structure was confirmed by its identity with a sample of the known compound prepared by a route involving the 2-metallation of amine (I).[‡] The scheme outlines both routes used in the synthesis of carbinol ether (IIIa).

A similar product (IIIb), m.p. 109–111°, was obtained in 90% yield (51% conversion) when methoxymethylferrocene (IIb) was metallated with *n*-butyl-lithium and condensed with benzophenone. Absorption spectra supported the assigned structure. An i.r. spectrum (Nujol) showed absorptions at 3.05, 8.05, 9.00, and 9.95 μm ., the last two bands indicative of homoannular substitution.¹² An n.m.r. spectrum exhibited a 3-proton singlet at τ 6.90 (CH_3), a complex 10-proton signal at τ 2.85 (phenyls) and a 5-proton singlet at τ 5.72 (C_5H_5 ring). The remaining six protons of the spectrum lay in a very broad and complex absorption from τ 5.8 to 6.8.



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[†] Yields are based on unrecovered starting material.

[‡] The usual criteria for identity of samples were satisfactorily met.

¹ D. W. Slocum and B. P. Koonsvitsky, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1968, Section ORGN, Paper 165.

² (a) D. W. Slocum, B. W. Rockett, and C. R. Hauser, *Chem. and Ind.*, 1964, 1831; (b) D. W. Slocum, B. W. Rockett, and C. R. Hauser, *J. Amer. Chem. Soc.*, 1965, **87**, 1241.

³ (a) D. W. Slocum, C. A. Jennings, T. R. Engelmann, B. W. Rockett, and C. R. Hauser, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Illinois, Sept. 1967, Section S, Paper 143; (b) *cf.* also D. W. Slocum, T. R. Engelmann, and C. A. Jennings, *Austral. J. Chem.*, 1968, **21**, 2319.

⁴ D. W. Slocum, S. Puckett, P. Shenkin, and T. R. Engelmann, Abstracts, Central Regional Meeting of the American Chemical Society, Akron, Ohio, May 1968, Paper 89.

⁵ F. N. Jones, M. F. Zinn, and C. R. Hauser, *J. Org. Chem.*, 1963, **28**, 663; F. N. Jones, R. L. Vaulx, and C. R. Hauser, *J. Org. Chem.*, 1963, **28**, 3461.

⁶ N. S. Narasimhan and A. C. Ranade, *Tetrahedron Letters*, 1966, 603.

⁷ W. H. Puterbaugh and C. R. Hauser, *J. Org. Chem.*, 1964, **29**, 853.

⁸ *cf.* H. Gilman and J. W. Morton, jun., *Org. Reactions*, 1954, **8**, 278, and references cited therein.

⁹ R. A. Finnegan and J. W. Altschuld, *J. Organometallic Chem.*, 1967, **9**, 193.

¹⁰ R. A. Benkeser, W. P. Fitzgerald, and M. S. Melzer, *J. Org. Chem.*, 1961, **26**, 2569.

¹¹ D. W. Slocum, R. Silverman, B. W. Rockett, and C. R. Hauser, *J. Org. Chem.*, 1967, **32**, 464.

¹² M. Rosenblum, Ph.D. Thesis, Harvard University, 1953; M. Rosenblum, *Chem. and Ind.*, 1958, 953; P. L. Pauson, *Quart. Rev.*, 1955, **9**, 391.