Intramolecular Ligand Exchange: the Reaction of Bisindenyliron with Boron Trifluoride Etherate

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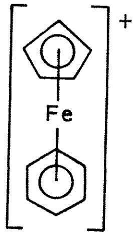
Summary Bisindenyliron reacts with $BF_3 \cdot Et_2O$ to give a cationic arene complex by a novel intramolecular ligand exchange.

IT has been shown by Nesmeyanov *et al.*[1] that intermolecular ligand exchange processes can be used to replace a cyclopentadienyl ligand in ferrocene to give cationic arene complexes (**1**) and the chemistry of these complexes has now been extensively investigated.[2] In connection with our work on the structure of the α-ferrocenyl-carbonium ion[3] we have studied the reaction of bisindenyliron (**2**) with a number of Lewis acids and report the first example of an intramolecular ligand exchange.



(1)

Bisindenyliron (**2**) was treated with $BF_3 \cdot Et_2O$ under nitrogen in the cold. A deep red solution resulted which on quenching with ammonium hexafluorophosphate gave a salt, $C_{18}H_{15}FePF_6$,[†] m.p. 200° (decomp.) in 15% yield as crimson needles. This cationic arene complex was assigned structure (**3**) on the basis of the following evidence. Hydride reduction gave an unstable neutral product, and hydrogenation, using Pd–C as catalyst, resulted in the uptake of 2·9 mol of hydrogen to give a new complex (**4**), $C_{18}H_{21}$-$FePF_6$ as golden rods, m.p. 200° (decomp.), in 88% yield. This complex (**4**) was synthesized unambiguously by an intermolecular ligand exchange when indane was treated with bistetrahydroindenyliron (**5**) in the presence of $AlCl_3$–Al in heptane under reflux. The properties of the arene complex obtained in this way were identical in all respects with (**4**) obtained by reduction of (**3**). Additionally, borohydride reduction of (**4**) gave a neutral species as an unstable red oil which exhibited a parent ion at *m/e* 294.

It appears that the formation of (**3**) from (**2**) involves an intramolecular shift of the ligand[‡] (possibly *via* a cationic intermediate).

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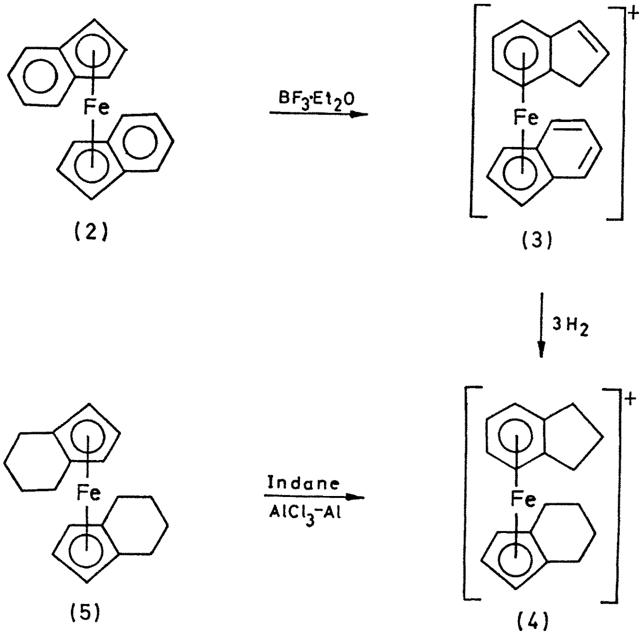

[†] All new compounds had satisfactory analytical and spectral data.

[‡] In a separate experiment lithium indenide was treated with $BF_3 \cdot Et_2O$ under nitrogen. The residue, after quenching with water, was examined by mass spectrometry and shown to consist of a mixture of dimers, trimers, tetramers, and other indene polymers.

[1] N. Nesmeyanov, N. A. Vol'Kenau, and I. N. Bolesova, *Tetrahedron Letters*, 1963, 1725.

[2] For a recent survey see M. I. Bruce, *Organometallic Chem. Rev.*, 1970, **6**, 705.

[3] W. M. Horspool and R. G. Sutherland, *Chem. Comm.*, 1967, 786.