

Synthesis and some Properties of Ferrocene Derivatives having a Long Alkyl Chain. Formation of a Regularly oriented Organometallic Complex in Monolayer Assemblies

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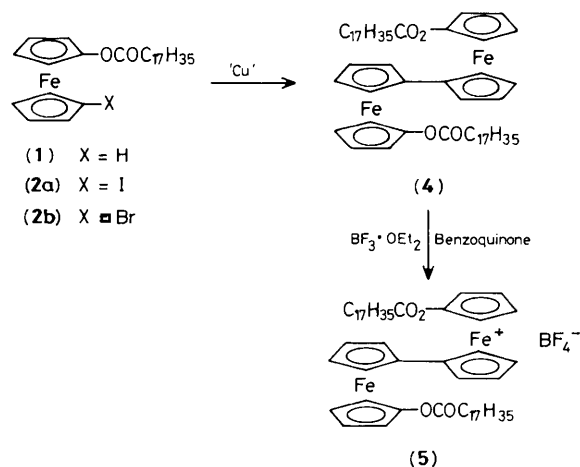
1',6'-Bis(stearoyloxy)biferrocene was synthesized and its Langmuir-Blodgett film was prepared, in which film the cyclopentadienyl rings of a ferrocene nucleus were orientated perpendicular to the film surface; Oxidation of the biferrocene derivative gave the mixed valence monocation complex which formed a stable monolayer on water.

It is known that regular ensembles of molecules with a well-defined order or orientation of groups can be obtained as Langmuir-Blodgett (L-B) films. These are currently of interest as molecular models of biological membranes and as organic electrical components. Ferrocene-containing multilayers with a well defined order were recently prepared¹ and films of simple ferrocene derivatives having long alkyl chains were used as a photodiode² and a modified electrode.³ We report here the synthesis of 1',6'-bis(stearoyloxy)biferrocene and its mono-cation, and their mono- and multi-layers.

Iodoferrocene was refluxed with stearic acid (m.p. 67.9–68.6°C) in the presence of copper(I) oxide in acetonitrile to give stearoyloxyferrocene (**1**) in good yield.⁴ A similar reaction of 1,1'-diiodoferrocene gave three products: stearoyloxyferrocene (**1**) (15%), 1'-iodo-1-stearoyloxyferrocene (**2a**) (16%), and 1,1'-bis(stearoyloxy)ferrocene (**3**) (12%). The ¹H n.m.r. spectrum (CDCl₃) of (**2a**) showed the presence of iodo-substituted (δ 4.19 and 4.44) and stearoyloxy-substituted (δ 3.97 and 4.44) cyclopentadienyl (Cp) ring protons, while (**3**) showed only the stearoyloxy-substituted Cp ring proton signals (δ 4.46 and 3.99). 1,1'-Dibromoferrocene reacted in a similar manner to give (**1**) (11%), (**2b**) (13%), and (**3**) (17%). The Ullmann coupling of (**2a**) and (**2b**) gave 1',6'-bis(stearoyloxy)biferrocene (**4**) as fine, orange needles (m.p. 84–85°C) in 75 and 40% yields, respectively. In the ¹H n.m.r. spectrum of (**4**), the Cp ring protons appeared as four triplets (*J*, 2 Hz) at δ 4.40 (4H), 4.27 (4H), 4.21 (4H), and 3.77 (4H). The δ 4.40 and 3.77 triplets were assigned to the protons of the stearoyloxy-substituted Cp rings and the δ 4.27 and 4.21 triplets were assigned to the fulvalene moiety of (**4**) in comparison with the spectra of (**1**) and biferrocene itself.⁵ The aliphatic protons showed a typical pattern of stearyl esters. The ¹H n.m.r. and mass spectra (*m/z* 934, *M*⁺) of (**4**) are in agreement with the proposed structure.

A monolayer of (**4**), spread on water at room temperature from a chloroform solution, formed a rigid condensed film

with a limiting area of *ca.* 45 Å² molecule⁻¹. Since an *s-trans* conformation has been reported for some biferrocene derivatives,⁶ the monolayer may also have this structure. The multilayers could be built up by the horizontal lifting method⁷ on quartz plates under a pressure of 30 mN molecule⁻¹ at 10°C. A hypsochromic shift (Δλ 12 nm) of the π-π* transition band in the multilayer film seems to be related to the close packing of ferrocene nuclei orientated with the Cp ring planes almost perpendicular to the surface, since this band is polarized parallel to the plane of the Cp rings of a ferrocene nucleus.⁸ This view is supported by the F.t.i.r. spectrum of the L-B film on Ge plates which showed that the C-C stretching (1410 cm⁻¹) band⁹ for the Cp rings of a ferrocene nucleus was intensified with perpendicularly polarized light, while the C-H bending¹⁰ band at 810 cm⁻¹ was enhanced with parallel polarized light.



Compound (4) was oxidized with benzoquinone and boron trifluoride-diethyl ether to give its monocation complex (5) as fine, dark violet crystals (m.p. 88–90°C) in low yield. Appearance of two carbonyl stretching absorptions at 1792 and 1762 cm^{-1} in the i.r. spectrum (KBr) and of absorption maxima at 558 nm ($\log \epsilon$ 3.30) and 1900 nm (2.86) in the visible-near i.r. spectrum (CH_2Cl_2) confirm that (5) has a mixed valence biferrocene ($\text{Fe}^{\text{II}} \text{Fe}^{\text{III}}$) cation structure.¹⁰ The surface pressure-area isotherm of (5) indicated the formation of a stable monolayer having a limiting area of ca. 48 \AA^2 molecule⁻¹. The absorption spectrum of the monolayer measured by a multichannel photodetector (MCPD system) showed an additional new absorption peak at 690 nm. However, this monolayer was gradually disrupted on standing, even at low temperatures. Attempts to build this monolayer onto a solid support are in progress.

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