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SYNTHESIS OF as-INDACENEBIS(CYCLOPENTADIENYLIRON)

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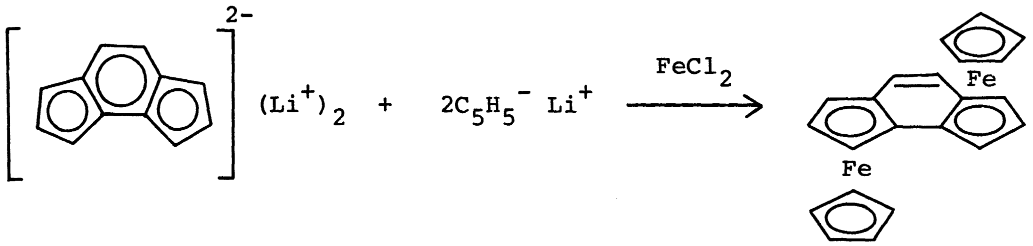
Iron(II) chloride reacts with a mixture of lithium cyclopentadienide and dilithium as-indacenide in tetrahydrofuran to give as-indacenebis(cyclopentadienyliron) (1). The results of NMR and solubility studies of (1) indicate that (1) is one of the new analogues of biferrocene or cyclopentadienyl(indenyl)iron rather than that of bis(as-indacenyliron).

It is known that some of the binuclear ferrocenium salts give iron atoms an intervalence state averaged between di- and trivalent states.[1,2] Recent studies indicate possibilities that there is a certain relation of the molecular structure of binuclear ferrocenium cations with the intervalence state.[3,4] However, only limited binuclear ferrocene derivatives, from which possible intervalent ferrocenium salts can be prepared, have so far been reported. Although [m,n](1,1')ferrocenophanes are known to have a number of analogues including bis(as-indacenyliron), only [2,2](1,2)ferrocenophanes[5] and some heterocyclic [0,3](1,2)ferrocenophanes[6] have so far been reported on the analogues of [m,n](1,2)ferrocenophanes. The present paper describes the synthesis of as-indacenebis(cyclopentadienyliron) (1), which is the dehydro-derivative of [0,2](1,2)ferrocenophane and is the first biferrocene compound with the structure fixed in trans form.

as-Indacenebis(cyclopentadienyliron) (1) was prepared from the reaction of iron(II) chloride with a mixture of lithium cyclopentadienide and dilithium as-indacenide prepared by the reaction of dihydro-as-indacene (2) with n-butyllithium:

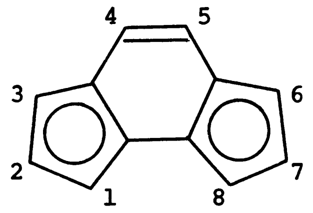


(1)

Dihydro-as-indacene (2) was prepared through the reaction of hexahydro-as-indacene with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in the yield of 25-47 %, according to the procedure of Wightman et al.[7] It is found by comparing the NMR and UV data of the product with the reported data,[8,9] that the dehydrogenation gives 1,8-dihydro-isomer exclusively in the reaction conditions.

To a solution of THF containing 0.62 g (4 mmol) of (2) cooled to -70°C, 2.64 g (40 mmol) of cyclopentadiene was added. 32 ml of solution of 1.5M n-butyllithium in hexane was, then, added in drops over a period of 15 min. The mixture was allowed to stand for about 15 min until the temperature rose to room temperature. After leaving the mixture for another 10 min, it was poured at room temperature into a suspension of iron(II) chloride prepared immediately before use. The solution turned instantly into deep purple. After being allowed to stand for 30 min under stirring, the solvent was evaporated off and then the residues were extracted with hexane. The extract was rapidly separated from ferrocene by column chromatography on alumina. as-Indacenebis(cyclopentadienyliron) (1) was obtained in the form of reddish needles in the yield of 3 %. m.p. 210-211°. Found: C, 66.79; H, 4.73. Calcd for $C_{22}H_{18}Fe_2$: C, 67.05; H, 4.60.

The NMR data on (1) was summarized in Table 1 and the positions of hydrogen atoms cited in Table 1 are shown below for the as-indacene skeleton involved in this compound. The chemical shifts of the five-membered ring protons are similar to those of biferrocene or cyclopentadienyl(indenyl)iron,[10] whereas the large spread of the chemical shifts of protons characteristic to bis(as-indacenyliron)[11] was not observed in the spectrum of (1). In contrast with most [m,n](1,1')ferrocenophanes including bis(as-indacenyliron), (1) is easily soluble in most organic solvents.



At 75 V, the mass spectrum showed as the most intense peak the parent ion with the most common isotopic abundances, i.e., m/e = 394. The less intense peak of one higher mass unit (m/e = 395) was that expected from the known abundances of other isotopes and the composition of (1). The other peaks found at m/e = 329, 273, 193, 152, 121 and 56 are ascribed to the peaks of $(C_{12}H_8)Fe_2(C_5H_5)^+$, $(C_{12}H_8)Fe(C_5H_5)^+$, $(C_{12}H_8)Fe_2(C_5H_5)_2^{2+}$, $C_{12}H_8^+$, $Fe(C_5H_5)^+$ and Fe^+, respectively.

Table 1. NMR data for as-indacenebis(cyclopentadienyliron)*

Protons	δ (ppm)	Relative intensity	Multiplicity	J (Hz)
H_4, H_5	6.89	1	s	
H_3, H_6**	4.80	1	dd	2.5, 1.0
H_1, H_8	4.58	1	dd	2.5, 1.0
H_2, H_7	4.18	1	t	2.5
Cp-protons	3.73	5	s	

* In $CDCl_3$. ** This assignment is verified by the fact that there is a small coupling between the protons resonating at δ = 6.89 and δ = 4.80. Irradiation at δ = 6.89 resolves the resonance at δ = 4.80 into a clean doublet of doublets.

The ^{57}Fe Mössbauer spectrum consists of only one quadrupole doublet, and this indicates the equivalency of the two irons in (1). The Mössbauer parameters are summerized together with the data of biferrocene for comparison in Table 2. (It is found that the data of biferrocene obtained in this work agree with the previous data reported by Wertheim and Herber.[12]) The quadrupole splitting (qs) of (1) is somewhat greater than that of biferrocene. This is similar to the relation between the qs of cyclopentadienyl(indenyl)iron, or diindenyliron and that of ferrocene.[13,14] It is known that e_{2g} electrons make a predominant contribution to the electric field gradient (efg) around the iron nucleus of ferrocene and the sign of the efg is positive consequently.[15] The large qs of (1) is ascribable to the donating effect of the π-electrons on C_4 and C_5 to the ferrocenyl moieties, which increases the nonbonding 3d character of the e_{2g} orbitals.

The visible and ultraviolet spectrum in cyclohexane showed absorptions at 482 (ε 855), 367 (4690), 320 (sh, 31200) and 251.5 (34000) nm.

The infrared spectrum (KBr) showed absorptions at 3100 (w), 3080 (w), 1502 (w), 1405 (m), 1105 (s), 1026 (m), 1002 (sh), 998 (s), 825 (m), 808 (s), 632 (s), 564 (s) and 465 (s, broad) cm^{-1}.

The results of the X-ray analysis indicate that two (η^5-C_5H_5)Fe moieties are substituted on the opposite sides of the indacene plane, i.e., giving trans-form with respect to iron atoms.[16]

The cyclic voltammogram of (1) in a CH_3CN solution containing n-Bu_4ClO_4 showed two steps of one-electron oxidation ($E_{1/2}$ = 0.63 and 0.23 V vs. SCE). The difference in the half-wave potentials has been used as the measure of the degree of the metal-metal interaction in a mono-oxidized binuclear ferrocene.[17] The larger difference in the half-wave potentials in (1) suggests that the metal-metal interaction in (1) is greater than that in the mono-cation of biferrocene ($E_{1/2}$ = 0.62 and 0.30 vs. SCE in biferrocene).

Oxidation of (1) in benzene with iodine gave mono-oxidized salt, $(C_{12}H_8)Fe_2$-$(C_5H_5)_2^+I_3^-\cdot0.5I_2$. Found: C, 29.23; H, 2.23. Calcd: C, 29.31; H, 2.06.

Table 2. Mössbauer parameters of as-indacenebis(cyclopentadienyliron) and biferrocene

Compound	Temperature (K)	Isomer shift* (mm sec^{-1})	Quadrupole splitting (mm sec^{-1})
as-Indacenebis(cyclopentadienyliron)	298	0.46	2.37
	78	0.55	2.42
Biferrocene	298	0.45	2.30
	78	0.55	2.34

* Relative to metallic iron foil.

The details will be published elsewhere concerning the oxidation state of the salt by means of Mössbauer spectroscopy.

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