The Enhanced Lewis Basicity of Ring-tilted Ferrocenes

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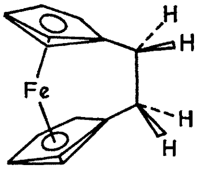
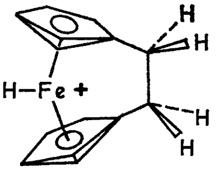
Summary. [2]Ferrocenophane, a ring-tilted ferrocene, is much more readily protonated than undistorted derivatives whose cyclopentadienyl rings occupy parallel planes.

FERROCENE is protonated by strong acids and the ^{1}H n.m.r. spectrum of this species reveals the presence of a strongly shielded proton bonded to the iron atom.[1] From molecular-orbital calculations,[2] it has been suggested that the cyclopentadienyl ring planes in this cation are mutually inclined and that the unique proton is co-ordinated to the central of three nonbonding metal orbitals located in the equatorial plane and oriented in the direction of the sandwich opening. In this connection, we earlier speculated[3] from indirect evidence that ring-tilted ferrocene derivatives should function as much stronger Lewis bases than their undistorted analogues and we now present confirmatory results.



(I)



(II)

[2]Ferrocenophane (alternatively 1,1′-dimethyleneferrocene) (I, m.p. 104—107°), a red sublimable solid, was prepared from the reaction of ferrous chloride with the dianion of 1,2-dicyclopentadienylethane which, in turn, was obtained by treatment of 1,2-dibromoethane with sodium cyclopentadienide.[4] The structure of the compound was established from elemental and spectral analysis. In particular, the ^{1}H n.m.r. spectrum ($CDCl_3$) consisted of two triplets (centred at τ 5·12, 6·00) and a sharp singlet (τ 6·99) in the intensity ratio 1 : 1 : 1. The large separation of the cyclopentadienyl α- and β-proton resonances is particularly diagnostic of a ring-tilted alkyl-bridged ferrocene derivative.[5]

The absorption maximum appearing at longest wavelength (430—480 nm) in the electronic spectra of ferrocene derivatives corresponds to the excitation of an electron from a nonbonding orbital (essentially 3*d*) located on the metal atom and we have earlier demonstrated[6] the sensitivity of this band to ring-tilting. In the spectrum of [2]ferrocenophane (I) in ethanol, this absorption appears at 472 nm (ϵ 450) but disappears upon addition to the solution of sulphuric acid in low concentration ($<0{\cdot}1\%$ v/v) whereupon a stable new species [probably (II)] is formed which lacks pronounced absorption at wavelengths longer than 400 nm. Under similar conditions, the spectra of ferrocene and its simple alkyl derivatives including [3]ferrocenophane (whose rings may be slightly tilted[7]) are not significantly affected by the presence of acid at much greater concentration (>100 times). The sensitivity of the protonation process to solvent effects has so far prevented determination of the ^{1}H n.m.r. spectrum of the cation and preliminary attempts to isolate a pure salt have been unsuccessful.

The results demonstrate, however, that ring-tilt distortion of the ferrocene nucleus is accompanied by an increase in Lewis basicity. Further investigation of the structure and reactivity of the protonated species should provide insight into the viability of the Ballhausen and Dahl bonding postulate[2] and permit evaluation of the process of proton exchange between the iron and ring carbon atoms.

(*Received, November 7th,* 1969; *Com.* 1689.)

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