Journal of Organometallic Chemistry, 194 (1980) C14—C18

Preliminary communication

SYNTHETIC STUDIES WITH IRON CARBONYL COMPLEXES, PROTONATION AND ACETYLATION OF TRICARBONYL-5-*exo*-(ISOPROPENYL)CYCLOHEXA-1,3-DIENEIRON(0)

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(Received April 8th, 1980)

Summary

Tricarbonyl-5-*exo*-(isopropenyl)cyclohexa-1,3-dieneiron(0) was prepared by the Wittig reaction. Protonation and acetylation of this complex gave 1-substituted cyclohexadienyl cations. The mechanistic implications of this observation are discussed.

Electrophilic attack on (triene)$Fe(CO)_3$ complexes generally results in the formation of dienyl cations [1]. We report below the formation of dienyl complexes by protonation and acetylation of a complex in which an sp^2 carbon atom separates the coordinated diene and the free olefinic portion of the molecule.

Tricarbonyl-5-*exo*-(isopropenyl)cyclohexa-1,3-dieneiron(0) (I) was obtained in two steps from tricarbonyl-5-*exo*-cyano(cyclohexa-1,3-diene)iron(0) [2] by treatment with methylmagnesium iodide [3] followed by a Wittig reaction on the resulting acetyl complex. Methyltriphenylphosphonium iodide was stirred with an equimolar amount of n-butyllithium for 15 minutes (Scheme 1). Tricarbonyl-5-*exo*-(acetyl)cyclohexa-1,3-dieneiron(0) was added and after 1 h the reaction was quenched, extracted into ether, and chromatographed to separate I from a little unreacted starting material. The complex has an olefin stretch at 1645 cm^{-1} in its IR spectrum and a bending mode at 898 cm^{-1} due to the olefinic methylene group. The PMR spectrum has a methyl group at τ 8.46 ppm. Decoupling at this position transforms the multiplet at 5.38 ppm to an AB spin system: the sp^2 methylene group. The inner and outer protons are found in the expected positions 4.70 and 7.07 ppm, and these and the signal at 5.38 ppm, all integrate for two protons each. The ^{13}C NMR spectrum is unusual as the two inner carbons are accidently degenerate at 85.1 ppm.

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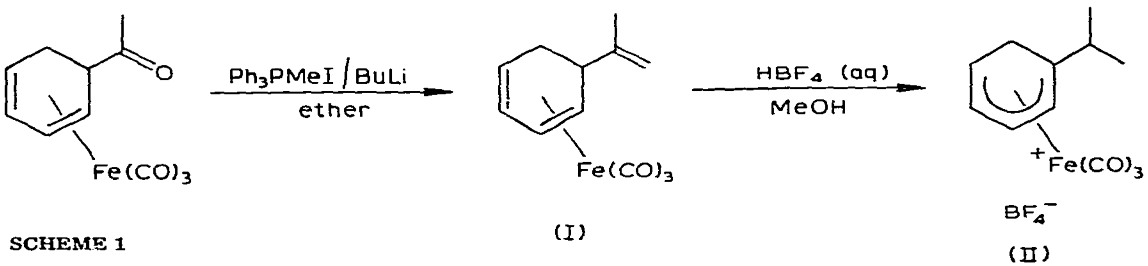


SCHEME 1

Protonation with HBF_4 in methanol forms tricarbonyl-1-isopropyl(cyclohexadienyl)iron(0) tetrafluoroborate (II). The ^{13}C NMR spectrum of II is conveniently recorded in acetonitrile since the methyl and cyanide resonances of the solvent neatly bracket the signals from the complex (Fig. 1). In comparing the ^{13}C NMR spectra of substituted dienyls with the parent complex, Birch and Pearson [4] comment that a methyl group at the 1-position shifts the resonance considerably downfield. The isopropyl group has a similar but larger effect, changing the order of the peaks so that C(1) is found at lowest field at 100.8 ppm. C(2) comes next at 99.5 ppm then C(4) (94.5 ppm), C(3) (85.3 ppm) and C(5) (61.0 ppm). The peak assignments are based on a gyrogated spectrum which clearly shows the signal at 100.8 ppm as a singlet.

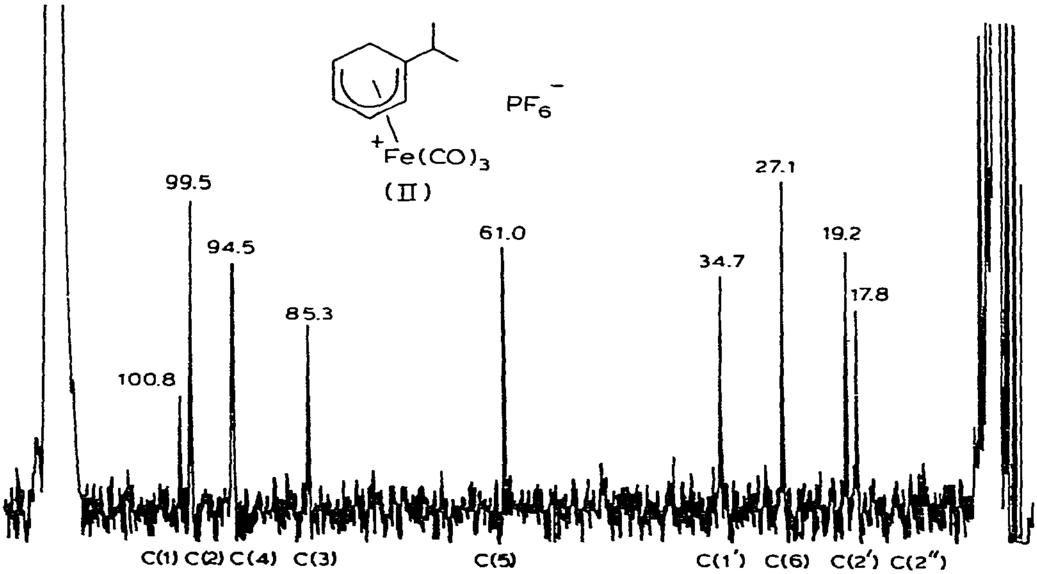
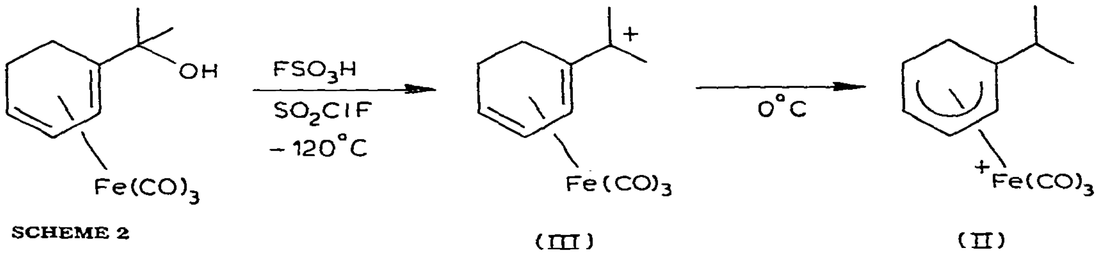
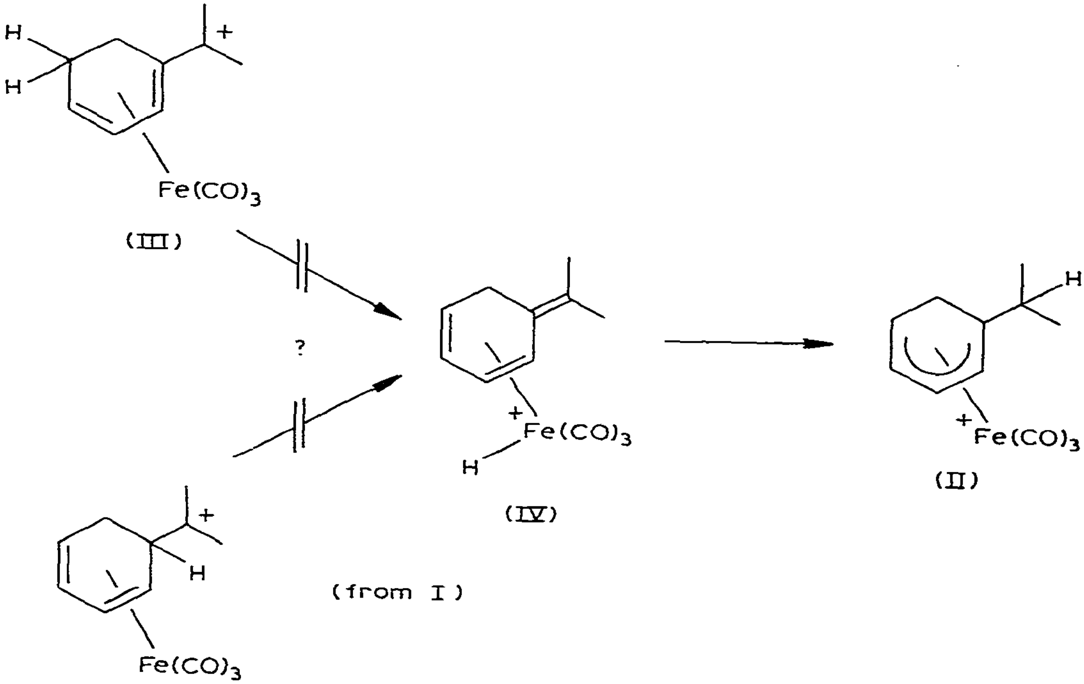


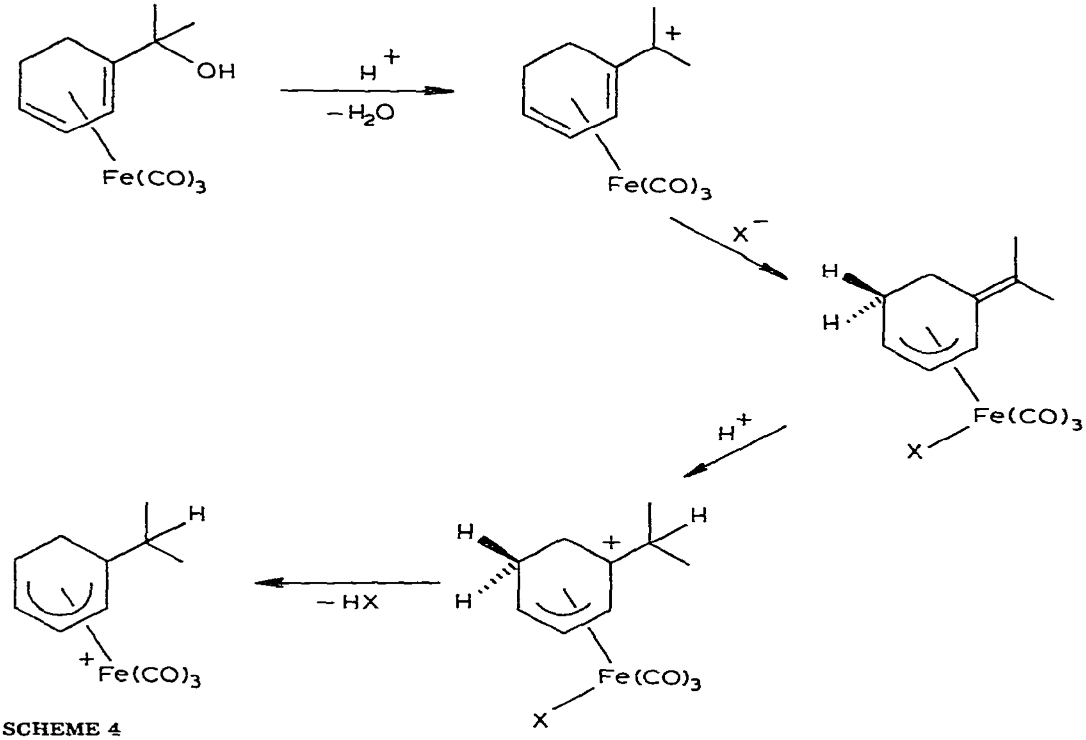
Fig. 1. ^{13}C NMR spectrum of compound II.



SCHEME 2

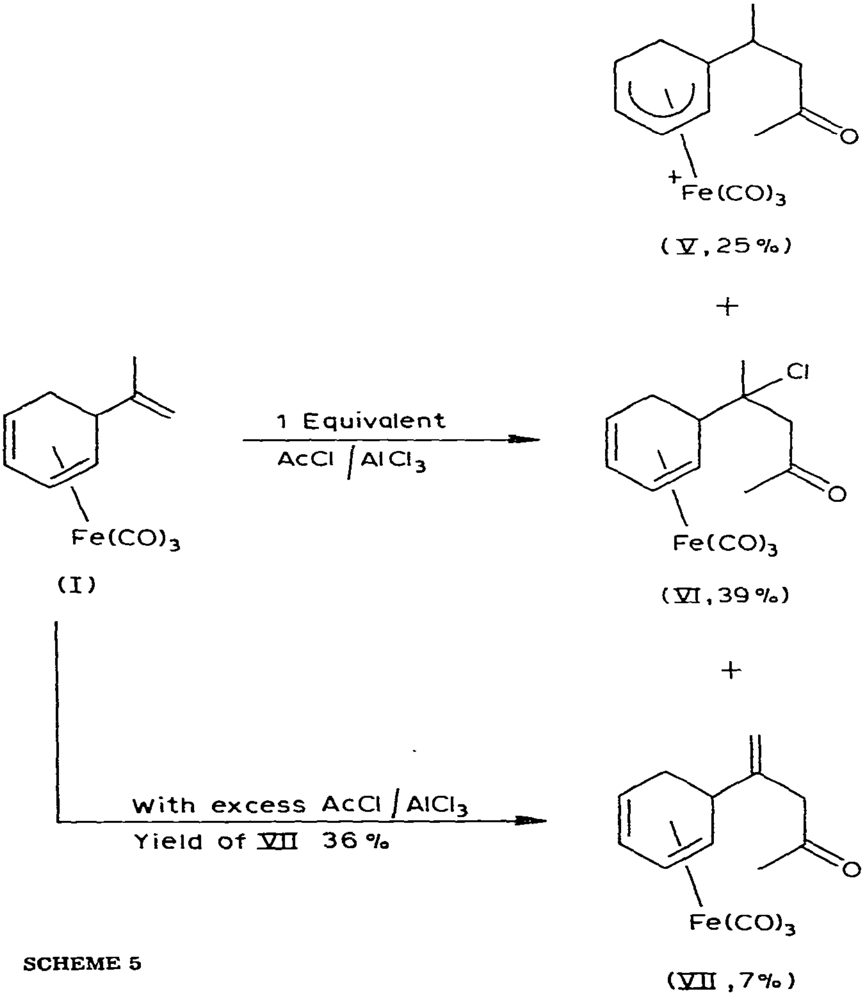


SCHEME 3



SCHEME 4

This complex is reported by Sorensen et al. [5] as the product of protonation of tricarbonyl-1-(1-hydroxyisopropyl)cyclohexa-1,3-dieneiron(0). Use of 1/3 FSO_3H/SO_2ClF at −120°C permitted the characterisation of the intermediate carbonium ion (III), the initial product of protonation (Scheme 2). Sorensen found III to be stable in this medium at temperatures up to 0°C, and to rearrange only slowly at this temperature to give II. The rearrangement is more extensive than that required to convert I into II, so it was decided to examine the temperature dependence of this latter process. Protonation was carried out by slow addition of FSO_3H to a solution of I in liquid SO_2 at −78°C. The ion formed was identified as II by its ^{13}C NMR spectrum. Even at this low temperature, the tertiary carbonium ion formed initially by protonation rearranges rapidly and is not observed. This might suggest that the triene intermediate IV is not involved, since this would be common to protonations of side-chains at both the 1- and 5-positions on the cyclohexadiene ring (Scheme 3). This leaves the possibility of an allyl intermediate, similar to that suggested by Sorensen to explain his deuterium-incorporation results. Coordination at the metal by the counterion



SCHEME 5

seems more probable than the dicationic intermediate previously proposed through an analogy with a report by Kaesz et al. [6]. These latter results have since been re-interpreted [7] and in the light of this, a revised mechanism is proposed in Scheme 4. For the protonation of a side-chain at the 5-position, reported here, a much simpler process may be involved, namely a 1,2-hydride shift (Scheme 5).

Acetylation of I was carried out by the Perrier method. A 1/1 mixture of acetyl chloride and aluminium trichloride was fused over a flame, dissolved in dichloromethane and a slight excess of this reagent was added by syringe to a stirred solution of I in dichloromethane at −78°C. The dienyl cation V was obtained by pouring the reaction mixture into ether, extracting with water, adding ammonium hexafluorophosphate and extracting again with dichloromethane. Other products were also formed, however, and were recovered from the ether fraction: tricarbonyl-5-*exo*-(1-methyl-1-chloro-3-oxobutanyl)cyclohexa-1,3-dieneiron(0) (VI) and tricarbonyl-5-*exo*-(1-acetonylethenyl)cyclohexa-1,3-dieneiron(0) (VII). The former is produced by chloride addition to the tertiary cation first produced in the acetylation process. Its formation is prevented by the use of a large excess of $AlCl_3/CH_3COCl$. In this case the major product is VII, obtained in 36% yield.

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