

Notes

Reactions of 2,3-Bis(carbomethoxy)-9,10-dichlorobicyclo[6.2.0]-deca-2,5-diene with $\text{Fe}_2(\text{CO})_9$

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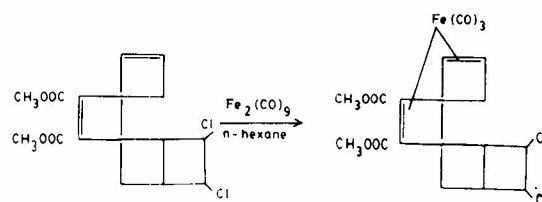
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The complex 2, 3-bis(carbomethoxy)-9, 10-dichlorobicyclo[6.2.0]-deca-2, 5-diene- $\eta^4(2, 5)$ -tricarbonyliron (II) has been synthesized by the reaction of 2, 3-bis(carbomethoxy)-9, 10-dichlorobicyclo[6.2.0]-deca-2, 5-diene (I) with $\text{Fe}_2(\text{CO})_9$. The complex has been characterized by IR, PMR, mass spectra and elemental analyses.

Diironenneacarbonyl, $\text{Fe}_2(\text{CO})_9$, is a good dehalogenating as well as a complexing agent. This remarkable property of the compound was utilized in the first synthesis of cyclobutadiene-tricarbonyliron by reacting it with *cis*-3, 4-dichlorocyclobutene^{1,2}. Similarly when $\text{Fe}_2(\text{CO})_9$ was reacted with 3, 4-bis(bromomethyl)-1, 3, 5-cycloheptatriene, dehalogenation and complexation took place giving rise to (3, 4-dimethylene-1, 5-cycloheptadiene)tricarbonyliron³. The title ligand of the present work, 2, 3-bis(carbomethoxy)-9, 10-dichlorobicyclo[6.2.0]-deca-2, 5-diene (I), is a precursor in the synthesis of *cis*-3, 4-dichlorocyclobutene by thermolytic decomposition⁴. The objective of the present work was to see if it was possible to dehalogenate (I) at 9, 10-positions introducing first an olefinic bond in the bicyclic ring and then coordinating this double bond with an $\text{Fe}(\text{CO})_3$ moiety.

Reactions of (I) with $\text{Fe}_2(\text{CO})_9$ under various conditions failed to produce any observable dehalogenation; on the other hand, a complex 2, 3-bis(carbomethoxy)-9, 10-dichlorobicyclo[6.2.0]-deca-2, 5-diene- $\eta^4(2, 5)$ -tricarbonyliron (II) was isolated as a yellow viscous oil in good yield [over 70% based on $\text{Fe}_2(\text{CO})_9$] which subsequently crystallized into plate like crystals; m.p., 130°. Mass spectra showed the parent ion peak at m/z 457, and the loss of three carbonyl groups. PMR: (C_6D_6) τ 4.1-4.3 (*t*, 2H, $J = 4.5$ Hz, $J = 5$ Hz), 5.9-6.1 (*m*, 2H), 6.2-6.3 (*m*, 4H), 6.6 (*s*, 6H), 7.4-7.7 (*m*, 2H). The signals were compared with those of the free ligand (I), which clearly showed upfield shift of protons at 5, 6-positions and also a slight upfield shift of methyl signals of the methylcarboxyl groups attached to double bonded carbons at 2, 3-positions. IR spectrum of the complex in cyclohexane showed three sharp peaks at 2060, 2010



Scheme 1

and 1986 cm^{-1} indicating a fairly high degree of deviation from C_3 local symmetry.

Thus, it is clear that $\text{Fe}_2(\text{CO})_9$ failed to dehalogenate the ligand (I); instead, coordination took place with $\text{Fe}(\text{CO})_3$ moiety at double bonds in 2 and 5 positions of the bicyclo ligand as shown in Scheme 1.

Experimental procedure

All the reactions of $\text{Fe}_2(\text{CO})_9$ and ligand (I) were carried out under oxygen-free dry nitrogen. Infrared spectra were recorded on a Beckman 4220 spectrophotometer, PMR spectra were taken on a Varian EM-390 (90 MHz) spectrometer. Mass spectra were recorded on an MS-12 high resolution spectrometer. Elemental analyses were performed in the Microanalytical Laboratory, Department of Chemistry, University of Manchester, U.K. Chlorine, used for the preparation of (I), was directly used from the reagent bottle. Low temperature (-30°), necessary during the preparation of (I), was maintained by an appropriate mixture of acetone and solid carbon dioxide. Cyclooctatetraene was freshly distilled over calcium hydride (42°, 20 mm Hg). Dimethylacetylene dicarboxylate was an Aldrich sample and it was used as such without further purification. Solvents were freshly distilled over appropriate drying agents. $\text{Fe}_2(\text{CO})_9$ was prepared by irradiating $\text{Fe}(\text{CO})_5$ in glacial acetic acid for 6 hr; yield was almost quantitative.

Preparation of (I)

The dichloro ligand (I) was prepared by well known methods^{4,5}. It was further crystallized from diethyl ether to white needle-shaped crystals; m.p. 80° . PMR: (CDCl_3) τ 3.3-3.5 (*t*, 2H, $J = 4.5$ Hz, $J = 5.0$ Hz), 5.6-5.9 (*m*, 2H), 6.1-6.2 (*m*, 4H), 6.25 (*s*, 6H), 7.1-7.3 (*m*, 2H). [Found: C, 52.9; H, 4.9; Cl, 22.0. $\text{C}_{14}\text{H}_{16}\text{O}_4\text{Cl}_2$ requires: C, 52.7; H, 5.0; Cl, 22.3%].

Reaction of (I) with $\text{Fe}_2(\text{CO})_9$

$\text{Fe}_2(\text{CO})_9$, 10 g (27.4 mmol) and the ligand 8.70 g (27.4 mmol) were stirred in the absence of light in *n*-hexane (100 ml) for 24 hr under nitrogen. Then, the

reaction mixture was refluxed for 18 hr. The course of the reaction was monitored by IR. IR monitoring indicated the formation of a monoolefin-Fe(CO)₄ complex, which, however, could not be isolated. At the end of the reaction, the solution was filtered over kieselguhr and the solvent was removed *in vacuo* when a greenish-yellow viscous mass was obtained. This was chromatographed over silica (sorbisil-60), eluting with toluene. This gave a single yellow band, which on stripping off the solvent *in vacuo* gave complex (II) as a thick viscous yellow liquid. It slowly crystallized into airstable plates (m.p., 130°) over a period of two months. IR: νCO 2060, 2010 and 1986 cm⁻¹. PMR: (C₆D₆) τ 4.1-4.3 (*t*, 2H, *J*=4.5 Hz, *J*=5.0 Hz), 5.9-6.1 (*m*, 2H), 6.2-6.3 (*m*, 4H), 6.6 (*s*, 6H), 7.4-7.7 (*m*, 2H).

Mass spectra showed the parent ion at 457 and the loss of three carbonyl groups. [Found: C, 36.9; H, 3.3; Cl, 15.2. C₁₇H₁₆FeO₇Cl₂ requires: C, 36.6; H, 3.5; Cl, 15.5%].

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