

Synthesis & Reactions of 1,5,9-Cyclododecatrienetricarbonyliron

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The complexes *trans, trans, trans*-1, 5, 9-cyclododecatrienetricarbonyliron(I) and *trans, trans, cis*-1, 5, 9-cyclododecatrienetricarbonyliron(II) have been synthesized by the photochemical reaction of *trans, trans, cis*-1, 5, 9-cyclododecatriene with $\text{Fe}(\text{CO})_5$. The complexes have been characterized by their IR, NMR and mass spectra. On reaction of complex(I) with $\text{Ph}_3\text{C}^+\text{BF}_4^-$, hydride ion abstraction occurs to give trienyl salt, $\text{C}_{12}\text{H}_{17}\text{Fe}(\text{CO})_3\text{BF}_4$ (III) of *trans, trans, trans*-1, 5, 9-cyclododecatrienetricarbonyliron, which reacts with anionic nucleophile like CN^- to give a transannularcyanoketone, $\text{C}_{12}\text{H}_{17}\text{CNCO}$ (IV).

Synthesis of metal olefin complexes by using metal carbonyls is well established¹. Nevertheless, this general reaction offers scope for further interesting work if the structural features of the coordinated olefin are such that its reactivity on coordination can be fruitfully utilized for the synthesis of organic compounds which are otherwise difficult to synthesise or are synthesised by circumlocutious reaction paths. 1, 5, 9-Cyclododecatriene is one such cycloolefinic ligand that merits attention in this respect.

Materials and Methods

All the reactions were carried out under dry nitrogen. Infrared spectra were recorded on a Beckman 4220 spectrophotometer and were calibrated against polystyrene. PMR spectra were taken on a Varian EM-390 (90 MHz) spectrometer. Mass spectra were recorded on an MS-12 high resolution spectrometer. GLC was recorded on a GCD gas chromatograph (Pye Unicam), APL (APIEZONL) column 100-120 mesh chromosorb W.DMCS; column temp., 140°. Photochemical reactions were carried out by irradiating with a 125 watt medium pressure mercury lamp. Elemental analyses were performed in the microanalytical laboratory, Department of Chemistry, Jahangirnagar University.

Photochemical reaction of *cis, trans, trans*-1,5,9-cyclododecatriene with $\text{Fe}(\text{CO})_5$

Iron pentacarbonyl (7.53 g, ~0.038 mol) and *cis, trans, trans*-1, 5, 9-cyclododecatriene (18.64 g, ~0.115 mol) were irradiated in benzene (25 ml) in a sealed tube for 45 hr. The reaction mixture was then filtered on a kieselgur and the solvent was removed *in vacuo* from the filtrate when a yellow oil was obtained. Chromatographic separation of the yellow oil on silica gave two distinct bands (elution with pet. ether 40-60°).

The first band on removal of solvent gave an yellow oil, which was redistilled at 0.05 mm Hg/60° to give yellow oily complex(I), *all-trans*-1, 5, 9-cyclododecatrienetricarbonyliron, $\text{C}_{12}\text{H}_{18}\text{Fe}(\text{CO})_3$ [64% based on $\text{Fe}(\text{CO})_5$]; IR: ν_{CO} (cyclohexane) 1995 and 1975 cm^{-1} ; PMR: (CDCl_3) τ 2.5-2.8 (m, 2H), 3.6-5.3 (m, 4H), and 7.7-8.2 (m, 12H); MS: m/z 302 (M^+), 274 ($\text{M}^+ - \text{CO}$), 246 ($\text{M}^+ - 2\text{CO}$) and 218 ($\text{M}^+ - 3\text{CO}$). [Found: C, 59.7; H, 5.9. $\text{C}_{15}\text{H}_{18}\text{FeO}_3$ requires: C, 59.6; H, 6.0%]. Since the PMR of this complex showed almost identical peaks with that of its isomeric complex *cis, trans, trans*-cyclododecatrienetricarbonyliron(II), it was further necessary for identification to carry out oxidation by ceric sulphate and substitution by triphenylphosphine in cyclohexane by the usual procedure. The olefinic ligand was then subjected to GLC and its retention time (16 min) was compared with that of an authentic sample of *all-trans*-1, 5, 9-cyclododecatriene.

The second band on the chromatographic column, on removal of the solvent and subsequent distillation at 0.05 mm Hg/60°, gave an yellow oily complex, *cis, trans, trans*-1, 5, 9-cyclododecatrienetricarbonyliron(II), $\text{C}_{12}\text{H}_{18}\text{Fe}(\text{CO})_3$ [28.8% based on $\text{Fe}(\text{CO})_5$]; IR: ν_{CO} (cyclohexane) 2040 and 1975 cm^{-1} ; PMR: (CDCl_3) τ 2.5-2.8 (m, 2H), 3.6-5.3 (m, 4H), 7.7-8.2 (m, 12H); MS: m/z 302 (M^+), 274 ($\text{M}^+ - \text{CO}$), 246 ($\text{M}^+ - 2\text{CO}$) and 218 ($\text{M}^+ - 3\text{CO}$). [Found: C, 59.7; H, 5.9. $\text{C}_{15}\text{H}_{18}\text{FeO}_3$ requires: C, 59.6; H, 6.0%]. As in the case of complex(I), complex(II) was also subjected to both ceric oxidation and substitution reaction by triphenylphosphine to remove the olefinic ligand, which was then examined by GLC under identical conditions. The retention time (11 min) was compared with that of the authentic sample of *cis, trans, trans*-1, 5, 9-cyclododecatriene (m.p. -18°) and also with that of *all-trans*-1, 5, 9-cyclododecatriene (m.p. 34°). The

excess ligand of the reaction was found to be isomerized to *all-trans*-1, 5, 9-cyclododecatriene to the extent of 65% under GLC examination.

Reaction of all-trans-1, 5, 9-cyclododecatrienetricarbonyliron(I) with trityltetrafluoroborate

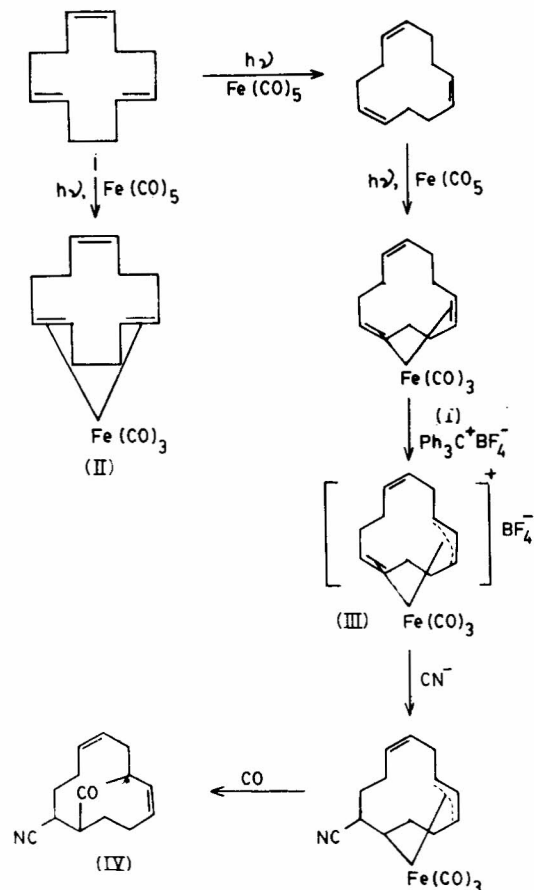
Solution of the complex(I) (0.5 g, ~ 0.0017 mol) dissolved in the minimum volume of dry dichloromethane and triphenylmethyltetrafluoroborate (0.66 g, ~ 0.002 mol) similarly dissolved in the same solvent were stirred together at room temperature under nitrogen for 1 hr; when a precipitate began to appear, dry diethyl ether was added to complete precipitation. The dirty yellow precipitate was filtered under nitrogen and the pale plate like crystals of *trans*-cyclododecatrienyltricarbonyliron tetrafluoroborate(III) were recrystallized from dichloromethane/diethyl ether (50/50, v/v), m.p. 280° (dec.); IR: $\nu_{\text{CO}}(\text{CH}_2\text{Cl}_2)$ 2140 and 2070 cm^{-1} . [Found: C, 46.3; H, 4.3. $\text{C}_{15}\text{H}_{17}\text{FeO}_3\text{BF}_4$ requires: C, 46.4; H, 4.4%]. Attempts to record PMR (SO_2 soln in a sealed tube) were, however, unsuccessful due to decomposition of the salt.

Reaction of the trienyl salt (III), $\text{C}_{12}\text{H}_{17}\text{Fe}(\text{CO})_3^+ \text{BF}_4^-$ with KCN

To an aqueous suspension (25 ml) (0.7 g, ~ 0.0018 mol) of the trienyl complex, potassium cyanide (0.116 g, ~ 0.0017 mol) in 25 ml water was added and the mixture was stirred for 1 hr under nitrogen. Then the reaction mixture was extracted with ether. Removal of the ether solution (duly dried with MgSO_4) gave a yellow solid. This on recrystallization at -80° from a mixture of ether and pentane (50/50, v/v) gave a pale yellow crystalline compound(IV), m.p. 76° (yield 30%); IR (nujol): 2215 (weak) and 1630 cm^{-1} (very strong), PMR: τ 3.1 (m, 4H), 5.1 (m, 1H), 7.0-8.2 (m, 12H); MS: m/z , 215, 189, 187 and 161. [Found: C, 78.3; H, 7.7; N, 6.4. $\text{C}_{14}\text{H}_{17}\text{ON}$ requires: C, 78.1; H, 7.9; N, 6.5%]. Compound IV readily reacted with 2, 4-dinitrophenylhydrazine (the usual procedure) to give a reddish-yellow hydrazone derivative, m.p. 148° (dec.) [Found: C, 52.1; H, 6.4; N, 21.6. $\text{C}_{14}\text{H}_{15}\text{O}_4$ requires: C, 52.0; H, 6.5; N, 21.7%].

Results and Discussion

Complexation of 1, 5, 9-cyclododecatriene with an $\text{Fe}(\text{CO})_3$ moiety has been reported earlier, but the product is not well identified possibly because of the isomerization of the ligand amongst its various conformational isomers due to influence of the metal ion in low oxidation state². As a result one may expect, in addition to the desired complex, isomeric forms of the complex. This indeed happens in the case of the thermal or photochemical reaction of 1, 5-



cyclooctadiene and iron pentacarbonyl. In addition to 1, 5-CODFe(CO)₃, 1, 3-CODFe(CO)₃ is also a major product³.

In the present work *cis*, *trans*, *trans*-1, 5, 9-cyclododecatriene was photochemically reacted with $\text{Fe}(\text{CO})_5$ to get a number of diene $\text{Fe}(\text{CO})_3$ complexes. Examination of the excess ligand by GLC indicated 65% isomerization of *cis*, *trans*, *trans*-1, 5, 9-cyclododecatriene to *all-trans*-1, 5, 9-cyclododecatriene. Of the three diene $\text{Fe}(\text{CO})_3$ complexes isolated from the reaction mass, *all-trans*, 1, 5, 9-cyclododecatriene $\text{Fe}(\text{CO})_3$ [64% based on $\text{Fe}(\text{CO})_5$] and *cis*, *trans*, *trans*-1, 5, 9-cyclododecatriene $\text{Fe}(\text{CO})_3$ were found to be major products. There was no indication of isomerization of the ligand by shifting of the double bond which would eventually give rise to a diene complex with $\text{Fe}(\text{CO})_3$ moiety bonded to a butadiene fragment.

We have also examined the reactivity of the coordinated ligand for complex(I) with respect to oxidation by triphenylmethyltetrafluoroborate (trityl) followed by nucleophilic attack (CN^-) on the resulting trienyl salt. No neutral complex, however, could be isolated. Instead, a transannulocyanoketone(IV) was obtained which was characterized by IR, PMR, mass spectra and by the usual ketone test. Such a

transannularcyanoketone was previously obtained by Lewis *et al.*⁴ by reaction of cyclooctadienyltricarboxyliron tetrafluoroborate with KCN in an atmosphere of carbon monoxide. It was explained that due to attack by a nucleophile on the dienyl salt, a neutral complex in which the iron atom is coordinated to the olefinic moiety by a π -allyl and σ -bond is first produced, which then undergoes CO insertion at the metal to carbon bond. The decomposition of the resulting acyl complex gives rise to the transannularcyanoketone. Indeed, it is separately shown that 1, 2, 3, 6-cyclooctadienetricarboxyliron, which has similar mode of bonding, undergoes a facile CO insertion, giving rise to a transannularketone³. Reactions described thus are summarized in Scheme 1.

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