Synthesis & Reactions of trans-1,4,9-Decatrienetricarbonyliron

S S ULLAH*, M E MOLLA & A H MOLLA
Department of Chemistry, Jahangirnagar University, Savar, Dhaka, Bangladesh
Received 18 June 1984; revised and accepted 16 August 1984

The complex trans-1,4,9-decatrienetricarbonyliron (complex-I) has been synthesized by the photochemical reaction between trans-1,4,9-decatriene and Fe(CO)₅. Complex (I) reacts with Ph₃C⁺ BF₄⁻, to give trienyl salt (II), C₁₃H₁₆Fe(CO)₅BF₄⁻.

The trienyl salt (II) reacts with NaBH₄ to give an isomeric neutral complex (III), all-trans-2,4,9-decatrienetricarbonyliron. The complexes have been characterized by their IR, PMR and mass spectra and elemental analyses.

Photochemical syntheses of complexes by the reaction of cycloolefins with Fe(CO)₅, are well established in a recent paper⁴ we reported the synthesis of all-trans- and trans,trans,cis-1,5,9-cyclooctadecatrienetricarbonyliron by the photochemical reaction of trans,trans,cis-1,5,9-cyclooctadecatriene with Fe(CO)₅. We also observed conformational isomerization of trans,trans,cis-1,5,9-cyclooctadecatriene to an all-trans isomer in the presence of Fe(CO)₅ and the formation of a new complex arising by the dimerization of the all-trans-complex⁴. Attempts to synthesize complexes of acyclic nonconjugated polyenes with Fe(CO)₅ are, however, few. With a view to synthesizing this type of complex trans-1,4,9-decatriene was allowed to react photochemically with Fe(CO)₅. Hydride ion abstraction followed by hydride ion attack on the resulting trienyl salt of the trans-1,4,9-decatrienetricarbonyliron complex thus obtained has also been investigated. The results are discussed in this paper.

Materials and Methods

For general remarks, i.e. the types of instruments used for recording the spectra, procedure for carrying out the photochemical reactions etc. see ref 4.

Photochemical reaction of trans-1,4,9-decatriene with Fe(CO)₅: Formation of trans-1,4,9-decatrienetricarbonyliron (complex-I)

A mixture containing pentacarbonyliron (10 g, 0.0511 mol) and trans-1,4,9-decatriene (6.96 g, 0.0511 mol) in benzene (20 ml) was irradiated in a sealed tube for 43 hr. Removal of solvent in vacuo afforded a yellow oil, which was subjected to column chromatography over silica. Elution of a distinct band (with pet. ether 60-80°) and evaporation of the solvent under reduced pressure yielded complex-I as a yellow oil; yield 65 % based on Fe(CO)₅; IR: vCO (cyclohexane) 2040 and 1975 cm⁻¹; PMR: (CDCl₃): 4.5-4.7 (m, 3H), 4.9-5.15 (m, 5H) and 7.2-8.5 (m, 8H); MS: m/z 276 (M⁺), 248 (M⁺ − CO), 220 (M⁺ − 2CO), 192 (M⁺ − 3CO) and 136 [M⁺ − Fe(CO)₅] (Found: C, 56.7; H, 5.6. C₁₃H₁₆FeO₃ requires C, 56.5; H, 5.7 %).

Reaction of complex-I with triphenylmethyldifluoroborate: Formation of complex-II

A solution of complex-I (4 g, 0.0145 mol) in minimum volume of dry dichloromethane was added to a solution of triphenylmethyldifluoroborate (5.26 g, 0.0159 mol) in the same solvent and the mixture stirred at room temperature under nitrogen for 3 hr. When a dark precipitate began to appear, dry ether was added to complete precipitation. The dark coloured trienyl salt was separated by decantation, dried in vacuo, redissolved in CH₂Cl₂, filtered and reprecipitated by adding dry ether to give dark violet complex-II; yield 73.3 %; IR: vCO (nujol mull) 2140, 2100 and 2075 cm⁻¹ (Found: C, 51.2; H, 4.7. C₁₃H₁₆FeO₃BF₄ requires C, 51.1; H, 4.9 %).

Reaction of complex-II with NaBH₄: Formation of complex-III

To an aqueous suspension (25 ml) of trienyl salt (complex-II, 1.5 g, 0.0042 mol) was added sodium borohydride (0.016 g, 0.0042 mol) in water (5 ml) and the mixture stirred for 1 hr under nitrogen atmosphere
Results and Discussion
The structure of complex-I has been confirmed on the basis of IR, PMR and mass spectra and elemental analyses. The signals at $\tau$ 4.5-4.7 have been assigned to the free olefinic protons and those at higher field at $\tau$ 4.9-5.15 to the olefinic protons at 1,4-double bonds involved in coordination. This upfield shift has been interpreted as being due to substantial negative charge on the coordinated olefinic system. The signals at $\tau$ 7.2-8.5 have been attributed to the methylene protons bonded to the $sp^3$ carbons. The mass spectrum of complex-I exhibited molecular ion peak at $m/z$ 276 and other important peaks at $m/z$ 248 ($P-CO$), 220 ($P-2CO$), 192 ($P-3CO$) and 136 ($M^+ - Fe(CO)_3$) (Found: $C$, 56.7; $H$, 5.6. $C_{13}H_{16}FeO_3$ requires $C$, 56.5; $H$, 5.7%).

Reduction of trienyl salt (II) with $NaBH_4$ yields a neutral complex (III) which is found to be all-trans-2,4,9-decatrienetricarbonyliron, an isomer of complex (I). The PMR signals in the region $\tau$ 4.5 to 4.7 in the PMR spectrum of III have been assigned to the free olefinic protons whereas those in the region $\tau$ 4.8-5.2 are attributed to the protons attached to the coordinated double bonds. The higher field signals at $\tau$ 7.2-8.5 have been assigned to the methylene protons bonded to the $sp^3$ carbons. The singlet at $\tau$ 9.2 is due to the methyl protons. The characteristic IR and PMR spectra indicate that two of the three double bonds are coordinated to an Fe(CO)$_3$ moiety. The neutral complex (III) exhibits parent peak at $m/z$ 276 in its mass spectrum. Other important peaks at $m/z$ 248, 220, 192 and 136 arise by the successive loss of three CO groups and Fe indicating the presence of Fe(CO)$_3$ moiety in the complex. The peak at $m/z$ 121 is due to the loss of CH$_3$ group from the isomerized all-trans-2,4,9-decatriene ligand. The spectral evidences lead to structure (III) for the product obtained by the reaction of trienyl salt (II) with $NaBH_4$. This is isomeric with complex-I.

Acknowledgement
We thank the Department of Chemistry, Tohoku University, Japan for PMR and mass spectra and elemental analyses.

References