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IRON CARBONYL COMPLEXES OF PENTALENE AND DIHYDROPENTALENE

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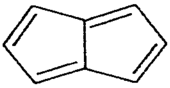
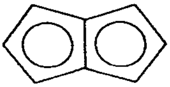
Summary

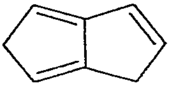
Treatment of 1,5-dihydropentalene with diiron enneacarbonyl affords iron carbonyl complexes of both pentalene and dihydropentalene.

Introduction

Theoretical calculations predict that the singlet ground state of pentalene (I) should be antiaromatic and possess the polyolefin structure Ia rather than the delocalized structure Ib [1]. In accord with these predictions all efforts to prepare pentalene by conventional synthetic organic methods have met with failure. Presumably this failure is due to the ease with which pentalene undergoes dimerization [2].


(Ia)


(Ib)

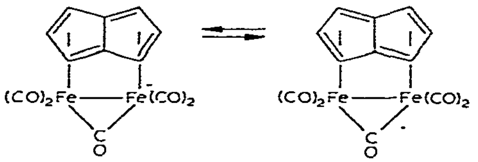

(II)

Recently it has been demonstrated that pentalene can be stabilized by coordination to various transition metals [2]. Starting materials for the preparation of these complexes include the pentalene dianion [2], cyclooctatetraene [2], and the pentalene dimer [3]. In this report we describe the conversion of 1,5-dihydropentalene (II) [4] to iron carbonyl complexes of both pentalene and dihydropentalene [6].

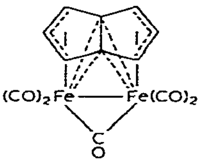
Discussion and results

In contrast to previous results obtained with substituted dihydropentalenes [5], reaction of 1,5-dihydropentalene (II) with $Fe(CO)_5$ at 105°C failed to yield an iron tricarbonyl complex of pentalene. Preparation of a pentalene iron carbonyl complex was achieved, however, on treatment of II with $Fe_2(CO)_9$ in ether at 45°C. This reaction produced at least five organometallic derivatives, three of which are described here.

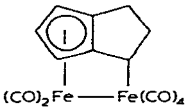
The $CI(CH_4)$ mass spectrum of the first compound isolated showed an abundant $M + 1$ ion characteristic of molecular weight at m/e 355. Fragmentation produced under EI conditions indicated the presence of five carbonyls, two metal atoms, and a C_8H_6 organic ligand. Both terminal and bridging carbonyl groups in the complex were indicated by strong signals in the IR at 1775 cm^{-1} and between 1900-2100 cm^{-1}. Information about the structure of the organic ligand was obtained from the 100 MHz PMR spectrum which exhibited two signals, a triplet and a doublet with intensities in the ratio of 1/2. Since protons on internal and terminal carbons of coordinated dienes possess different chemical shifts [7], a pattern of three signals having intensities in the ratio 1/1/1 would be expected for a pentalene ligand with a fixed polyolefin structure IIIa. Only a rapidly equilibrating mixture of structures IIIa and IIIb or the bis-π-allyl structure IV fit the observed data. Based on the X-ray crystallographic data for pentalene ruthenium carbonyl complex obtained by Stone et al. [2], we tentatively formulate the structure of the isolated compound as IV.



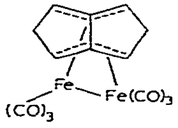
(IIIa) (IIIb)



(IV)



(V)



(VI)

The second compound isolated had a molecular weight of 384 as determined from the $CI(C_4H_{10})$ mass spectrum which exhibited an abundant $M + 1$ ion at m/e 385. High resolution mass spectrometry defined the elemental composition of the complex as $C_{14}H_8Fe_2O_6$. The presence of a dihydropentalene ligand, six carbonyls, and two iron atoms in the complex was evident from the EI fragmentation pattern. Since the IR spectrum showed five absorptions in the terminal carbonyl region and the pattern compared favorably with those published for 6-substituted fulvene diiron hexacarbonyl complexes [8], structure V was assigned to the isolated compound. This assignment was confirmed by the PMR spectrum which exhibited 3 signals in the region (τ 4.5-6.0) characteristic of cyclopentadienyl protons and 5 resonances at high field characteristic of protons bonded to saturated carbon.

Like V, the third compound isolated was shown to contain six carbonyls, two iron atoms, and a molecule of dihydropentalene by conventional EI mass spectrometry. $CI(CH_4)$ mass spectrometry was used to confirm the molecular weight assignment of 384. Only terminal carbonyl units were detected in the IR and the PMR spectrum consisted of a multiplet and two doublets with intensities in the ratio of 1/2/1. A coupling constant of 20 Hz, characteristic of geminal protons, was also observed. This information coupled with the integration data suggested that the coordinated dihydropentalene ligand contained a symmetrical bis-π-allyl unit. Accordingly, the compound was formulated as VI.

In an effort to determine which of the dihydropentalene complexes might be precursors to the pentalene complex, toluene solutions of V and VI were heated under nitrogen at 100°C for 1 h. Under these conditions VI was recovered in 95% yield. In contrast a 25 mg sample of V decomposed completely to a mixture containing IV (4%) and VI (28%).

Experimental

Reaction of 1,5-dihydropentalene (II) [4] with $Fe_2(CO)_9$

A suspension of 1.56 g (15 mmol) of 1,5-dihydropentalene (II) [4], 7.30 g (20 mmol) of $Fe_2(CO)_9$, and 100 ml of freshly distilled diethyl ether was stirred and heated at 45°C for 10 h under nitrogen. The reaction mixture was then cooled to room temperature, filtered through Celite and separated into three fractions using dry column chromatography on neutral Silica Gel with 1/1 benzene/hexane as the eluent.

Isolation of (1,2,3,3a,4,6a-hexahapto-1,2-dihydropentalene)-hexacarbonyldiiron-(Fe—Fe) (V).

Sublimation of the red liquid residue from Fraction I at 45°C (0.1 mm) afforded 193 mg(3.4%) of V as an air sensitive red oil; IR (CCl_4) 2062 (C≡O), 2036 (C≡O), 1986 (C≡O), 1962 (C≡O), and 1936 (C≡O) ±5 cm^{-1}; mass spectrum (70 eV), *m/e* (rel. intensity) 384 (2), 356 (7), 328 (10), 300 (21), 272 (19), 270 (20), 242 (33), 216 (51), 214 (73), 158 (100), and 102 (73); PMR (CS_2) τ 5.05 (d, 1, J = 2.0 Hz), 5.38 (t, 1, J = 2.0 Hz), 6.08 (d, 1, J = 2.0 Hz), 7.20 (m, 2), and 7.78 (m, 3). Anal. High resolution CI-MS (Ar-H_2O) [9]. Found: 384.9098. $C_{13}H_8Fe_2O_6 + H^+$ calcd.: 384.9096.

Isolation of (1,3,3a,4,6,6a-hexahapto-2,5, dihydropentalene)hexacarbonyldiiron(Fe—Fe) (VI).

Preparative TLC (neutral Silica Gel using 1/1 benzene/hexane as the eluent) of the residue remaining after sublimation of material in Fraction I afforded 50 mg (0.9% of VI as a yellow-orange solid: IR (CS_2) 2065s (C≡O), 2020vs (C≡O), 1990 vs (C≡O), 1980s (C≡O), 1960s (C≡O) ±5 cm^{-1}; mass spectrum (70 eV), *m/e* rel. intensity) 384 (15), 356 (46), 328 (27), 300 (22), 272 (16), 270 (25), 242 (50), 216 (50), 214 (79), 158 (100), and 102 (44); PMR (acetone-d_6) τ 6.07 (d, 2, J = 3.0 Hz), 6.42 (m, 1), and 7.60 (d, 1, J = 20 Hz), Anal. Found: C, 43.78; H, 2.15; Fe, 29.38. $C_{14}H_8Fe_2O_6$ calcd.: C, 43.80; H, 2.10; Fe, 29.09%.

Isolation of (octahapto-pentalene)-μ-carbonyl-tetracarbonyldiiron(Fe—Fe) (IV)

The residue from Fraction II contained 25 mg (0.4%) of IV as a green-black solid: IR (CCl_4) 2075 (C≡O), 2045 (C≡O), 2005 (C≡O), 1975 (C≡O), and 1775 (>C=O) ±5 cm^{-1}; mass spectrum (70 eV), *m/e* (rel. intensity) 354 (22), 326 (32), 298 (16), 270 (27), 242 (86), 214 (95), 158 (98), and 102 (100) PMR (acetone-d_6) τ 3.72 (t, 1, J = 1.5 Hz) and 6.18 (d, 2, J = 1.5 Hz) Anal. High resolution CI-MS (Ar-H_2O) [9]; Found: 354.9003. $C_{13}H_6Fe_2O_5 + H^+$ calcd.: 354.8991.

Acknowledgement

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