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Preliminary communication

Phenylpentalenediiron pentacarbonyl

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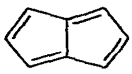
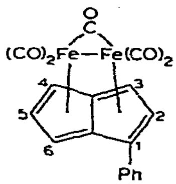
In recent years a number of examples have been reported in which coordination to an iron carbonyl moiety markedly enhances the stability of highly reactive organic molecules. Cyclobutadiene[1], heptafulvene[2], norbornadien-7-one[3], trimethylenemethane[4], and *cis*-cyclononatetraene[5], for example, have all been isolated and characterized in the form of iron tricarbonyl complexes.

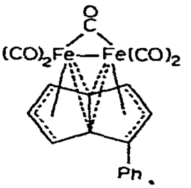
Pentalene (I), the lower homolog of naphthalene, is another example of a theoretically interesting hydrocarbon which is incapable of existing in the free state at ambient temperatures but might form a stable iron carbonyl complex★. To test this hypothesis, we have recently examined a number of reactions between derivatives of dihydropentalene and various iron carbonyls. In this report we describe the preparation and physical properties of (*octahapto*-1-phenylpentalene)-μ-carbonyltetracarbonyldiiron (Fe–Fe) (II), a stable transition metal π-complex of phenylpentalene.



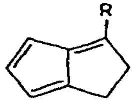
(I)



(IIa)



(IIb)



(IIIa) R = $(CH_3)_2N$
(IIIb) R = Ph

★ Hexaphenyl-[6] and bis(1,3-dimethylaminopentalene)[7] have been synthesized and found to be relatively stable, and evidence supporting the existence of 1-methylpentalene at –196° has recently been obtained[8]. Organometallic complexes of pentalenes, bis(pentalenylnickel)[9], diallylpentalenedinickel[10], tetraallylpentalenedichromium[10], hexaallylpentalenedizirconium[10], pentalenyl-1,5-cyclooctadienerhodium anion[11], and the dipentalenyliron anion [12] have been prepared recently. An approach to the synthesis of the benzopentalenylcyclopentadienyliron cation has also been reported[13].

Treatment of 3-dimethylamino-1,2-dihydropentalene (IIIa) with phenyllithium according to the procedure of Kaiser and Hafner[14] afforded 3-phenyl-1,2-dihydropentalene (IIIb) in 62% yield as a maroon solid. A 100 MHz NMR spectrum (acetone-d_6) of purified IIIb (sublimation at 75°/0.1 mm) displayed the following signals (τ): 2.22, 2.64 (5,m) C_6H_5; 3.22 (1,m) H_5; 3.60 (1,d, J = 5 Hz) H_6; 4.20 (1,m) H_4; 6.60, 7.30 (4,m) CH_2CH_2. Assignments were confirmed by double-resonance experiments.

Preparation of II was accomplished by heating a magnetically stirred solution of 3-phenyl-1,2-dihydropentalene (900 mg, 5 mmole) and iron pentacarbonyl (12 ml, 89 mmole) in 60 ml of deoxygenated methylcyclohexane at 110° for 12 h under nitrogen. The reaction mixture was then cooled, filtered through Celite, and concentrated under reduced pressure (20 mm). Preparative TLC of the residue on neutral Silica Gel using 5/1 benzene–acetone as the eluent afforded 260 mg (12%) of II as a dark green solid; m.p. 133–135° (N_2.) (Found: C, 53.10; H, 2.33; Fe, 25.89. $C_{19}H_{10}O_5Fe_2$ calcd.: C, 53.08; H, 2.35; Fe, 25.98%.)

The mass spectrum (70 eV) of II shows a molecular ion at *m/e* 430 (16) and abundant fragment ions corresponding to the successive loss of five carbon monoxide ligands and two iron atoms at *m/e* 402 (25), 374 (18), 346 (25), 318 (65), 290 (83), 234 (88), and 178 (100). The fragment ion at *m/e* 178 ($C_{14}H_{10}$) suggested the presence of a phenylpentalene ligand in the complex and provided the first indication that the starting material, 3-phenyl-1,2-dihydropentalene (IIIb), had been oxidized under the reaction conditions. The molecular weight of II was confirmed by a CI(CH_4) mass spectrum[15] of II which shows an abundant M+1 ion at *m/e* 431.

The presence of a bridging carbonyl in II is indicated by the IR spectrum (CCl_4) which shows a strong absorption at 1785 ± 5 cm^{-1}. Bands due to the terminal carbonyls in II occur at 1975, 2010, and 2040 ± 5 cm^{-1}.

The 100 MHz NMR spectrum of II contains signals at (τ) 2.62 (5,m) C_6H_5; 3.90 (1,d, $J_{2,3}$ = 3 Hz) H_2; 4.40 (1,t, $J_{4,5} = J_{5,6}$ = 3 Hz) H_5; 5.34 (1,d) H_4; 5.70 (2.m) H_3 and H_6. Assignments were confirmed by double-resonance experiments.

Although the above spectral data define the gross structural features of the phenylpentalene complex, differentiation of structures IIa and IIb must await X-ray analysis. Cyclooctatetraenediiron pentacarbonyl, which also contains a cyclic 8π-electron ligand, has recently been shown to have a structure similar to IIb [16].

Experiments designed to liberate the phenylpentalene ligand from the iron carbonyl complex and also to explore the chemistry of the coordinated pentalene ring system are planned in the near future.

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