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STABILIZATION OF HIGHLY REACTIVE CYCLIC POLYOLEFINS BY COORDINATION TO IRON CARBONYLS

METHYLPENTALENEDIIRON PENTACARBONYL

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Summary

Thermolysis of (*cis*-bicyclo[6.1.0]nonatriene)diiron hexacarbonyl (Fe—Fe) involves rearrangement of the starting organic moiety with formation of four iron carbonyl complexes. The major product is the known *cis*-8,9-dihydroindeneiron tricarbonyl complex (VI). Two complexes have the same formula, $C_9H_8Fe_2(CO)_5$ (VII and VIII); VII can be also obtained by reaction of VI with $Fe_2(CO)_9$, while VIII is a methylpentalenediiron pentacarbonyl complex and represents a further example of stabilization of this reactive organic molecule by coordination; IX is probably a polycyclic cyclopentadienyl derivative $[C_9H_9Fe(CO)_2]_2$.

Possible mechanisms for the formation of the four compounds are discussed.

Introduction

Metal carbonyls, and especially iron carbonyls, have been found to be very efficient in stabilizing reactive organic molecules. Thus stable iron tricarbonyl complexes of cyclobutadiene [1], heptafulvene [2], and *cis*-cyclononatetraene [3] have been obtained.

Pentalene (I) is another example of a highly reactive organic molecule which has been obtained in a relatively stable form only as the hexaphenyl- [4] or bis(1,3-dimethylamino-) [5] derivative. I and its 1-methyl-, 2-methyl-, and 1,3-dimethyl-derivatives have only been prepared at —196°. They show a great tendency to form dimeric products II.

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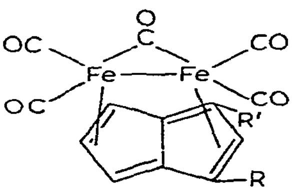
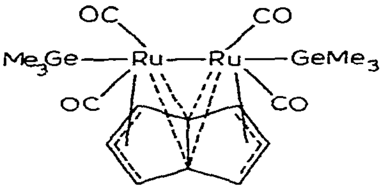
(I) (II)

Recently, stabilization of the pentalene moiety has been achieved by coordination to metal carbonyls. Thus, reaction of the corresponding 1,2-dihydropentalenes with $Fe(CO)_5$ involves formation of 1-phenyl- and 1-dimethylaminopentalenediiron pentacarbonyl (IIIa, b) [7]; fission of the corresponding pentalene dimers (II) with $Fe_2(CO)_9$ yields the 1,3-dimethyl- and the unsubstituted pentalene—$Fe_2(CO)_5$ complexes (IIIc, d) [8]; dehydrogenative transannular cyclization of cyclooctatetraene with *cis*-$Ru(CO)_4(GeMe_3)_2$ gives the bis(trimethylgermyldicarbonylruthenium)pentalene complex* (IV) [9].



(III)



(IV)

(a: R = phenyl, R' = H;
b: R = dimethylamino, R' = H;
c: R = R' = H;
d: R = R' = methyl.)

We report below the isolation and characterization of the similar 1-methylpentalenediiron pentacarbonyl complex, formed together with other complexes in the thermolysis of (*cis*-bicyclo[6.1.0]nonatriene)diiron hexacarbonyl (Fe—Fe) (V).

Experimental

The preparation and handling of the compounds were carried out under nitrogen. Solvents were dried before use. Infrared spectra were recorded on Perkin—Elmer Model 457 or 521 spectrometers. PMR spectra were measured on Varian T-60 or HA-60 spectrometers using TMS as an internal reference. The mass spectra were obtained on a Hitachi—Perkin—Elmer RMU-6D spectrometer. Melting points are uncorrected. Elemental analyses were carried out by Dörnis and Kolbe, Mülheim (West Germany).

cis-Bicyclo[6.1.0]-2,4,6-nonatriene [10] and *cis*-8,9-dihydroindene

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* The X-ray crystal and molecular structures of this complex have been resolved [9] and the complex can be depicted as IV. The spectroscopic data of III are similar to those for this structure.

[11] were prepared by published methods. The preparation of $C_9H_{10}Fe_2(CO)_6$ (V) and $C_9H_{10}Fe(CO)_3$ (VI) has been described previously [3a].

Thermolysis of $C_9H_{10}Fe_2(CO)_6$ (V)

A solution of $C_9H_{10}Fe_2(CO)_6$ (1.0 g, 2.5 mmol) in 15 ml of toluene was refluxed in nitrogen until no starting material remained (ca 15 h) the progress of the reaction being monitored by TLC. The brown mixture was filtered to remove solid material, and evaporated under reduced pressure to give a brown oil. This was transferred to an alumina (Merk, activity 2) column (2 × 30 cm). Elution with hexane gave a yellow band, and a brown band which remained at the head of the column. The yellow solution was evaporated to give 393 mg (yield 61%) of a yellow oil, which afforded pale yellow needles on crystallization at —50° from hexane. The spectroscopic features of this compound are identical to those of *cis*-8,9-dihydroindeneiron tricarbonyl (VI) [3].

Elution with a 1/1 benzene/hexane mixture allowed partial removal of the brown band at the head of the column. Three new bands appeared, a red band and a green band which were well separated at the bottom of the column, and a brown band which remained almost at the head of the column. The red fraction was evaporated to give 12 mg (yield 1.5%) of a red compound (VII) which shows the same spectroscopic characteristics as the compound obtained in the reaction of VI with $Fe_2(CO)_9$ in boiling *p*-xylene (see below).

The green fraction was evaporated to give 135 mg (yield 16%) of VIII, a dark green compound, which was recrystallized from CH_2Cl_2/hexane (m.p. 124—126°). The mass spectrum exhibited a parent ion peak at *m/e* 368, and those peaks expected for $P-(CO)_x$ ($x = 1-5$). The IR spectrum (cyclohexane) showed bands at 2024, 1998m, 1980 (terminal CO) and 1798 cm^{-1} (bridging CO). The PMR spectrum (C_6D_6) exhibited signals at τ 5.64 (1, t), 5.82 (1, d), 6.88 (1, d), 7.18 (1, d), 7.25 (1, d) and 8.82 ppm (3, s). (Analysis found: C, 45.57; H, 2.23; Fe, 30.11. $C_{14}H_8Fe_2O_5$ calcd.: C, 45.62; H, 2.19; Fe, 30.43%).

The brown band was eluted with benzene. The solution was evaporated to give a dark red solid (IX, 17 mg, yield 3%) which was crystallized from CH_2Cl_2/hexane (m.p. 174—176°). The mass spectrum exhibited a parent ion peak at *m/e* 458, and those peaks expected for $P-(CO)_x$ ($x = 1-4$). The IR spectrum (CS_2) showed a weak band at 2030 cm^{-1} (impurity?) and three strong bands at 1990, 1943 (terminal CO) and 1775 cm^{-1} (bridging CO).

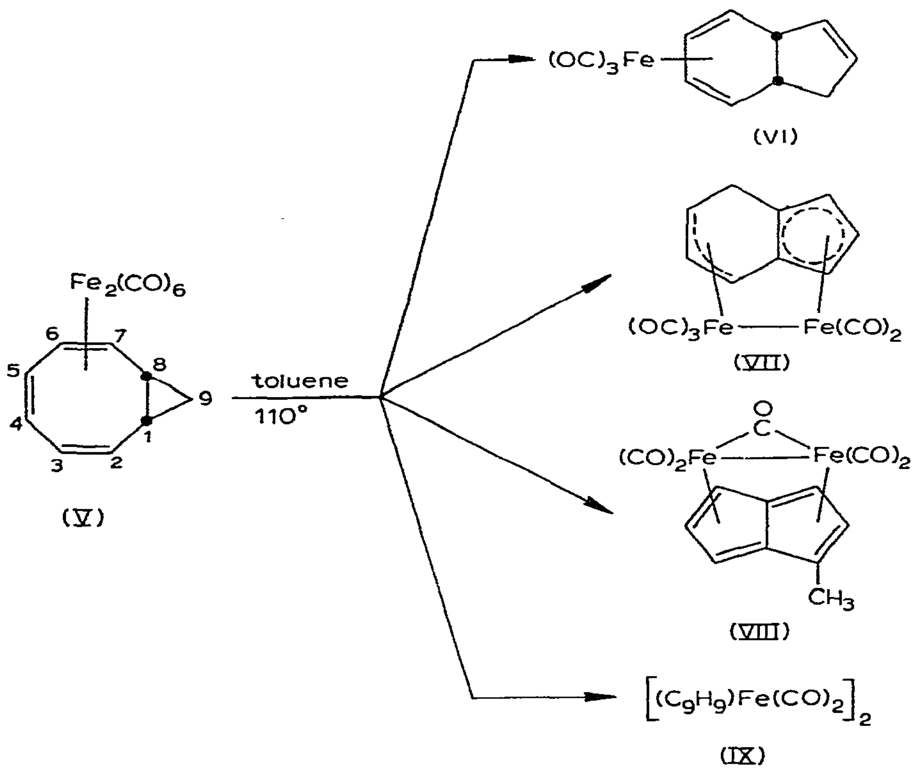
Preparation of $C_9H_8Fe_2(CO)_5$ (VII) from $C_9H_{10}Fe(CO)_3$ (VI) and $Fe_2(CO)_9$

The complex $C_9H_{10}Fe(CO)_3$ (516 mg, 2 mmol) was dissolved in 10 ml of *p*-xylene and $Fe_2(CO)_9$ (3 g, 8.25 mmol) was added. The mixture was stirred and refluxed under nitrogen for 3 h. It was then filtered and the solvent removed under reduced pressure. The dark red residue was chromatographed on an alumina (Merk, activity 2) column (2 × 20 cm) with hexane to give 230 mg of unreacted VI and a red band at the head of the column. Elution with a 1/1 mixture of benzene/hexane gave 86 mg of VII (20% based on $C_9H_{10}Fe(CO)_3$ consumed). The product was crystallized from hexane (m.p. 135—137°). The mass spectrum exhibited a parent ion peak at *m/e* 368, and those peaks expected for $P-(CO)_x$ ($x = 1-5$). The IR spectrum (CS_2) showed strong bands at 2034, 1988 and 1975 cm^{-1}. The PMR spectrum ($CDCl_3$) exhibited signals at

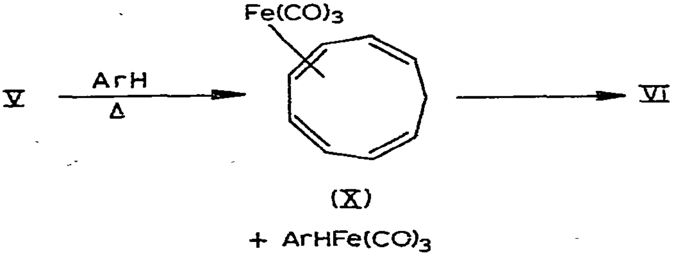
τ 4.6 (1, t), 5.05 (1, d), 5.1 (1, t), 5.25 (1, d), 6.05 (1, d), 6.8 (1, m), 7.75 (1, d) and 8.35 ppm (1, dd). (Analysis found: C, 45.55; H, 2.16; Fe, 30.25. $C_{14}H_8Fe_2O_5$ calcd.: C, 45.62; H, 2.19; Fe, 30.43%.)

Results and discussion

Thermolysis of $C_9H_{10}Fe_2(CO)_6$ (V) in boiling toluene gives the four compounds VI—IX.

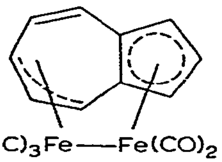


The formulation of VI as *cis*-8,9-dihydroindeneiron tricarbonyl is based on comparison of its PMR and IR spectra with those of an authentic sample prepared from $Fe_2(CO)_9$ and *cis*-bicyclo[6.1.0]nonatriene or *cis*-8,9-dihydroindene [3a]. The mechanism of formation of VI from V may involve rupture of the C_1—C_8 bond together with loss of an $Fe(CO)_3$ group. Breaking of the iron—iron bond assisted by the aromatic solvent has been proposed in other similar systems [12, 13]:

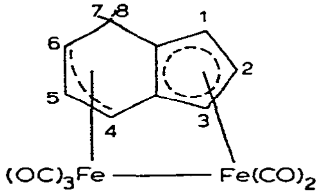


The formation of *cis*-cyclononatetraeneiron tricarbonyl (X) as an intermediate is plausible, since it has been isolated in the room temperature reaction of *cis*-bicyclo[6.1.0]nonatriene with $Fe_2(CO)_9$ [3]. Under the conditions of thermolysis, however, X has been shown to rearrange to the more stable VI.

Compound VII, a red crystalline material, has been analysed as $C_9H_8Fe_2(CO)_5$ (mass spectrum: $P = m/e$ 368 and fragment ions corresponding to the successive loss of five carbonyl groups and two iron atoms). The infrared spectrum shows no bridging carbonyl but only three strong bands at 2034, 1988 and 1975 cm^{-1}, which are indicative of an $Fe(CO)_3$—$Fe(CO)_2$ group. A well-known precedent for such an $Fe_2(CO)_5$ group coordinated to an organic moiety is azulene—$Fe_2(CO)_5$ [14] for which the following structure has been determined by X-ray analysis [15]:



We believe that the PMR spectrum (Fig. 1) is consistent with the structure VII:



(VII)

H_5 (τ 4.6 ppm) appears as a triplet coupled (J 6 Hz) to H_4 (doublet at τ 5.01) and to H_6 (τ 6.8 ppm) which is a multiplet due to further coupling to H_7 (J

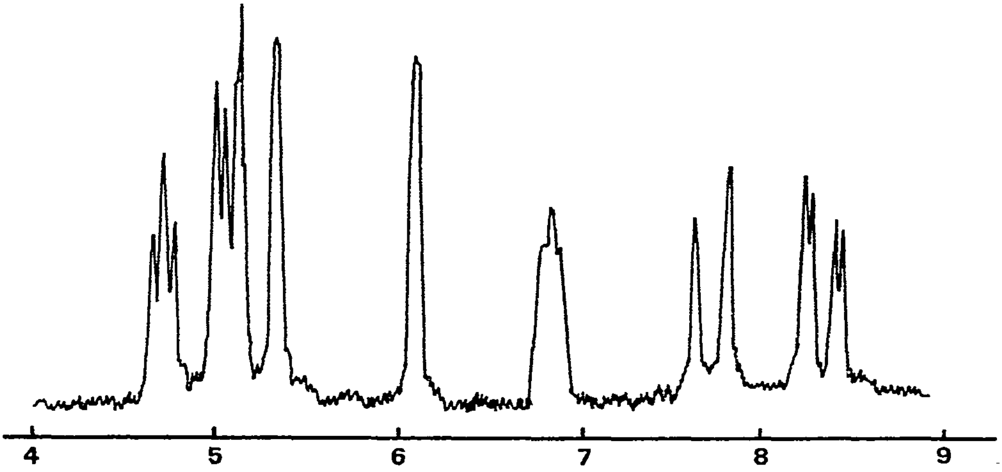


Fig. 1. The 60 MHz PMR spectrum of $C_9H_8Fe_2(CO)_5$ (VII) in $CDCl_3$ solution.

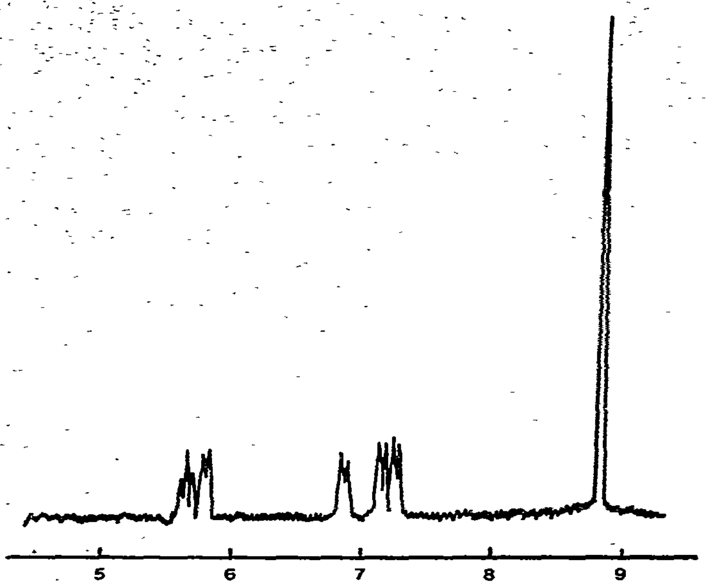


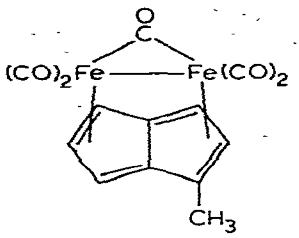
Fig. 2. The 60 MHz PMR spectrum of $C_9H_8Fe_2(CO)_5$ (VIII) in C_6D_6 solution.

4.8 Hz). The methylene protons (H_7, H_8) appear as an AB quartet centered at τ 8.05 ppm. H_2 is assigned to the triplet at τ 5.1 weakly coupled (J 2 Hz) to H_3 and H_1 (τ 5.25 and 6.05 ppm).

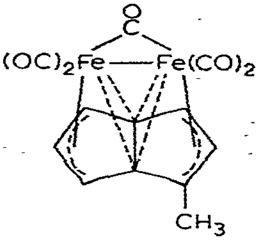
A plausible mechanism which accounts for the formation of VII involves further reaction of VI with $Fe(CO)_3$ groups originating by the breaking of the iron—iron bond of V. The low yield of VII is consistent with the above interpretation. Further evidence is the high temperature reaction of VI with $Fe_2(CO)_9$ which gives better yield of the same compound. The process must involve dehydrogenation and hydrogen shift steps.

Reaction of *cis*-8,9-dihydroindene with $Fe_2(CO)_9$ in boiling *p*-xylene gives again VI and VII and another compound [16] which shows different spectroscopic characteristics from VIII and IX, suggesting that they arise directly from V. The dark green complex VIII represents a further example of stabilization of the pentalene unit by an iron carbonyl. Its mass spectrum shows the characteristic pattern of an $Fe_2(CO)_5$ group ($P = m/e$ 368 and fragment ions corresponding to the successive loss of five carbonyl groups and two iron atoms). The infrared spectrum exhibits three strong bands (2024, 1998 and 1980 cm^{-1}) in the terminal CO region and a medium-strong band (1798 cm^{-1}) in the region of bridging carbonyls. The PMR spectrum (Fig. 2) shows a triplet (H_5, J 2.4 Hz) at τ 5.64 coupled to two doublets at 7.18 and 7.25 (H_4 and H_6), two doublets (J 2.7 Hz) at 5.82 and 6.88 (H_2 and H_3), and a singlet at 8.82 ppm (CH_3). Similar chemical shift and coupling constants have been reported for the other pentalene- or substituted pentalene-$Fe_2(CO)_5$ complexes [7, 8].

Both configurations VIIIa and VIIIb are consistent with the above spectral data, which provide only the general structures:

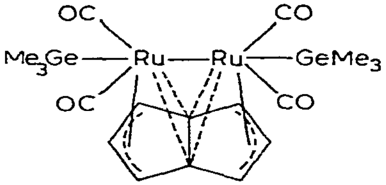


(VIIIa)



(VIIIb)

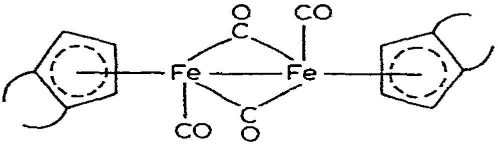
A recent X-ray determination on pentalene$Ru_2(CO)_4(GeMe_3)_2$ has shown that in the solid the configuration which best fits the data is [9]:



There is the possibility that the pentalene$Fe_2(CO)_5$ complexes also have a similar configuration in the solid. A precedent for this type of structure is cyclooctatetraene$Fe_2(CO)_5$ [17] which is fluxional at room temperature [18]. Complex VIII, however, does not exhibit fluxional behavior in solution.

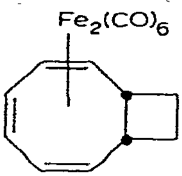
The mechanism of formation of VIII is obscure. The process must involve an intramolecular cyclization of the C_8 polyene ring in V, accompanied by dehydrogenation of the polyolefin. Abstraction of the two hydrogens by the metal is indeed favoured by loss of a carbonyl group which makes coordination sites available for Fe—H bonds. In addition the methyl group must arise from breaking of the C_8—C_9 bond in V, transfer of a hydrogen to the methylene group, and formation of a double bond at C_1—C_8. Whether the dehydrogenative transannular cyclization follows, accompanies, or precedes the formation of the methyl group cannot be established, owing to the absence of evidence for any intermediate in the thermolysis of V.

Compound IX has not been fully characterized, although the spectroscopic data suggest that it may be a polycyclic cyclopentadienyl derivative. Thus the mass spectrum shows a molecular ion at *m/e* 458, and the IR spectrum presents a bridging carbonyl band at 1775 cm^{-1} and two bands of comparable intensities in the terminal carbonyl region (1990 and 1943 cm^{-1}). The existence of two bands in the terminal CO region in the unsubstituted $[(C_5H_5)Fe(CO)_2]_2$ complex [19] is indicative of the presence of both *cis* and *trans* isomers rapidly interconverting [20] and it is likely that the same process occurs in our complex.

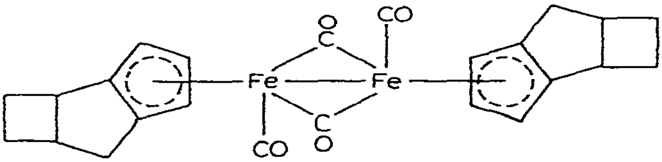


(IX)

A similar complex $[(C_{10}H_{11})Fe(CO)_2]_2$ has been obtained by thermolysis of $C_{10}H_{12}Fe_2(CO)_6$ (XI) [21] and characterized by X-ray crystallography as XII [13]. Thus our complex IX may be similar to XII with a cyclopropane ring in place of the cyclobutane ring, with a similar mechanism of formation. However, a different configuration of the cycles attached to the cyclopentadienyl ring is possible.



(XI)



(XII)

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