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cis-Cyclononatetraene Tricarbonyliron Complexes

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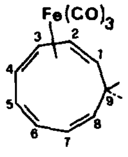
Several examples have been recently reported of enhanced stability of highly reactive organic molecules by coordination to iron carbonyl groups [1]. Cyclobutadiene [2], trimethylenemethane [3], norbornadien-7-one [4] are among the most interesting cases. More recently the ability of iron carbonyls in the stabilization of cyclic polyolefins has become well documented; thus heptafulvene [5–7], pentalene [8–10], cyclononatetraene [11, 12], bicyclo-[4.3.0.0^{2,4}]nona-6,8-diene [13] and bicyclo-[4.4.0.0^{2,5}]deca-7,9-diene (13, 14] have been isolated as iron carbonyl complexes.

The asymmetric complex [Fe(CO)$_3$(1–4 η^4-C$_9$H$_{10}$)] (1) (C$_9$H$_{10}$ = cyclonona-1,3,5,7-tetraene)



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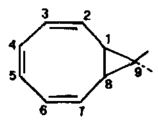

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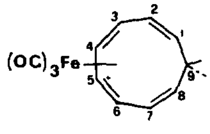


3

has been isolated independently by Reardon and Brookhart [11] in the photochemical rearrangement of bicyclo[6.1.0]nona-2,4,6-triene (2) in the presence of Fe(CO)$_5$, and by us [12] in the thermal rearrangement of the same polyolefin in the presence of Fe$_2$(CO)$_9$. The coordination of Fe(CO)$_3$ in 1 has been established on the basis of its unsymmetric ^{1}H NMR spectrum [11, 12]. Here we wish to describe the symmetric isomer [Fe(CO)$_3$ (3–6 η^4-C$_9$H$_{10}$)] (3)** which has been isolated by repeated chromatography of the first fraction (A$_1$) of the room temperature reaction of 2 with Fe$_2$(CO)$_9$ [12], after elimination of the dihydroindene tricarbonyl iron complex (4). The ratio of 1 to 3 is about 9:1 and is reproducible. The mass spectrum of 3 shows a parent peak at 258 m/e followed by peaks due to the loss of three carbonyl groups. The IR spectrum of 3 in the carbonyl region presents the usual three bands characteristic of Fe(CO)$_3$ complexes. These data do not discriminate between the asymmetric (1) and symmetric (3) derivatives which however present noticeable differences in their ^{1}H NMR spectra. As expected the ^{1}H NMR spectrum of 3 shows the presence of a symmetric plane bisecting the organic unit on C$_{4,5}$ and passing through C$_9$. This fact is particularly manifested in the multiplets due to protons H$_{4,5}$ and H$_{3,6}$ (Fig. 1) in comparison with the corresponding inner and outer protons of the diene unit in 1.*

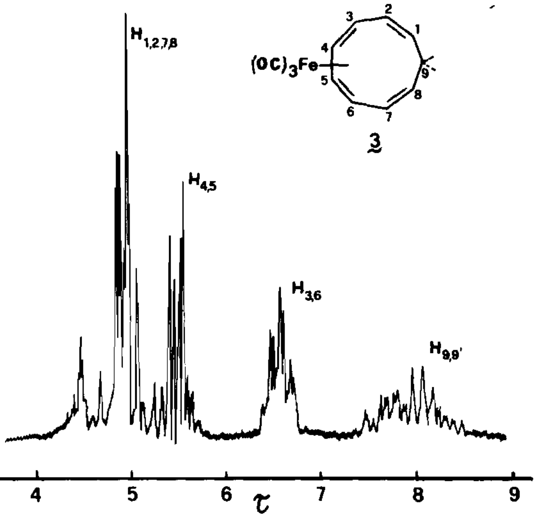
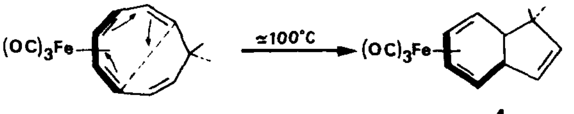


Fig. 1. The ^{1}H NMR spectrum of [Fe(CO)$_3$(3–6 η^4-C$_9$H$_{10}$)] (3) in C$_6$D$_6$.

As does the 1–4 η^4-C$_9$H$_{10}$ complex [11, 12], 3 undergoes thermal rearrangement to 4 and, similarly, a 1,2-shift [11] of the tricarbonyl iron group must be involved in such transformation:



3 4

Two major considerations arise from the obtainment of both 1 and 3 in the same reaction. They are related to: a) the absence of interconversion 1 ⇌ 3 at least at the temperature of the reaction; b) the mechanism of formation of the two cyclononatetraene complexes. While point a) does not deserve further comments, point b) may have two ways of resolution, *i.e.* that 1 and 3 are formed by rearrangement of two different intermediates or by coordination of an active iron carbonyl species to the labile cyclononatetraene.

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**This complex has been mentioned in ref. 12; at that time its formation was not established, owing to the obtainment of a very impure sample.

*The ^{1}H NMR spectrum in C$_6$D$_6$ of [Fe(CO)$_3$(1–4 η^4-C$_9$H$_{10}$)] (1) shows multiplets at τ 4.47(H$_{5,6,7,8}$), 5.58(H$_{2,3}$), 6.68(H$_{1,4}$), 7.71(H$_9$) and 8.38(H$_{9'}$).

Attempts to isolate a cyclononotetraene complex from the rearrangement of bicyclo[5,2,1]nona-2,5,8-triene tetracarbonyl iron [12], which is a reasonable precursor to **1**, were unsuccessful. We believe that the coordination of the metal group is a step following the promotion by iron carbonyls [15] of the rearrangement of **2** to *cis*-cyclononatetraene. If this is true there should be a way to obtain **1** and **3** directly from reaction of cyclononatetraene and an iron carbonyl source. We are currently investigating this point as well as the possibility of synthesizing other metal cyclononatetraene complexes.

Acknowledgments

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