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STABILIZATION OF HIGHLY REACTIVE CYCLIC POLYOLEFINS BY COORDINATION TO IRON CARBONYLS: *cis*-CYCLONONATETRAENE-IRON TRICARBONYL*

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SUMMARY

Reaction of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (C_9H_{10}) (I) with $Fe_2(CO)_9$, at room temperature, yields a number of complexes (IV)–(IX). One of these, (IX), is the $Fe_2(CO)_6$ derivative of the starting polyolefin (I), whereas the others are $Fe(CO)_3$ or $Fe(CO)_4$ complexes of isomeric C_9H_{10} polyolefins.

(IV) is (h^4-1,2,3,4-*cis*-8,9-dihydroindene)iron tricarbonyl, (V) is tentatively formulated as (h^2-8,9- or h^2-5,6-*cis*-bicyclo[5.2.0]nona-2,5,8-triene)iron tetracarbonyl, (VI) has been characterized only as $C_9H_{10}Fe(CO)_3$, and (VII) and (VIII) are the asymmetric and symmetric isomers (h^4-*cis*-cyclononatetraene)iron tricarbonyl.

Characterization of the complexes has been obtained through PMR, IR, and mass spectra.

Peculiar features of this reaction are the promotion of the polyolefin (I) rearrangement by iron carbonyls and the stabilization of highly reactive intermediates through coordination to the metal carbonyl groups.

INTRODUCTION

Metal carbonyls and particularly iron carbonyls have been found to be very effective in promoting rearrangement of cyclic polyolefins under mild conditions[1–3], and in some cases[1] the same organic product, obtained by higher temperature rearrangement of the polyolefin, can be isolated:

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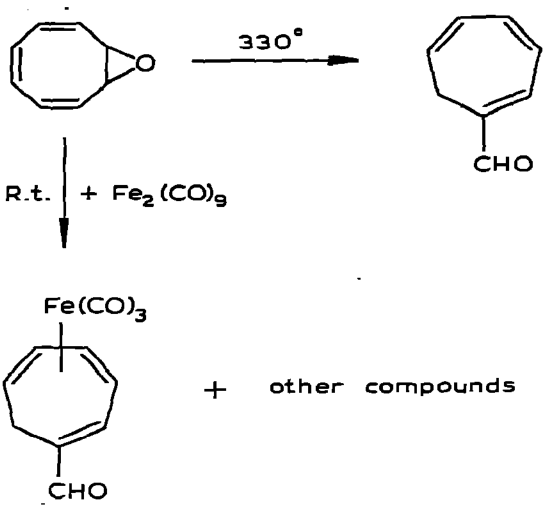
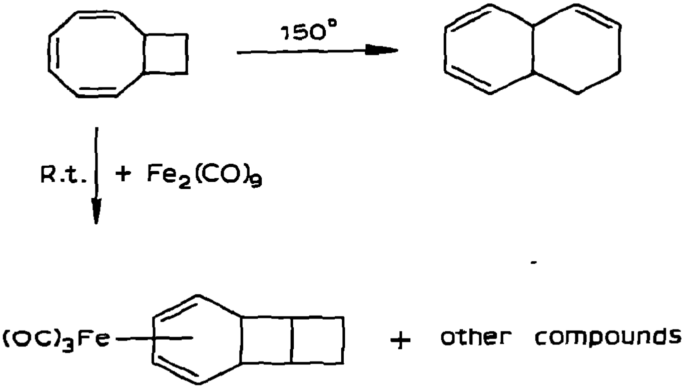
[*] Work presented in part at the 3rd International Symposium on Reactivity and Bonding in Transition Organometallic Compounds, Venice, September 9–10, 1970.

[**] Most of the work was carried out in Boston College, where G.D. was on leave of absence, during 1970.

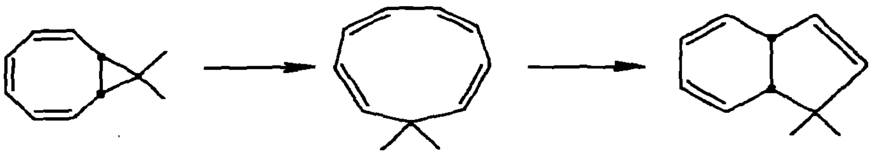


In other cases new products are obtained[2,3]:



suggesting a change in the rearrangement pathway provoked by the metal carbonyl. Another feature of metal carbonyls is the stabilization of highly reactive organic molecules by coordination, for example, stable iron carbonyl complexes of cyclobutadiene[4], heptafulvene[5-7], trimethylenemethane[8], and methyl-[9] or phenylpentalene[10] have been reported.

cis-Cyclononatetraene (II) has been widely studied as a possible intermediate in the rearrangement of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (I) to *cis*-8,9-dihydroindene (III)[11,12]:



(I) (II) (III)

III has been isolated from the reaction of 9-chloro-*cis*-bicyclo[6.1.0]nona-2,4,6-triene and lithium and by successive quenching of the cyclononatetraene anion with water[13]; its half life at 23° is ≈50 min[14].

Some attempts have been made to stabilize (II) as a metal complex but so far no report has appeared on the isolation of a metal derivative of *cis*-cyclononatetraene*. The formation of a molybdenum tricarbonyl complex of (II) by reaction of (III) with $Mo(CO)_6$ was reported[16] by King but subsequently retracted[17]. Iron carbonyls react with (III) to give several complexes[16,18]: none of these, however, is a derivative of (II)[18].

cis-Bicyclo[6.1.0]nona-2,4,6-triene (I) appears to be a better precursor of (II) and in this paper we report isolation of the stable (h^4-1,2,3,4-*cis*-cyclonona-1,3,5,7-tetraene)iron tricarbonyl and of a number of other complexes obtained in the room temperature reaction of (I) with $Fe_2(CO)_9$.

EXPERIMENTAL

All the reactions and working up of the compounds in solution were carried out in an atmosphere of pure nitrogen. Solvents were dried before use. Melting points are uncorrect.

Elemental analyses were performed by Dörnis und Kolbe, Mülheim (West Germany). IR spectra were recorded on Perkin–Elmer, Model 457 or 521 spectrometers. The mass spectra were obtained on a Hitachi–Perkin–Elmer RMU-6D spectrometer. The PMR spectra were recorded on Varian T-60 or HA-60 spectrometers.

Preparation of the ligands

cis-Bicyclo[6.1.0]*nona*-2,4,6-*triene* (*I*) was prepared with the method suggested by Staley and Henry[19] from cyclooctatetraene and lithium amide in liquid ammonia at −33°. Slow addition of CH_2Cl_2, in ether, to this mixture gives (I) in 80–90% yield, after aqueous work-up and distillation.

cis-8,9-*Dihydroindene* (*III*) was prepared by published methods[13] from 9-chlorobicyclo[6.1.0]nona-2,4,6-triene and lithium. The reaction mixture was quenched by water to give (III), in ≈80% yield.

Reaction between (*I*) *and* $Fe_2(CO)_9$

Reactions were carried out at room temperature for 2–4 days in solvents such as petroleum ether, benzene, diethyl ether, *etc.* All reactions gave comparable results as typically described below: C_9H_{10} (I) (4.72 g, 40 mmol) in anhydrous diethyl ether (350 ml) and $Fe_2(CO)_9$ (25.4 g, 70 mmol) were stirred at room temperature for four days. The reaction mixture was filtered and the resulting dark-red solution concentrated under reduced pressure to give an orange-red oil, which was chromatographed on a 60 × 3 cm alumina column (Merk, reactivity 2, 100-200 mesh). Elution with petroleum ether gave a diffuse pale yellow band (A); elution with ether an orange-red band (B). The solution from band A was concentrated to leave an orange-yellow oil which was rechromatographed on a 60 × 3 cm alumina column (Merk, reactivity 1, 100-200 mesh). Elution with petroleum ether gave two large pale-yellow bands. The first was concentrated and cooled at −50° to give pale yellow needles (IV), melting at

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* An iron tricarbonyl complex of *cis*-cyclononatetraene has been quoted in the literature[10].

TABLE 1

ANALYTICAL AND SPECTROSCOPICAL DATA OF THE COMPLEXES (IV)–(IX)

Complex (color, m.p.) Yield(%)	*Analysis found/(calcd.) (%)*			*Infrared spectra*[a] *ν(CO)*	*PMR spectra*[b] *(area)*	*Mass spectra*
	C	*H*	*Fe*			
$C_9H_{10}Fe(CO)_3$ (yellow, ≈10°) (IV) 30–32	55.78 (55.81)	3.85 (3.87)	21.65 (21.70)	2040s 1994s 1986s	4.68(4), 6.86(3) 7.02–8.42(3) in CS_2	258(M^+) 230(−CO) 202(−2CO) 174(−3CO)
$C_9H_{10}Fe(CO)_4$ (yellow, oil) (V) 8–10	54.48 (54.54)	3.58 (3.49)	19.31 (19.58)	2078s 2000s 1988s	3.65–5.02(6) 6.43(2) 6.6(1) 7.4(1) in CS_2	286(M^+) 258(−CO) 230(−2CO) 202(−3CO) 174(−4CO)
$C_9H_{10}Fe(CO)_3$ (yellow, oil) (VI)	55.70 (55.81)	3.89 (3.87)		Contaminated by (VII) and (VIII)		258(M^+)
$C_9H_{10}Fe(CO)_3$ (orange-yellow, ≈30°) (VII) 7–9	55.92 (55.81)	3.78 (3.87)	21.60 (21.70)	2042s 2001s 1990s	4.02–4.96(4) 5.58(2), 6.68(2) 7.71(1), 8.38(1) in C_6D_6	258(M^+) 230(−CO) 202(−2CO) 174(−3CO)
$C_9H_{10}Fe(CO)_3$ (orange-yellow, oil) (VIII)	55.79 (55.81)	3.85 (3.87)		Contaminated by (VII)		258(M^+)
$C_9H_{10}Fe_2(CO)_6$ (red-orange, 125°) (IX) 20–25	54.20 (54.27)	2.47 (2.51)	27.88 (28.06)	2053s 2012s 1992s 1988(sh) 1968s	6.5(2), 5.9(2) 7.2(2), 8.96(3) 9.5(1) in CS_2	398(M^+) 370(−CO) 342(−2CO) 314(−3CO) 286(−4CO) 258(−5CO) 230(−6CO)

[a] In cyclohexane solution. [b] In ppm (τ), relative to TMS.

room temperature. The analytical data for this and the other compounds discussed here are listed in Table 1.

The crystallization solvent for (IV) and the second pale-yellow band from the original band A, were combined (A_1) and rechromatographed on alumina. Sometimes more than one chromatographic separation was necessary, because only a small quantity of A_1 can be used in each run if efficient separation is to be achieved but it is possible to obtain five compounds (IV)–(VIII) (Table 1) by elution with petroleum ether.

The orange-red band B was concentrated and the resulting orange-red oily solid crystallized from petroleum ether and sublimed in high vacuum to give (IX).

Reaction of (III) with $Fe_3(CO)_{12}$

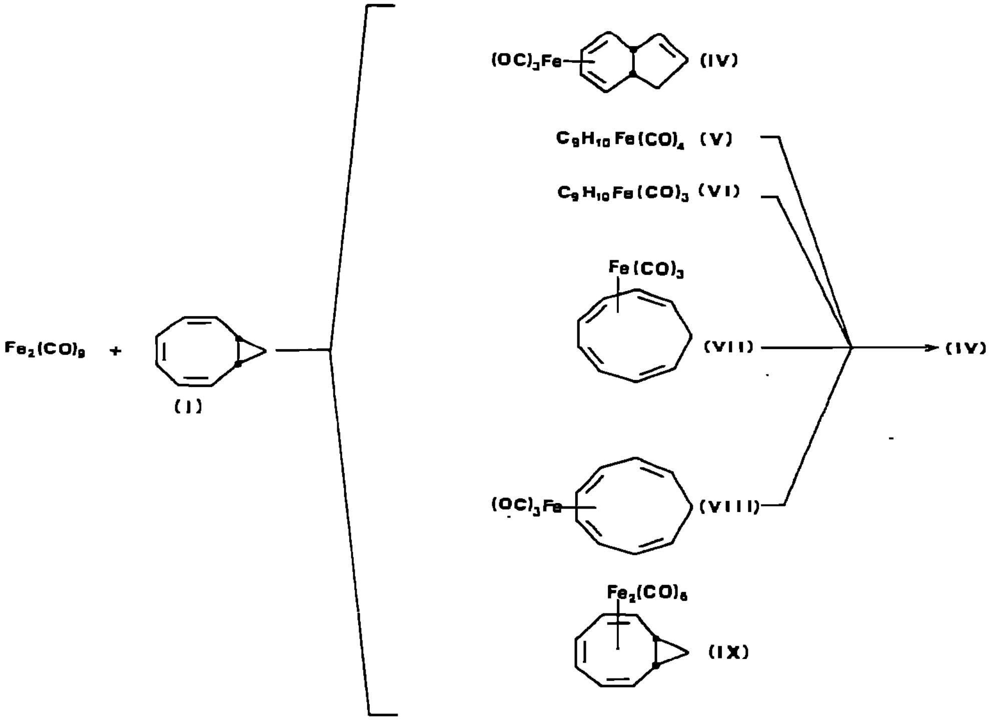
This reaction was carried out at room temperature in boiling benzene or boiling xylene. Each run gave a good yield of (IV) in addition to other complexes[18].

The spectroscopic data of (IV) obtained from these reactions are completely identical to those of (IV) obtained in the reaction of (I) with $Fe_2(CO)_9$.

RESULTS AND DISCUSSION

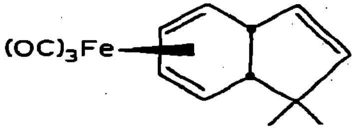
The products isolated in the room temperature reaction of (I) with $Fe_2(CO)_9$ are set out in Scheme 1. Increasing the temperature of the reaction results in a decrease in yield of all compounds (V)–(IX) in favor of (IV) and a number of new complexes are formed. Similar results are obtained by thermolysis of (IX) and will be reported later[9].

SCHEME 1

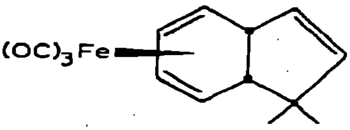


Complex IV

cis- and *trans*-8,9-Dihydroindene (III) are obtained in a ratio of 9/1 in the thermal (90°) rearrangement of (I)[10]. When $Fe_2(CO)_9$ reacts with (I), however, the rearrangement to (III) occurs much faster since yields higher than 30% in (IV) are obtained, at room temperature. At present it is not clear if this is due to the instability of an intermediate $Fe(CO)_3$ complex of (I) which rearranges to the more stable (IV) or to a promotion of the rearrangement (I)→(III) by the metal, followed by coordination of the strong dienophile $Fe(CO)_3$. The isolation of stable complexes of (II), however, should support the second interpretation although other mechanisms which interconvert the $Fe(CO)_3$ complex of (I) to (IV) cannot be ruled out. That (IV) contains the *cis*-configuration follows from the fact that the same complex has been obtained by reaction of pure (III) with $Fe_3(CO)_{12}$[18]. Since *cis*→*trans*-dihydroindene isomerization is unlikely we assign one of the above *cis*-structures as compound (IV).



(IVa)



(IVb)

The choice between (IVa) and (IVb) is difficult on the basis of the PMR spectrum (Fig. 1) since the absorption in the range of H_5 and H_9 appears rather complicated. IR and mass spectra of (IV) have been reported in the experimental section (Table 1) and are in agreement with the given formulation.

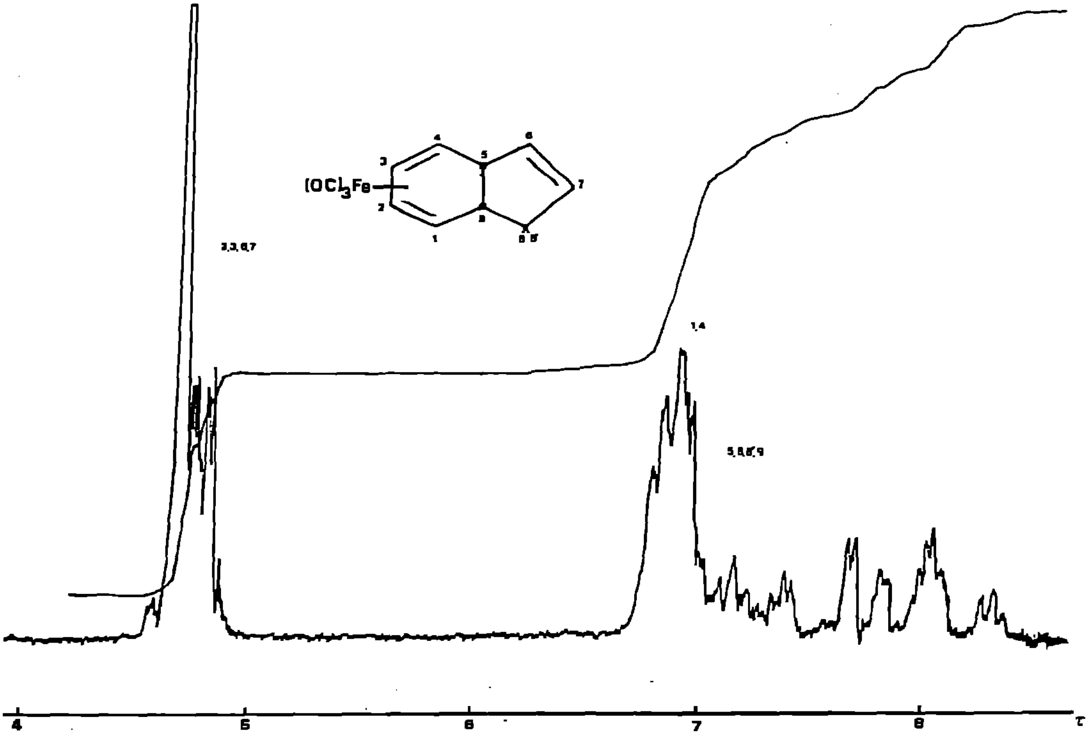


Fig. 1. The 60 MHz PMR spectrum of $C_9H_{10}Fe(CO)_3$ (IV) in CS_2 solution.

Complex (V)

Although (V) has been fully characterized by IR, PMR, and mass spectra, we are not able to give a definitive formulation of it. On the basis of the PMR spectrum (Fig. 2) and mass spectra ($M^+ = 286$ and following pattern showing loss of four car-

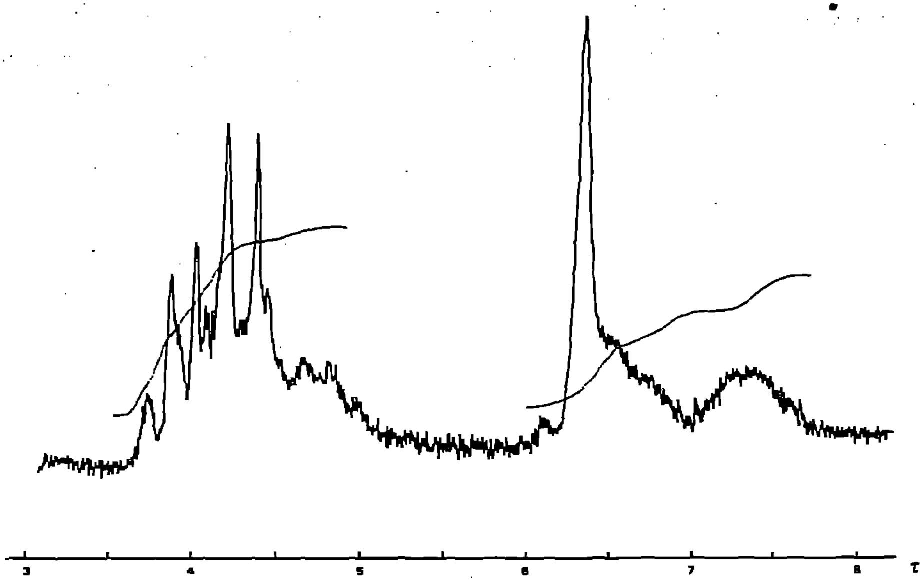
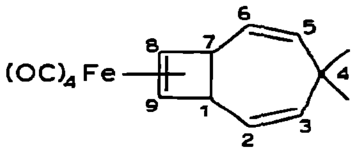
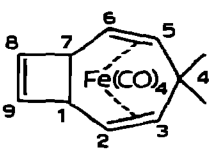


Fig. 2. The 60 MHz PMR spectrum of $C_9H_{10}Fe(CO)_4$ (V) in CS_2 solution. See discussion.

bonyl groups) we are inclined to the tentative formulation of (V) as an $Fe(CO)_4$ complex of *cis*-bicyclo[5.2.0]nona-2,5,8-triene:



(Va)



(Vb)

The broadening of the spectrum in the region of protons 4 and 4′ favours the (Vb) configuration. In this case the symmetrical spectrum could be obtained by rapid interconversion of the two equivalent forms (h^2-5,6-$Fe(CO)_4$) and (h^2-2,3-$Fe(CO)_4$)*. Further studies are in progress to check this possibility. The organic unit which we suggest has been postulated as a possible precursor of (II) in the rearrangement of (I) to (III)[12]. If the formulation of (V) as (h^2-8,9-) or (h^2-5,6-bicyclo[5.2.0]nona-2,5,8-triene)iron tetracarbonyl is correct it would represent a further example of stabilization of a highly reactive polyolefin by metal coordination. However, such a stabilization by an $Fe(CO)_4$ group is unprecedented.

Complex (VI)

(VI) analyzes as $C_9H_{10}Fe(CO)_3$ but its PMR spectrum shows that some (VII) and (VIII) are still present and we are not able to assign an exact configuration for it. In addition the very low yield in (VI) precluded further purification and characterization.

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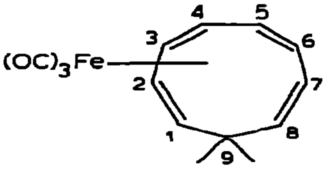
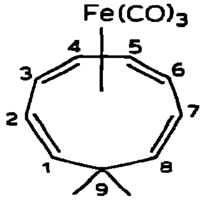
* We thank Prof. M. Graziani for helpful discussion on this point.

Complex (VII) and complex (VIII)

Coordination of an $Fe(CO)_3$ group to *cis*-cyclonona-1,3,5,7-tetraene (II) can be obtained via a diene–metal linkage in the 1,2,3,4 and 3,4,5,6 positions, for example:



(VII)



(VIII)

Both complexes have indeed been isolated and the ratio between the asymmetric (VII) and symmetric (VIII) isomers is ca. 9/1. PMR, IR and mass spectra are consistent with the formulation of (VII) as (h^4-1,2,3,4-*cis*-cyclonona-1,3,5,7-tetraene)iron tricarbonyl. The absence of cyclopropyl protons (Fig. 3), the presence of four uncoordinated olefinic protons (τ 4.2–4.9), and the characteristic inner ($H_{2,3}$) and outer ($H_{1,4}$) protons of a coordinated diene unit* support the monocyclic configuration. The asymmetry of the spectrum particularly in $H_{5,6,7,8}$ and $H_{1,4}$ proves that coordination of the $Fe(CO)_3$ group must involve the 1,2,3,4 carbons.

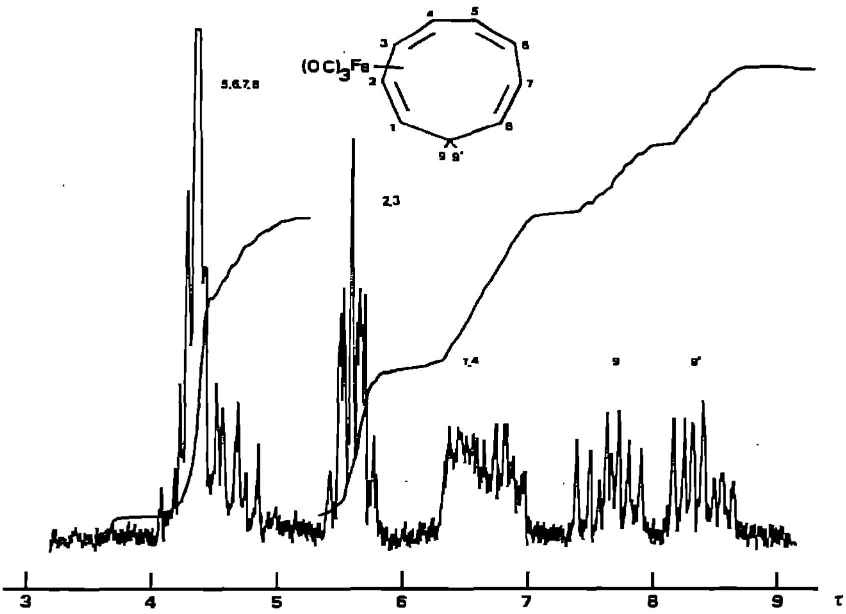


Fig. 3. The 60 MHz PMR spectrum of $C_9H_{10}Fe(CO)_3$ (VII) in C_6D_6 solution.

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* For a review article on PMR spectra of diene complexes, see ref. 20.

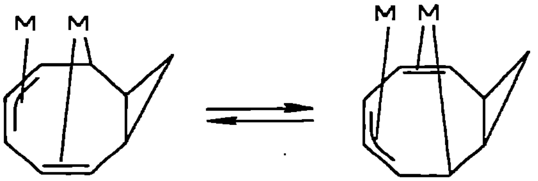
The symmetric isomer (VIII) has also been isolated, albeit in an impure state. The presence of (VII) complicates the assignment of its PMR spectrum.

Pure (VII) as well as a mixture of (V), (VI), (VII), (VIII) undergoes very slow rearrangement to (IV) (Scheme 1) at ≈ 100°. These experiments may be taken as supporting (*vide supra*) an enhanced rearrangement of the starting ligand (I) to *cis*-8,9-dihydroindene (III) promoted by iron carbonyls. Coordination and stabilization of the intermediate polyolefins by $Fe(CO)_3$ or $Fe(CO)_4$ groups occur in a second, less rapid step.

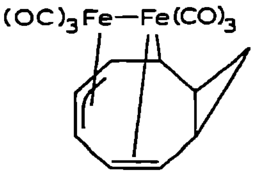
Other metals can bring about the rearrangement of these polyolefins. For example the rearrangement of (I) to (III) is stereospecifically catalyzed by $[Rh(CO)_2Cl]_2$[21].

Complex (IX)

This is the only complex which maintains the organic moiety of the starting polyolefin. The IR spectrum shows five bands in the terminal carbonyl region [ν(CO) at 2053, 2010, 1992, 1988(sh), and 1968, all ±5 cm^{-1}] and the mass spectrum shows a molecular ion at 398 and fragmentation according to the loss of six carbonyl groups and two iron atoms. Its PMR spectrum is symmetric and the assignments are reported (Fig. 4). The fact that the PMR spectrum of IX does not change on lowering the temperature to −90° could be due to a real symmetry of the molecule in solution or to a very low activation energy for the interconversion of two energetically equivalent, asymmetric, configurations (see *e.g.* ref. 22).



The presence of two carbonyls peaks (2/1 intensity ratio) in the ^{13}C NMR spectrum of (IX), however, has been taken as evidence of non-fluxional behavior[23] in agreement with the former hypothesis. X-ray crystal structure determination[24]



proved to be similar to other complexes which show fluxional behavior[23,25,26]. The only plausible interpretation we can give is that (IX) displays a rigid, symmetric configuration in solution, like $C_7H_8Fe_2(CO)_6$[27], but as shown by X-ray analysis, in the solid, it prefers an asymmetric structure, such as $C_8H_{10}Fe_2(CO)_6$ or $C_{10}H_{12}Fe_2(CO)_6$.

$C_9H_{10}Fe_2(CO)_6$ (IX) when heated at ≈ 100° is converted to a series of new

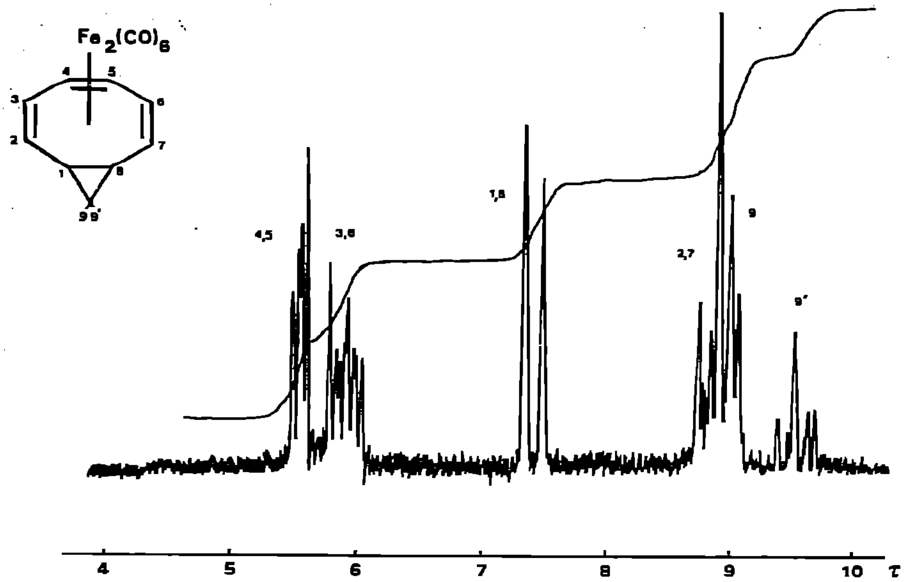
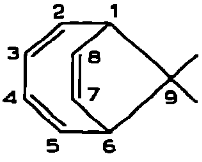


Fig. 4. The 60 MHz PMR spectrum of $C_9H_{10}Fe_2(CO)_6$ (IX) in CS_2 solution.

complexes[9], none of these however being a derivative of bicyclo[4.2.1]nona-2,4,7-triene (X):



(X)

The stable $Mo(CO)_3$ complex of (X) has been reported in the thermolysis of the $Mo(CO)_3$ derivative of (I)[28].

ACKNOWLEDGEMENTS

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