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^{13}C AND ^{1}H NMR OF IRON CARBONYL COMPLEXES: AN UNUSUAL DIMERIZATION OF *syn*-(1-METHYLPENTADIENYL)IRON TRICARBONYL CATION

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SUMMARY

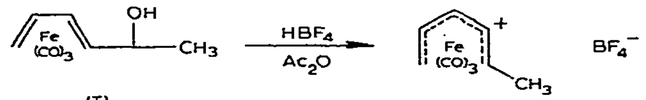
syn-(1-Methylpentadienyl)iron tricarbonyl fluoroborate reacts with basic alumina to give initially *syn*-(1-vinylbutadiene)iron tricarbonyl. Prolonged reaction results in the formation of a dimer, $C_{18}H_{16}Fe_2O_6$, and small amounts of higher molecular weight material. Mass spectroscopy, PMR, and ^{13}C NMR show that the dimer consists of two diastereomers of *syn,syn*-1,3,8,10-(5-methyl-1,3,6,8,10-undecapentaene)diiron hexacarbonyl.

INTRODUCTION

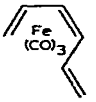
Cations coordinated to the iron tricarbonyl group are well-known, but few reactions other than the addition of simple nucleophiles have been described[1,2]. Several other possibilities remain for investigation, and in this account proton abstraction from a coordinated cation to give new complexes is reported.

RESULTS

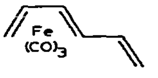
The alcohol (I) dissolves in anhydrous fluoroboric acid to form *syn*-(1-methylpentadienyl)iron tricarbonyl fluoroborate (II), which is isolable as a stable crystalline solid[3]. Removal of a proton from the cation in (II) could theoretically give either *anti*-(1-vinylbutadiene)iron tricarbonyl (III) or the *syn*-isomer (IV), which has previously been obtained in low yield from the reaction of $Fe_2(CO)_9$ with 1,3,5-hexatriene[4]. Upon being heated with excess triethylamine the salt (II) gives an addition product [probably(V)] instead of compounds resulting from proton abstraction.



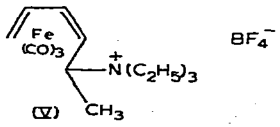
(I) (II)



(III)



(IV)



(V)

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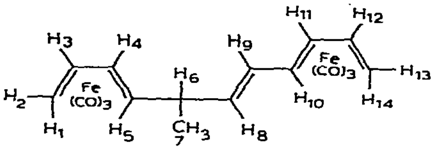
However, when a suspension of (II) in methylene chloride is stirred at room temperature with basic alumina [(II)/Al_2O_3 1/10 *w/w*] a neutral complex is rapidly formed. After one hour the volatile *syn*-complex (IV) can be isolated in 30% yield. The infrared spectrum of this material is identical with that reported previously[4] and the NMR spectrum is compatible with the *syn*-structure.

If the reaction with alumina is allowed to continue for 60 h, complex (IV) is completely converted into two new components. The major component, A (90%), has the empirical formula $C_{18}H_{16}Fe_2O_6$ (established by high-resolution mass spectroscopy). The minor component, B, consists of a mixture of higher molecular weight products (mainly $C_{27}H_{20}Fe_3O_6$) and has not been examined further.

The fragmentation pattern in the mass spectrum of A corresponds to the formula: $C_{12}H_{16}Fe_2(CO)_6$ and the infrared spectrum contains intense absorptions in the 2000 cm^{-1} region typical of dieneiron tricarbonyl complexes. Absorptions at 965 and 1640 cm^{-1} suggest the presence of a *trans*-substituted non-complexed double bond. Inspection of the ^1H and ^{13}C NMR spectra of compound A shows that it consists of two closely related isomers of *syn,syn*-1,3,8,10-(5-methyl-1,3,6,8,10-undecapentaene)-diiron hexacarbonyl (VI):



(VI)

^1H NMR

The 220 MHz ^1H NMR spectral data of compound A (VI) are summarized in Table 1. The most informative features of this spectrum are the two high-field absorptions at 0.28 and 0.47 ppm. Their position and multiplicity are characteristic of *anti*-protons of the terminal methylene groups in dieneiron complexes[5]. The dieneiron groups must therefore occupy terminal positions in the molecule. Thus, the arrangement of eight carbon atoms is accounted for by these two absorptions.

In the olefinic region, two absorptions (at 5.38 and 5.58 ppm) are typical of protons attached to a *trans*-substituted double bond (*J* 15 Hz) and the remaining four-proton multiplet in this region is assigned to the central protons of the dieneiron units. As there are no absorptions between 1.95 and 5.15 ppm, the remaining four carbon atoms of the polyene ligand in compound A must be attached in a *syn* fashion to the two complexed dienes. If there was *anti* substitution, the corresponding *syn* protons would absorb in the 2.5–3.0 ppm region[5].

The arrangement of the four central carbon atoms is shown clearly by decoupling experiments carried out at 220 MHz.

The double absorptions observed for the methyl group and protons 6 and 8 are due to isomerism, because careful chromatography of compound A gives partial separation into two mixtures in which one or other isomer is predominant. A corresponding reversal of intensity of the relevant peaks is observed in the NMR spectrum. As the absorptions due to the rest of the protons in the two isomers are identical, the structures must be very closely related. The probable origin of the two isomers is discussed below.

TABLE 1

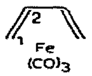
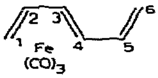
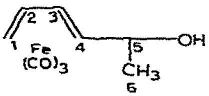
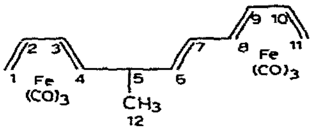
220 MHz ^{1}H NMR SPECTRAL DATA FOR (VI)
($CDCl_3$ SOLUTION)

Chem. shift of absorption (ppm)	*Number of protons*	*Multiplicity*[a]	*Decoupling*[b] *experiments*		*Assignment*	*Coupling constants, (Hz)*
0.28	1	dd		d(9.0)	1	$J_{1,3}$ 9.0; $J_{1,2}$ 2.0
0.47	1	dd		d(0.9)	14	$J_{12,14}$ 9.0; $J_{13,14}$ 2.5
0.82	1	t	d(9.0)		5	$J_{4,5}$ $J_{5,6}$ 9.0
1.12	3	d[c]	s[c]		7	$J_{6,7}$ 6.5
1.75	3	m		↓	2,10,13	
1.95	1	m	↓		6	$J_{5,6}$ 9.0; $J_{6,7}$ 6.5; $J_{6,8}$ 7.0
5.14	3	m			3,4,12	
5.27	1	q		d(5.0)	11	$J_{10,11}$ 8.5; $J_{11,12}$ 5.0
5.38	1	q		d(15.0)	9	$J_{8,9}$ 15.0; $J_{9,10}$ 9.5
5.58	1	q[c]	d(15.0)[c]		8	$J_{8,9}$ 15.0 $J_{6,8}$ 7.0

[a] s = Singlet; d = doublet; t = triplet; q = quartet; m = multiplet; dd = double doublet. [b] ↓ Denotes signal irradiated; remaining coupling constants shown in parentheses. [c] Additional splitting in these peaks is due to isomerism.

TABLE 2

^{13}C CHEMICAL SHIFTS (in ppm) RELATIVE TO EXTERNAL $^{13}CS_2$, AND ASSIGNMENTS FOR FOUR IRON TRICARBONYL POLYENE COMPLEXES

Carbon number	 (VII)	 (IV)	 (I)	 (VI)
1	151.7	153.6	152.8	152.8
2	107.0	107.0	108.1	105.5
3		111.5	111.4	111.5[a]
4		130.7	123.7[b]	123.3
5		54.2	121.7[b]	150.5 150.9 } diastereomers
6		78.4	166.8	55.9
7				63.1
8				130.4
9				111.2[a]
10				107.2
11				153.3
12				170.8 170.5 } diastereomers

[a] These two assignments could be reversed. [b] These two assignments could be reversed.

^{13}C *NMR*

The complete ^{13}C assignment which is presented in Table 2 has been facilitated by the study of several related model compounds; it confirms the structural assignment reached with ^1H NMR. The ^{13}C shifts of the simplest of these models, 1,3-butadieneiron tricarbonyl (VII), have been reported in the literature[6].

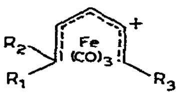
The fully coupled spectrum of (VII) shows a doublet for carbons 2 and 3, each component of which is broadened through long-range coupling with protons on adjacent carbons into a vague doublet with a width at half height of 17 to 18 Hz. This observation removes the ambiguity of the assignment of carbons 2 and 3 in the two model compounds (IV) and (I), which have signals in their decoupled spectra at 107.0 and 111.5 ppm (IV) and 108.1 and 111.4 ppm (I). In both these compounds C_2 is in very much the same environment with regard to spin coupling as C_2 in (VII). Thus in the fully coupled mode we expect the components of the doublet of C_2 to appear as broad signals with a width at half height equal to that in (VII), namely 17 to 18 Hz. This was found to be the case for the lines at 107.0 (IV) and 108.1 ppm (I), having widths of 18.5 and 17.5 Hz, respectively. The other decoupled signals at 111.5 (IV) and 111.4 ppm (I) gave, in the fully coupled mode, doublets whose components had linewidths of 9 and 9.5 Hz, respectively.

The other signals of (IV) and (I) can be assigned without difficulty, although a slight uncertainty remains for C_4 and C_5 in (I). As can be seen in Table 2, compound (IV) resembles the right-hand side and compound (I) the left-hand side of (VI). This facilitates the assignment of the eight carbon atoms involved in the π-complexes in (VI), namely atoms 1, 2, 3, 4 and 8, 9, 10, 11. Of the still unassigned carbons 5, 6, 7 and 12, C_6 and C_7 are normal olefinic carbons. Their assignment may be made with the aid of the predictive formulae reported in the literature[7], according to which C_6 would appear at 57.7 ppm (observed 55.9) and C_7 at 64.4 ppm (observed 63.1). An attempt to predict the shift of C_5 using aliphatic shift parameters[8] leads to a value of 161.0 ppm. The only lines which are close to this position and give the expected doublet in the partially decoupled mode are the two lines at 150.5 and 150.9 ppm. The presence of two lines is accounted for by the existence of diastereomers. The discrepancy between the predicted and observed line positions has an interesting bearing on the configuration within the molecule. It has been reported previously[7] that carbons α to a *trans*-substituted double bond appear 3 to 4 ppm to lower field than their counterparts in the corresponding alkane. The fact that C_5 is at a field about 10 ppm lower than predicted for the corresponding alkane implies that C_5 is in a *trans,trans* configuration. This further supports the conclusions drawn from the ^1H NMR spectrum.

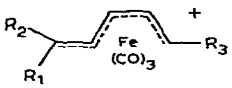
In view of the appearance of quartets in the partially decoupled mode the two lines at 170.8 and 170.5 ppm are assigned to the remaining carbon, C_{12}, in the CH_3 group. The presence of diastereomers again accounts for the doubling of the CH_3 signal.

DISCUSSION

In order to explain the formation of two isomers of (VI) a plausible mechanism for the reaction of (II) with alumina must be presented. Most additions to pentadienyliron tricarbonyl cations (VIII) give products derived from the *trans*-species (IX)[2].

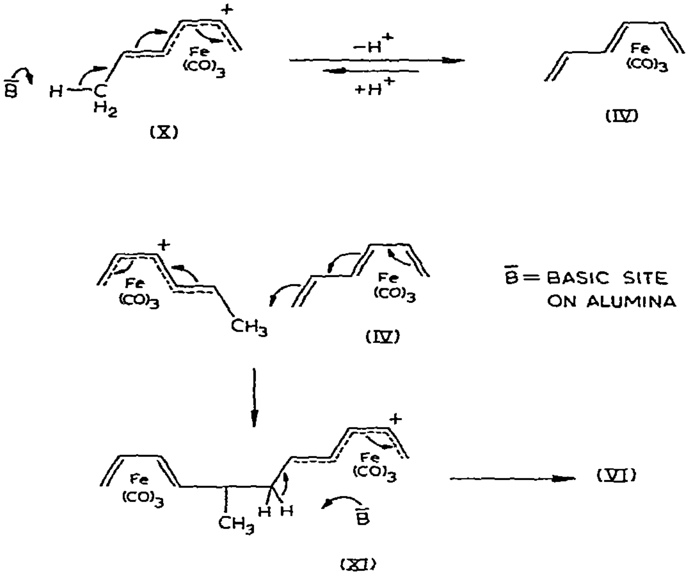


(VIII)

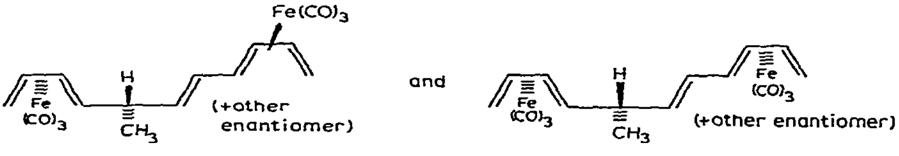


(IX)

The *cis/trans* equilibrium (VIII) ⇄ (IX) has recently been demonstrated for the pentadienyliron tricarbonyl cation (VIII), ($R_1=R_2=R_3=CH_3$)[9]. A likely explanation of our results is that a small equilibrium concentration of the *trans*-cation (X) absorbed on the alumina reacts thus:



Presumably for steric reasons, addition reactions of pentadienyliron tricarbonyl cations give products derived from attack of the incoming group on the side opposite to the iron atom[10]. Thus, if the same rule applies to the formation of (VI), the configuration of the methyl-bearing carbon will be fixed relative to the neighbouring dieneiron group. Owing to their asymmetry (X) and (IV) are racemates and their combination can be expected to give two diastereomers. Considering these points, the isomers of (VI) present in "compound A" are probably:



The reaction of (II) with basic alumina gives a 60% yield of (VI) and is effectively a highly specific dimerization of 1,3,5-hexatriene.

EXPERIMENTAL

Spectra

The ^{13}C NMR spectra were recorded on a Varian HA 100 spectrometer in the pulse Fourier transform mode, $^{13}CS_2$ was used as the external standard and also served as the lock. The ^{1}H NMR spectra were recorded on a Varian HR 220 spectrometer. The double resonance experiments were carried out in the field sweep mode.

Infrared spectra were recorded on a Perkin–Elmer 457 spectrophotometer.

Mass spectra were obtained with an AEI MS-902 spectrometer.

Starting material

syn-(1-Methylpentadienyl)iron tricarbonyl fluoroborate (II) was prepared from *syn*-(2,4-hexadien-1-ol)iron tricarbonyl in 82% yield[3].

Reaction of syn-(1-methylpentadienyl)iron tricarbonyl fluoroborate (II) with basic alumina/methylene chloride

(*a*). *Short reaction time.* A suspension of the salt (II) (1.6 g) and basic aluminium oxide (Woelm grade I, 10.0 g) in dry methylene chloride (50 ml) was stirred under argon for one hour at room temperature. The reaction mixture was filtered and the alumina was washed well with methylene chloride. Evaporation of the filtrate under reduced pressure followed by pumping down to 0.1 mmHg for two hours afforded *syn*-(1-vinylbutadiene)iron tricarbonyl (IV) (301 mg, 26%) as a volatile orange liquid. (Substantial amounts were probably lost during pumping.)

The infrared spectrum of (IV) was identical with that published previously[4] and the ^{1}H NMR spectrum was compatible with the *syn*-structure. The high-resolution mass spectrum showed a fragmentation pattern indicative of the formula $C_6H_8Fe(CO)_3$. (Found: C, 50.0; H, 4.0. $C_9H_8FeO_3$ calcd.: C, 49.2; H, 3.7%.)

(*b*). *Long reaction time.* A suspension of the salt (IV) (6.2 g) and basic aluminium oxide (Woelm grade I, 60 g) in dry methylene chloride (150 ml) was stirred under argon for 64 h at room temperature. The reaction mixture was filtered and the alumina washed several times with methylene chloride. Evaporation of the filtrate under reduced pressure afforded an orange oil (3.18 g). This material was chromatographed on silica gel (Merck, 70–325 mesh) using hexane as the eluant. Three yellow bands were obtained. The early fractions collected contained the vinyl complex (IV) (77 mg), identified by infrared spectroscopy. Fractions containing the second (major) band gave a mobile orange oil (2.65 g) identified as *syn,syn*-1,3,8,10-(5-methyl-1,3,6,8,10-undecapentaene)diiron hexacarbonyl (VI). The ^{1}H NMR and ^{13}C NMR data are collected in Tables 1 and 2. The high-resolution mass spectrum showed sequential loss of six carbonyl groups and two iron atoms, leaving a $C_{12}H_{16}^{+}$ ion. Apart from the characteristic bands of an iron tricarbonyl complex[5], the infrared spectrum contained bands at 965 and 1640 cm^{-1} typical of a *trans*-substituted non-complexed double bond. (Found: C, 49.7; H, 3.9. $C_{18}H_{16}Fe_2O_6$ calcd.: C, 49.2; H, 3.7%.)

The third yellow band was removed from the column with pentane + 2% ether. The viscous orange gum obtained (407 mg) appeared to be a complex mixture of higher molecular weight iron carbonyl complexes (mass spectroscopic evidence) and was not investigated further.

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