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ROOM TEMPERATURE ^{13}C NMR SPECTRA OF FLUXIONAL AND NON-FLUXIONAL COMPLEXES OF THE TYPE (POLYOLEFIN)$Fe_2(CO)_6$*

G. DEGANELLO

Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del C.N.R., Facoltà di Chimica Industriale, Università "Ca' Foscari", Venezia (Italy)

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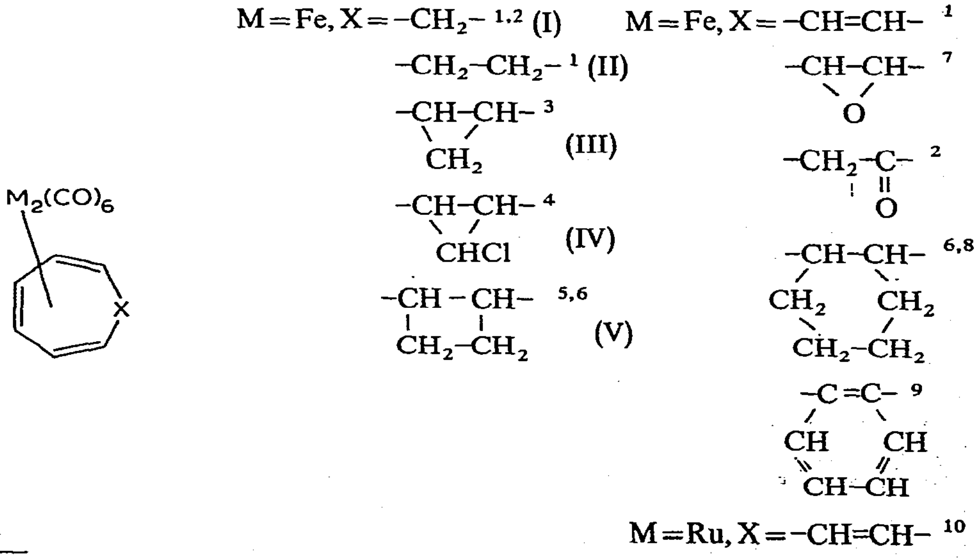
SUMMARY

Room temperature ^{13}C NMR spectra of five (polyolefin)$Fe_2(CO)_6$ complexes (I)–(V) {polyolefin = cycloheptatriene [(I), C_7H_8], cyclooctatriene [(II), C_8H_{10}], bicyclo[6.1.0]nona-2,4,6-triene [(III), C_9H_{10}], and its 9-chloro derivative [(IV), C_9H_9Cl], bicyclo[6.2.0]deca-2,4,6-triene [(V), $C_{10}H_{12}$]} are reported. All spectra are symmetric in the organic region, since the molecules have a real or apparent symmetry plane. However, they differ in the carbonyl region, and from the number of ^{13}CO peaks it is possible to anticipate the fluxional or non-fluxional behavior of these types of molecules.

INTRODUCTION

Several complexes of the type (polyolefin)$M_2(CO)_6$ containing an M–M bond have been recently reported[1–10]:



M = Fe, X = $-CH_2-$ [1,2] (I)
$-CH_2-CH_2-$ [1] (II)
$-CH-CH-$ bridged by CH_2 [3] (III)
$-CH-CH-$ bridged by CHCl [4] (IV)
$-CH-CH-$ with CH_2-CH_2 [5,6] (V)

M = Fe, X = $-CH{=}CH-$ [1]
$-CH-CH-$ bridged by O [7]
$-CH_2-C(=O)-$ [2]
$-CH-CH-$ with CH_2, CH_2, CH_2-CH_2 [6,8]
$-C{=}C-$ with CH, CH, $CH-CH$ [9]

M = Ru, X = $-CH{=}CH-$ [10]

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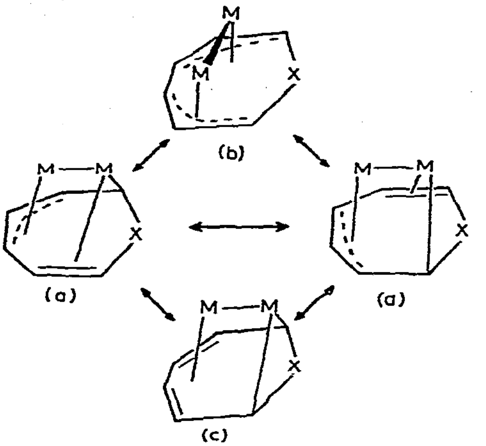

Fig. 1. Fluxional behavior of (polyolefin)$M_2(CO)_6$ complexes.

Most of these complexes are "fluxional"[11], and the most satisfactory explanation for their behavior in solution is indeed a rapid interconversion of two asymmetric, energetically equivalent, configurations[12-15] (*a* and *d* in Fig. 1). Whether these interconversions involve a symmetric intermediate (*b* or *c*) and what kind of intermediate is the most likely to be involved, remains an open question[15,16].

There are, however, a few examples, namely $Fe_2(CO)_6$ complexes of cycloheptatriene (I)[16], bicyclo[6.1.0]nonatriene (III)[3], and cyclooctatetraene oxide[7], which do not show any changes in the ^1H NMR spectrum at various temperatures, suggesting the presence of a real symmetry plane at least in solution. The fact that a compound of the type (polyolefin)$Fe_2(CO)_6$ shows an invariant NMR spectrum because of its non fluxional behavior, does not mean that in the crystalline state the molecule must be symmetric. Although in the only case so far studied crystallographically[16] $C_7H_8Fe_2(CO)_6$ displays the same symmetric structure in the crystal (*b* in Fig. 1) as is suggested in solution, other cases might be found in which the compound becomes symmetric and rigid in solution although showing an asymmetric structure in the solid.

Thus for (polyolefin)$M_2(CO)_6$ complexes (M = Fe, Ru) a distinction between fluxional and non-fluxional molecules at room temperature is not feasible on the basis of ^1H NMR techniques. In both cases the ^1H NMR spectra show a symmetry plane; a real symmetry plane is found in the non-fluxional molecules, whereas only an apparent one, resulting from a time averaging process (Fig. 1), exists for fluxional molecules of this type. Only a variable temperature investigation of the ^1H NMR spectra can detect the interconversion between energetically equivalent configurations (*a* and *d*). An X-ray crystal and molecular determination is also of great help. Difficulty is often caused by limited solubility of the compounds at low temperatures, which does not allow the ^1H NMR spectra to be recorded and it is often hard to obtain good crystals and to prevent their decomposition in the X-ray beam. Furthermore the length of time required for such investigations must be considered.

We present here a simple criterion by which one can anticipate the fluxionality or non-fluxionality of compounds of the type (polyolefin)$Fe_2(CO)_6$. This criterion is based on an analysis of the room temperature ^{13}C NMR spectra of such compounds both in the organic as well as in the carbonyl regions.

EXPERIMENTAL

The complexes $C_7H_8Fe_2(CO)_6$ (I)[1], $C_8H_{10}Fe_2(CO)_6$ (II)[2], $C_9H_{10}Fe_2(CO)_6$ (III)[3], $C_9H_9ClFe_2(CO)_6$ (IV)[4], and $C_{10}H_{12}Fe_2(CO)_6$ (V)[5], were prepared according to published methods and purified by column chromatography, crystallization or sublimation.

^{13}C NMR spectra were recorded at 22.63 MHz on a Brüker HX-90 or at 25.2 MHz on a Varian XL-100 spectrometer* equipped with a Fourier transform capability, in C_6D_6 as the solvent with TMS as internal standard reference. All proton spectra were decoupled and deuterium was used as an internal field frequency lock. Low temperature spectra were measured using CS_2/CF_2Cl_2/TMS mixtures.

RESULTS AND DISCUSSION

The organic region of the ^{13}C NMR spectra at room temperature is similar for all compounds investigated. As expected for molecules which display a symmetry plane (real or apparent) a single line is found for each pair of carbon atoms (Fig. 2a, b).

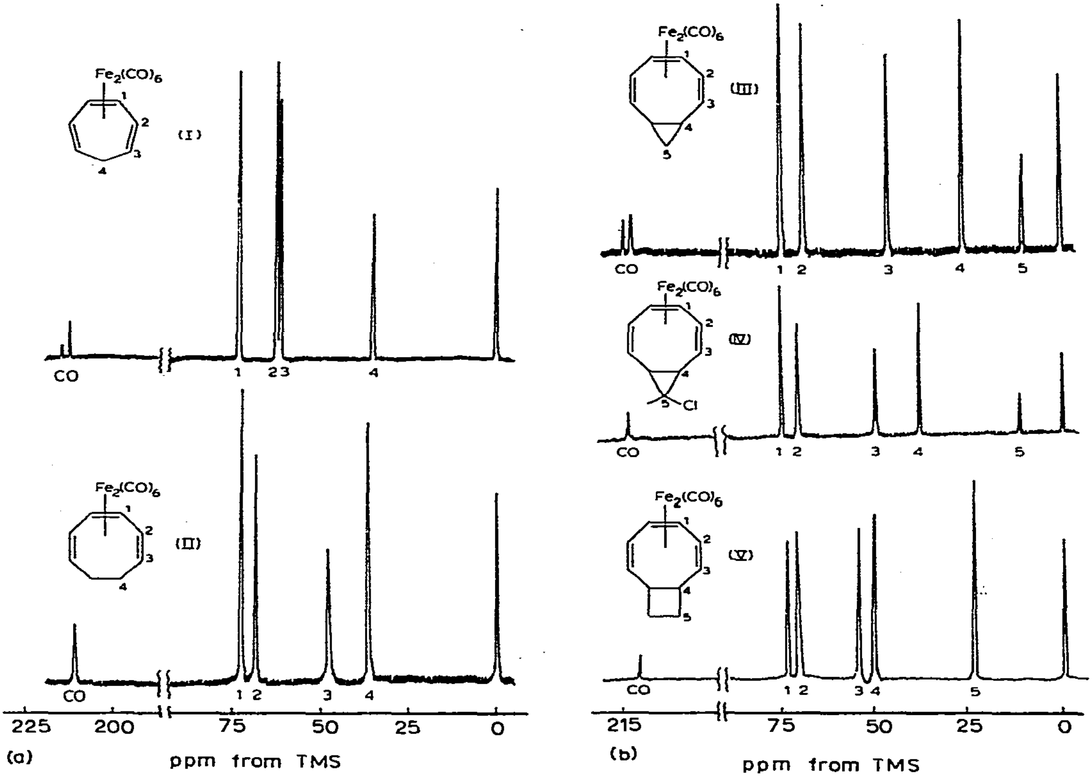

Fig. 2. ^{13}C NMR Spectra of (polyolefin)$Fe_2(CO)_6$ complexes recorded on: (a), Varian XL-100; (b), Brüker HX-90 in C_6D_6, at room temperature. Assignments are tentative.

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* We thank Drs. R. Price (Brüker AG, Karlsruhe, Germany) and F. W. Wherly (Varian AG. Zug, Switzerland) for running some of the spectra reported herein.

TABLE 1

^{13}C NMR SPECTRA (NUMERICAL VALUES) OF SOME (POLYOLEFIN)$Fe_2(CO)_6$ COMPLEXES AT 30°[a]

Complexes		*CO region*[b]	*Organic region*[b]		
$C_7H_8Fe_2(CO)_6$	(I)[c]	215.03	74.93	63.95	63.32
		212.66	40.34		
$C_8H_{10}Fe_2(CO)_6$	(II)[c]	211.73	74.05	69.68	48.65
			41.29		
$C_9H_{10}Fe_2(CO)_6$	(III)[d]	213.07	77.88	68.46	45.85
		211.38	25.57	9.27	
$C_9H_9ClFe_2(CO)_6$	(IV)[d]	211.88	74.10	69.61	48.62
			36.85	10.21	
$C_{10}H_{12}Fe_2(CO)_6$	(V)[d]	211.38	72.86	70.18	53.87
			49.58	22.87	

[a] In C_6D_6 solution. [b] In ppm from TMS. [c] Varian XL-100. [d] Brüker HX-90.

Numerical values of the chemical shifts are listed in Table 1.

However, in the carbonyl region some complexes, namely (I) and (III), show two peaks (in an intensity ratio of ca. 2/1), whereas (II), (IV), and (V) display a single peak.*,**

An interpretation can be made on the basis of simple considerations. For a compound, which is not fluxional the plane of symmetry must be real and symmetry considerations predict three pairs of magnetically non-equivalent carbonyl groups. The fact that in (I) and (III) only two peaks of different intensity are obtained may be due to accidental superposition. For a fluxional compound, the appearance of a single peak in the carbonyl region indicates that at least two distinct processes occur. First, interconversion shown in Fig. 1 occurs; this time-averaging process however, should lead to a ^{13}C NMR spectrum very similar to that found for the non-fluxional molecules of the type (polyolefin)$Fe_2(CO)_6$[(I) and (III)], since the rapid interconversion between the two asymmetric configurations (*a* and *d* in Fig. 1) is equivalent, for the spectrometer, to a molecule displaying a rigid symmetric configuration. This behavior is found in the NMR spectrum of fluxional compounds in the solid state, where only the organic unit is mobile[18]. In solution, in addition to this process, another one is operating which involves rapid interchange (scrambling) of the carbonyl groups, thus accounting for the single peak in the ^{13}C NMR spectra at room temperature. This proves, in our opinion, unequivocally that the carbonyl groups also independently participate in the fluxional behavior of these molecules.

Preliminary observations of variable temperature ^{13}C NMR investigations reveal very complicated behavior between +23° and −100° for both (II) and (V), and suggest that at least two rearrangement processes are involved. One of these

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* The occurrence of a single ^{13}CO peak at room temperature in (V) was observed independently by F. A. Cotton and O. Gansow who have subsequently confirmed our observation of a single peak also in (II) (Personal communication).

** While this manuscript was in preparation it was reported[17] that the carbonyl region ^{13}C NMR spectrum of cyclooctatetraene $Fe(CO)_3$ exhibits one peak at room temperature and two peaks (2/1 ratio in intensity) below −120°.

would be due to the interconversion $a \leftrightarrow d$ and another to the independent interchange (scrambling) of the carbonyl groups[19,20].

In principle, other cases might occur in this series of complexes, at room temperature, such as a spectrum which is asymmetric in the ^{13}C organic region and displays six peaks in the ^{13}CO region. This spectrum should belong to an asymmetric molecule and the fluxionality of the compound should appear at higher temperatures. This would be an exception among (polyolefin)$Fe_2(CO)_6$ complexes since it would require a very high activation energy; no such cases have been reported so far.

The ^{13}C NMR spectrum of (V) at ca. −130° shows, as expected for its "frozen" configuration (*a* or *d*), six distinguishable carbonyl peaks[19].

The interpretation of the ^{13}C NMR spectra given here is fully in agreement with the fluxional [(II) and (V)] or non-fluxional behavior [(I) and (III)] found through variable temperature studies with ^1H NMR techniques. By a logical extension of the above described criterion we can anticipate that (IV) will be fluxional and will display an asymmetric crystal and molecular structure, very similar to the other fluxional complexes of the series[21].

The factors which influence the fluxional behavior are not yet clear and much work is needed on this aspect since several competitive effects must be responsible for the contrasting behavior found in the above series [(I)–(V)].

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