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IRON-57 SATELLITES IN ^{13}C NMR SPECTRA: AN AID TO ELUCIDATION OF "HIDDEN-PROCESSES" IN THE DYNAMICS OF METAL CARBONYLS

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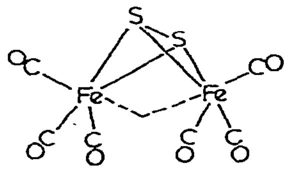
Summary

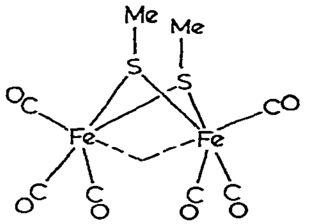
The observation of ^{57}Fe satellites in ^{13}C NMR spectra of $Fe_2(CO)_6S_2$, *syn*- and *anti*-$Fe_2(CO)_6(SCH_3)_2$ isomers and $Fe_3(CO)_{12}$ adds new information to the understanding of the dynamic behaviour of these molecules.

In recent years, the availability of NMR spectrometers operating in the FT mode has permitted determination of the NMR parameters of many nuclei of low sensitivity. This can be accomplished either by direct observation or via the detection of the satellites subspectra in more accessible spectra (e.g. ^1H, ^{13}C, ^{31}P...) [1]. Although direct observation of ^{57}Fe resonances (I = ½) is hindered by several factors (low natural abundance, very small magnetic moment, very long relaxation times), ^{57}Fe NMR spectra have been recently recorded for 35 organoiron complexes, and all the known values for ^1J(Fe—C) coupling constants in Fe(CO)$_n$ fragments (n = 2,3,4,5) have been summarized [2]. Since all the values fall in the range 23—32 Hz, it is evident that the coupling constants for Fe—CO bonds exhibit only a small dependence on the nature of the other ligands bonded to iron. We show below how the use of ^{57}Fe-satellites can assist in elucidation of the dynamic processes occurring in molecules containing more than one iron atom in cases in which the ^{13}C spectra are consistent with a fast intramolecular CO exchange at room temperature.

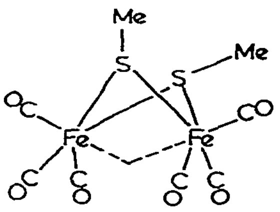
The variable temperature ^{13}C NMR spectra of I, II and III have shown that carbonyl exchange occurs [3]. For I and II, two resonances with integrated intensities 2/1 and for III three resonances of equal intensity are observed in the low temperature limiting spectra. In each case resonances merge into a single peak at high temperature.



I



II



III

In the light of the symmetry of the molecules, the variable temperature observation enables a decision to be made between the two types of process which can lead to averaging of the carbonyl resonances; viz. a polytopal rearrangement within each $M(CO)_n$ moiety or an exchange of CO's between metal centres. Determination of the metal—carbon coupling constants in the spectra corresponding to the fast exchange limit can help in making this choice.

Among the molecules containing one carbon-13 atom (multiply labelled molecules are not observable), 4.4% have one iron-57 atom. In half of them the iron-57 is directly bonded to the carbon-13 atom, whereas in the other half the iron-57 and the carbon-13 are two bonds away. Two different subspectra are then expected for the isotopomers containing ^{57}Fe atoms according to the mechanism of carbonyl exchange: (i) when there is only a polytopal rearrangement within each $Fe(CO)_3$ moiety, the ^{57}Fe satellite subspectrum consists of two doublets, with inner separations corresponding to ^1J(Fe—C) and ^2J(Fe—C), respectively. It is likely that the smaller doublet will be hidden under the main resonance, since ^2J(Fe—C) is expected to be very small (as found for ^2J(Rh—C)) [4].

(ii) If exchange between metal centres is involved only a doublet will be observed, with a separation corresponding to $\frac{1}{2}(^1J(\text{Fe—C}) + {}^2J(\text{Fe—C}))$; the magnitude of this separation is expected to be in the range 13—18 Hz, or lower if an inversion in the sign of the coupling constants occurs.

For each of the compounds under study, only a doublet was detected, with separation 29.3, 27.0 and 26.9 H_2 for I, II, and III, respectively. These values are in good agreement with those expected for one-bond carbon-iron couplings and the results can thus be interpreted in terms of process with $^2J(\text{Fe—C}) <$ 5 Hz.

Recently, Cotton and Hanson reported the observation of the iron satellites subspectrum in the ^{13}C NMR spectrum of $Fe_3(CO)_{12}$, which appears as a doublet with an inner separation of 8.3 Hz [5]. We have also observed this spectrum for a ^{13}CO enriched (65%) sample of $Fe_3(CO)_{12}$ (IV) (see figure).

The solid state structure of $Fe_3(CO)_{12}$ [6] reveals that two different types of iron atoms are present in the molecule and different iron-carbon coupling constants would be expected for the one apical and two basal iron atoms of the isosceles triangle. At the fast CO exchange limit there should be one doublet of satellites corresponding to the averaged coupling constants of all the CO's with the unique iron atom for one set of molecules and a second doublet (twice intense) corresponding to the averaged coupling constants of all the CO's with the basal iron atoms for the other set of molecules. It would

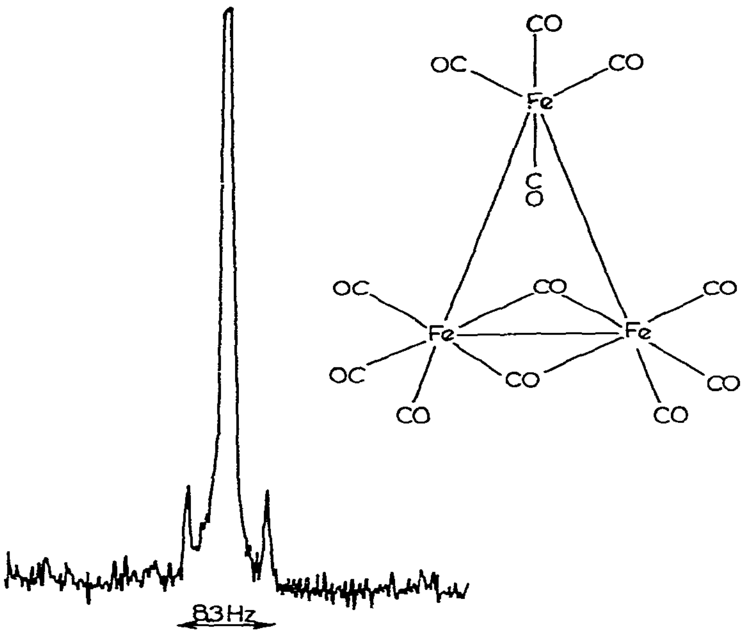


Fig. 1. ^{13}C NMR spectrum of a 65% ^{13}CO enriched sample of $Fe_3(CO)_{12}$ (IV).

certainly be possible in our experiments to observe the expected satellites pattern if the iron—carbon coupling constants at the unique iron and the two basal ones differ by at least 0.3 Hz. However, since the doublet observed at room temperature remains unchanged down to −80°C, we conclude that a fast rearrangement in the iron framework is occurring to make the three iron atoms equivalent on the NMR time scale. This is consistent with the two mechanisms suggested by Cotton [7] and Johnson [8] to account for the exchange of CO groups.

Experimental

Complexes II and III were moderately ^{13}CO enriched (10%) and IV was highly ^{13}CO enriched: the enrichment was performed by stirring for a few days in a sealed ampoule at +40°C in presence of 90% enriched ^{13}CO (Monsanto Research Corporation). ^{13}C NMR spectra were recorded on a Jeol PFT 100 instrument operating in the Fourier Transform mode at 25.1 MHz. Solutions in $CDCl_3$ or CD_2Cl_2 were sealed in vacuo in 10 mm tubes. For I, II and III accumulations of 1500—2000 transients were necessary at a spectral width of 1 kHz. For IV, a digital resolution of 0.05 Hz was obtained when 100—150 transients were accumulated using a 200 Hz spectral window.

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