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*Short Communication*

# $^{13}$C-NMR Spectroscopy of Tricarbonyl[3-6-η-((*E*)-6-methyl-3,5-heptadien-2-one)]iron at Low Temperatures*

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**Summary.** The dynamic behaviour of Tricarbonyl[3-6-$\eta$-((*E*)-6-methyl-3,5-heptadien-2-one)]iron in solution has been investigated by low temperature $^{13}$C-NMR spectroscopy. Preliminary results are discussed.

**Keywords.** [Fe(CO)$_3$($\eta^4$-diene)] complex; Carbonyl scrambling; Dynamic $^{13}$C-NMR spectroscopy; Heteronuclear NOE effect.

**Tieftemperatur-$^{13}$C-NMR-Spektroskopie von Tricarbonyl[3-6-η-((*E*)-6-methyl-3,5-heptadien-2-on)]-eisen (Kurze Mitt.)**

**Zusammenfassung.** Das dynamische Verhalten von Tricarbonyl[3-6-$\eta$-((*E*)-6-methyl-3,5-heptadien-2-on)]eisen in Lösung wurde mittels Tieftemperatur-$^{13}$C-NMR-Spektroskopie untersucht. Vorläufige Resultate werden vorgestellt.

Carbonyl scrambling in [Fe(CO)$_3$($\eta^4$-diene)] complexes has attracted considerable attention since the process was observed for the first time in the early seventies by low temperature $^{13}$C-NMR spectroscopy [1–3]. The influence of the electronic properties of the organic ligand on activation barriers has been discussed and exchange mechanisms have been proposed [4–6]. Recent developments are reviewed in Refs. [7] and [8].

Tricarbonyl[3-6-$\eta$-((*E*)-6-methyl-3,5-heptadien-2-one)]iron (**1**), synthesized in the context of the preparation of isoprenoid tricarbonyliron complexes [9], shows a considerable broadening of the averaged Fe(CO)$_3$ resonance at room temperature and an observation frequency of 25 MHz. An estimation of the energy barrier of the exchange process from a correlation of the free energy of activation with the $^{13}$C chemical shift of the Fe(CO)$_3$ moiety in the fast exchange limit yields a $\Delta G^{\neq}$ value of about 50 kJ mol$^{-1}$ [4, 10]. This should allow the monitoring of the carbonyl scrambling process at temperatures not far below room temperature at 5.87 T.

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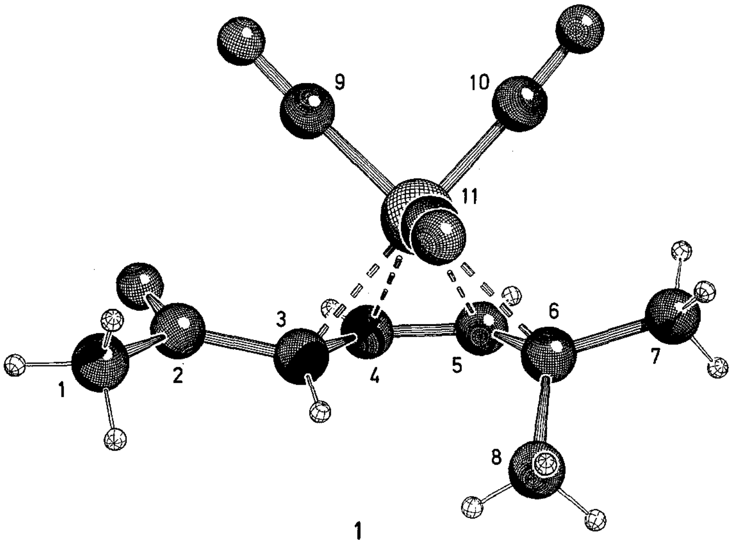
* Dedicated to Prof. Dr. K. Schlögl on the occasion of his 65th birthday



**1**

Fig. 1 shows the carbonyl region of the $^{13}$C-NMR spectrum of **1**. It is obvious that the Fe(CO)$_3$ resonances behave exactly as predicted. The three nonequivalent sites give rise to three well separated peaks at low temperatures. The slow exchange limit is reached at about $-60$°C as can be seen from the intensities of the Fe(CO)$_3$ resonances compared to the peak due to the ligand carbonyl group, whereas an approach to the fast exchange limit failed because of the thermal instability of **1** (at elevated temperatures **1** rearranges partly to the corresponding unstable enone complex; compare [9]).

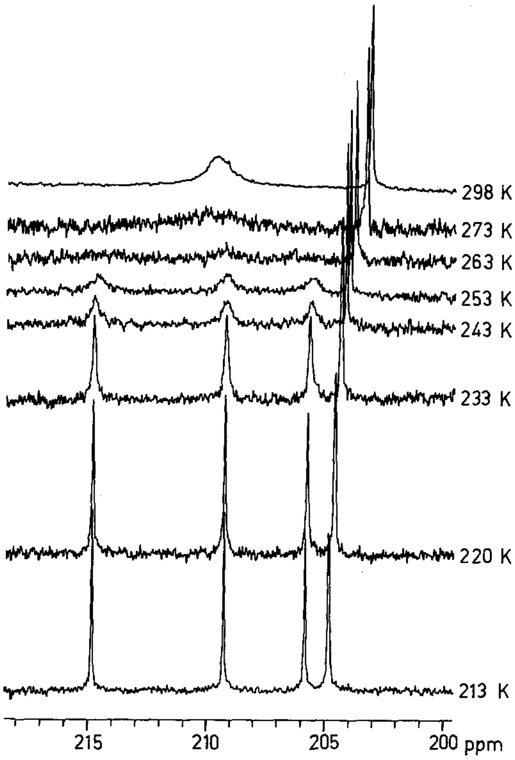


**Fig. 1.** Carbonyl region of the $^{13}$C-NMR spectrum of **1** in CDCl$_3$ at different temperatures

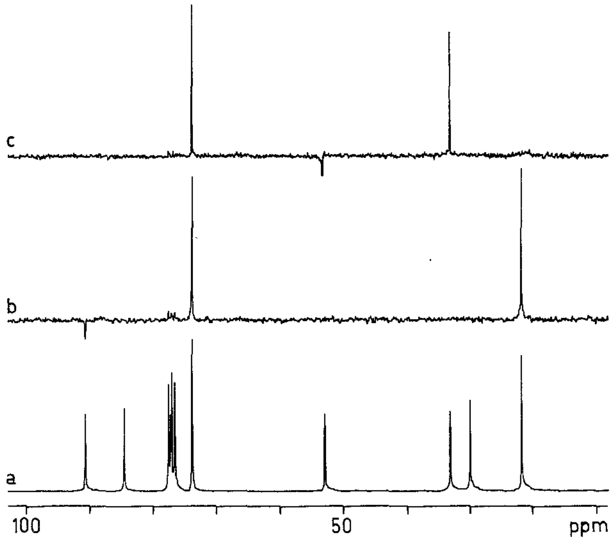


**Fig. 2.** $^{13}$C{$^1$H} NOE difference spectra of **1**. *a*: Reference spectrum; *b*: irradiation at H—C(7); *c*: irradiation at H—C(8). The enhancement of the signal due to C(6) could be unambiguously detected after 16 scans

The position of the $^{13}$C-NMR signal of C(2) shows a considerable temperature dependance. All other $^{13}$C shift values of the ligand carbon atoms remain virtually constant when the temperature is varied. Therefore, in addition to the three site exchange, a second dynamic process concerning the ligand in the region of its carbonyl group must be taken into consideration.

The assignment of the $Fe(CO)_3$ resonances in the slow exchange limit (Table 1) is deduced from a comparison with values given in the literature for complexes with symmetric organic ligands [6]. It is in accordance with a small temperature dependance of the $^{13}$C chemical shift of C(9) at low temperatures, probably caused by the above cited temperature dependant phenomenon at the nearby situated C(2).

**Table 1.** $^1$H and $^{13}$C chemical shifts of **1** (ppm relative to internal *TMS*); a: $^1$H, 250.13 MHz, $CDCl_3$, 220 K; b: $^{13}$C, 62.9 MHz, $CDCl_3$, 220 K; c: $^1$H, 400 MHz, $C_6D_6$, 300 K; d: $^{13}$C, 100.9 MHz, $C_6D_6$, 300 K. Shift values in $C_6D_6$ are taken from Ref. [9]. The assignment of C(9), C(10) and C(11) in column b is tentative

| No. C | a | b | c | d |
|---|---|---|---|---|
| 1 | 2.14 | 29.9 | 1.76 | 32.4 |
| 2 | — | 204.8 | — | 199.0 |
| 3 | 2.48 | 52.9 | 2.17 | 57.0 |
| 4 | 5.77 | 84.5 | 5.69 | 86.8 |
| 5 | 5.28 | 90.6 | 4.42 | 92.1 |
| 6 | — | 73.7 | — | 74.9 |
| 7 | 1.55 | 33.0 | 1.13 | 36.0 |
| 8 | 1.25 | 21.6 | 0.82 | 25.0 |
| 9 | — | 205.7 | — | 208.1 |
| 10 | — | 209.2 | — | 208.1 |
| 11 | — | 214.8 | — | 208.1 |

However, to the best of the authors knowledge no method for an unambiguous assignment is available. In **1**, the intramolecular distances as derived from an x-ray study of the solid compound [9] seem suited for the generation of $^{13}C\{^1H\}$ nuclear Overhauser effects at the $Fe(CO)_3$ carbons starting from the protons attached to C(7). Therefore, an assignment of C(10) by one-dimensional heteronuclear NOE difference spectroscopy [11–14] should be possible provided the exchange process is sufficiently slow. No unequivocal results could be obtained so far, mainly due to artefacts caused by the sensibility of the chemical shifts of C(2) and, to a much lesser extent, C(9) to small temperature deviations. Nevertheless, heteronuclear NOE experiments proved to be a valuable tool for the acquisition of structural information in crowded molecules. In **1**, direct as well as indirect $^{13}C\{^1H\}$ NOE effects could be observed on irradiation at H—C(7) and H—C(8), respectively (Fig. 2). The results are in accordance with the assignment of the $^1H$- and $^{13}C$-NMR spectra of **1** based on informations derived from chemical shifts and coupling constants (Table 1) [9].

A quantitative investigation on the dynamic properties of **1** is in progress and will be published elsewhere.

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## Experimental Part

The synthesis of **1** has been described elsewhere [9]. $CDCl_3$ was stored over $Al_2O_3$ (Aluminiumoxid 90, stand., act. II–III, 70–100 mesh, Fa. Merck) for several days prior to use. An approx. 1 *M* solution of **1** in $CDCl_3$ was prepared and transferred to a 10 mm NMR tube provided with a teflon stopcock via a short column of $Al_2O_3$. The solution was degassed by a stream of argon for approx. 10 min and the NMR tube was closed. All manipulations were carried out in an inert atmosphere.

$^{13}C$-NMR spectra were measured on a Bruker WM 250 NMR spectrometer equipped with an Aspect 2000 online computer at 62.9 MHz using a 10 mm tunable probehead. Field-frequency stabilization was provided by a deuterium lock channel. The temperature was adjusted and kept constant by the variable temperature unit of the spectrometer.

Spectra of the carbonyl region: size, 4 K data points; sweep width, 1 300 Hz; digital resolution, 0.63 Hz/point; pulse width, 10 $\mu$s (36°); relaxation delay, 10 s; number of scans, 160 (exception: $T = 298$ K, NS = 7 600); exponential weighting, 1 Hz.

$^{13}C\{^1H\}$ NOE difference spectra: size, 32 K data points; sweep width, 16 666 Hz; digital resolution, 0.98 Hz/point; pulse width, 25 $\mu$s (90°); irradiation period, 10 s; irradiation power, 45 L; number of scans, 400; exponential weighting, 1.5 Hz.

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