

Tricarbonyliron Complexes – Observation of $^{13}\text{C}(\text{CO})$ NMR Signals via Polarization Transfer

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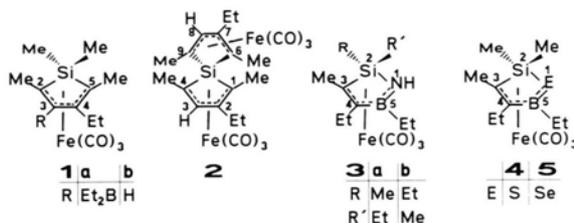
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Tricarbonyliron Complexes, Cyclic Dienes,
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Improvements in the detection of $^{13}\text{C}(\text{CO})$ resonances by using polarization transfer techniques, based on long-range coupling constants $^nJ(^{13}\text{C}(\text{CO})^1\text{H}) = 1 \pm 0.1 \text{ Hz}$ ($n > 3$), are reported. Coupling constants between $^{13}\text{C}(\text{CO})$ and other rare spin-1/2 nuclei have been observed, and long-range $^{13}\text{C}(\text{CO})$ – ^1H coupling have been traced by two-dimensional (2D) $^{13}\text{C}/^1\text{H}$ heteronuclear shift correlations (HETCOR). Seven tricarbonyliron complexes **1** to **5** serve as examples in which the $[\text{Fe}(\text{CO})_3]$ fragment is linked to cyclic dienes (siloles: **1a, b**; 1,1'-spirobisilole: **2**), and to cyclic heterodienes derived from substituted 2,5-dihydro-2,5-silaboroles [1-aza (**3a, b**); 1-thia (**4**); 1-selena (**5**)]. In the case of complex **5**, it was possible to resolve the ^{77}Se satellites with $^2J(^{77}\text{Se}^{13}\text{C}(\text{CO})) = 4.4 \text{ Hz}$. In 2D $^{13}\text{C}(\text{CO})/^1\text{H}$ HETCOR experiments it was shown that polarization transfer originates mainly from C-methyl groups [$^4J(^{13}\text{C}(\text{CO})^1\text{H}(\text{Me}))$], adjacent to the "terminal" carbon atom(s) of the cyclic diene or heterodiene system which are linked to the $[\text{Fe}(\text{CO})_3]$ fragment.

Tricarbonyliron-diene complexes are important compounds in organometallic chemistry and organic synthesis [1–3]. At first sight, it seems that little NMR spectroscopic information on the $[\text{Fe}(\text{CO})_3]$ fragment can be gained in addition to the $\delta^{13}\text{C}(\text{CO})$ values which are accessible by routine ^{13}C NMR measurements. Useful information on spin–spin coupling of $^{13}\text{C}(\text{CO})$ to other nuclei such as ^1H or rare spin-1/2 nuclei is frequently not available because of insufficient resolution (if the

magnitude of the coupling constants is small) or insufficient signal-to-noise ratio if satellites of low intensity have to be detected. We report here on the application of polarization transfer, based on long-range coupling constants $^nJ(^{13}\text{C}(\text{CO})^1\text{H})$ ($n > 3$) to improve the detection of the $^{13}\text{C}(\text{CO})$ NMR signals for the complexes **1–5** in one- (1D) and two-dimensional (2D) experiments.



Recently, we have prepared tricarbonyliron complexes of substituted siloles (**1**) [4], 1,1'-spirobisiloles (**2**) [5], and also of several cyclic heterodienes (**3** [6], **4** [7], **5** [8]), derived from the substituted 2,5-dihydro-2,5-silaborole system. In the course of characterizing these compounds by ^{13}C NMR, the $^{13}\text{C}(\text{CO})$ NMR signals could always be observed without much difficulty. However, it proved rather time consuming to detect satellite signals, e.g. due to $^1J(^{55}\text{Fe}^{13}\text{C}(\text{CO}))$, and sometimes the satellites were not well resolved from the central signal, e.g., for $^2J(^{77}\text{Se}^{13}\text{C}(\text{CO}))$ in **5**. Coupling constants $^nJ(^{13}\text{C}(\text{CO})^1\text{H})$ were never resolved in ^1H -coupled ^{13}C NMR spectra of **1–5**.

Results

Since rather small long-range coupling constants $|^nJ(^{13}\text{C}(\text{CO})^1\text{H})|$ are to be expected ($< 2 \text{ Hz}$), it is important for the present purpose to consider which polarization transfer technique should be used. The refocused INEPT pulse sequence with ^1H -decoupling [9] proved more efficient than DEPT [10], owing to shorter delays and consequently smaller loss of transverse magnetization. For all complexes **1–5**, it was found that the best results are obtained with delays corresponding to $|^nJ(^{13}\text{C}(\text{CO})^1\text{H})| = 1 \pm 0.1 \text{ Hz}$, and that the relative intensities of the $^{13}\text{C}(\text{CO})$ signals differ only slightly when the refocusing delay is tuned according to coupling of the $^{13}\text{C}(\text{CO})$ nucleus with 2, 3, 4, 5 or 6 protons. An example of the improved quality of 1D NMR spectra is shown for compound **5** in Fig. 1. In addition to the gain in the signal-to-noise ratio, the INEPT experiments yield

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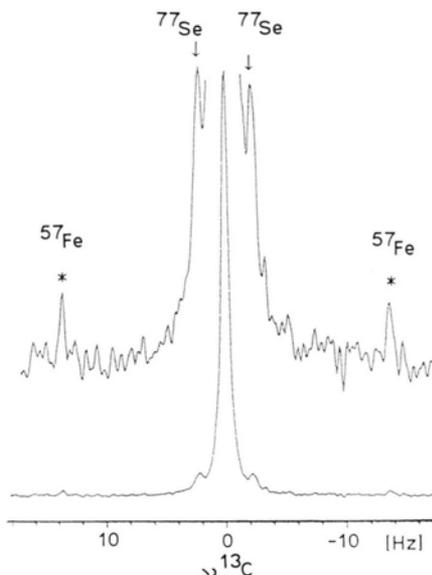


Fig. 1. 125.7 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **5** ($25 \pm 1^\circ\text{C}$; $\approx 5\%$ in C_6D_6) showing the $^{13}\text{C}(\text{CO})$ resonance signal ($\delta^{13}\text{C}$ 212.1) recorded via the refocused INEPT sequence, based on $^1J(^{13}\text{C}(\text{CO})^1\text{H}(\text{Me}^3)) = 1$ Hz (result of 400 scans; acquisition time 3 s; recycle delay 8 s; spectrometer time ≈ 1.5 h). The satellites due to ^{57}Fe [$^1J(^{57}\text{Fe}^{13}\text{C}(\text{CO})) = 27.3$ Hz] and ^{77}Se [$^2J(^{77}\text{Se}^{13}\text{C}(\text{CO})) = 4.4$ Hz] are indicated by asterisks (*) and arrows (\downarrow), respectively.

more narrow lines when compared with routine $^{13}\text{C}\{^1\text{H}\}$ spectra, because temperature gradients in the sample (particularly annoying at higher field strengths B_0), due to dielectric heating by continuous ^1H -decoupling, decay during the recycling delays of the pulse sequence, and in the case of the $^{13}\text{C}(\text{CO})$ resonance signals, a low level of decoupling power can be used.

In Fig. 1, the ^{57}Fe satellites are clearly visible [$^1J(^{57}\text{Fe}^{13}\text{C}(\text{CO})) = 27.3$ Hz] and the ^{77}Se satellites [$^2J(^{77}\text{Se}^{13}\text{C}(\text{CO})) = 4.4$ Hz] which are close to the central $^{13}\text{C}(\text{CO})$ resonance are clearly resolved. For all complexes studied here, the magnitude of values $^1J(^{57}\text{Fe}^{13}\text{C}(\text{CO}))$ covers a small range of 27.7 ± 0.5 Hz.

It was of interest to find out which protons are mainly responsible for the successful polarization transfer. The 1D approach (off resonance, selective ^1H -decoupling experiments) is rather tedious, since the choice of the correct power level for ^1H -decoupling is critical owing to the small magnitude of $^1J(^{13}\text{C}(\text{CO})^1\text{H})$. Similarly, selective population inversion (SPI) experiments are not straightforward because of overlapping signals in the ^1H NMR spectra. Therefore, simple INEPT

based 2D $^{13}\text{C}/^1\text{H}$ heteronuclear shift correlations (HETCOR) [11] were applied, taking advantage of the fairly precise knowledge of the value $^1J(^{13}\text{C}(\text{CO})^1\text{H})$. It turned out that the by far most intensive cross peaks in the contour plots of the HETCOR experiments for all complexes **1–5** stem from the methyl groups in 2,5-position (**1**), in 1,4,6,9-position (**2**) and in 3-position (**3, 4, 5**). All other coupling constants $^1J(^{13}\text{C}(\text{CO})^1\text{H})$ must be ≤ 1 Hz. A typical example is given for complex **2a** in Fig. 2. There are neither cross peaks of appreciable intensity for $\text{H}^{3,8}$ (not shown), although this would be a coupling across three bonds, nor for the CH_2 -protons of the ethyl groups in 2,7-position. Each of the methyl groups in **1–5** with cross peaks to $^{13}\text{C}(\text{CO})$ is attached to a "terminal" carbon atom of the diene or heterodiene system. Although only a small number of tricarbonyliron complexes has been studied in this way, the observation of the same effect for all complexes **1–5** points towards a general phenomenon which deserves further attention.

In Fig. 2, the intensities of the two cross peaks are different, indicating that one coupling constant, $^1J(^{13}\text{C}(\text{CO})^1\text{H}(\text{Me}^{1,6}))$, is ≈ 1 Hz (the experiment was set up for this value which gave best

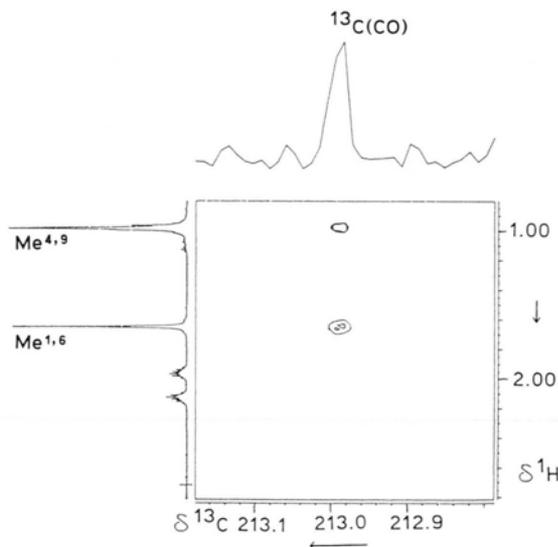


Fig. 2. Contour plot of the 2D $^{13}\text{C}(\text{CO})/^1\text{H}$ HETCOR experiment [based on $^1J(^{13}\text{C}(\text{CO})^1\text{H}) = 1$ Hz] for complex **2** ($25 \pm 1^\circ\text{C}$; $\approx 5\%$ in C_6D_6 ; 1 K data points for F_2 (1000 Hz) and 2500 Hz with 256 experiments of 32 scans each for F_1 ; Gaussian multiplication and zero-filling in both dimensions; recycle delay 2.5 s; spectrometer time ≈ 8 h), showing the projections F_2 ($\delta^{13}\text{C}$) and F_1 ($\delta^1\text{H}$, range of Me and Et groups). Only the $\text{Me}^{1,6}$ and $\text{Me}^{4,9}$ groups show cross peaks of appreciable intensity.

results in the 1D spectra) and the magnitude of the other one, $|^4J(^{13}\text{C}(\text{CO})^1\text{H}(\text{Me}^{4,9}))|$, is somewhat smaller. In the case of **1a** the stronger cross peak is observed for the methyl group in 5-position, whereas there is hardly any difference in the cross peak intensities for the methyl groups in 2- and 5-position of **2b**. This shows that further work is necessary in order to determine systematically the influence of substituents on these long-range coupling constants. Although the distance between the iron atom and the "terminal" carbon atoms of the diene system is in general longer than to the "central" carbon atoms [2], the long-range coupling is apparently better transmitted through the "terminal" carbon atom. Future work, including other carbonylmetal diene complexes, will show whether there is a dependence on $\sigma(\text{metal-C})$ bonding.

In the case of complex **5**, the $^{13}\text{C}/^1\text{H}$ HETCOR experiment was run until the signal-to-noise ratio was sufficient to detect cross peaks for ^{57}Fe and ^{77}Se satellites. Since there was no tilt observed for these cross peaks [12], the coupling constant $|^3J(^{57}\text{Fe}^1\text{H})|$ must be very small (<0.3 Hz, accord-

ing to the digital resolution of the experiment), as expected because of the small magnetic moment of the ^{57}Fe nucleus.

Experimental

All samples were handled under an Ar atmosphere, using carefully dried solvents and glassware. The synthesis of the complexes **1–5** has been described, and most of their NMR data have been reported [4–8]. Complex **2** was isolated as the *meso*-isomer, and its molecular structure has been determined by X-ray analysis [5]. The compounds were dissolved in C_6D_6 (**1**, **2**, **4**, **5**) or $[\text{D}_8]$ toluene (**3**) and sealed in 5 mm tubes. The NMR spectra were recorded using Bruker ARX 250 and AM 500 spectrometers (see also Fig. 1 and 2 for experimental details).

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- [1] A. J. Pearson, *Acc. Chem. Res.* **13**, 463 (1980).
[2] C. Krüger, B. L. Barnett, D. Brauer, in E. A. Koerner von Gustorf, F.-W. Grevels, I. Fischler (eds): *The Organic Chemistry of Iron*, Vol. 1, pp. 1–112, Academic Press, New York (1978).
[3] a) R. B. King, in E. A. Koerner von Gustorf, F.-W. Grevels, I. Fischler (eds): *The Organic Chemistry of Iron*, Vol. 1, pp. 525–625, Academic Press, New York (1978);
b) A. J. Pearson, in F. R. Hartley (ed.): *The Chemistry of the Metal-Carbon Bond*, Vol. 4, Chapter 10, Wiley, Chichester (1987);
c) H.-J. Knölker, in K. H. Dötz, R. W. Hoffmann (eds): *Organic Synthesis via Organometallics* (Volkswagen-Stiftung, Proceedings of the 3rd Symposium), pp. 119–147, Vieweg, Braunschweig (1991).
[4] R. Köster, G. Seidel, J. Süß, B. Wrackmeyer, *Chem. Ber.* **126**, 1107 (1993).
[5] R. Köster, G. Seidel, I. Klopp, C. Krüger, G. Kehr, J. Süß, B. Wrackmeyer, *Chem. Ber.* **126**, 1385 (1993).
[6] R. Köster, G. Seidel, B. Wrackmeyer, D. Schlosser, *Chem. Ber.* **122**, 2055 (1989).
[7] R. Köster, G. Seidel, R. Boese, B. Wrackmeyer, *Chem. Ber.* **121**, 709 (1988).
[8] R. Köster, G. Seidel, R. Boese, B. Wrackmeyer, *Chem. Ber.* **121**, 1955 (1988).
[9] a) G. A. Morris, *J. Magn. Reson.* **41**, 185 (1980);
b) D. P. Burum, R. R. Ernst, *J. Magn. Reson.* **39**, 163 (1980).
[10] D. T. Pegg, D. M. Doddrell, M. R. Bendall, *J. Chem. Phys.* **77**, 2745 (1982).
[11] R. Freeman, G. A. Morris, *J. Chem. Soc. Chem. Commun.* **1978**, 684.
[12] A. Bax, R. Freeman, *J. Magn. Reson.* **45**, 177 (1981).