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Solid state ^{13}C CP-MAS NMR spectra of iron (alkyne) carbonyl compounds

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Abstract

The solid state ^{13}C NMR spectra of a series of iron (alkyne) carbonyl complexes, enriched in ^{13}C at the carbonyl groups, have been obtained using ^{13}C-{^{1}H} cross-polarisation (CP) and slow magic angle spinning (MAS). In general, more resonances are observed from the solid state than from samples in solution; this may be due either to crystal packing effects lifting the degeneracy of certain signals or to a slowing of carbonyl fluxionality in the solid state. The intensities of the spinning side bands in the ^{13}C spectra have been used to derive values for the components of the ^{13}C shielding tensor. The component of the shielding tensor assigned to the C–O bond axis (σ_{33}) is sensitive to the bonding of the CO group, i.e. whether it is a terminal or asymmetrically bridging group.

Introduction

Recent applications of solid state NMR spectroscopy to metallo-carbonyls have shown that the stereochemical non-rigidity exhibited by these compounds in solution is not usually found in the solid state [1,2] as, for example, in systems such as

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$Ru_3(CO)_{12}$ [1] and $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ [2]. However, in the case of $Fe_3(CO)_{12}$, high resolution solid state ^{13}C NMR spectroscopy has shown [3] the occurrence of a dynamic process attributed to motion of the Fe_3 moiety inside the cluster of carbonyl ligands, motion which can be "frozen out" only at low temperatures. Simple systems, such as (arene)$M(CO)_3$, show fluxionality in the solid state and variable temperature experiments [4] may be used to distinguish between carbonyl scrambling within the $M(CO)_3$ unit and rotation of the π-arene ring. In general it can be said that these observations prompt new studies in order to define more systematically the main features which characterise the ^{13}C CP-MAS spectra (see Experimental) of carbonyl compounds and establish what new information may be available through the use of this technique applied to this class of compounds.

With this aim we have examined the solid state ^{13}C CP-MAS spectra of four binuclear iron derivatives obtained from the reactions of iron carbonyls with alkynes.

In solution spectra the resonances are centred at the isotropic shielding, σ_{iso}, as are the centre bands of a solid state ^{13}C spectrum; σ_{iso} is given by:

$$\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3 \tag{1}$$

where the σ_{ii} are the principle components of the shielding tensor. The value of σ_{iso} for the solution and solid states may be somewhat different because the components may be different in different media. In solid state slow MAS ^{13}C spectra the intensities of the spinning side bands for each resonance (see Fig. 1) are a function of the three chemical shift components and the spinning speed, and can be analysed [5,6] to provide the individual components for each resolved ^{13}C resonance. Knowledge of the σ_{ii} values can provide a more detailed basis for assignment and for a discussion of the localised bonding characterisatics of a carbonyl group than knowledge of σ_{iso} only. The methods to derive the σ_{ii} values from the side band intensities of slow MAS experiments have been described. Maricq and Waugh [5] used a moment analysis of the intensities, but as noted by Clayden et al. [7], to derive accurate values for the shielding tensor components by this method requires spectra with excellent signal-to-noise ratios, particularly for the higher order side bands. A subsequent analysis, due to Herzfeld and Berger [6] which does not suffer from this constraint, considers the experimental ratio of the intensity of a given ^{13}C resonance in the ith spinning side band to the corresponding intensity in the centre band to be a function of μ and ρ:

$$\mu = \nu_0(\sigma_{33} - \sigma_{11})/\nu_r \tag{2}$$

$$\rho = (\sigma_{11} + \sigma_{33} - 2\sigma_{22})/(\sigma_{33} - \sigma_{11}) \tag{3}$$

where ν_0 is the ^{13}C resonance frequency (here 50.3 or 75.5 MHz) and ν_r the spinning speed. The intensity ratio for a given side band may be plotted as a function of μ and ρ and when this procedure is repeated for all the spinning side bands of the same resonance a characteristic contour plot is obtained. Ideally the contours corresponding to the different side bands should intersect at a single point exactly defining μ and ρ. In practice, owing to experimental errors, they intersect over a finite region. Once this region is defined the best values of μ and ρ may be selected and the shielding tensor components calculated from eqs. (2) and (3).

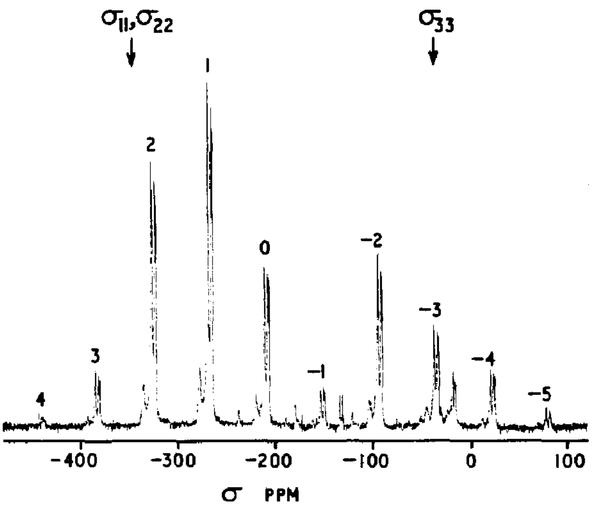
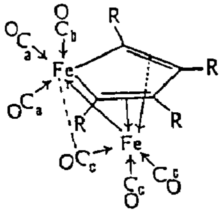
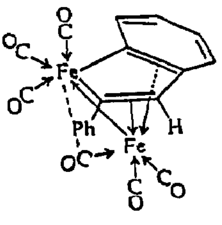


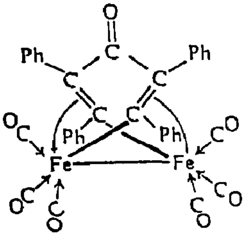
Fig. 1. 50.3 MHz ^{13}C CP/MAS spectrum of (^{13}CO)-enriched I; the spinning speed was 2.92 kHz. Numbers above the spectrum are the assignment of the spinning side bands.



I, R=Et
II, R=Ph



III



IV

Finally, the shielding tensor anisotropy ($\Delta\sigma$), and the shielding asymmetry parameter, η, are defined by:

$$\Delta\sigma = \sigma_{33} - (\sigma_{11} + \sigma_{22})/2 \tag{4}$$

$$\eta = (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma_{iso}) \tag{5}$$

We use the same convention as Herzfeld and Berger [6], i.e. $\sigma_{33} \geqslant \sigma_{22} \geqslant \sigma_{11}$. Both $\Delta\sigma$ and η turn out to be useful diagnostic parameters for the type of carbonyl.

Results and discussion

Compounds I, II and III are structural analogues [8,9]; their bonding scheme is characterized by the formation of a metallo-cyclopentadiene system coordinated to another $Fe(CO)_3$ unit which releases back the excess of electron density through the semibridging carbonyl "c". We have not found any published data on the crystal structure of I, but the structure of the tetraphenyl analogue (II) has been determined

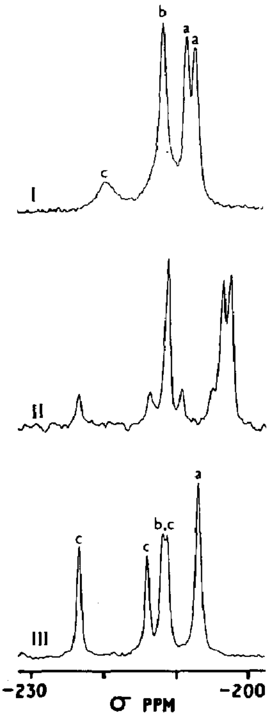


Fig. 2. Centre band regions of the ^{13}C CP/MAS spectra of (^{13}CO)-enriched I, II and III; the spectra of I and II were recorded at 50.3 MHz, and that of III at 67.8 MHz.

by X-ray diffraction [10]. The compound crystallises in the non-centrosymmetric space group $P2_1$ with two molecules/unit cell and one molecule as the asymmetric unit. Compound III crystallises [11] in the space group $P\bar{1}$ with two molecules/unit cell and again with one molecule as the asymmetric unit. Therefore there may be up to six resolved isotropic shieldings for the carbonyl groups of II and III in their solid state ^{13}C spectra, and in the absence of information to the contrary we will assume the same to be true for I. The solution ^{13}C NMR spectra [12,13] of I, II and III show distinct resonance for carbonyls "a" and "b", but only a single averaged resonance for carbonyl "c"; the intensities of these three signals are in the ratio 2/1/3. Only with bulky t-Bu substituents on the metallo-cycle ring and at low temperature was it possible to slow down the exchange of the "c" carbonyls and detect [12] separate semi-bridging and terminal carbonyl resonances.

The centre-band regions of the ^{13}C CP-MAS spectra of I, II and III are shown in Fig. 2 (see also Fig. 3A for II). In II and III the π-bonded $Fe(CO)_3$ units show three distinct signals for the carbonyls "c"; at -211.7, -214.0, and -223.7 ppm for II and at ca. -211.3, -214.1, and -223.4 ppm for III. The averages of these signals for II and III (-216.5, -216.3) agree well with the isotropic values found in solution in the presence of fast exchange (-216.2, -215.4). The appearance of three peaks for the "c" carbonyls is due to crystal packing effects, as is the splitting of carbonyls "a" in both I and II. Obviously, the rate of exchange of the different carbonyls in the solid state at ambient temperatures depends critically upon the nature of the substituents on the metallo-cyclopentadiene ring. Presumably the "c"

Table 1

Shielding tensor component analysis [a] for the carbonyl groups of I–IV

	σ_{iso}	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$	η	SSB's [b]
I	−219.6 [c]						
	−211.5	−345.2	−345.2	65.8	411.0	0	+4 to −5
	−208.2 −207.0 [d]	−342.9	−242.9	64.9	407.8	0	+4 to −5
II	−223.7 [e]						
	−214.0 [e]						
	−211.7	−347.6	−347.6	60.1	407.7	0	+3 to −4
	−209.6 [e]						
	−205.3 [e]						
	−204.0 −203.0 [d]	−340.1	−340.1	69.8	409.9	0	+3 to −5
III	−223.4	−350.2	−350.2	30.0	380.2	0	+3 to −5
	−214.1	−351.4	−351.4	60.5	411.9	0	+3 to −5
	−211.6 −211.0 [d]	−348.9	−348.9	63.9	412.9	0	+3 to −5
	−207.0	−345.7	−345.7	70.4	416.1	0	+3 to −5
IV	−211.8 [f]						
	−209.8	−342.2	−342.2	55.1	397.2	0	+3 to −4
	−206.9	−338.4	−338.4	56.2	394.6	0	+3 to −4
	−202.8	−336.8	−336.8	65.1	401.9	0	+3 to −4
	−193.9	−299.0	−163.7	−119.1	112.3	1.81	+2 to −2

[a] The shieldings are referenced to external TMS, with the convention that high frequency shieldings are negative and that high frequency side bands are positive. For chemical shifts on the δ scale, the signs of σ should be reversed. [b] These spinning side bands were those used to derive the tensor components. [c] Broad resonance. [d] The average of these isotropic shieldings was used in the calculation of the shielding tensor components. [e] These are the low intensity resonances (see Fig. 3d). [f] The side band intensities for this resonance gave an unacceptably large area in the μ,ρ contour plot (see text), and hence we are unable to define μ and ρ with any confidence.

carbonyls in I are close to their coalescence temperature and give rise to the broad hump at ca. −220 ppm.

The intensity of a resonance is proportional to the sum of the intensities of the resonance over the centre band and all its side bands. However, when comparing the intensities of two resonances, it is sufficient, if the three shielding components are very similar, to compare the intensities within the centre band (or indeed any single side band group). On the other hand, if the shielding tensor components are very different, e.g. the terminal carbonyls and the ketonic carbonyl of IV (see Table 1), then the relative intensities within the centre band will not provide an accurate estimate of the relative populations of the chemical environments. The peaks due to carbonyls "c" in II are are of relatively low intensity, but as they are sharp this is unlikely to be due to an exchange process. We checked the possibility that the relatively low intensity was due to differences in the efficiency of the cross-polarisation for different carbonyls by repeating the spectrum with different contact times in the range 1 to 10 ms. No marked effect on the relative signal intensities was found. Subsequently we noted that spectra run on the same sample of II at intervals of several days show (Fig. 3) significant intensity changes, starting with a set of six

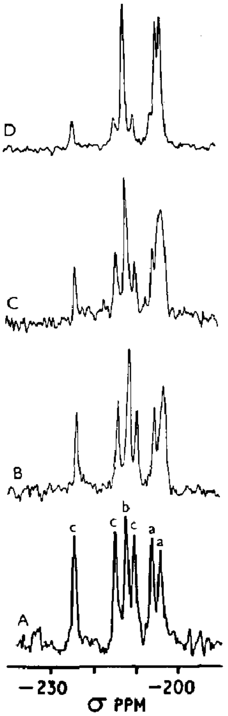


Fig. 3. Time dependence of the centre band region of the ^{13}C CP/MAS spectrum of (^{13}CO)-enriched II; the spectra were recorded at (A) ca. 1 d, (B) ca. 10 d, (C) ca. 24 d, and (D) ca. 40 d after crystallisation.

equally intense resonances. We found that the same result could be obtained more quickly with a sample left for a few hours under vacuum (0.5 mmHg), and therefore conclude that the observed change is probably due to the elimination of solvent molecules from the crystal.

The X-ray structural analysis of IV showed [14] the molecule to crystallise in the space group $P2_1/n$ with four molecules/unit cell and the asymmetric unit to contain one molecule. Therefore up to six metal-bound carbonyl ^{13}C signals and one ketonic carbonyl ^{13}C signal might be expected in the solid state spectrum. The centre-band region of the ^{13}C CP-MAS spectrum of IV (Fig. 4) shows resolved peaks at −211.8, −206.9, −207.8, −202.8 and −193.9 ppm. The signal at −193.9 ppm can be readily assigned to the ketonic carbonyl group on the ligand, both from its isotropic shielding and from its low chemical shift anisotropy. The solution state shielding [12] is −195.5 ppm (cf. −193.9 for the solid state, see Table 1) and the shielding anisotropy $\Delta\sigma$ is 112.3 ppm which is very similar to that for the carbonyl carbon of benzophenone [15] (108 ppm). The following discussion is concerned only with the remaining metal-bound carbonyl groups, which in the solution state are known [12] to exhibit fluxional behaviour. On the basis of the preceding discussion we would expect up to six resonances for IV. Summation of the intensities of the four observed resonances over the whole spinning side-band manifold shows that the intensity ratio is 1/2/2/1, i.e. two sets of carbonyls exhibit a degeneracy. Again, the weighted average of the observed carbonyl shieldings (−208.0) is in good agreement with the value found [12] for the exchanging system in solution (−207.7 ppm).

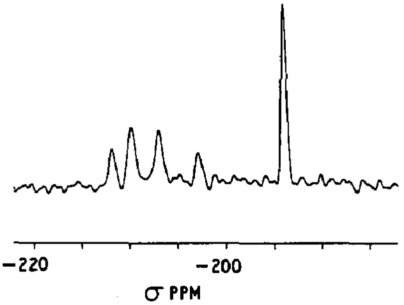


Fig. 4. Centre band region of the ^{13}C CP/MAS spectrum of (^{13}CO)-enriched IV.

Table 1 shows the results of the analysis for the shielding tensor components for all four compounds. As the main limitation to obtaining reliable values for the tensor components is a reasonable signal-to-noise ratio in the ^{13}C spectrum, we have considered only the most intense peaks in each experiment (see Table 1, final column).

The results of the sideband analysis show that all the metal-bonded carbonyls have axial symmetry. This is not expected for the "semibridging" CO ($\sigma_{iso} = -223.4$ ppm) in III but we note that its σ_{33} component is significantly to higher frequency than the values found for the other resonances, which are expected to be truly terminal resonances. The resulting $\Delta\sigma$ is then smaller too (380.2 ppm) and this must be an indication of its partial bridging character. Gleeson and Vaughan [16] proposed that the σ_{33} component may reasonably be assigned to the shielding along the C–O bond axis. As pointed out by Mahnke and coworkers [17], σ_{33} values in systems with axial symmetry are very sensitive to back bonding and the higher frequency found for this carbonyl is then indicative of the release of negative charge from the iron atom involved in the metallo-cycle. As expected the symmetry of the organic keto-group in IV is non axial. Kempf et al. [15] assigned the shielding tensor components for the ketonic carbon of benzophenone as $\sigma_{11} = -272$, $\sigma_{22} = -229$, $\sigma_{33} = -99$ ppm, where the σ_{22} component is that directed along the C–O bond. The values found for the ketonic carbon of IV are (see Table 1) −299.0, −163.7, and −119.1 ppm, and if we follow the above assignment, then σ_{11} and σ_{33} are reasonably similar for the two carbons while σ_{22} shows the greatest difference between the two. Therefore, as with the metal-bonded carbonyls, it is possible that the shielding along the C–O bond axis is the most sensitive to chemical environment.

Experimental

Compounds II and IV were prepared as described previously [18] starting from ^{13}C-enriched $Fe_3(CO)_{12}$. Compounds I and III were prepared [13] analogously by reaction of ^{13}C-enriched $Fe_3(CO)_{12}$ with 3-hexyne or diphenylacetylene in refluxing n-hexane for 6 and 4 h respectively. The products were isolated by thin layer chromatography. This starting material was ^{13}C enriched by stirring a solution in n-hexane under an atmosphere of ^{13}CO in sealed ampoules at 40 °C for 2 d. The level of ^{13}C enrichment was typically 20%. The solid state ^{13}C spectra of I, II and IV were recorded on a Bruker CXP-200 spectrometer (4.7 T) operating at 50.3 MHz for

^{13}C observation. The spectra were obtained with the samples placed in a 7 mm i.d. rotor made of deuterated polymethylmethacrylate (PMMA). The magic angle was optimized using potassium bromide [19] and spinning speeds were in the region 1.5 to 3.2 kHz. ^{13}C-$\{^1H\}$ cross polarisation (CP) was used with flip-back and phase alternation of the ^1H 90° pulse [20]. The proton 90° pulse length varied between 5–6 μs, corresponding to a ^1H field strength of ca. 45 kHz. For the CP technique, a contact time of 2 ms was found to be optimum for this class of compounds. The ^{13}C CP/MAS spectrum of III was obtained with a JEOL GX-270 spectrometer (6.3 T), operating at 67.8 MHz for ^{13}C, equipped with a Chemagnetic solid state accessory. The sample was contained in a 10 mm o.d. rotor made of delrin, the spinning speed was ca. 3.5 kHz, and the ^1H 90° pulse length was 6.5 μs. ^{13}C chemical shifts were referenced to external liquid tetramethylsilane (TMS), using as secondary reference the $^{13}CH_2$ signal of adamantane at -38.25 ppm (to high frequency) from TMS. The ^{13}C shielding tensor components were obtained from the intensities of the spinning side bands by the method of Herzfeld and Berger [6]. Our Herzfeld and Berger analysis was computer-automated in a manner to be described elsewhere [21].

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