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SOLID STATE NMR SPECTROSCOPY OF METAL CARBONYLS. THE INFLUENCE OF SITE SYMMETRY ON THE SOLID STATE SPECTRUM OF *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ *

HARRY C. DORN, BRIAN E. HANSON *
Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061 (U.S.A.)

and EDWIN MOTELL
Department of Chemistry, San Francisco State University, San Francisco, California 94132 (U.S.A.)

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Summary

Solid state carbon-13 NMR spectra of metal carbonyls are readily obtained using commercial instrumentation. The observed isotropic chemical shifts are in good agreement with solution values. Furthermore there is a one-to-one correspondence between crystallographically unique carbonyls and magnetically distinguishable carbonyls in the absence of accidental degeneracies. For *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ the site symmetry is C_1 while the molecular symmetry is C_{2v}. The lower solid state symmetry gives rise to more resonances in the solid spectrum than in solution. Magic angle tuning and chemical shifts were obtained using hexamethylbenzene as a standard.

Introduction

As part of a study of metal carbonyls using solid state NMR spectroscopy, we chose to look at $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ as a model system. This molecule has played a pivotal role in the development of the solution dynamics of metal carbonyls as studied by infrared and NMR spectroscopy.

The dimer, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$, has been shown to exist in solution in two and perhaps three isomeric forms by infrared spectroscopy [1,2,3]. These isomers are in rapid equilibrium. The equilibrium concentrations of these three species is solvent and temperature dependent with the *cis* isomer, Ib, predomin-

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[*] A preliminary account of this work was presented at the Southeast-Southwest Regional ACS meeting in New Orleans, Dec. 10—13th, 1980.

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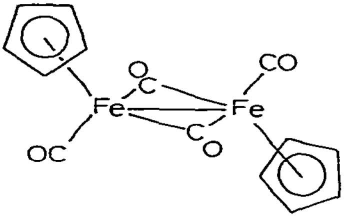
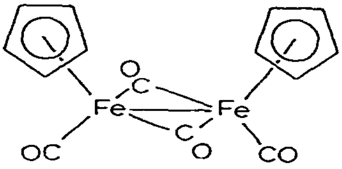


(Ia)



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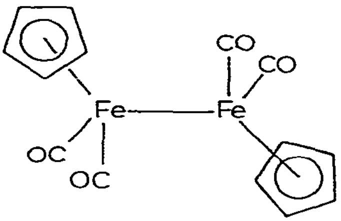


(Ic)

ating in polar solvents and at low temperatures. Isomer Ic is proposed as an intermediate in the interconversion of Ia and Ib [4] and is present in solution only in very small concentrations.

On the NMR time scale only one resonance is observed in the solution ^1H NMR spectrum [4,5] for the C_5H_5 rings at room temperatures. The same result is observed by ^{13}C NMR [6]. A consequence of the isomerization is the exchange of bridging and terminal CO ligands. In the slow exchange limit distinct bridging and terminal CO resonances are observed for the *cis* isomer only [6].

The *trans* isomer, Ia, can be selectively crystallized at room temperature. Its crystal structure has been studied extensively by X-ray and neutron diffraction studies [7—9]. In the solid Ia lies on a crystallographic inversion center in the space group $P2_1/c$. Thus in solution Ia has C_{2h} symmetry while in the solid it occupies a site of Ci symmetry.

The *cis* isomer, Ib, is crystallized from solution at —78°C from polar solvents. This molecule, which has C_{2v} molecular symmetry in solution, occupies a general position in the space group $P2_1/c$ [10]. Thus its maximum symmetry in the solid is C_1.

The non-bridged isomer, Ic, has not been observed in the solid.

It is against this background that we present the solid state NMR spectra for Ia and Ib. The difference in their solid state symmetry allows us to see directly the influence of site symmetry on the NMR spectra of solids. We also report NMR data on several other metal carbonyl complexes in the solid state.

Previously, solid state NMR spectroscopy has been used to study metal carbonyl compounds including $Fe(CO)_5$ [11], $(C_8H_8)_2Ru_3(CO)_4$ [12,13], $(C_8H_8)Fe(CO)_3$ [13], $(C_8H_8)Fe_2(CO)_6$ [13], and $(C_8H_8)Fe_2(CO)_5$ [13]. For iron pentacarbonyl it was deduced that rapid axial—equatorial exchange occurs in the solid. For $(C_8H_8)_2Ru_3(CO)_4$ and the iron complexes $(C_8H_8)Fe(CO)_3$ and $(C_8H_8)Fe_2(CO)_5$ it was shown that rotation of the cyclooctatetraene ring is rapid in the solid as well as in solution [13]. Recent work on the ruthenium complex by high resolution solid state NMR showed that the rotation exchanges distinct carbons [12]. Molecular rotations about axes of high symmetry are, in general, facile in the solid and readily studied by NMR techniques. A classic example is the rotation of benzene about the C_6 axis in the solid [14].

Experimental

All solid state NMR spectra were obtained using a JEOL FX60QS spectrometer operating at 15.0 MHz. Samples were packed in special kel-F rotors supplied

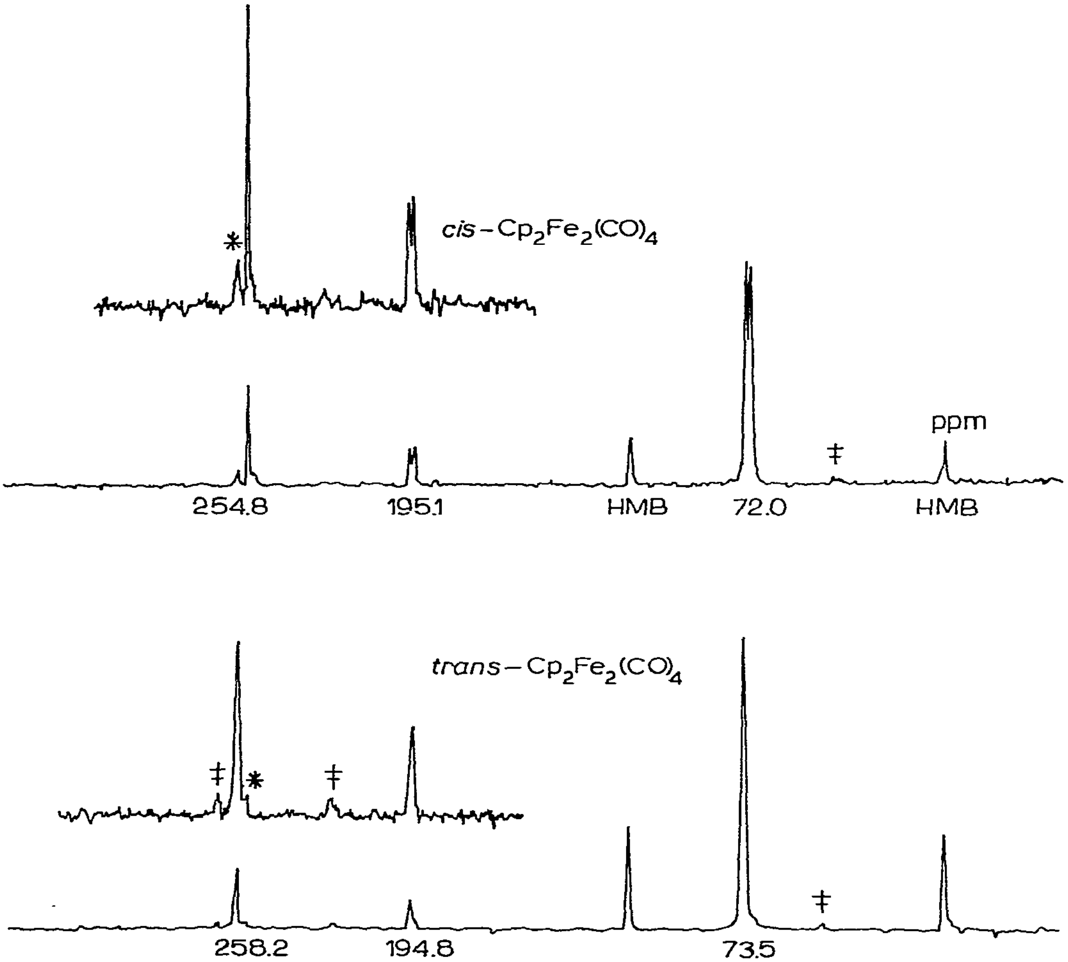


Fig. 1. High resolution solid state NMR spectra for compounds Ia and Ib. The peaks labeled HMB are due to hexamethylbenzene (0 and 114.8 ppm). The asterisked peak in the spectrum of the *cis* isomer is due to a trace of the *trans* isomer. The asterisked peak in the spectrum of the *trans* isomer is due to a trace of the *cis* isomers. The daggered peaks in the spectrum of the *trans* isomer are due to spinning bands. Isotopically normal samples were used for these spectra.

by JEOL. Spinning rates were approximately 2300 cps. Hexamethylbenzene was added to each rotor in a layer ca. 1.5 mm thick at the top. For air sensitive samples the rotor was loaded under N_2 and sealed with plasticine.

Figure 1 shows the solid state NMR spectra for the *cis* and *trans* isomers of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$. A comparison of solution and solid chemical shifts for various metal carbonyls are given in Table 1. Enrichment in ^{13}CO was necessary for the observation of the solid state spectrum of $Fe_2(CO)_9$. Some samples were enriched to provide adequate signal to noise in a reasonable period of time e.g., $Fe_3(CO)_{12}$, $Cp_2Fe_2(CO)_4$, and $Co_2(CO)_8$. Levels of enrichment were typically 10% or less (by infrared spectroscopy). No line broadening due to ^{13}C—^{13}C dipolar couplings were observed at these levels of enrichment.

The spectra of samples containing protons were recorded with the Hartman-Hahn pulse sequence to improve sensitivity [15]. For binary carbonyls a normal

FT pulse sequence was used, i.e. a pulse width of 5 μs (30°) and a delay time of 2 to 10 s. A typical spectrum required 2000 to 5000 pulses.

Discussion

(η^5-C_5H_5)$_2$$Fe_2(CO)_4$

The NMR spectrum of solid *trans*-(η^5-C_5H_5)$_2$$Fe_2(CO)_4$ is consistent with the crystal structure. It should be noted that the solution spectrum of Ia in the slow bridge—terminal exchange limit has not been observed. This is because of the low concentration of Ia in solution and the rapidity of the exchange process [6].

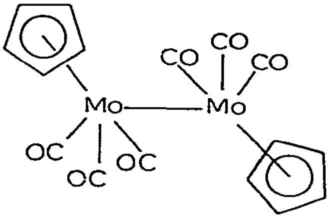
The sharp peak at 73.5 ppm vs. HMB is assigned to the two η^5-C_5H_5 rings, which are related by an inversion center in the crystal. All ten carbons in the two rings are equivalent on the NMR time scale, giving just one resonance implying rapid rotation about the C_5 axis. Crystallographically the thermal motions for the C_5H_5 ring reveal oscillation about this axis [8]. Also there is considerable NMR evidence for rapid rotation of pi-bonded C_5 rings in other organometallic compounds [16—19]. In the carbonyl region the peaks at 258.2 and 194.8 ppm vs. HMB are assigned to the bridging and terminal CO groups respectively. These chemical shifts are consistent with those obtained for many iron carbonyl complexes in solution [20]. The observation of distinct carbonyl resonances shows that rapid bridge terminal exchange does not occur in the solid.

In the spectrum for the *cis* isomer it is immediately obvious that there are now two resonances in the C_5H_5 region and two peaks in the terminal CO region. The bridging CO's appear as a single resonance. Since the two bridging CO groups in Ib are not related by any crystallographically imposed symmetry, the single peak must be due to an accidental superposition of the resonances or an exchange process. The latter makes little sense in terms of the accepted mechanism for bridge—terminal exchange, although it is conceivable that a rapid molecular vibration or oscillation could generate a time-averaged mirror plane that would relate bridging CO's but not the terminal CO's or the C_5H_5 rings. The non-equivalence of the terminal CO's and the C_5H_5 rings is a direct consequence of the C_1 site symmetry of the general position that the molecule occupies. The description of the molecular packing in the crystal [10b] readily reveals the differences. The closest intermolecular contact involving non-hydrogen atoms is between symmetry-related terminal carbonyl oxygen atoms (3.12 Å) [10b]. Also, one C_5H_5 ring makes more "short" intermolecular contacts than the other. Furthermore, this C_5H_5 ring shows more clearly defined carbon positions than the other ring (smaller amplitude of thermal motion). Although C_5H_5 rotation for both rings is fast on the NMR time scale, such rotation cannot equivalence the two rings.

Thus, site symmetry alone can account for the observed spectrum of Ib. The increase in the number of resonances in going from Ia to Ib is a direct consequence of the change in symmetry from C_i to C_1. The appearance of one resonance for the bridging CO's in Ib is not inconsistent with the lower site symmetry.

(η^5-C_5H_5)$_2$$Mo_2(CO)_6$, II

This molecule represents another example where the crystallographic site symmetry is lower than the molecular symmetry. In solution two carbonyl resonances of relative intensity 2 : 4 are observed while in the solid state three resonances of equal intensity are observed. Crystallographically the molecule lies on an inversion center but contains no mirror planes [21]. Only one resonance, as expected, is observed for the cyclopentadienyl rings.



(II)

Other carbonyl compounds

For obvious reasons insoluble compounds represent a class for which solution NMR methods are unavailable. Two compounds studied dissolve only with concomitant reaction. These are $Fe_2(CO)_9$, III, and $Ru_2(O_2CCH_3)_2(CO)_4$, IV. These very important compounds are used extensively as intermediates in inorganic synthesis.

The structure of $Fe_2(CO)_9$ is a classic in metal carbonyl chemistry [22,23]. It consists of two $Fe(CO)_3$ groups linked by three bridging CO groups. Each iron atom lies at the center of an octahedral array of CO ligands. The molecule has a crystallographically imposed three fold axis and a mirror plane that bisects the Fe—Fe bond. Thus only two CO's need be defined crystallographically, one bridging and one terminal. This is completely consistent with the observed NMR spectrum (see Table 1) in which just two carbonyl resonances are observed in a ratio of 3 : 6. The chemical shift of the bridging CO, 218.4 ppm, appears quite far upfield when compared to those observed for substituted iron carbonyl derivatives [10]. It must be noted, however, that this represents the first observation of a distinctly bridging CO in a neutral binary iron carbonyl compound by NMR spectroscopy.

The solid state structure of $Ru_2(O_2CCH_3)_2(CO)_4$, IV, is not known. Some of its derivatives, e.g. $Ru_2(O_2CCH_3)_2(CO)_4(py)_2$ [24], have been examined crystallographically. Unfortunately, there is not sufficient resolution in the solid state NMR spectrum of IV to gain any structural information. The peak at 183.7 ppm is assigned to the four CO groups (this resonance is broad with no discernible fine structure). It is impossible to determine from this single resonance whether the 4 CO ligands are crystallographically related or if the resolution is too poor to see individual CO resonances or an exchange process is occurring.

The NMR spectra of the remaining complexes in Table 1 are consistent with the known or accepted solid state structures, with the exceptions of $Co_2(CO)_8$, V, $Fe_3(CO)_{12}$, VII, and (toluene)$Cr(CO)_3$, XIII. In each of these cases fewer than the number of expected carbonyl resonances observed. For $Fe_3(CO)_{12}$ the spectrum has been shown to be consistent with a dynamic process in the solid [25]. It is possible that the observed spectra for $Co_2(CO)_8$ and (toluene)$Cr(CO)_3$

TABLE 1

SOLID STATE CARBON-13 NMR DATA FOR SOME METAL CARBONYLS

Compound	Chemical shifts			Solution chemical shifts
	(ppm vs HMB)	(ppm vs TMS) [a]		
Ia, *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$	254.8	272.3	bridging CO	274.7 [b]
	195.9	213.4	terminal CO	210.5 [b]
	194.3	211.8		
	72.7	90.2	Cp rings	
	71.4	88.9		
Ib, *trans*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$	258.2	275.7		
	194.8	212.3		
	73.5	91.0		
II, $Cp_2Mo_2(CO)_6$	219.2	236.7		233.9 [c]
	211.4	228.9		227.1
	209.4	226.9		
	76.1	93.6		
III, $Fe_2(CO)_9$	218.4	235.9		
	187.0	204.5		
IV, $Ru_2(OAc)_2(CO)_4$	183.7	201.2		
	170.1	187.6		
	7.3	24.8		
V, $Co_2(CO)_8$	187.8	205.3		202.5 [c]
VI, $CpFe(CO)_2I$	197.9	215.4		213.6 [c]
	68.8	86.3		
VII, $Fe_3(CO)_{12}$	208.6	226.1		
	207.0	224.5		
	196.6	214.1		212.5 [c]
	192.7	210.2		
	185.7	203.2		
	184.3	201.8		
VIII, $Cr(CO)_6$	193.5	211.0		211.2 [c]
IX, $Mo(CO)_6$	184.7	201.2		201.7 [c]
X, $W(CO)_6$	175.6	193.1		191.4 [c]
XI, $(toluene)Mo(CO)_3$	207.1	224.6		223.1 [c, d]
	101.6	118.1		
	83.1	100.6		
	5.5	23.0		
XII, $(toluene)Cr(CO)_3$	217.1	234.6		233.6 [e]
	93.5	111.0		110.3
	77.9	95.4		94.9
	71.7	89.2		93.4
	70.5	88.0		90.2
	0	17.5		20.4

[a] $\delta(TMS) = \delta(HMB) + 17.5$. [b] Data from ref. 6. [c] Data from ref. 20. [d] Chemical shift for carbonyls in $(mesitylene)Mo(CO)_3$. [e] Data from ref. 26.

can be explained by a dynamic process in the solid. The similarity of the solution and solid state chemical shifts in V is indicative of potential bridge—terminal exchange in the solid. For $(\eta^6\text{-arene})Cr(CO)_3$ molecules rotation of the arene with respect to the $Cr(CO)_3$ group is well known in solution [36]. However, in the solid for $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ rotation appears to be slow since three components for the ^{13}C shielding tensor (σ_l, σ_t, σ_r) can be evaluated for the benzene ring. Clearly, confirmation of potential carbonyl exchange processes in the solid state requires a low temperature study. We are currently modifying our spectrometer to allow us to collect data at low temperature on these and other carbonyl compounds.

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