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A MAGIC ANGLE SPINNING ^{13}C NMR STUDY OF ^{13}CO-LABELLED TRICARBONYL(HEXAHAPTO-HEXAMETHYLBENZENE)CHROMIUM(0) AND TRICARBONYL(HEXAHAPTO-DURENE)CHROMIUM(0)*

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Abstract—At 293 K, the slow magic angle spinning carbonyl subspectrum of crystalline ^{13}CO-labelled tricarbonyl(hexahapto-hexamethylbenzene)chromium(0) (**1**) displays an extensive manifold of spinning side bands. These have been analysed to yield the principal elements of the shielding tensor which are appropriate to an axially symmetric anisotropy pattern. In contrast, only a single signal at a position corresponding to the isotropic chemical shift is observed at 293 K for the carbonyl carbon atoms of ^{13}CO-labelled tricarbonyl(hexahaptodurene)chromium(0) (**2**). The intensity of this signal is highly temperature-dependent and the changes are considered in the context of the known crystal and molecular structures of **1** and **2**.

As variable-temperature solid-state Cross Polarization/Magic Angle Spinning (CP/MAS) NMR facilities become more generally available, there is increasing interest in applying the technique to determine the effect(s) of intermolecular interactions on the intramolecular motions of organometallic complexes.[1] For isolated organometallic molecules of the type $(\eta^6\text{-}C_6R_nH_{(6-n)})M(CO)_3$, it is well-established that unless the R group is sufficiently large to cause intramolecular steric hindrance, the barrier to rotation about the (η^6-arene)–metal bond is so low that rapid rotation on the NMR time scale occurs at any experimentally-accessible temperature.[2] However, intermolecular interactions may be significant in the solid state and then, as Braga has pointed out,[3] that particular rotational barrier becomes dependent on the shape of the arene. A discoidal moiety of six-fold symmetry, e.g. benzene or hexamethylbenzene, creates little intermolecular steric hindrance, whereas an arene of lower symmetry, e.g. mesitylene (1,3,5-trimethylbenzene) or durene (1,2,4,5-tetramethylbenzene), causes rotation about the (η^6-arene)–metal bond to become very much less favoured.[4] Methyl groups protruding from the arene ring interlock with neighbouring molecules in the crystal unit cell such that reorientation is forbidden and any significant movement away from the equilibrium position results in a short contact with the surrounding atoms and strong intermolecular repulsion.

Rotation of the conic cog-like $M(CO)_3$ moiety relative to the boundaries of the unit cell involves interactions with corresponding fragments and/or the arenes of adjacent molecules, and is predicted to be energetically very unfavourable even for complexes of discoidal arenes,[4] although relatively low barriers for this process have been claimed for $(\eta^6\text{-}C_4H_5CH_3)Cr(CO)_3$ (65 kJ mol^{-1}) and $(\eta^6\text{-}C_6H_5CH_3)Mo(CO)_3$ (71 kJ mol^{-1}) by variable-temperature CP/MAS ^{13}C NMR spectroscopy at 22.63 MHz.[5]

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* Dedicated to Professor E. W. Abel, on the occasion of his retirement.

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Braga has, however, been able to reconcile these latter observations with the calculated high barriers to $M(CO)_3$ rotation by pointing out that the crystal packing does not oppose extensive "swinging" of the $M(CO)_3$ and toluene fragments around the coordination axis, and this would be sufficient to mimic the effects of full rotation.[6]

Prompted by a very recent report of the solid-state ^{13}C NMR spectrum of benzenetricarbonylchromium(0),[7] we now describe the results of a variable-temperature CP/MAS 75.5 MHz ^{13}C NMR study of ^{13}CO-labelled (η^6-hexamethylbenzene) tricarbonylchromium(0) (**1**) and (η^6-1,2,4,5-tetramethylbenzene)tricarbonylchromium(0) (**2**), complexes for which both X-ray crystallographic determinations and ^1H NMR relaxation studies have been reported,[3] shedding further light on the motional processes occurring in the crystalline phases. A previous report of the ^{13}C CP/MAS spectrum of **1** concentrates on the arene carbon subspectrum and makes no comment about the carbonyl carbon resonance.[8]

EXPERIMENTAL

Syntheses of (η^6*-arene*)*tricarbonylchromium*(0)

These complexes were prepared as described previously.[9]

^{13}CO*-labelling experiments*

Labelling of the (η^6-arene)tricarbonylchromium(0) complexes was carried out using ^{13}CO (MSD Isotopes, 99 atom% ^{13}C) by a previously described procedure.[10] After initial labelling, typically 30–35% of the total carbonyl content was ^{13}CO as determined by mass spectroscopy. The relative amounts of (η^6-arene)$Cr(^{13}CO)_3$, (η^6-arene) $Cr(^{13}CO)_2(CO)$, (η^6-arene)$Cr(^{13}CO)(CO)_2$ and (η^6-arene)$Cr(CO)_3$ were calculated on the basis of stepwise equilibria, where the ratios of the stepwise formation constants used in the calculations were based on statistical arguments.[11] An isotope effect of unity was assumed for the exchange of free and uncomplexed CO. The ^{13}CO as a proportion of the total carbonyl content was adjusted to 13% by UV irradiation of heptane solutions of the initially-labelled product mixed with the calculated amount of (η^6-arene)tricarbonylchromium(0) prepared from natural abundance material. Scrambling of the ^{13}CO labels occurred to give a mixture of (η^6-arene) $Cr(^{13}CO)_3$ (1%), (η^6-arene)$Cr(^{13}CO)_2(CO)$ (4%), (η^6-arene)$Cr(^{13}CO)(CO)_2$ (30%) and (η^6-arene) $Cr(CO)_3$ (65%), as confirmed by mass spectroscopy.

Mass spectroscopy

Mass spectra were obtained with a VG Analytical 11-250J instrument using electron ionization.

NMR spectroscopy

Variable-temperature CP/MAS ^{13}C solid-state NMR spectra were obtained at 75.5 MHz using either Bruker AM300WB fitted with a Chemagnetics MAS unit or Chemagnetics CMXLite 300 instruments, attached to a Chemagnetics Pencil® MAS probe using 7.0 mm zirconia rotors. Dry nitrogen gas from liquid nitrogen boil-off was used to spin the rotors up to a maximum of 7 kHz over the temperature range 133–293 K. The effects of cross-polarization on ^{13}C signal intensities were examined over the contact time range 0.5–5.0 ms. Chemical shifts were referred to tetramethylsilane at 0.0 ppm.

RESULTS AND DISCUSSION

The solution $^{13}C\{^1H\}$ NMR spectra of both **1** and **2** have been reported previously.[9] In the MAS spectra of solid samples, cross-polarization gave surprisingly modest enhancement of the carbonyl carbon signals of either **1** or **2**, although the methyl and arene carbon signals were satisfactorily enhanced. Recourse to ^{13}CO labelling was therefore necessary to obtain an acceptable signal-to-noise ratio in a reasonable time. Moreover, the parameters necessary to achieve the Hartmann–Hahn condition were highly temperature-dependent. Spectra were therefore obtained using only MAS combined with high power ^1H decoupling, a 90° ^{13}C pulse and a relaxation delay of 5 s between pulses.

At a slow spinning rate of 2 kHz, the carbonyl subspectrum of 35% ^{13}CO-labelled **1** at 293 K displayed a complete manifold of spinning side bands (SSBs) extending over 490 ppm (Fig. 1). Even when the sample was spun at 7 kHz the line associated with the isotropic chemical shift ($\delta_{iso} - 232$ ppm) was far from being the most intense. The SSB manifold could have arisen from incomplete averaging of either chemical shift anisotropy (CSA) or ^{13}C–^{13}C dipole–dipole interactions [at 35% CO labelling, the sample contained 49.5% (η^6-$C_6(CH_3)_6$) $Cr(^{13}CO)(CO)_2$ and 24% (η^6-$C_6(CH_3)_6$)$Cr(^{13}CO)_2$ (CO)]. To eliminate the latter possibility, the ^{13}CO labelling was reduced to 13%, corresponding to a still high (η^6-$C_6(CH_3)_6$)$Cr(^{13}CO)(CO)_2$ content of 30% but only a 4% content of (η^6-$C_6(CH_3)_6$)Cr $(^{13}CO)_2CO$. The SSB manifold remained intact, confirming that it arose from incompletely averaged CSA. The intensity profile of the SSB pat-

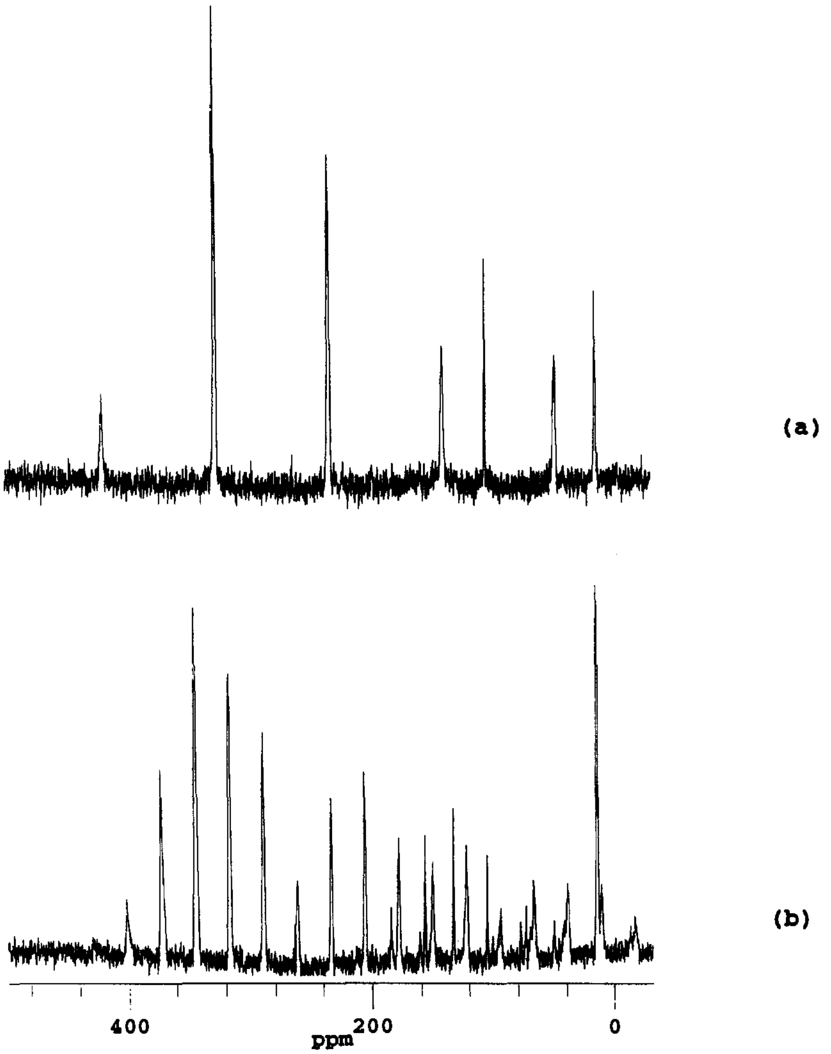

Fig. 1. 75.5 MHz ^{13}C MAS NMR spectra of 13% CO-labelled **1** recorded at 7.05 kHz (a) and 2.05 kHz (b). The spectra were obtained with high power ^{1}H decoupling at 293 K.

tern approximates the static line shape.[12] The three principal elements of the shielding tensor were extracted using the method of Herzfeld and Berger[13] at spinning rates of 2.05, 5.03 and 6.05 kHz to give: $\delta_{11} = \delta_{22} = -377$ ppm, $\delta_{33} = 39$ ppm (relative to TMS = 0 ppm). The shielding anisotropy, $\Delta\sigma$, is given by:

$$\Delta\sigma = \delta_{33} - 0.5(\delta_{11} + \delta_{22}) = 416\,\text{ppm}.$$

The very large shielding anisotropy for the carbonyl carbons of **1** is similar to those reported for $Ni(CO)_4$ (396 ppm) and $Fe(CO)_5$ (426 ppm),[14] and is much greater than the complete range of isotropic chemical shifts which are found in solution ^{13}C NMR studies. A shielding anisotropy of over 400 ppm would require an impracticably high spinning rate of more than 31 kHz to completely eliminate the SSBs in the 75.5 MHz ^{13}C carbonyl subspectrum. The δ_{11}, δ_{22} and δ_{33} values for **1** are very similar to those obtained for $(\eta^6\text{-}C_6H_6)Cr(CO)_3$.[7]

The occurrence of a molecular motion will give a partial averaging of the CSA pattern.[12] The classic example is polycrystalline hexamethylbenzene itself, whose aromatic carbon atoms give an asymmetric anisotropic pattern, which at high temperature is reduced to one of axial symmetry.[15] In the change, δ_{11} and δ_{22} average, but δ_{33} is unchanged. From the known orientation of the principal shielding elements derived from single crystal studies, the motion was deduced as being the in-plane reorientation of the aromatic ring. For the powdered sample of **1** it is not possible to relate the principal elements to the molecular axis system, but there is partial averaging of δ_{11} and δ_{22} to give an axially symmetric anisotropy pattern, as is also the case for $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ at 293 K.[7]

At slow spinning rates, an axially symmetric anisotropy pattern, interdigitated with the carbonyl SSB manifold, was also observed for the arene carbon subspectrum with $\delta_{11} = \delta_{22} = -148$ ppm; $\delta_{33} = -25$ ppm; $\delta_{\text{iso}} = -105$ ppm; $\Delta\delta = 123$ ppm. At 5 kHz, by far the most intense line was that corresponding to δ_{iso}; by 7 kHz all SSBs had disappeared. This behaviour is consistent with rapid rotation of the hexamethylbenzene about its bond to the chromium atom at 293 K, as is expected given the energy of activation of 25.9 kJ mol^{-1} to such rotation determined by variable-temperature ^{1}H T_1 measurements for **1**.[4] While the ^{13}C T_1 values were not determined, the efficient recovery of signal intensity, despite a relaxation delay of only 5 s, indicated quite a short value for the spin-lattice relaxation time of the carbonyl carbon atoms. We consider that this results from the molecular organization in the crystal lattice in which the arene and carbonyl moieties are interlocked by placing the tricarbonyl in the small cavities formed by four rapidly rotating hexamethylbenzene groups[16,17] (Fig. 2). The carbonyl carbons are therefore in close proximity to the relaxing effects of the protons of neighbouring molecules.

In contrast to **1**, no SSBs were observed for the

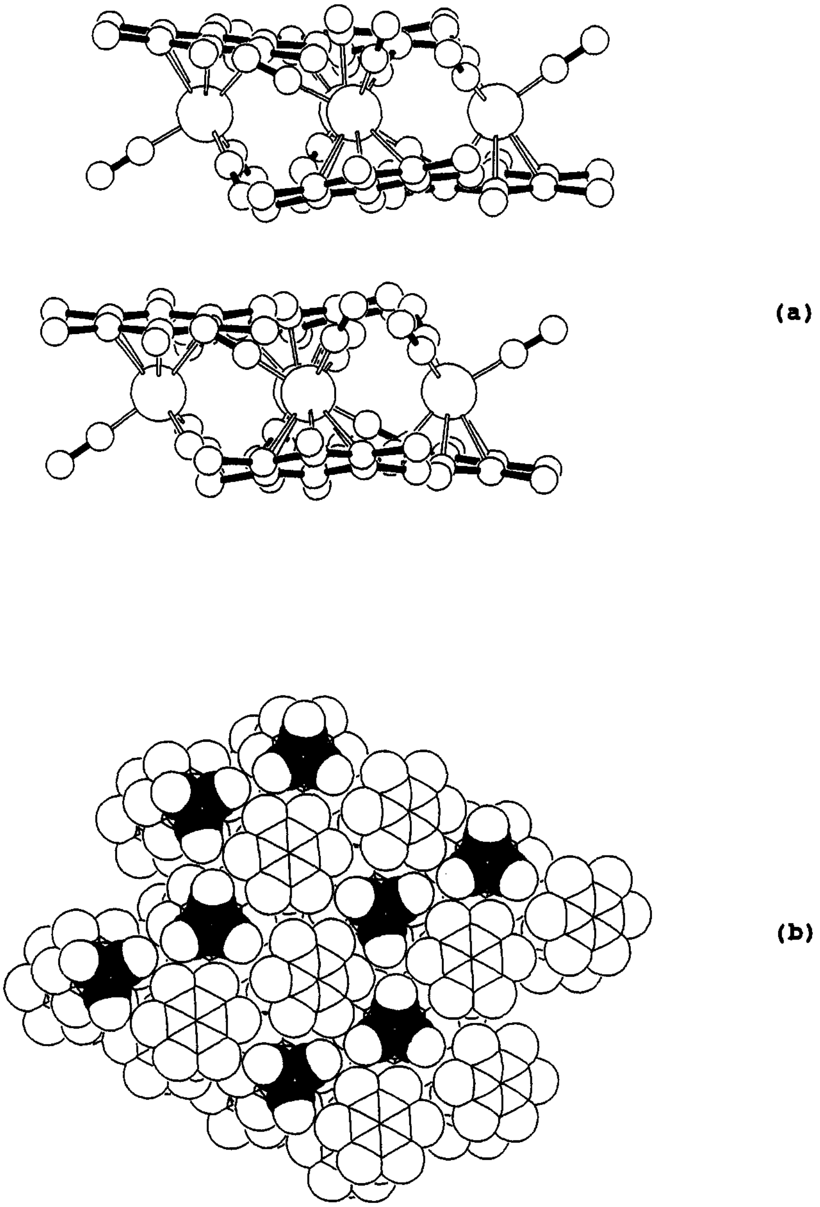

Fig. 2. Crystal and molecular structures of **1**:[17] (a) viewed parallel to the layers of chromium atoms; (b) space-filling view normal to a hexamethylbenzene and tricarbonyl layer (after Braga and Grepioni[16]). The carbonyl carbons are filled in black.

carbonyl carbon subspectrum of 30% ^{13}CO-labelled **2**, only the line corresponding to $\delta_{iso} = 232$ ppm being seen. The intensity of this signal was very temperature dependent, decreasing with falling temperature and finally disappearing into the background noise at 220 K. Without cross-polarization, the intensity of the methyl carbon signal (15 ppm) was also strongly temperature dependent, except that in this case there was a decrease with rising temperature, a strong signal observed at 133 K having disappeared by 220 K. This temperature coincides with an inflection in the plot of log T_1 versus temperature for the ^{1}H spectrum.[4] The linear plot below 220 K then becomes non-linear up to 330 K, when a phase transition occurs leading to a sudden collapse of the crystal lattice. An energy of activation of 5.2 kJ mol^{-1} was obtained from the plot up to 220 K, this being in the range of values expected for methyl group rotation. We consider that the temperature-dependent variations in the intensities of the carbonyl and methyl carbon signals of **2** can be rationalized if it is assumed that the major source of ^{13}C relaxation is the motion of nearby protons. Below 220 K, the rate of methyl group rotation is appropriate for efficient relaxation of those carbon atoms; above that temperature methyl group rotation is too rapid for efficient relaxation. Below 220 K, relative motion of the arene and Cr(CO)$_3$ moieties is too slow to relax the carbonyl carbon atoms; above that temperature the extensive swinging motion of these moieties described by Braga is sufficiently rapid to produce a relaxation effect. Figure 3 shows the molecular organization in crystalline **2**, from which it can be

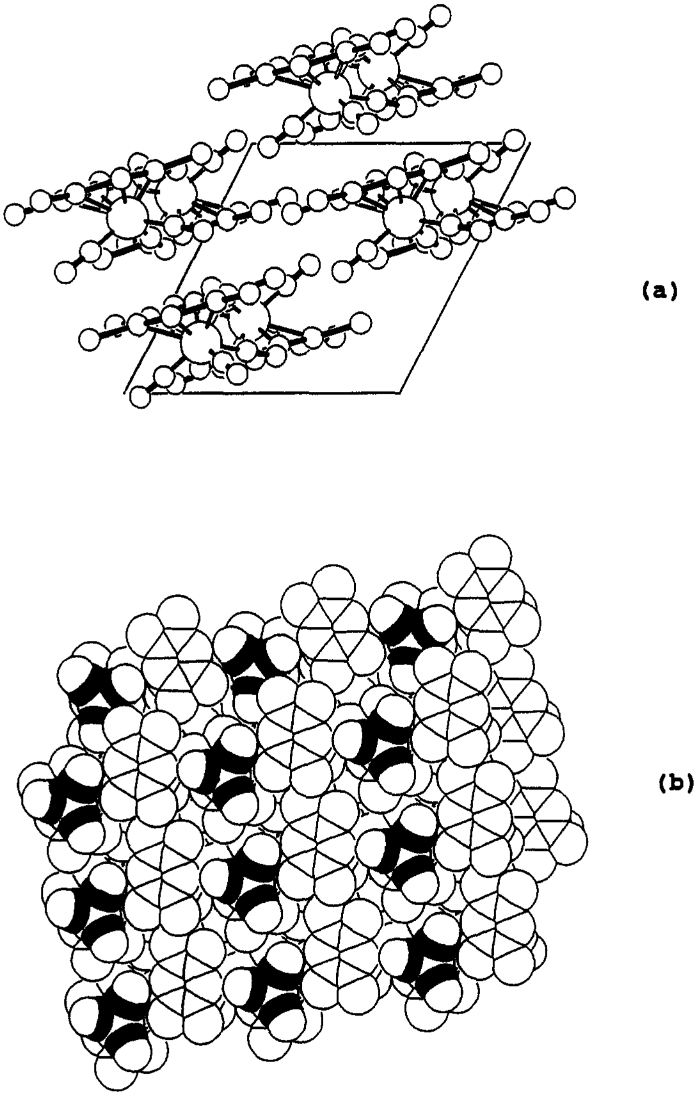

Fig. 3. Crystal and molecular structures of **2**:[4] (a) viewed parallel to the arene layers; (b) space-filling view normal to a durene and tricarbonyl layer. The carbonyl carbons are filled in black.

seen that substantial motions of the arene and tricarbonyl moieties can be accommodated before major interference occurs.

It is not at all obvious why large CSAs should be observed for the carbonyl carbons of **1** and benzenetricarbonylchromium(0) but not of **2**. Harris *et al.*[7] consider that, for benzenetricarbonylchromium(0), the observation of an axially symmetric anisotropy pattern at 293 K allied with a coalescence phenomenon at 310 K in the centre band indicate that rapid reorientation of the tricarbonyl moiety occurs at sufficiently high temperature. We do not observe a coalescence phenomenon for the isotropic signal of **1**, but the anisotropy pattern is very similar to that of benzenetricarbonylchromium(0), suggesting that the two molecules behave in the same fashion. While we find that $\delta_{11} = \delta_{22}$ also for **1**, such are the possible errors involved in obtaining the principal elements of the shielding tensor[18] that a small asymmetry could easily be masked. We therefore consider it premature to conclude that, at least for **1**, full rotation of the $Cr(CO)_3$ moiety occurs at 293 K. The carbonyl carbon atom environments are rather similar for **1** and **2**, except that for the latter complex they lie rather closer to the plane described by the arene carbons. There is also significantly greater opportunity for swinging motion than can occur for **1**.

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