Molecular Dynamics of Tricarbonyl(pentamethylbenzene)chromium: A ^{13}C Solid-state Nuclear Magnetic Resonance Study

Patrick J. Barrie,*[a] **Christiana A. Mitsopoulou**[b,c] **and Edward W. Randall**[c]
[a] *Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK*
[b] *Inorganic Chemistry Laboratory, Department of Chemistry, University of Athens, Panepistimiopolis, 15 771 Athens, Greece*
[c] *Department of Chemistry, Queen Mary and Westfield College, Mile End Road, London E1 4NS, UK*

Carbon-13 cross polarization magic angle spinning NMR spectra of $[Cr(\eta^6-C_6HMe_5)(CO)_3]$ have shown unambiguously that there is rapid exchange between the CO groups at room temperature in the solid state. Chemical shift anisotropy measurements at 296 and 155 K have indicated that the angle between the C–O bond and the axis of rotation is 127.4 ± 0.2°. The activation energy barrier for the process was estimated to be 31 ± 4 kJ mol^{-1}, which is significantly lower than that observed in related complexes. The aromatic group appears not to be undergoing rapid rotation at room temperature.

The dynamics of molecules in the solid state has become a topic of increasing importance. For organometallic complexes, both local reorientations of individual groups and whole-molecule reorientations are possible over a wide range of time-scales.[1] One topic of interest is the possibility of rapid CO rotation in the $[Cr(\eta^6\text{-arene})(CO)_3]$ system (arene = a C_6 aromatic ring). The conformations of such complexes in solution have been widely studied to establish the orientation of the CO groups relative to the aromatic ring (staggered or eclipsed) and the activation barriers for the reorientation of the CO groups.[2] In the solid state, it has been known for many years that there is rapid hopping of the benzene about its C_6 axis in $[Cr(\eta^6-C_6H_6)(CO)_3]$.[3–6] However, it is only recently[7] that ^{13}C solid-state NMR spectroscopic studies have suggested that the CO groups undergo $2\pi/3$ jumps about the approximate molecular C_3 axis at high temperatures. Similarly ^{13}C solid-state NMR studies of the methyl derivative $[Cr(\eta^6-C_6H_5Me)(CO)_3]$, and the molybdenum analogue $[Mo(\eta^6-C_6H_5Me)(CO)_3]$, by Wagner and Hanson[8] were interpreted in terms of rotation of the CO groups while the aromatic group remained static. This motion has, however, been questioned by other workers[9] who calculated a large barrier to this process on the basis of atom–atom potential energy calculations, and suggested that the NMR results might be due to large-amplitude librations rather than a full reorientation of the $Cr(CO)_3$ moiety relative to the arene ring.

Here we report variable-temperature solid-state ^{13}C NMR results on $[Cr(\eta^6-C_6HMe_5)(CO)_3]$, which demonstrate unambiguously that CO exchange does indeed occur. In this case the reorientation is rapid even at room temperature. Furthermore, measurements of the ^{13}C chemical shift anisotropy of the CO group enable the angle about which CO rotation takes place to be determined accurately, thus giving an elegant demonstration of the power of solid-state NMR spectroscopy to provide both detailed structural and dynamic information.

Experimental

The NMR spectra were obtained at 75.47 MHz on a Bruker MSL300 spectrometer using magic angle spinning (MAS) and high-power proton decoupling. Cross-polarization (CP) was normally used, though some spectra were acquired using only single-pulse excitation. The 90° pulse was 4.4 μs, and spinning rates were in the range 600–5000 Hz. The temperature was controlled using a Bruker VT-1000 unit after the thermocouple had been calibrated to ±2 K on the basis of the temperature-dependent ^{13}C shifts of solid samarium acetate.[10] Despite this calibration, the uncertainty in the sample temperature may be as large as 5 K at some temperatures due to the problems associated with frictional heating upon MAS and the effect of the decoupling field. Spinning sideband intensities were simulated using an iterative-fit program based on the method of Herzfeld and Berger[11] to give the principal components of the chemical shift tensor (δ_{11}, δ_{22} and δ_{33}).[12] There are a confusing number of different conventions for reporting shielding tensor components; in this paper we quote the span and the skew according to the recent proposal of Mason[13] designed to clarify the situation, and we also quote the anisotropy and asymmetry parameter according to Haeberlen's[14] convention to allow easy comparison with existing data in the literature. Definitions of these parameters are given in the footnote to Table 1. Simulations considering the combined effects of MAS, chemical shift anisotropy and dynamic exchange were performed using the program CARLA, kindly made available by Dr. Melinda Duer (University of Cambridge).[15]

Results and Discussion

Fig. 1 shows ^{13}C CP MAS NMR spectra of $[Cr(\eta^6-C_6HMe_5)(CO)_3]$ at 296 and 155 K. The low-temperature spectrum [Fig. 1(*a*)] shows a broad range of spinning sidebands arising from the CO environments. Simulation of the intensities of these sidebands indicates that the shielding tensor is axially symmetric with an anisotropy of 436 ± 10 ppm; this is comparable with the reported anisotropy for the CO group in $[Cr(\eta^6-C_6H_6)(CO)_3]$.[7,16]

The structure of $[Cr(\eta^6-C_6HMe_5)(CO)_3]$ has not been reported, to our knowledge, though it is believed to be isomorphous to that of $[Cr(\eta^6-C_6Me_6)(CO)_3]$ whose structure is known.[17,18] If this is the case, then the three CO sites will be crystallographically distinct, and so would be expected to give rise to three CO peaks in an NMR spectrum recorded at the low-temperature limit. The structures of several other methyl-substituted benzene tricarbonylchromium derivatives are known and in some of these, such as $[Cr(\eta^6-C_6H_6)(CO)_3]$ itself,[19,20] one of the CO sites lies on a crystallographic mirror plane, and so two ^{13}CO peaks are observed in the ratio 2:1 at the low-temperature limit.[7] It seems likely that the linewidth and lack of resolution in the observed spectrum at 155 K (the lowest temperature accessible on the MAS probe used) indicate that the low-temperature limit may not yet have been reached.

In contrast to the spectrum at 155 K, that at 296 K [Fig. 1(*b*)] shows a single sharp peak, with barely detectable sidebands, arising from the CO sites. Reduction of the MAS rate to less than 1000 Hz [Fig. 1(*c*)] enables the principal components of the shielding tensor of the CO sites to be measured at this temperature, and it is found that the anisotropy at 296 K is only 22.9 ± 1.0 ppm. The results of these simulations, and of those performed on the other ^{13}C environments, are reported in Table 1. Clearly a process is occurring in the solid state which is responsible for the reduction of the shielding anisotropy from that observed at 155 K. That this is a continuous dynamic process, rather than due to a structural change at a specific temperature, is established by differential scanning calorimetry (DSC) measurements which show no detectable phase transition between 173 and 373 K. It is also apparent that the dynamic process does not involve molecular reorientation of the whole complex, as the anisotropies of the aromatic carbon nuclei are little affected.

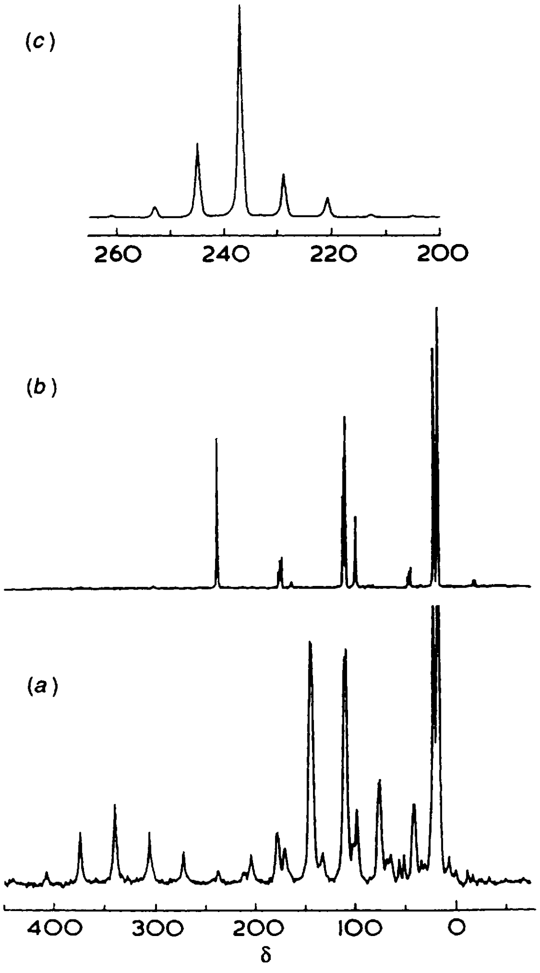

Fig. 1 The ^{13}C CP MAS NMR spectra of $[Cr(\eta^6\text{-}C_6HMe_5)(CO)_3]$: (*a*) 155 K, spinning speed 2570 Hz; (*b*) 296 K, spinning speed 4830 Hz; (*c*) 296 K, spinning speed 610 Hz. For (*c*) only the region of the ^{13}CO resonance is shown

Fig. 2 shows typical ^{13}C CP MAS NMR spectra of the ^{13}CO region at intermediate temperatures. Upon cooling the sample from room temperature there is a gradual broadening of the

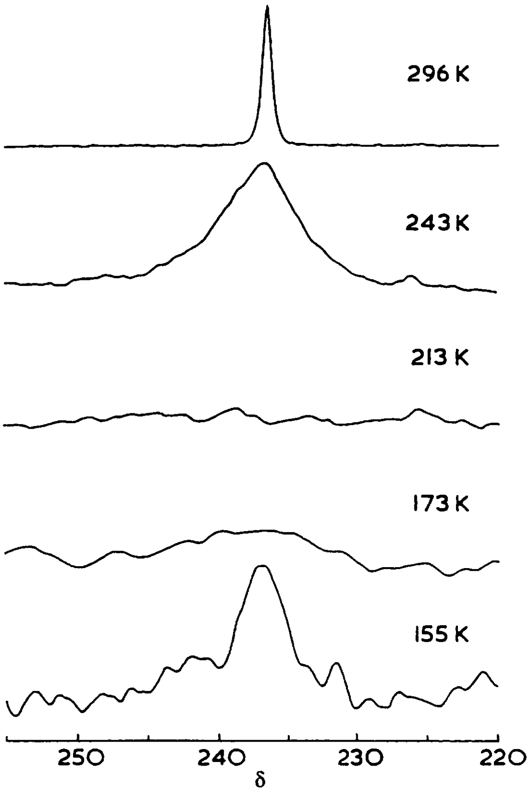

Fig. 2 The ^{13}C CP MAS NMR spectra of $[Cr(\eta^6\text{-}C_6HMe_5)(CO)_3]$ at various temperatures (*T*/K) (only the region of the isotropic ^{13}CO resonance is shown)

Table 1 Principal components of the ^{13}C chemical shift tensor of $[Cr(\eta^6\text{-}C_6HMe_5)(CO)_3]^*$

	T/K	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	$\Delta\sigma$	η	Ω	κ
CO	296	236.5	244.1	244.1	221.2	22.9	0.0	22.9	1.00
	155	237.2	382.6	382.6	−53.5	436	0.0	436	1.00
C_6 ring	296	110.8	163.7	147.7	20.9	134.8	0.18	142.8	0.78
	296	109.5	165.6	146.1	16.9	138.9	0.21	148.7	0.74
	296	107.8	159.9	144.2	19.2	132.8	0.18	140.7	0.78
	296	98.0	139.0	113.7	41.3	85.0	0.45	97.7	0.48
Me	296	21.2							
	296	17.3							
	296	16.8							

* The chemical shifts are given in ppm relative to $SiMe_4$ using the convention $\delta_{11} > \delta_{22} > \delta_{33}$. Following the proposal of Mason,[13] the other parameters given are the span, Ω $(\delta_{11} - \delta_{33})$, and the skew, κ $[3(\delta_{22} - \delta_{iso})/\Omega]$. To enable easy comparison with existing literature, values of the anisotropy, $\Delta\sigma$, and asymmetry parameter, η, are also quoted. When $\delta_{11} - \delta_{22} < \delta_{22} - \delta_{33}$, $\Delta\sigma = 0.5(\delta_{11} + \delta_{22}) - \delta_{33}$ and $\eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{iso})$; when $\delta_{11} - \delta_{22} > \delta_{22} - \delta_{33}$, $\Delta\sigma = 0.5(\delta_{33} + \delta_{22}) - \delta_{11}$ and $\eta = (\delta_{22} - \delta_{33})/(\delta_{11} - \delta_{iso})$.[14] The estimated uncertainties (95% confidence levels) of $\Delta\sigma$ for ^{13}CO are ± 1 ppm at 296 K and ± 10 ppm at 155 K. The errors in the individual tensor components for the peaks arising from the aromatic carbons are ± 3.5 ppm.

^{13}CO peak (as seen, for instance, in the spectrum recorded at 243 K). Between 183 and 223 K no peak due to ^{13}CO can be detected in a reasonable time period, even though narrow aromatic and methyl peaks are still detected with high sensitivity. Upon cooling to 173 K a weak ^{13}CO peak can be detected, together with spinning sidebands of significant intensity, and this peak gradually narrows on further cooling as is evident in the spectrum at 155 K. Similar results are obtained using single-pulse excitation rather than CP.

There are a number of ways in which dynamic processes in the solid state can influence NMR linewidths. At slow rates of exchange between non-equivalent groups there may be conventional peak coalescence as is commonly observed in solution NMR studies of fluxional processes, and this process may well be affecting the ^{13}C linewidth seen for $[Cr(\eta^6\text{-}C_6HMe_5)(CO)_3]$ at 155 K. At faster rates of exchange, there may be additional broadening when the rate of exchange becomes comparable with the dipolar coupling to hydrogen nuclei due to interference between the motion and the proton decoupling field.[21] Another important broadening mechanism for sites with appreciable chemical shift anisotropy occurs when the rate of exchange becomes comparable with the magnitude of the anisotropy, as is likely to be the case for exchange between CO groups.

Fig. 3 shows some theoretical simulations of the combined effect of MAS and chemical shift anisotropy on a system of three equivalent CO groups undergoing exchange (strong collision model). The shielding tensor of each site was taken to be axially symmetric with an anisotropy of 32 900 Hz {which corresponds, in the magnetic field used, to 436 ppm as was observed for CO in $[Cr(\eta^6\text{-}C_6HMe_5)(CO)_3]$ at 155 K}. The angle between the C–O bond and the axis of rotation for fast exchange was taken to be 127.4° (see below), while the MAS rate was chosen to be 4000 Hz. As can be seen, there is substantial peak broadening when the rate of exchange becomes comparable with the anisotropy of the shielding tensor. Given that the intensities of the simulated spectra in Fig. 3 are arbitrary, it is readily apparent why the peaks due to the CO sites in $[Cr(\eta^6\text{-}C_6HMe_5)(CO)_3]$ are broadened beyond detectability between 183 and 223 K. It is also relevant that at exchange rates less than the anisotropy there can still be appreciable broadening of the spinning sidebands in an MAS spectrum.

Useful structural information is available from the chemical shift anisotropy measurement at 296 K. In the fast-exchange limit the peak from the CO groups is narrow, and the chemical shift anisotropy is averaged over the motion. Fast three-site exchange between identical CO sites with axially symmetric shielding tensors is expected to result in a shielding tensor with anisotropy, $\Delta\sigma'$, which is modified from the static anisotropy, $\Delta\sigma$, by the factor $(3\cos^2\theta - 1)/2$ (where θ denotes the angle between the C–O bond and the axis of rotation). This prediction is also borne out by computer simulations of very fast exchange performed in the same manner as those shown in Fig. 3. In the case of $[Cr(\eta^6\text{-}C_6HMe_5)(CO)_3]$, the results reported in Table 1 imply that the angle, θ, is 127.4 ± 0.2°. Thus the knowledge of the high- and low-temperature limiting shielding anisotropies provides accurate structural information. This angle may be compared to those known from X-ray structural work of related complexes; for instance, the angles between the centre of the aromatic ring and the Cr–CO bond in $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$ at 78 K are 128.7° (two of them) and 122.2° (giving an average angle of 126.5°).[20] The reduction of the chemical shift anisotropy upon motional averaging is particularly dramatic in the case studied here as the angle between the C–O bond and the axis of rotation is close to the magic angle (54.7° or, equivalently, 125.3°), and it provides unambiguous evidence that rapid $Cr(CO)_3$ rotation takes place in the solid.

In principle it is possible to simulate the ^{13}C spectra obtained at intermediate temperatures in order to gain the rates of carbonyl exchange as a function of temperature and hence obtain an accurate activation energy. However, this is complicated by the different broadening interactions that may be occurring at the same time. In the case of $[Cr(\eta^6\text{-}C_6HMe_5)(CO)_3]$ there is the added problem that the spectrum at the low-temperature limit has probably not yet been achieved. The rates of exchange, k, at 233, 238, 243 and 248 K were estimated by comparison with simulations that assumed that the ^{13}CO linewidth results principally from chemical shift anisotropy averaging at these temperatures; this gives estimated rates $k_{233} = 1.1 \times 10^6$ and $k_{248} = 4 \times 10^6$ Hz. This range of temperatures is too small, however, for an accurate activation energy to be obtained. Simulation of the linewidths at 163 and 173 K, again assuming that the effect of motional averaging of the chemical shift anisotropy is the dominant broadening interaction, gives estimated exchange rates $k_{163} = 1500$ and $k_{173} = 3800$ Hz. Such rates may be sufficiently high that chemical shift coalescence broadening is small, and sufficiently low that maximum dipolar broadening is also small; while clearly a potential source of error, it is expected that these estimated rates are at least comparable with the true values.

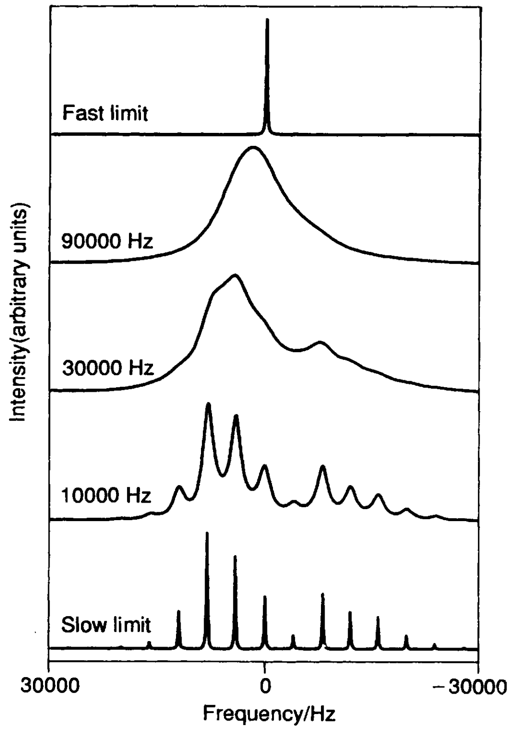

Fig. 3 Theoretical simulations of the combined effect of MAS (4000 Hz) and chemical shift anisotropy (axial symmetry with $\Delta\sigma = 32\,900$ Hz) on a system of three equivalent CO groups undergoing chemical exchange (strong collision model). The angle between the C–O bond and the axis of rotation for fast exchange was chosen to be 127.4°. The rates of exchange are indicated

Fitting these estimated rates to the standard Arrhenius equation gives an activation energy, E_a, of 30.6 ± 1.5 kJ mol^{-1}, with a pre-exponential factor, A, of 8.7×10^{12} s^{-1}. Given the assumptions made in estimating the exchange rates, the possible error in E_a is larger than the uncertainty calculated from the fit, and we suggest a more realistic value for the activation energy is $E_a = 31 \pm 4$ kJ mol^{-1}. This barrier to carbonyl exchange is significantly less than that for related systems. Activation energies in $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$, $[Cr(\eta^6\text{-}C_6H_5Me)(CO)_3]$ and $[Mo(\eta^6\text{-}C_6H_5Me)(CO)_3]$ have been estimated to be in the range 65–71 kJ mol^{-1},[7,8] though a consideration of the effect of ^{13}CO chemical shift anisotropy averaging on the reported spectra suggests that these values may be slightly overestimated. It is, as yet, unclear why carbonyl exchange is so much more facile for $[Cr(\eta^6\text{-}C_6HMe_5)(CO)_3]$, but it presumably reflects differences in crystal packing.

There remains the question about possible motion of the aromatic group in [Cr(η^6-C_6HMe_5)$(CO)_3$]. The fact that the chemical shift anisotropies of the aromatic carbon nuclei (Table 1) deviate from axial symmetry suggests that fast rotation of the pentamethylbenzene unit does not take place at 296 K. The ^1H MAS NMR spectrum (not shown) at a spinning rate of 4.5 kHz consists of a set of broad spinning sidebands, covering about 40 kHz, which is also suggestive of a static aromatic group, though there is almost certainly fast rotation of the methyl groups. However, the dynamics of the aromatic group would perhaps be investigated better by ^1H relaxation time studies, as have been performed on some other members of the methyl-substituted [Cr(η^6-C_6H_6)$(CO)_3$] family.[22]

Acknowledgements

We are grateful to the University of London Intercollegiate Research Services (ULIRS) for providing solid-state NMR facilities (UCL) and DSC equipment (Birkbeck College).

References

1 D. Braga, *Chem. Rev.*, 1992, **92**, 633.
2 M. J. McGlinchey, *Adv. Organomet. Chem.*, 1992, **34**, 285.
3 P. Delise, G. Allegra, E. R. Mognaschi and A. Chierico, *J. Chem. Soc., Faraday Trans. 2*, 1975, 207.
4 G. Lucazeau, K. Chhor, C. Sourisseau and A. J. Dianoux, *Chem. Phys.*, 1983, **76**, 307.
5 K. Chhor and G. Lucazeau, *J. Raman Spectrosc.*, 1982, **13**, 235.
6 A. E. Aliev, K. D. M. Harris and F. Guillaume, *J. Phys. Chem.*, 1995, **99**, 1156.
7 A. E. Aliev, K. D. M. Harris, F. Guillaume and P. J. Barrie, *J. Chem. Soc., Dalton Trans.*, 1994, 3193.
8 G. W. Wagner and B. E. Hanson, *Inorg. Chem.*, 1987, **26**, 2019.
9 D. Braga and F. Grepioni, *Polyhedron*, 1990, **9**, 53.
10 J. F. Haw, G. C. Campbell and R. C. Crosby, *Anal. Chem.*, 1986, **58**, 3172.
11 J. Herzfeld and A. E. Berger, *J. Chem. Phys.*, 1980, **73**, 6021.
12 G. E. Hawkes, K. D. Sales, L. Y. Lian and R. Gobetto, *Proc. R. Soc. London, Ser. A*, 1989, **424**, 93.
13 J. Mason, *Solid State Nucl. Magn. Reson.*, 1993, **2**, 285.
14 U. Haeberlen, *Adv. Magn. Reson. Suppl.*, 1976, **1**, 9.
15 M. J. Duer, CARLA Fortran computer program, University of Cambridge, 1992.
16 Y. Huang, D. F. R. Gilson, I. S. Butler and F. G. Morin, *Inorg. Chem.*, 1992, **31**, 322.
17 H. J. Buttery, G. Keeling, S. F. A. Kettle, I. Paul and P. J. Stamper, *J. Chem. Soc. A*, 1969, 2224.
18 M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1298.
19 M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1314.
20 B. Rees and P. Coppens, *Acta Crystallogr., Sect. B*, 1973, **29**, 2515.
21 W. P. Rothwell and J. S. Waugh, *J. Chem. Phys.*, 1981, **74**, 2721.
22 S. Aime, D. Braga, R. Gobetto, F. Grepioni and A. Orlandi, *Inorg. Chem.*, 1991, **30**, 951.

Received 1*st February* 1995; *Paper* 5/00596E