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Molecular dynamics of (η^6-arene)tricarbonylchromium complexes in the solid state: carbon-13 nuclear magnetic resonance and crystal structure of [Cr(η^6-C_6HMe_5)(CO)$_3$]

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Variable-temperature solid-state ^{13}C NMR spectra have been recorded for a series of [Cr(η^6-arene)(CO)$_3$] complexes. In all cases there is evidence for carbonyl exchange in the solid state at elevated temperatures. Both the isotropic chemical shifts and the chemical shift anisotropies of the ^{13}CO groups were obtained. The relative ease of the carbonyl exchange depended on the extent of methyl substitution of the arene ring. It was more facile in those complexes with less symmetric arene rings. The single-crystal structure of [Cr(η^6-C_6HMe_5)(CO)$_3$] was determined at 150 K. X-Ray data recorded at room temperature led to a misleading structural refinement due to molecular motion.

The intermolecular interactions and the dynamics of organometallic complexes in the solid state have become an important research topic.[1] Both local reorientations of individual groups and whole-molecule reorientations are now known to be possible over a wide range of time-scales;[2] such motions are important in structural characterisation and can affect reactivity. Complexes of the type [Cr(η^6-arene)(CO)$_3$] have been studied for many years by solution NMR techniques to establish the orientation of the CO groups relative to the aromatic ring (*e.g.* staggered or eclipsed) and to obtain the activation barriers for the tripodal reorientation of the CO groups.[3] Dynamics in solids may also be investigated using NMR techniques.[4] For solid-state NMR studies it needs to be remembered that there are several anisotropic interactions present that can influence spectra, and the combined effect of molecular motion and anisotropic interactions needs to be considered.

In a recent paper we demonstrated using variable-temperature solid-state ^{13}C NMR spectroscopy that rapid exchange between the CO groups occurs even at room temperature in the solid state for [Cr(η^6-C_6HMe_5)(CO)$_3$].[5] Broadening of the peak originating from the ^{13}CO groups was observed when the exchange rate was comparable to the magnitude of the ^{13}C chemical shift anisotropy. Spectra obtained when the carbonyl exchange was rapid enabled the angle between the C−O bond and the axis of rotation to be obtained. In this paper, we extend our solid-state NMR studies to include measurements on other members of the family of [Cr(η^6-arene)(CO)$_3$] complexes. A range of dynamic behaviour is observed depending on the extent and position of methyl substitution on the aromatic ring. A crystal structure is reported for the pentamethylbenzene complex which was previously studied using NMR spectroscopy. An initial attempt at refining crystallographic data at room temperature for this complex was not successful due to the motional processes occurring; a sensible crystallographic structure was obtained only by using data collected at low temperature (150 K).

Experimental

Sample preparation

The [Cr(η^6-arene)(CO)$_3$] complexes were synthesized for the arenes benzene, 1,3-dimethyl-, 1,2,3-trimethyl-, 1,2,4-trimethyl-, 1,3,5-trimethyl-, 1,2,3,5-tetramethyl-, 1,2,4,5-tetramethyl-, pentamethyl- and hexamethyl-benzene. The preparations were based on reported methods,[6] and all of the complexes gave satisfactory elemental analyses. As an example, the preparation of [Cr(η^6-C_6HMe_5)(CO)$_3$], which gave crystals of sufficient quality for a crystal structure determination, is outlined. Pentamethylbenzene (10 g) and [Cr(CO)$_6$] (3 g) were dissolved in a mixture of diglyme (2,5,8-trioxanonane, 40 cm^3) and heptane (40 cm^3) in a nitrogen atmosphere. This was then held under reflux at 150 °C for 40 h, cooled and the solvent evaporated. The resulting green oil was dissolved in boiling heptane (200 cm^3) and filtered while hot. The yellow filtrate was collected and cooled to −10 °C. The yellow crystals deposited were washed with cold heptane and dried at 25 °C. Yield 56%, m.p. 156–158 °C.

NMR spectroscopy

The solid-state ^{13}C NMR spectra were obtained at 75.47 MHz on a Bruker MSL-300 spectrometer using magic angle spinning (MAS) and high-power proton decoupling. Cross-polarisation (CP) was normally used, though a few spectra were also acquired using single-pulse excitation for comparative purposes. The 90° pulse was typically 4.4 μs, and spinning rates were in the range 600–5000 Hz. The temperature was controlled using a Bruker VT-100 unit. The thermocouple was calibrated on the basis of established solid-state phase transitions (above room temperature) and on the temperature-dependent ^{13}C chemical shifts of solid samarium acetate (below room temperature).[7] Despite this calibration, the uncertainty in the sample temperature may be as large as 5 K for some spectra due to the problems associated with frictional heating upon MAS and the effect of the decoupling field. Owing to instrumental limitations the temperature limits were 155–400 K. Spinning sideband intensities were simulated using an iterative-fit program based on the method of Herzfeld and Berger[8,9] to give the principal components of the chemical shift tensor (δ_{11}, δ_{22} and δ_{33}). The magic angle was set accurately by maximising the spinning sidebands from the ^{23}Na resonance of solid NaNO$_3$ before running spectra on each complex to avoid any distortions in the spinning sidebands that would affect the analysis. Chemical

Table 1 Summary of the low-temperature-limiting ^{13}C NMR results for [Cr(η^6-arene)(CO)$_3$] complexes

Arene	T/K	δ_{iso}	Intensity ratio	$\Delta\sigma$/ppm[a]
Benzene	296	235.8, 233.9	2:1	436 ± 6
1,3-Dimethylbenzene	296	236.4, 233.3	2:1	430 ± 8
1,2,3-Trimethylbenzene	213	237.3, 235.8	1:2	437 ± 2
1,2,4-Trimethylbenzene	213	236.2, 235.3	2:1	430 ± 2
1,3,5-Trimethylbenzene	296	237.1, 236.4, 234.9	1:1:1	430 ± 5
1,2,3,5-Tetramethylbenzene	296	236.6, 236.0	2:1	426 ± 2
1,2,4,5-Tetramethylbenzene	253	237.0, 236.6, 235.8	1:1:1	435 ± 3
Pentamethylbenzene	155	237.2[b]	—	436 ± 10
Hexamethylbenzene	296	237.1, 236.3	2:1	422 ± 6

[a] Axial symmetry was assumed in all cases. [b] Low-temperature limit probably not reached.

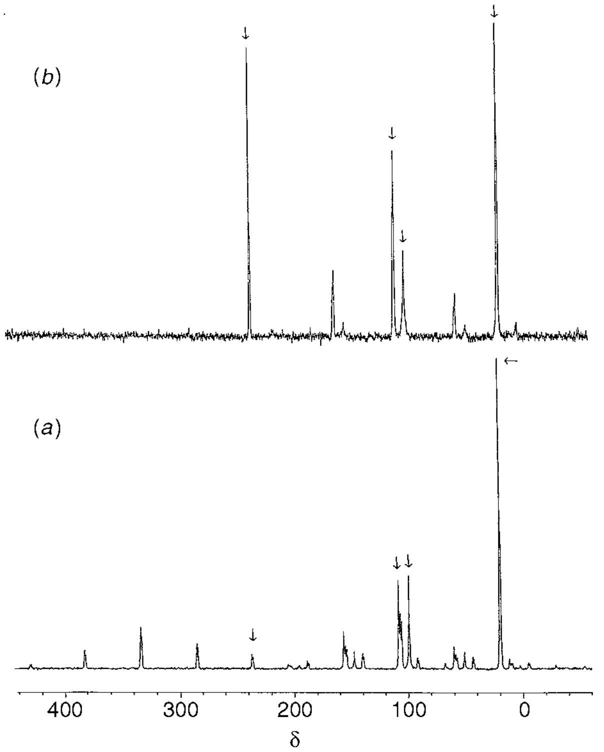

Fig. 1 The ^{13}C CP MAS NMR spectra of [Cr(η^6-C$_6$H$_2$Me$_4$-1,2,4,5)-(CO)$_3$] at (*a*) 253 K, spinning rate 3650 Hz, and (*b*) 362 K, spinning rate 4025 Hz. Isotropic peaks are marked by arrows; the other peaks are spinning sidebands

shifts are quoted relative to external SiMe$_4$. The anisotropy parameter, $\Delta\sigma$, is defined as $0.5(\delta_{11} + \delta_{22}) - \delta_{33}$ when the principal components are chosen such that $|\delta_{33} - \delta_{\text{iso}}| > |\delta_{11} - \delta_{\text{iso}}| > |\delta_{22} - \delta_{\text{iso}}|$ where δ_{iso} is the isotropic chemical shift $(\delta_{11} + \delta_{22} + \delta_{33})/3$.[10] Error estimates in the values of $\Delta\sigma$ quoted represent 95% probability limits.

Crystallography

Diffraction intensity data were collected at both room temperature and 150 K for [Cr(η^6-C$_6$HMe$_5$)(CO)$_3$] using a CAD4 diffractometer operating in the ω–2θ scan mode. The room-temperature data led to an incorrect structure determination due to the dynamic processes occurring (see below). For the low-temperature data, the unit-cell parameters were determined by a least-squares refinement of 25 automatically centred reflections in the range $10 < \theta < 13°$. The structures were solved by the heavy-atom method using the SHELXS 86 and SHELXL 93 programs and refined with full-matrix least-squares techniques.[11,12] All hydrogen-atom positions were calculated geometrically using the AFIX command of the SHELXL program. An empirical absorption correction was applied to the data based on ψ scans of three reflections;[13] minimum and maximum transmission factors were 0.70 and 0.99. The program PLUTON was used for drawing the molecular structures.[14]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/326.

Results

At low enough temperatures the solid-state ^{13}C NMR spectra of all the complexes show the behaviour expected for static molecules. A typical spectrum, in this case for [Cr(η^6-C$_6$H$_2$Me$_4$-1,2,4,5)(CO)$_3$] at 253 K, is shown in Fig. 1(*a*).

Results obtained at low temperatures are summarised in Table 1. The carbonyl groups show a large anisotropy which is manifested by a wide array of spinning sidebands separated by integral multiples of the spinning speed from the isotropic resonance. The chemical shift anisotropy can be obtained by analysis of the spinning sideband intensities and is found to be in the range 422–437 ppm for the complexes studied, as expected for terminal M–C–O units.[15] Interestingly, more than one isotropic ^{13}CO peak is observed at low temperatures for all complexes, indicating that the carbonyl sites are crystallographically inequivalent.

As the temperature is raised, for all complexes it is observed that the ^{13}CO peaks merge and gradually broaden until they are no longer detected in the spectrum. There are several line-broadening mechanisms that can occur in solids. In our previous paper[5] we showed that a major effect for the ^{13}CO peaks in these type of complexes was when the rate of the carbonyl-exchange process became comparable with the magnitude of the chemical shift anisotropy. In this intermediate regime the ^{13}CO peak is not detected. The temperature at which the peak is first not detected (T_{dis}) and that at which it reappears (T_{reapp}) for the complexes studied are shown in Table 2. Data for [Cr(η^6-C$_6$H$_5$Me)(CO)$_3$] are estimated from ref. 16.

For three of the samples further heating enabled the high-temperature-limiting spectrum to be obtained. In this case a single narrow ^{13}CO peak is observed with a very small anisotropy. This is shown for [Cr(η^6-C$_6$H$_2$Me$_4$-1,2,4,5)(CO)$_3$] at 362 K in Fig. 1(*b*). As in the case of the pentamethylbenzene complex previously reported,[5] very slow spinning speeds are necessary to obtain sidebands from which the ^{13}CO chemical shift anisotropy may be derived. Fast carbonyl exchange modifies the static shielding anisotropy by the factor $(3\cos^2\theta - 1)/2$, where θ is the average angle between the centre of the aromatic ring and the C–O vectors, in an intramolecular molecular process akin to the magic-angle spinning experiment.[17] Results obtained on those complexes for which the high-temperature limit was reached are also shown in Table 2. For the other complexes a high-temperature limit was not obtained, either due to sample melting (in the case of the 1,2,4-trimethylbenzene complex) or because the probe used was limited to a maximum temperature of about 400 K.

Table 2 Summary of the intermediate- and high-temperature-limiting ^{13}C NMR results for [Cr(η^6-arene)(CO)$_3$] complexes

	Intermediate regime		High-temperature regime		
Arene	T_{dis}/K	T_{reapp}/K	T_{meas}/K	$\Delta\sigma$/ppm	θ/°
Pentamethylbenzene	183	223	296	22.9 ± 1.0	127.4 ± 0.2
1,2,3-Trimethylbenzene	290	295[a]	360	41.9 ± 0.6	129.0 ± 0.1
1,2,4-Trimethylbenzene	293	303		Melts	
Toluene[b]	≈300	≈310[b]			
1,2,4,5-Tetramethylbenzene	310	340	360	36.1 ± 1.2	128.6 ± 0.1
Benzene	340	380			
1,3-Dimethylbenzene	350	(>380)			
Hexamethylbenzene	360	(>400)			
1,2,3,5-Tetramethylbenzene	365	(>400)			
1,3,5-Trimethylbenzene	380	(>400)			

[a] A structural phase transition probably occurs at this temperature. [b] Estimated from ref. 16.

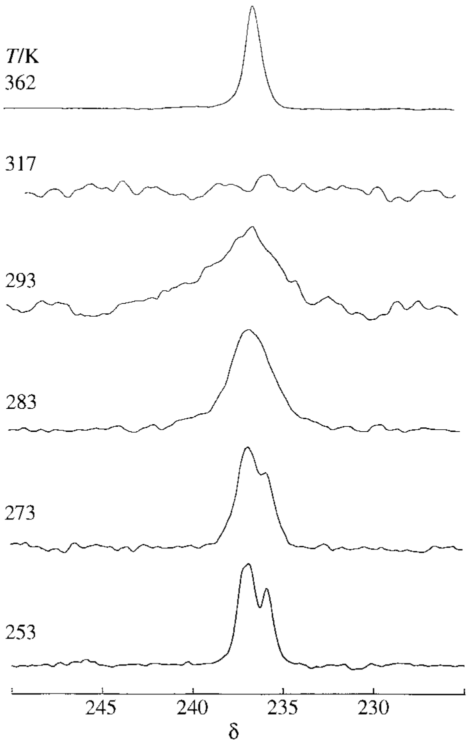

Fig. 2 Expansion of the ^{13}CO isotropic peak region of the ^{13}C CP MAS NMR spectra of [Cr(η^6-C$_6$H$_2$Me$_4$-1,2,4,5)(CO)$_3$] at the temperatures indicated

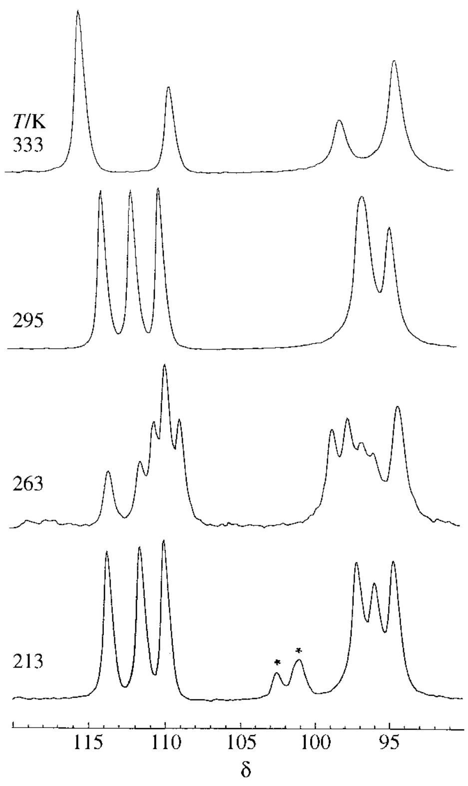

Fig. 3 Expansion of the aromatic peak region of the ^{13}C CP MAS NMR spectra of [Cr(η^6-C$_6$H$_3$Me$_3$-1,2,3)(CO)$_3$] at the temperatures indicated; the asterisks denote spinning sidebands from the ^{13}CO groups

Fig. 2 shows an expansion of the isotropic ^{13}CO peak for [Cr(η^6-C$_6$H$_2$Me$_4$-1,2,4,5)(CO)$_3$] at various temperatures to illustrate in more detail the behaviour observed: narrow peaks at low temperatures, broadening followed by disappearance at intermediate temperatures, until eventually a narrow peak with low anisotropy is observed at high temperatures.

An interesting series of spectra was obtained for [Cr(η^6-C$_6$H$_3$Me$_3$-1,2,3)(CO)$_3$] as the temperature was changed (Fig. 3). The ^{13}CO peak behaved as described above, but with a sharp transition between the low- and high-temperature-limiting cases (Table 2). However, it is clear from spectra of the aromatic region (Fig. 3) that crystallographic phase changes must also be occurring. At low temperatures six aromatic peaks are observed as might be expected. About 245 K there is a transition, and at least ten aromatic peaks occur at 263 K, probably indicating that there are now two molecules in the asymmetric part of the unit cell. Another transition occurs at 290 K, and six aromatic sites are once again observed (with two overlapping). Another transition occurs at 323 K, so that at 333 K four aromatic peaks are observed as expected due to symmetry if there is free molecular rotation. Similar complicated changes occur in the ^{13}C methyl region, and these changes were found to be reversible. It is clear that for this sample structural transitions may play an important role in determining the molecular dynamics: the ^{13}CO peaks indicate that the high-temperature limit is reached as soon as the transition at 290 K is overcome.

In the light of our previous NMR results on [Cr(η^6-C$_6$HMe$_5$)(CO)$_3$] showing dynamic CO exchange above 223 K,[5] we decided to examine the crystal structure in the hope that it would shed more light on the dynamic process involved. The structure has not been previously published to our knowledge, though Buttery *et al.*[18] in 1969 stated that they believed it to be isomorphous to the hexamethylbenzene analogue. Refinement of diffraction data obtained on a single crystal of [Cr(η^6-C$_6$HMe$_5$)(CO)$_3$] at room temperature gave a startling result: six methyl groups appeared. The space group used was *Pbca*, the same as the refinement at 150 K, and the refined unit-cell dimensions at 293 K were $a = 13.349(1)$, $b = 13.578(1)$ and $c = 15.138(2)$ Å. The thermal ellipsoids were, however, very

Table 3 Crystal data for [Cr(η^6-C_6HMe_5)(CO)$_3$] and details of structure refinement

Empirical formula	$C_{14}H_{16}CrO_3$
M	284.27
T/K	150(2)
λ/Å	0.710 69
Crystal system	Orthorhombic
Space group	*Pbca*
a/Å	13.229(1)
b/Å	13.408(1)
c/Å	14.998(2)
U/Å^3	2660.3(5)
Z	8
D_c/g cm^{-3}	1.420
μ/mm^{-1}	0.857
F(000)	1184
Crystal size/mm	0.22 × 0.18 × 0.12
θ Range for data collection/°	2.55–25.02
hkl Ranges	−15 to 15, −10 to 15, −17 to 11
Reflections collected	7581
Independent reflections	2110 [R(int) = 0.0481]
Refinement method	Full-matrix least squares on F^2
Data, restraints, parameters	2107, 0, 165
Goodness of fit on F^2	0.978
$R1$, $wR2$	
[$I > 2\sigma(I)$]	0.0565, 0.1525
(all data)	0.0787, 0.1667
Largest difference peak and hole/e Å^{-3}	1.515, −0.400

$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$. Goodness of fit $= [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$ where n is the number of reflections, p is the total number of refined parameters and $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 4 Selected bond lengths (Å) and angles (°) in [Cr(η^6-C_6HMe_5)(CO)$_3$] at 150 K

Cr–C(12)	1.847(3)	Cr–C(1)	2.229(4)
Cr–C(13)	1.833(2)	Cr–C(2)	2.244(4)
Cr–C(14)	1.831(2)	Cr–C(3)	2.239(4)
C(12)–O(1)	1.151(4)	Cr–C(4)	2.241(4)
C(13)–O(2)	1.157(4)	Cr–C(5)	2.227(4)
C(14)–O(3)	1.160(4)	Cr–C(6)	2.216(4)
C(1)–C(2)	1.419(7)	C(1)–C(7)	1.520(7)
C(2)–C(3)	1.444(6)	C(2)–C(8)	1.501(6)
C(3)–C(4)	1.401(5)	C(3)–C(9)	1.505(5)
C(4)–C(5)	1.411(6)	C(4)–C(10)	1.527(6)
C(5)–C(6)	1.380(7)	C(5)–C(11)	1.531(5)
C(6)–C(1)	1.405(7)		
O(1)–C(12)–Cr	178.4(3)	C(6)–C(1)–C(7)	113.7(5)
O(2)–C(13)–Cr	177.7(3)	C(2)–C(1)–C(7)	126.8(5)
O(3)–C(14)–Cr	178.6(3)	C(1)–C(2)–C(8)	122.1(4)
C(12)–Cr–C(13)	89.41(10)	C(3)–C(2)–C(8)	119.1(4)
C(12)–Cr–C(14)	90.84(10)	C(2)–C(3)–C(9)	119.4(4)
C(13)–Cr–C(14)	89.32(10)	C(4)–C(3)–C(9)	120.9(3)
C(1)–C(2)–C(3)	118.8(4)	C(3)–C(4)–C(10)	120.8(3)
C(2)–C(3)–C(4)	119.7(4)	C(5)–C(4)–C(10)	118.8(4)
C(3)–C(4)–C(5)	120.4(4)	C(4)–C(5)–C(11)	120.9(4)
C(4)–C(5)–C(6)	119.9(4)	C(6)–C(5)–C(11)	119.2(4)
C(5)–C(6)–C(1)	121.6(4)		
C(6)–C(1)–C(2)	119.6(4)		

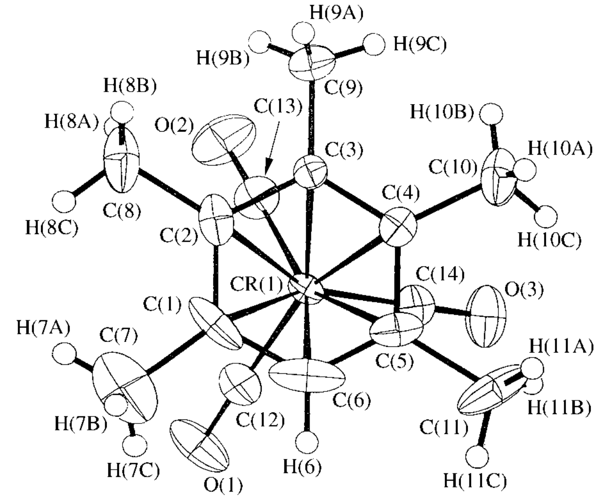

Fig. 4 An ORTEP projection of the structure of [Cr(η^6-C_6HMe_5)(CO)$_3$] at 150 K

large. This misleading result must be due to a dynamic process occurring in the complex; the NMR experiments show this to be a carbonyl exchange. It is thus unsurprising that previous X-ray work on this complex at room temperature suggested that it was isomorphous to the hexamethylbenzene analogue. A second data collection was required, this time at 150 K, and it was only refining this data that led to the correct structure (Tables 3 and 4). An ORTEP[19] plot of the structure at 150 K is shown in Fig. 4.

As can be seen from Fig. 4 the three carbonyl groups are in staggered positions relative to the aromatic ring methyl groups. The Cr–C (CO) bond distances average 1.837(2) Å, with the longest being Cr–C(12) which has the least steric hindrance from overlying methyl groups. The C–O distances average 1.156(4) Å and are the same within experimental error. Both these bond lengths are in the range expected based on related structures.

The Cr–C (ring) distances in [Cr(η^6-C_6HMe_5)(CO)$_3$] at 150 K average 2.233(4) Å. This is the same as that found when the arene is hexamethylbenzene,[20] but slightly longer than when it is benzene or toluene (2.221 and 2.213 Å respectively)[21,22] in line with increasing steric repulsion with an increasing number of methyl groups; care needs to be taken over such a comparison as the data were obtained at different temperatures. The distance between the chromium and the carbon bearing no methyl substitutent [*i.e.* Cr–C(6)] is the shortest due to less steric hindrance.

The aromatic ring is almost perfectly flat, but slightly distorted: the six C–C bond lengths range from 1.380(7) to 1.444(6) Å with an average of 1.410 Å (similar to that observed for the hexamethylbenzene analogue[20]). The C(5)–C(6) bond is the shortest, which corresponds to the bond to the non-methyl-bearing carbon without a carbonyl group below it, while the

C(2)–C(3) bond on the opposite side of the aromatic ring is the longest. The C–C (Me) bond distances are also not equivalent and range from 1.501(6) to 1.531(5) Å, with the shortest being those furthest from the non-methyl-bearing carbon atom.

From the thermal ellipsoids shown in Fig. 4 it is interesting that the main librational motion of the molecule is not around an axis through the Cr atom and the cente of the aromatic ring, but appears to be closer to the C(3) carbon atom. This is presumably a reflection of the presence of hydrogen attached to C(6) rather than a bulky methyl group.

Discussion

More than one ^{13}CO site is normally detected in the low-temperature-limiting spectrum of the complexes under discussion (see Table 1). For $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$ it is known that one of the CO sites lies on a mirror plane, while the other two are related by this mirror plane.[21] Hence in this case two ^{13}CO NMR peaks are expected in the ratio 2:1 and this is indeed what is observed at low temperatures.[23] In the general case, however, the CO sites will be on general positions in the unit cell and so three peaks are expected in a 1:1:1 intensity pattern. This is observed for two of the complexes. In the other cases it may simply be lack of spectral resolution that prevents resolution of the three individual peaks rather than the crystallographic symmetry. For the pentamethylbenzene complex the low-temperature-limiting spectrum has almost certainly not been reached at the lowest temperature accessible with the probe used (155 K), and so the three ^{13}CO peaks expected on the basis of the crystal structure are not resolved.

The chemical shift anisotropies, $\Delta\sigma$, measured by simulating the spinning sideband intensities at low temperature are all in the range 422–437 ppm (Table 1) and are virtually identical within experimental error. This similarity in $\Delta\sigma$ values indicates little difference in the Cr–C–O electronic environment between the complexes. There is no obvious correlation of the exact magnitude of $\Delta\sigma$ with the extent of methyl substitution.

From the intermediate-temperature ^{13}C NMR results in Table 2 it is clear that all complexes show dynamic behaviour involving carbonyl exchange in the solid state. It should be noted that a simple arene-ring reorientation process could not affect the ^{13}CO anisotropy in the fashion observed. Similarly the fact that the anisotropy of the aromatic carbons does not change dramatically in magnitude in the temperature range studied rules out other motions such as whole-molecule tumbling. All complexes show broadening and eventual disappearance of the ^{13}CO peak(s). For three complexes a high-temperature-limiting spectrum could be obtained, which gave a greatly reduced value of $\Delta\sigma$ compared to that from the low-temperature data. The actual values of $\Delta\sigma$ can be used to obtain the angle, θ, between the centre of the aromatic ring and the rapidly exchanging C–O vectors. This angle is given in Table 2 for the three cases in which high-temperature $\Delta\sigma$ was obtained. It can be seen that the high-temperature $\Delta\sigma$ is a sensitive function of molecular geometry. Thus the small difference in geometry between the pentamethyl- and 1,2,3-trimethylbenzene complexes is manifest by a large difference in high-temperature $\Delta\sigma$.

The complexes in Table 2 are arranged in order of the ease of rotation of the CO group, based on when the intermediate carbonyl-exchange regime is reached. It is recognised that both intra- and inter-molecular effects will be important in determining the ease of exchange. Inspection of Table 1 reveals that in general it is the $[Cr(\eta^6\text{-arene})(CO)_3]$ complexes with arenes of low symmetry that show carbonyl exchange at lower temperatures. For instance, the pentamethylbenzene complex can be viewed as similar to the hexamethylbenzene one but with a ‘hole’ where there is a missing methyl group, and this must facilitate the exchange. The complexes with arenes of higher symmetry show more resistance to exchange. Thus the NMR experiments indicate that the complex of 1,3,5-trimethylbenzene has the largest barrier to exchange. This is most likely due to the fact that there is approximate three-fold symmetry of the arene ring above the chromium atom and of the $Cr(CO)_3$ unit; carbonyl exchange probably involves moving from energetically favourable positions through a stage where there will be unfavourable interactions with all three methyl groups at the same time (which would not be the case for complexes of lower-symmetry arenes).

It has been widely accepted that for organometallic complexes in the solid state ‘the more regular the ligand shape, the easier the rotational phenomenon’ as ‘ligands with more protruding groups . . . are more easily locked in place by the surrounding molecules’.[2] While lower-symmetry ligands are less likely to show dynamic behaviour themselves, this work shows that they may facilitate dynamic exchange of other parts of the molecule. The link between molecular symmetry and dynamic exchange is thus a complex one. For instance, organometallic complexes containing the cyclohexa- and cyclohepta-dienyl groups have recently been found to show complicated dynamic behaviour: whole-molecule tumbling has been observed to occur for $[Fe(C_6H_7)(CO)_3]BF_4$ and $[Fe(C_7H_9)(CO)_3]BF_4$ above a solid-state phase transition, notwithstanding the steric protuberance of the diene ligands.[24]

Braga and Grepioni[25,26] have calculated barriers to carbonyl rotation for $[M(\eta^6\text{-arene})(CO)_3]$ complexes using atom–atom potential-energy calculations and concluded that such rotations were unlikely. However, our results show that exchange does indeed occur. While there are several molecular motions that can broaden NMR peaks in solids, only carbonyl exchange could result in the reduced chemical shift anisotropy values observed in Table 2. It thus seems that vibrations and possible concerted intermolecular motions in the solid must have a major effect in overcoming the large potential-energy barriers to rotation calculated based on atoms in fixed positions.

The dynamics of some $[Cr(\eta^6\text{-arene})(CO)_3]$ complexes have previously been investigated by Aime *et al.*[27] using variable-temperature ^{1}H relaxation-time measurements. They observed a large reduction in T_1 above 330 K for $[Cr(\eta^6\text{-}C_6H_3Me_3\text{-}1,2,3)(CO)_3]$ and $[Cr(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,5)(CO)_3]$ which they suggested might be due to the onset of reorientation of the arene fragment. It is clear from this work that the dynamic process responsible for the reduction in ^{1}H T_1 must also involve carbonyl exchange.

Another critical feature affecting molecular dynamics in solids is the possibility of phase transitions. For instance, the spectra of $[Cr(\eta^6\text{-}C_6H_3Me_3\text{-}1,2,3)(CO)_3]$ shown in Fig. 3 clearly indicate that phase transitions occur. For this complex as soon as the temperature is raised above the phase transition at 290 K the carbonyl exchange suddenly becomes rapid. This is in contrast to the situation for the other $[Cr(\eta^6\text{-arene})(CO)_3]$ complexes studied which have a gradual increase in the rate of exchange over a wider temperature range. The spectral changes observed were all reversible. However, prolonged heating at high temperatures did in some cases cause small irreversible changes in relaxation times for some samples, possibly relating to trace amounts of paramagnetic species being formed from partial sample decomposition. This effect has been noticed previously for similar complexes,[24,27] but was not studied in any detail here.

As can be seen from Fig. 4, the three carbonyl groups of $[Cr(\eta^6\text{-}C_6HMe_5)(CO)_3]$ are in staggered positions relative to the aromatic ring methyl groups. This is also known to be the case for the $[Cr(\eta^6\text{-arene})(CO)_3]$ complexes of benzene,[21] 1,2,3-trimethyl-,[27] 1,2,4,5-tetramethyl-[27] and hexamethyl-benzene.[20] It should be noted, however, that the energetic preference for the staggered conformation is not large, and the eclipsed conformation is found when the arene is toluene[22] or hexaethylbenzene.[28] The identity of the metal can also make a difference to the conformation adopted in the solid: $[Mo(\eta^6\text{-}C_6H_5Me)(CO)_3]$ is staggered[25] in contrast to the chromium analogue. It must be the close similarity in energy between the staggered and eclipsed conformations that enables the carbonyl exchange in these complexes to occur in the solid state.

It is interesting to consider the failed structural refinement of [Cr(η^6-C_6HMe_5)$(CO)_3$] at room temperature. The fact that six methyl sites were apparently located could be used as evidence that there is rapid reorientation of the arene ring at room temperature. However, the NMR results indicate that carbonyl exchange is occurring, and it may be the carbonyl rotational process and resulting pseudo-symmetry of the complex which cause the incorrect structural refinement. This provides a nice example where crystallography and NMR spectroscopy are complementary techniques: while in many cases crystallography provides the 'definitive' answer over the structure of a solid, solid-state NMR techniques are needed when disorder or motional processes are important in order to avoid misleading X-ray structural refinements.

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