Solid-state ^{13}C Nuclear Magnetic Resonance Investigations of Molecular Dynamics in Crystalline Benzenetricarbonylchromium

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Lineshape changes in the solid-state ^{13}C NMR spectrum of $[Cr(\eta^6-C_6H_6)(CO)_3]$ over the temperature range 203–393 K have been shown to be consistent with reorientation of the $Cr(CO)_3$ unit (with free energy of activation estimated to be 70 ± 5 kJ mol^{-1}), and in-plane reorientation of the benzene molecule.

The dynamic properties of organometallic complexes in the solid state[1] represent an interesting area of study in view of the diversity of dynamic processes, ranging from local reorientational motions of individual ligands to whole-molecule reorientational processes that may occur over a wide range of time-scales. An organometallic complex that exhibits interesting solid-state dynamic properties is benzenetricarbonylchromium, $[Cr(\eta^6-C_6H_6)(CO)_3]$. Its crystal structure has been determined previously from X-ray and neutron diffraction data.[2-4] At room temperature, the crystal structure is monoclinic with space group $P2_1/m$; there are two molecules in the unit cell and the asymmetric unit is half the molecule, with the molecule lying on a mirror plane. Thus, there are two crystallographically distinct CO environments in the crystal structure; for each molecule, one CO group lies on a mirror plane, whereas the other two CO groups are symmetry related across this mirror plane. The dynamic behaviour of the benzene molecules in crystalline $[Cr(\eta^6-C_6H_6)(CO)_3]$ has been investigated using several techniques, including ^1H spin-lattice relaxation time measurements,[5] incoherent quasielastic neutron scattering,[6] potential energy calculations,[7] Raman spectroscopy,[8] and ^2H NMR lineshape analysis and ^2H spin-lattice relaxation time measurements.[9] The results from all of these approaches support the view that the benzene molecule undergoes $2\pi/6$ jumps about its molecular C_6 symmetry axis. The reported values of the energy barrier for this motion fall within a comparatively narrow range, 15.5–19.7 kJ mol^{-1}.[5-9]

It has been argued[6] that heat capacity results can be accounted for by a model in which the $Cr(CO)_3$ unit is fixed, and conclusions from potential-energy calculations[7] have supported the view that rotation of this unit does not occur in the crystal. For the methyl derivative $[Cr(\eta^6-C_6H_5Me)(CO)_3]$, on the other hand, it has been suggested[10] that rotation of the $Cr(CO)_3$ unit occurs in the crystal in the temperature range 273–333 K, but that the arene ring remains fixed. In view of these results for $[Cr(\eta^6-C_6H_5Me)(CO)_3]$, it is important to reconsider the question of motion of the $Cr(CO)_3$ unit in $[Cr(\eta^6-C_6H_6)(CO)_3]$.

Here we report solid-state ^{13}C NMR studies of a sample of $[Cr(\eta^6-C_6H_6)(CO)_3]$ with natural isotopic abundances. All spectra were recorded at 75.5 MHz on a Bruker MSL300 spectrometer using a standard Bruker magic angle sample spinning (MAS) probe with double-bearing rotation mechanism. Both ^1H–^{13}C cross-polarization (CP) and 'single-pulse' techniques were employed (^{13}C 90° pulse duration = 3.5 μs; ^1H 90° pulse duration = 4 μs), with high-power ^1H decoupling applied during acquisition. The accuracy of the temperature measurements was *ca.* ±3 K. Carbon-13 chemical shifts are given relative to $SiMe_4$.

In a polycrystalline powder there are molecules in all possible orientations with respect to the external magnetic field, giving rise to a well defined distribution of chemical shifts [known as chemical shift anisotropy (c.s.a.)], and, consequently, producing a broad resonance line ('powder pattern'). From lineshape analysis of the observed powder pattern, the principal components of the c.s.a. tensor [σ_{11}, σ_{22} and σ_{33} (with $\sigma_{33} \geqslant \sigma_{22} \geqslant \sigma_{11}$)] can be determined. (Note that $\delta_{ij} = -\sigma_{ij}$, in the traditional chemical shift convention.) The chemical shift anisotropy, $\Delta\sigma$, and asymmetry, η, are defined as: $\Delta\sigma = [(\delta_{11} + \delta_{22})/2] - \delta_{33}$ and $\eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{iso})$, where $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$ is the isotropic chemical shift. The occurrence of fast molecular motion with correlation time much shorter than the inverse of the total spectral width of the static powder pattern may significantly modify the observed ^{13}C NMR lineshape.[11]

We consider first the portion of the ^{13}C NMR spectrum due to the CO groups (Fig. 1). In the crystal structure of $[Cr(\eta^6-C_6H_6)(CO)_3]$ at room temperature,[2-4] the molecule lies on a crystallographic mirror plane, such that one CO group (denoted A) lies on this mirror plane, and the other two CO groups (denoted B) are symmetry related by reflection across this mirror plane. Thus, there are two different crystallographic environments (A and B) for the CO groups, with a 1:2 ratio between the numbers of CO groups in environments A and B. At sufficiently low temperature, each CO group remains in one or other of these environments over the time-scale of the ^{13}C NMR measurement, giving rise to peaks at δ 233.9 for environment A and at δ 235.8 for B, with a 1:2 ratio of the integrated intensities (Fig. 1). As the temperature is increased from 293 to 393 K, these resonance lines broaden considerably and coalesce in a manner indicative of exchange of each CO group between environments A and B (coalescence temperature 333–363 K). The rapid rotation of the benzene molecule and the continued existence of a strong ^{13}C NMR signal (not shown in Fig. 1) from the benzene carbons at these temperatures rules out other possible broadening mechanisms, such as effects arising from maximum dipolar broadening or CP dynamics (the latter can also be ruled out from the fact that the same phenomena are observed in the sets of spectra recorded using the CP and 'single-pulse' techniques as a function of temper-

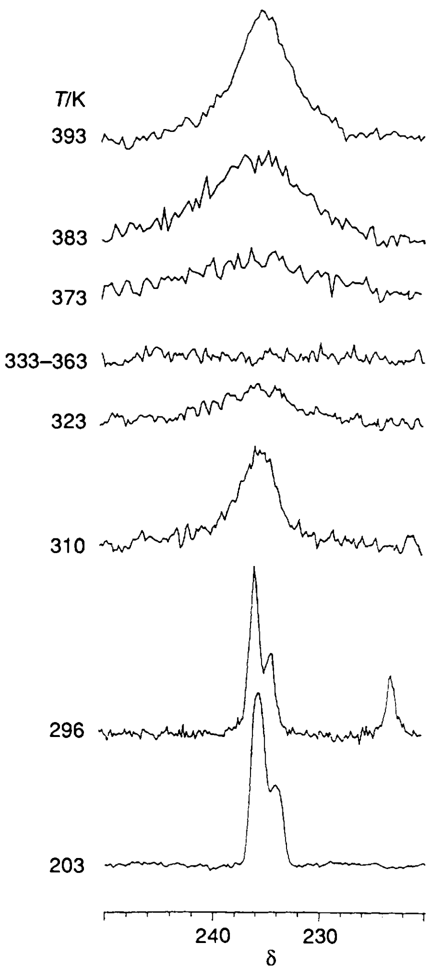

Fig. 1 The carbonyl region of the high-resolution solid-state ^{13}C NMR spectrum of [Cr(η^6-C_6H_6)(CO)$_3$] recorded as a function of temperature. The spectra were recorded using the single-pulse technique with high-power ^{1}H decoupling and MAS (spinning frequency ≈4–5 kHz). Peaks in the region δ 220–223 in the spectra recorded at 296 and 310 K are spinning sidebands due to benzene carbons

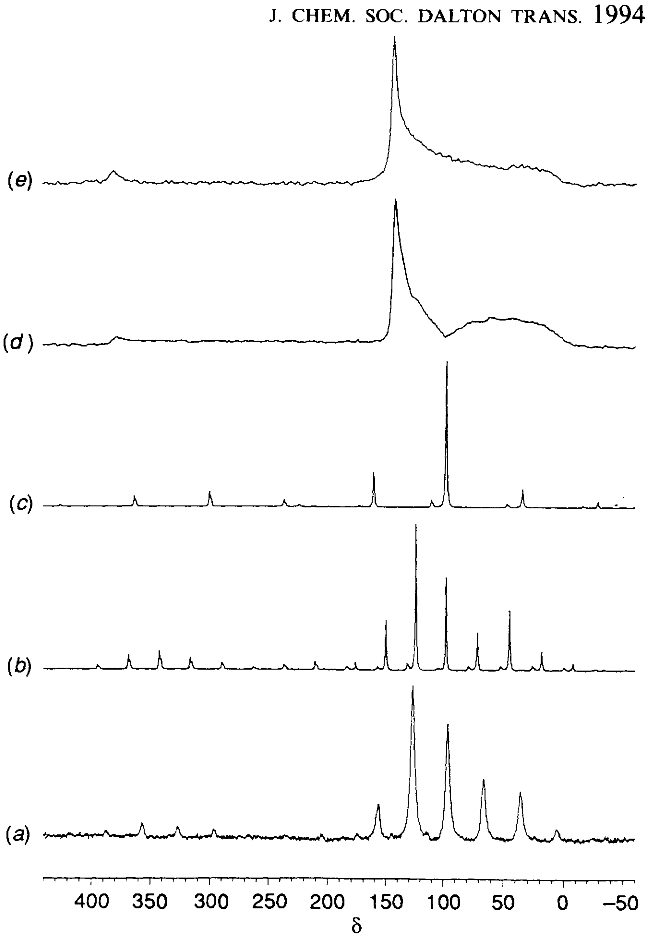

Fig. 2 High-resolution solid-state ^{13}C NMR spectra of [Cr(η^6-C_6H_6)(CO)$_3$] recorded: (*a*) at 129 K with MAS frequency = 2.28 kHz; (*b*) at 293 K with MAS frequency = 1.98 kHz; (*c*) at 293 K with MAS frequency = 4.76 kHz. Broadline solid-state ^{13}C NMR spectra of [Cr(η^6-C_6H_6)(CO)$_3$] recorded: (*d*) at 293 K for a static sample using the CP technique (CP contact time = 0.5 ms); (*e*) at 293 K for a static sample using the 'single-pulse' technique. The linewidths for the benzene carbons are broader at 129 K than at 293 K; this may be because the ^{1}H decoupler frequency (*ca.* 70 kHz) is comparable to the frequency of benzene ring rotation at 129 K (*ca.* 500 kHz[9]). At 293 K, on the other hand, the frequency of benzene ring rotation (*ca.* 10^7 kHz[9]) is several orders of magnitude larger than the ^{1}H decoupler frequency

ature). [Note that at all temperatures in the range 293–393 K, the spectral contribution from the benzene carbons is the same as that shown in Fig. 2(*c*).] The observed spectral changes in the portion of the ^{13}C NMR spectrum due to CO groups are consistent with rotation of the Cr(CO)$_3$ unit such that, at sufficiently high temperature, the average environment (averaged over the time-scale of the measurement) of each CO group in the molecule is equivalent. It is plausible to propose that this motion of the Cr(CO)$_3$ unit takes the form of $2\pi/3$ jumps about the approximate molecular C_3 symmetry axis, although the data recorded here do not allow a definitive assignment of the mechanism for this motion.

The ^{13}C NMR spectrum contains spinning sidebands for the CO carbons at all temperatures studied. Typical examples of the distribution of the spinning sidebands at two different MAS frequencies (1.98 and 4.76 kHz) at 293 K are shown in Fig. 2, and using the modified Herzfeld–Berger method,[12,13] the following parameters for the CO carbons have been obtained: $\delta_{11} = \delta_{22} = 379$, $\delta_{33} = -51$, $\delta_{iso} = 235.7$, $\Delta\sigma = 431$ ppm, $\eta = 0$. These values are typical for terminal CO groups.[13] Although lineshape analysis for spectra containing spinning sidebands requires consideration of the whole spinning sideband pattern rather than just the isotropic peak,[14] we have estimated the free energy of activation using a method, described elsewhere,[15] based on considering the coalescence temperature for a pair of lines of unequal intensity. The value of $\Delta G^\ddagger$ predicted is 70 ± 5 kJ mol^{-1} for the temperature range 333–363 K. This is close to the 'activation barrier' of 65 kJ mol^{-1} reported[10] for rotation of the Cr(CO)$_3$ unit in the related material [Cr(η^6-C_6H_5Me)(CO)$_3$] (however, it is not clear from ref. 10 if this 'activation barrier' is a free energy of activation $\Delta G^\ddagger$, so we do not attempt to discuss further the comparison between this 'activation barrier' and the value of $\Delta G^\ddagger$ reported here). In summary, our ^{13}C NMR studies indicate that reorientation of the Cr(CO)$_3$ unit occurs at sufficiently high temperature, although this motion is several orders of magnitude slower than the reorientational motion of the benzene molecule.[5–9] To our knowledge, this work provides the first evidence for reorientational motion of the Cr(CO)$_3$ unit in crystalline [Cr(η^6-C_6H_6)(CO)$_3$], and contradicts the conclusions from previous studies[6,7] of the dynamics of this material.

We now consider the portion of the ^{13}C NMR spectrum due to the benzene molecule in crystalline [Cr(η^6-C_6H_6)(CO)$_3$], which supports the view (see above) that in-plane rotation of the benzene molecule occurs. For this motion, which can be classified as a uniform uniaxial rotation, the c.s.a. shielding tensor will be only partially averaged, giving rise to an axially symmetric powder pattern.[11] As a result, the direction of the rotation axis relative to the principal axis system of the c.s.a. tensor can be deduced from comparison of the static and motionally averaged c.s.a. tensors. Fig. 2 shows ^{13}C NMR spectra of $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$ recorded at 293 K under various conditions, and the ^{13}C CP MAS NMR spectrum recorded at 129 K. The intensities of the spinning sidebands for the benzene carbons recorded at 129 K were analysed by the Herzfeld–Berger method[12,13] and the following parameters were determined: $\delta_{11} = 158$, $\delta_{22} = 126$, $\delta_{33} = 3$, $\delta_{iso} = 95.7$, $\Delta\sigma = 139$ ppm, $\eta = 0.35$ (δ_{iso} was measured directly from the position of the isotropic peak in the spectrum). On increasing the temperature, rapid in-plane rotation of the benzene molecule averages the δ_{11} and δ_{22} components, and the spectrum [Fig. 2(*e*)] recorded *via* a single-pulse experiment with high-power proton decoupling is an axially symmetric powder pattern. From the spectra recorded at 293 K using two different MAS frequencies, and employing the Herzfeld–Berger method, the following parameters were obtained: $\delta_{11} = \delta_{22} = 141$, $\delta_{33} = 8$, $\delta_{iso} = 96.8$, $\Delta\sigma = 133$ ppm, $\eta = 0$. The 5 ppm difference in δ_{33} on changing the temperature from 129 to 293 K can be attributed to a small temperature dependence of the chemical shifts and to the errors associated with application of the Herzfeld–Berger method.[13,16] That δ_{33} is essentially independent of temperature suggests that the angle between the rotation axis of the benzene molecule and the *z* axis of the c.s.a. tensor (in its principal axis system) is zero, consistent with previous results for hexamethylbenzene[11] and benzene.[17] Spectra [Fig. 2(*d*)] recorded for a static polycrystalline sample under CP conditions (with CP contact times in the range 0.5–24 ms) show characteristic distortions in the lineshape of the powder pattern due to the fact that CP is inefficient for those molecular orientations for which the angle between the rotation axis of the benzene molecule and the external magnetic field B_0 is close to the magic angle. Finally, we note that the values of δ_{11}, δ_{22}, δ_{33} and $\Delta\sigma$ determined for the benzene carbons of $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$ lie between those determined for benzene ($\delta_{11} = \delta_{22} = 187$, $\delta_{33} = 13$, $\Delta\sigma = 174$ ppm) and $[Cr(\eta^6\text{-}C_6H_6)_2]$ ($\delta_{11} = \delta_{22} = 114$, $\delta_{33} = 0$, $\Delta\sigma = 114$ ppm).[17] At a qualitative level, this reflects the differing electron-density distributions around the benzene carbons in these different molecular systems.

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