Fast carbonyl exchange in the solid state for β-cyclodextrin/(arene)Cr$(CO)_3$ inclusion complexes

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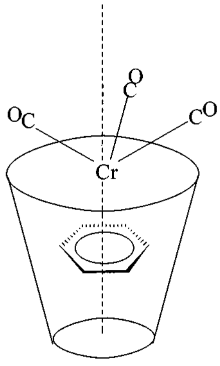
The exchange of carbonyls is a common feature for metal carbonyl compounds in solution whereas in the solid state high interatomic potential energy barriers cause this occurrence to be highly unlikely; it is shown that the compartmentalization of (arene)Cr$(CO)_3$ in the β-cyclodextrin cavity removes any constraint and thereby facilitates the rotation of the Cr$(CO)_3$ group in the solid state.

Cyclodextrins (CDs) that are naturally occurring oligomers of amylose which consist of six to eight glucose units are known to form inclusion compounds with various moieties including neutral molecules and organometallic complexes.[1] The ability of the cyclodextrin molecule to include guest compounds into its internal hydrophobic cavity has been extensively studied and found to be dependent on the size of the internal cavity which can vary from 5 to 7 to 8 Å for α-, β- and γ-cyclodextrins respectively.

Although properties of cyclodextrin inclusion compounds have been studied extensively there have been relatively few reports on their molecular dynamics in the solid state. With regards to organometallic complexes, reports on the inclusion compound formed between ferrocene and β-cyclodextrin (β-CD) indicated that inclusion into the cavity altered the dynamics in the solid state of the guest molecule compared to that observed for the pure compound.[2–5]

We were interested in investigating motion in the solid state of other previously reported inclusion compounds formed between β-cyclodextrin and organometallic complexes whose solid state dynamics of the pure compound had been well documented. This was found to be the case for (arene)Cr$(CO)_3$ (arene = C_6H_6, C_6H_5Me, $C_6H_4Me_2$) complexes where the motion in the solid state had been previously investigated by several authors.[6–8]



It was found that in a polycrystalline sample of $(C_6H_6)Cr(CO)_3$, the arene rotates freely along its principal coordination axis whereas the carbonyl moiety is rigid on the NMR timescale at ambient temperature. Calculations based upon the X-ray crystal structure showed that there is a large potential energy barrier for the rotation of the Cr$(CO)_3$ unit as a consequence of the strong interatomic interactions with the neighbouring molecules.[9,10] This situation is clearly depicted in the ^{13}C CP MAS NMR spectrum [Fig. 1(*a*)] which shows single resonances for the C_6H_6 ligand at δ 95 and the carbonyl group (isotropic peak at δ 234) each showing the typical spinning side band (SSB) manifold which for the carbonyl resonance is indicative of a chemical shift anisotropy of *ca*. 390 ppm. Such a value has been commonly observed for solid state specimens of metal carbonyls containing terminal bound CO.[11]

In the β-CD/$(C_6H_6)Cr(CO)_3$ adduct the arene is reorienting freely as observed in the polycrystalline specimen.[6] This is proven firstly by the observation of a single ^{13}C resonance for the benzene ring in the ^{13}C CP MAS NMR spectrum [Fig. 1(b)] at the same chemical shift as the pure compound. Further support for the occurrence of free arene rotation is gained by looking at the ^{2}H NMR solid state spectrum of the inclusion compound containing as a guest molecule the perdeuterated $(C_6D_6)Cr(CO)_3$ isotopomer.† A typical powder pattern[12] with an inner separation between the main components of 71.0 kHz is observed at 300 K. This behaviour is consistent with the occurrence of a fast-exchange regime ($> 10^8$ s^{-1}) for the arene ring executing six-site nearest-neighbour jumps within the β-cyclodextrin cavity.

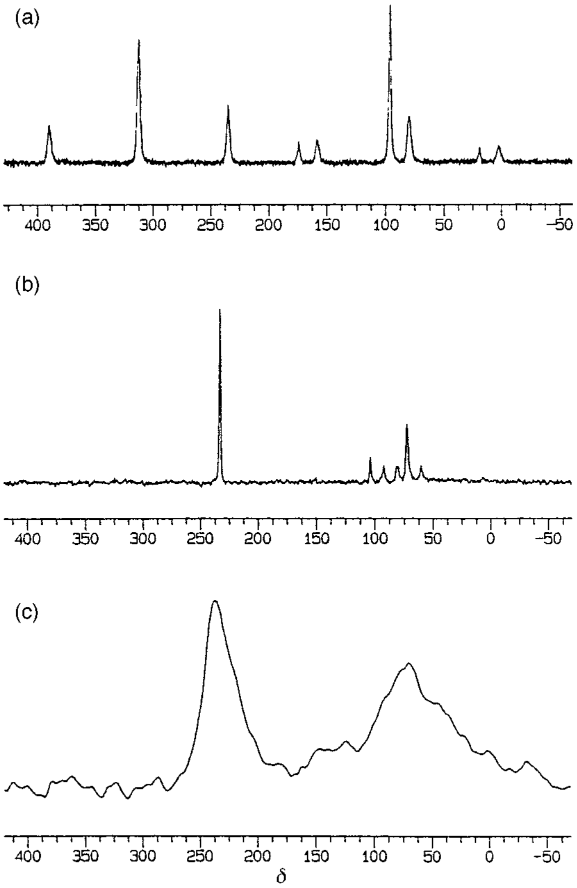


Fig. 1 Solid state ^{13}C NMR spectra recorded at 67.8 MHz for (a) CP MAS of $(C_6H_6)Cr(CO)_3$, (b) CP MAS of β-CD/$(C_6H_6)Cr(CO)_3$ adduct and (c) CP-static β-CD/$(C_6H_6)Cr(CO)_3$ adduct. All spectra was recorded for ^{13}CO enriched‡ samples, with cross polarization (contact time 5 ms) and a recycle delay of 20 s. For (a) and (b) the sample spinning speed was 5000 Hz.

Contrary to what is observed for the polycrystalline sample, in the inclusion compound, the carbonyl moiety acquires a substantial mobility which averages out the CSA responsible for the appearance of the SSB manifold in the high field ^{13}C NMR spectra of metal carbonyls under magic angle spinning [Fig. 1(b)]. Thus the ^{13}C CP MAS NMR spectrum of $(C_6H_6)Cr(CO)_3$ compartmentalized in the β-CD cavity is strictly analogous to the solution spectrum.

At ambient temperature the T_1 of the ^{13}CO resonance in the crystalline $(C_6H_6)Cr(CO)_3$ specimen is *ca*. 30 s, a value significantly shorter than those reported[13] for binary metal carbonyl resonances. This behaviour is likely to be the result of the dipolar interaction to the arene protons modulated by the intramolecular motion of the π-bonded C_6H_6 ring. At the same temperature and magnetic field strength, the T_1 of the CO resonance in the inclusion compound is only 1 s. This observation clearly indicates a high mobility of the carbonyl moiety. It is also worth noting that, in chloroform solution at 6.7 T and 298 K, the T_1 of the carbonyl resonance of $(C_6H_6)Cr(CO)_3$ is 23 s. Indeed the concurrence of a short T_1 and of the lack of the SSB manifold allows the attainment of higher sensitivity of the ^{13}C NMR spectrum of the included species than that of the crystalline sample and even of the solution spectrum.

Further evidence of the dynamic state of the carbonyl moiety has been obtained by recording the static spectrum of the inclusion compound [Fig. 1(c)]. The ^{13}CO resonance displays a bandwidth at half height of *ca*. 20 ppm, *i.e.* remarkably smaller than that commonly found in the static spectra of metal carbonyls.[11]

The motion of the carbonyl ligands is still in fast exchange also at temperatures as low as −100 °C where the ^{13}C CP MAS NMR spectrum is identical to that recorded at ambient temperature. This observation unambiguously shows that the high rotational barrier of the carbonyls[14] is overcome when the metal complex is included in the CD.

The observation of a narrow ^{13}C NMR carbonyl resonance in the static spectrum and the almost negligible asymmetry of its shape appear to be in agreement with the fast rotation of the $M(CO)_3$ unit around its principal coordination axis. A consequence of this type of motion is that the anisotropy of the axially symmetric ^{13}CO tensor is reduced by a factor of $(3\cos^2\beta - 1)/2$ where β is the angle between the principal chemical shift tensor axis and the rotational axis.[15] In the case of the β-CD/$(C_6H_6)Cr(CO)_3$ adduct the structure of the guest molecule[16] is such that the angle β is close to the value of the magic angle. Thereby rotation about the principal rotation axis would be expected to decrease the chemical shift anisotropy to a value close to zero also in the static spectrum.[14] An isotropic (or almost isotropic) reorientation of the whole molecule, which in principle would justify the absence of chemical shift anisotropy, has to be ruled out on the basis of the features of the deuterium NMR spectrum which is typical of a C_6 rotation.

The scrambling of carbonyls is a very common feature in metal carbonyl compounds in solution but it is highly unlikely in the solid state. Our findings show that the stereochemical non-rigidity of the carbonyl moieties may be re-established in a solid sample provided that the intermolecular interactions responsible for the high potential energy barriers in the crystalline framework of the pure compound are removed.

The observed behaviour would seem to suggest that the β-CD cavity provides a lower energy pathway for the rotation of the $M(CO)_3$ group.

Analogous results have been obtained by recording the ^{13}C CP MAS spectra of the inclusion complexes of β-CD with (toluene)$Cr(CO)_3$ and (*o*-xylene)$Cr(CO)_3$.

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Notes and references

† ^{13}C enriched $(C_6H_6)Cr(CO)_3$ was prepared by irradiating the compound in a benzene solution under 1 atm of ^{13}CO (99% enriched) using a 125 W high pressure mercury lamp for 2 h.[17]

‡ $(C_6D_6)Cr(CO)_3$ was obtained by reacting $(C_6H_6)Cr(CO)_3$ in a 1 : 1 mixture of C_6D_6 and $(CD_3)_2CO$ in a sealed vessel at 142 °C for 18 h, in a manner similar to that previously reported for other arene substitutions in ref. 18.

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