Solid State ^{13}C Cross-polarisation/Magic Angle Spinning N.M.R. Spectroscopy of Titanium and Magnesium Chloride Complexes with Ethyl Acetate

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Two complexes of ethyl acetate with metal chlorides, $[TiCl_4(MeCO_2Et)]_2$ and $[MgCl_2TiCl_4(MeCO_2Et)_4]$ were examined by solid-state ^{13}C CP/MAS n.m.r. spectroscopy and the isotropic ^{13}C chemical shift of the carbonyl carbon was found to be relatively insensitive to co-ordination, though large changes of up to 41 p.p.m. were seen in the σ_{22} component of the chemical shift tensor.

Ziegler–Natta catalysts supported on anhydrous magnesium chloride are of great importance in the production of polypropene. The stereoregularity of the polymer made using such catalysts is known to be affected by the presence of ester such as ethyl benzoate and dialkyl phthalate.[1,2] Despite the importance of this behaviour, the exact mode of action is unclear. Two views are held; first that the ester inhibits atactic sites[3] and second, that the ester converts atactic into isotactic sites.[4] At the simplest level it is unclear whether the ester binds to a magnesium or titanium atom at the surface. To clarify the nature of the interaction between esters and Ziegler–Natta catalysts two model complexes $[TiCl_4(EA)]_2$, (EA = ethyl acetate) and $[MgCl_2TiCl_4(EA)_4]$ were studied by ^{13}C CP/MAS n.m.r. The aim was to establish the background n.m.r data necessary to interpret the complex real catalyst systems by using relatively well characterised ester complexes.

Adducts of titanium tetrachloride with Lewis bases are well established and in general involve octahedral co-ordination of the titanium(IV). Thus $[TiCl_4(EA)]_2$ is a dimer with two chlorine bridges. *X*-Ray diffraction studies of this complex[5] indicate the ethyl acetate co-ordinates through the non-bonding electrons on the oxygen of the carbonyl group, giving a relative short Ti–O bond length of 2.03 Å. Less is known about the complexes of esters with magnesium chloride. Well characterised complexes of the magnesium halides are restricted to those with ethers such as $\mathrm{MgBr_2(OEt_2)_2}$[6] and mixed metal ester complexes, for example $[\mathrm{MgCl_2TiCl_4(EA)_4}]$, where *X*-ray diffraction has established ester co-ordination to the magnesium.[7] The ^{13}C CP/MAS n.m.r. spectrum of $[\mathrm{TiCl_4(EA)}]_2$, Figure 1, illustrates the narrow linewidths seen for both complexes, consistent with a well-defined ester environment. An interesting feature of the spectrum shown is that the two methyl resonances at 15.3 and 22.4 p.p.m. are broadened to differing extents. This is because the methyl group giving rise to the resonance at 22.4 p.p.m. has a more restricted motion about its C_3 axis, caused by a degree of steric crowding of this methyl group. In the case of $[\mathrm{TiCl_4(EA)}]_2$ all the resonances are singlets, consistent with the presence of a centre of inversion in the crystal structure of the dimer. Contrasting with this $[\mathrm{MgCl_2TiCl_4\,(EA)_4}]$ shows a multiplicity of resonances for each carbon type reflecting the lower symmetry of the complex. The chemical shifts found for the two complexes are listed in Table 1 together with the shifts expected for the free ester.

A feature of the chemical shift data is the similarity of the chemical shifts for the ester carbonyl in the free EA and in the complexes. Rather larger differences of up to 10 p.p.m. have been observed in complexes with ethyl benzoate.[8] Indeed the largest changes are seen for the carbon adjacent to the acyl oxygen in the alkyl group. It is somewhat surprising that the strong interaction between the ester and titanium, as reflected in the short Ti–O bond length, causes such a small change in the carbonyl ^{13}C isotropic chemical shift. In a solid the three principal components of the chemical shift tensor can be seen and it is possible that the small isotropic chemical shift variations obscure larger but opposing changes in the chemical shift tensor components. To explore this possibility the slow MAS spectra of the complexes with ethyl acetate were obtained, and the intensities of the spinning sidebands analysed using the Herzfeld–Berger method.[9] Computer simulation of the MAS spectrum was used to ensure the uniqueness of the chemical shift tensor.[10] Chemical shift tensor components derived from this analysis are shown in Table 2.

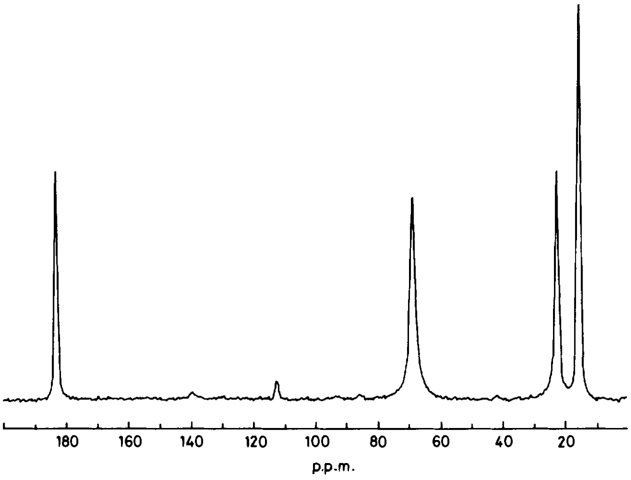

Figure 1. 50.32 MHz ^{13}C CP/MAS n.m.r. spectrum of $[\mathrm{TiCl_4(EA)}]_2$.

Table 1. Isotropic chemical shifts for free ethyl acetate and the metal complexes.

	$\mathrm{H_3}\mathit{C}\text{–}\mathrm{CO}$ (p.p.m.)	$\mathrm{H_3C}\text{–}\mathit{C}\mathrm{O}$ (p.p.m.)	$\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$ (p.p.m.)	$\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$ (p.p.m.)
EA	20.3	180.0	60.4	14.3
$[\mathrm{TiCl_4(EA)}]_2$	22.4	182.9	68.7	15.3
$[\mathrm{MgCl_2TiCl_4(EA)_4}]$	23.9	177.4	65.8	16.7
	22.3	179.5		15.6
				14.3

An examination of the chemical shift tensors confirms that the small changes seen in the isotropic chemical shift of the carbonyl resonance are caused by a cancellation of opposing larger changes within the tensor components. Thus for $[\mathrm{TiCl_4(EA)}]_2$ σ_{11} is shielded by 23.5 p.p.m. and σ_{22} deshielded by 41 p.p.m. Hence at a qualitative level the chemical shift tensor is far more sensitive to the interaction between ethyl acetate and the metal centres than the isotropic chemical shifts.

Having observed significant differences in the chemical shift tensors, it is of interest whether they can be related to changes in the electronic structure of the ester, caused by bonding to the metal centre. The chemical shielding, σ, can be defined as the sum of two terms,[11] a diamagnetic shielding, σ^d, and a paramagnetic shielding, σ^p. For ^{13}C the two terms are of comparable magnitude. The paramagnetic term is dependent upon matrix elements involving unoccupied excited states and their excitation energies, equation (1). This means that a full quantitative analysis of the chemical shielding tensor would require accurate *ab initio* MO calculations. However, a qualitative analysis can be presented in the absence of such calculations for the system under study by using data for the simplest carbonyl, methanal.[12,13] For methanal it is possible to identify the three principal components of the chemical shielding tensor with different electronic transitions as shown in Figure 2. On the basis of this analysis only small variations in σ_{33} should be seen because the σ–σ* energies will be least sensitive to structural change. A large variation is expected and is indeed seen for σ_{22} in carbonyl compounds, consistent with the known variations in the *n*–π* excitation energy, while smaller changes are seen for σ_{11}. As the σ-donor behaviour of an ester involves the non-bonding orbital on the ester carbonyl, large changes are predicted in the *n*–π* excitation energy and thus σ_{22}. Hence the strength of the interaction between the ester and the metal centre will be reflected in σ_{22} and indeed a strong interaction between the ester and metal centre is observed as indicated by the significant changes in σ_{22}

$$\sigma^p = \frac{-e^2}{m^2c^2}\sum_{jj'}\sum_{\nu\mu}\sum_{\lambda\rho}\frac{a^*{}_{\nu j}a_{\mu j}a^*{}_{\lambda j'}a_{\rho j}}{\Delta E_{jj'}} \times$$

$$\{<\phi_\nu(k)|\,\frac{l(k)}{r^3}\,|\phi_\mu(k)><\phi_\lambda(k)|l(k)|\phi_\rho(k)>\} \quad (1)$$

Table 2. Chemical shift tensor components for the ester carbonyl.

	σ_{11} (p.p.m.)	σ_{22} (p.p.m.)	σ_{33} (p.p.m.)	σ_{iso} (p.p.m.)
Methyl acetate[a,15]	261	159	119	180.0
$[\mathrm{TiCl_4(EA)}]_2$	237.5	200	111.5	182.9
$[\mathrm{MgCl_2TiCl_4(EA)_4}]$	254.0	175.9	108.3	179.5
	252.6	174.5	106.6	177.4

[a] Closest model for ethyl acetate.

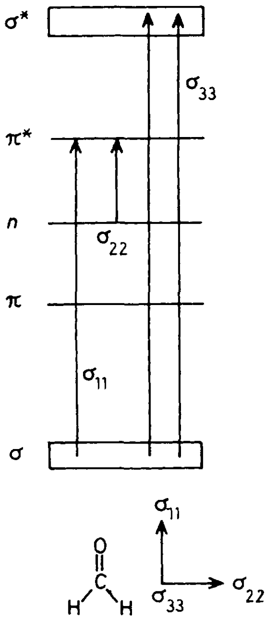

Figure 2. Simplified MO description of methanal showing the correlation between the chemical shift tensor components and the electronic transitions.

shown in Table 2. A comparison of σ_{22} for $[TiCl_4(EA)]_2$ where the ester is co-ordinated to the titanium and for $[MgCl_2TiCl_4(EA)_4]$ where the co-ordination is to magnesium indicates a stronger perturbation to the ester electronic environment by the titanium. This suggests a stronger bond to titanium, which would be consistent with the respective Lewis acidities of $MgCl_2$ and $TiCl_4$. However, a detailed analysis reveals that the sign of the differences in σ_{22} is inconsistent with the model discussed above. That is, the interaction of the ester carbonyl non-bonding orbital with the metal will tend to increase the n–π^* excitation energy and thus lead to a shielding effect, contrary to the experimental result.

The origin of this discrepancy is the neglect of the $<r^{-3}>_{2p}$ term. In the case of hydrogen bond formation, where the carbonyl oxygen similarly acts as a σ-donor, two opposing effects are present. An increase in $E(n$–$\pi^*)$ does indeed occur but this is more than offset by the increase in $<r^{-3}>_{2p}$.[14] Changes in $<r^{-3}>_{2p}$ can be understood in a straightforward manner; σ-donation from the oxygen to the metal centre will enhance the polarisation of the carbonyl bond so that the remaining $2p$ electrons on the carbon are under a higher effective nuclear charge. As a consequence the nuclear – $2p$ electron distance, r, decreases and $<r^{-3}>_{2p}$ increases. Both the increase in $E(n$–$\pi^*)$ and $<r^{-3}>_{2p}$ are correlated to the degree of interaction between the ester carbonyl and the metal centre. Thus it is reasonable to use changes in σ_{22} as a measure of the strength of the bonding between an ester and a metal.

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