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A Study of Titanium and Magnesium Chloride Complexes with Dialkyl Phthalates by Solid State ^{13}C CP MAS NMR Spectroscopy

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A series of dialkyl phthalate complexes with magnesium chloride and titanium(IV) chloride has been prepared and characterised by ^{13}C CP MAS NMR spectroscopy. The isotropic chemical shift of the ester carbonyl group did not allow co-ordination to magnesium or titanium to be distinguished in general.

Examination of the ester carbonyl chemical shift tensor as characterised by the parameters δ and η, however, reveals a clear distinction between titanium complexes where $\eta < 1$ and magnesium complexes where $\eta > 1$. Both complexes give a similar δ value.

Modern Ziegler–Natta catalysts for the polymerisation of propene are composed of titanium tetrachloride on a magnesium chloride support.[1,2] The stereoregularity of the basic catalyst is modified by the use of an internal donor such as dialkyl phthalates[3] and external donors such as phenyl- and alkyl-alkoxysilanes.[4] Characterisation of the precise mode of interaction between the internal donor and the catalyst system is essential in order to understand the manner in which the donor modifies the stereoregularity of the polymer. IR spectroscopy has been the mainstay technique for studying ester interactions, especially in what one can call 'real catalytic systems' while X-ray diffraction has been used to obtain the structure of model crystalline compounds. More recently, solid state ^{13}C NMR spectroscopy [5–7] and EXAFS [8] have been applied in order to gain more information regarding the interactions.

The emphasis in the solid state ^{13}C NMR studies [5,6] has been on changes in the isotropic chemical shift of the carbonyl resonance. In the case of monoesters significant differences of up to 7 ppm are seen in the chemical shift upon complexation with magnesium or titanium(IV) chloride. On the other hand, very similar chemical shifts are seen for dialkyl phthalate complexes and hence for these complexes it is not possible to differentiate between a phthalate complexed to a magnesium or titanium centre. In the desire to achieve high resolution solid state ^{13}C NMR spectra comparable to solution NMR important additional information has been removed, namely the anisotropic component to the chemical shift.[9] The importance of this contribution has been demonstrated in a study of titanium and magnesium chloride complexes with ethyl acetate.[7] Although the isotropic chemical shift of the carbonyl resonance shows only a small change of 2.9 ppm from the free ester to [TiCl$_4$(ethyl acetate)$_2$], very significant changes are seen in the chemical shift tensor components, thus σ_{11} is shielded by 23.5 ppm and σ_{22} deshielded by 41 ppm. Moreover, the difference between the magnesium and titanium complexes was marked. Using δ and η to describe the chemical shift tensor ($\delta = \sigma_{33} - \sigma_{\text{iso}}$, $\eta = (\sigma_{22} - \sigma_{11})/\delta$ we can clearly see this: for [TiCl$_4$(ethyl acetate)$_2$] $\delta = -71.4$ ppm and $\eta = 0.52$ and for [MgCl$_2$:TiCl$_4$(ethyl acetate)$_4$] $\delta = -71.2$ ppm and $\eta = 1.10$, hence the η value is a good indicator of the metal to which the ester is bound. In the light of this observation, a series of magnesium and titanium complexes with dialkyl phthalates were prepared in order to ascertain whether similar changes occur in the chemical shift tensor of the carbonyl group and thus allow the characterisation of the ester bonding site in a typical catalyst system.

Experimental

Materials.—MgCl$_2$:*(diethyl phthalate) complex.* Anhydrous MgCl$_2$ was milled for 2 h in a vibration ball mill equipped with steel balls to produce a finely subdivided material, 3.71 g (39.0 mmol) of which was suspended in anhydrous diethyl phthalate (50 cm^3) with stirring under a nitrogen atmosphere. The temperature was raised to 150 °C for 4 h. Excess ester was removed by filtration at 100 °C and the filter cake was washed with dry heptane (3 × 30 cm^3) at 85 °C. The washed cake was dried *in vacuo*.

MgCl$_2$:*(di-isobutyl phthalate) complex.* The above procedure was repeated using 2.95 g (31.0 mmol) of MgCl$_2$ and di-isobutylphthalate (50m cm^3).

TiCl$_4$:*(diethyl phthalate) complex.* Neat TiCl$_4$ (5 cm^3, 45.5 mmol) was added to dry heptane (80 cm^3) under nitrogen. Diethyl phthalate (9 cm^3, 45 mmol) was added dropwise with stirring. A bright yellow precipitate formed immediately. The solid was filtered and washed with heptane before being dried at 50 °C *in vacuo*.

TiCl$_4$:*(di-isobutyl phthalate) complex.* Di-isobutylphthalate (18 cm^3, 67 mmol) was dissolved in dry dichloroethane (80 cm^3) under nitrogen. Neat TiCl$_4$ (10 cm^3, 91 mmol) was added with stirring. A clear yellow solution was formed which precipitated a bright yellow solid on standing. The solid was filtered, washed with heptane (3 × 80 cm^3) and dried at 50 °C *in vacuo*.

TiCl$_4$:*(dicyclohexyl phthalate) complex.* Neat TiCl$_4$ (5.45 cm^3, mmol) was dissolved in dry toluene (50 cm^3) under nitrogen. Dicyclohexyl phthalate (26.5 g, 50 mmol) dissolved in dry toluene (50 cm^3) was added dropwise with stirring. A lemon-yellow solid precipitated after *ca.* 40 cm^3 of this solution had been added. The solid was filtered and washed with dry heptane (2 × 70 cm^3) before being dried at ambient temperature *in vacuo*.

MgCl$_2$:TiCl$_4$:*(di-isobutyl phthalate) complex.* Anhydrous MgCl$_2$ was milled for 2 h in a vibration mill containing steel balls. The resulting material (3.44 g) was suspended in di-isobutyl phthalate (300 cm^3) with stirring and TiCl$_4$ (6.90 g, 4 cm^3) was syringed in. The temperature was raised to 120 °C for 30 min when the solid suspension cleared. A slight haze was removed by filtration through Kieselguhr.

A yellow oil separated on addition of heptane (280 cm^3). The oil was separated, shaken with dry toluene (60 cm^3), and gradually formed crystals when allowed to stand.

NMR Measurements.—Solid state ^{13}C NMR spectra were

Table. Chemical shift tensors for the carbonyl resonance in dialkyl phthalates and their complexes.

	$-\delta$ (ppm)	η	δ_{iso}[a] (ppm)	Q[b]
Dicyclohexyl phthalate	56.4	2.27	167.7	0.63
Dineopentyl phthalate	58.9	2.03	166.7	0.37
$TiCl_4$:(diethyl phthalate)	69.5	0.70	174.6	0.43
$TiCl_4$:(di-isobutyl phthalate)	71.5	0.77	174.3	0.84
$TiCl_4$:(di-cyclohexyl phthalate)	71.2	0.91	172.7	0.40
$MgCl_2$:(diethyl phthalate)	66.7	1.00	169.4	0.18
	69.1	1.03	171.7	0.42
$MgCl_2$:(di-isobutyl phthalate)	73.9	1.19 (0.16)	175.6	0.47
	73.6	1.14 (0.04)	174.8	0.005
	65.4	1.05	173.7	0.54
	61.6	1.27	171.5	0.001
	55.6	1.57 (0.02)	169.5	0.61
$MgCl_2$:$TiCl_4$:(di-isobutyl phthalate)	66.9	1.12	173.7	0.58
	66.1	1.09	172.9	0.95
	63.7	1.12	172.0	0.75
	64.1	1.14	171.8	0.74
	62.1	1.25	171.3	0.83

[a] Measured with respect to TMS using an external secondary reference of adamantane. [b] Goodness-of-fit.

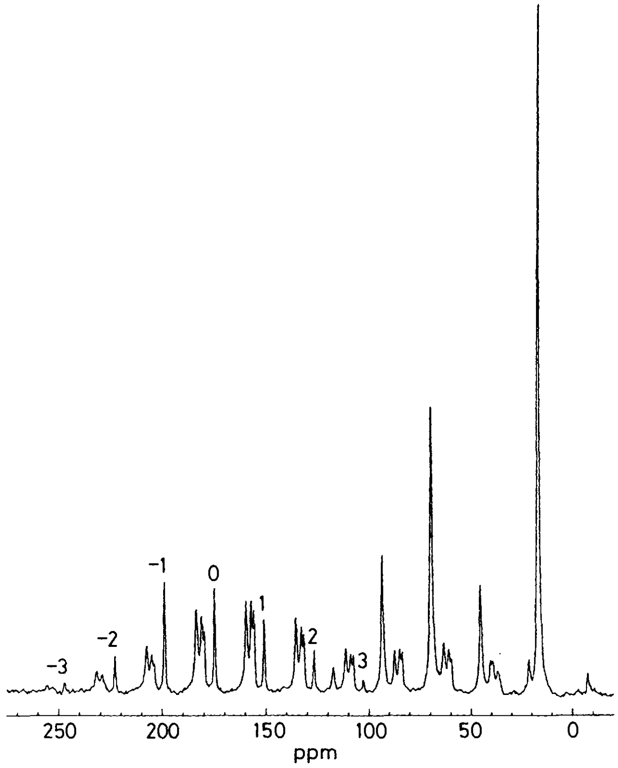

Figure 1. 50.32 MHz ^{13}C CP Slow MAS NMR spectrum of $TiCl_4$: (diethyl phthalate). The spinning sidebands of the carbonyl resonance are labelled -3 to 3. A spinning speed of 1 212 Hz was used.

acquired on a Bruker MSL200 NMR spectrometer operating at 50.32 MHz. To obtain high resolution spectra, magic angle spinning and high power proton decoupling were used while the sensitivity was enhanced by cross polarisation through a spin-lock pulse sequence with a contact time of 1 ms. MAS speeds of 4 kHz were used except for the slow-spinning experiments when speeds of *ca.* 1 kHz were necessary.[10] The chemical shift tensors were derived from the spinning sideband intensities in the slow spinning spectra by computer simulation of the MAS spectrum using a SIMPLEX routine.[11] The standard deviation for the sideband intensities was determined from the experimental noise level allowing the minimum χ^2 value found in the SIMPLEX routine to be tested for the goodness-of-fit.[11] The goodness-of-fit, Q, is the probability that the observed χ^2 value would be obtained given the experimental noise level and the correctness of the model. A value of $Q > 0.1$ was deemed to be acceptable.

Results and Discussion

The chemical shift tensor data for the carbonyl resonance derived from the slow spinning sideband intensities for each of the phthalate complexes is shown in the Table. A typical slow spinning spectrum is shown in Figure 1. Two solid dialkyl phthalates were studied to provide reference chemical shift tensors for free phthalate esters and the results for these are also included in the Table. In the case of $MgCl_2$:(di-isobutyl phthalate) very poor fits were found to the sideband intensities using a unique η value and a more sophisticated model involving a normal distribution of η for a single δ value was tried. The justification for such an approach is that despite the range in η found for magnesium and titanium complexes, δ varies to a lesser extent, hence it is possible that a resonance with a given chemical shift may represent an overlap of a number of resonances with different η. For those complexes where the goodness-of-fit to a unique η was unacceptable, the distribution of η fit was tested in a SIMPLEX routine allowing δ, η, and the standard deviation of the normal distribution to vary; these fits are indicated by the standard deviation of η in parentheses after the η values.

A comparison of the isotropic chemical shifts of the carbonyl resonances for the titanium and magnesium chloride complexes confirms the view that these cannot be used to differentiate between the ester complexing to one or other of the metals. However, for all the complexes studied to date, no magnesium chloride complex has been found with an η value <1 while all the titanium(IV) chloride complexes have $\eta < 1$. This is not to say that complexes will not be found which blur the distinction, indeed $TiCl_4$:(dicyclohexyl phthalate) with $\eta = 0.91$ is close to the border, but for a given ester, we can expect the η value to define whether the ester is bound to magnesium or titanium. The reason for the clear differences is that magnesium chloride and titanium(IV) chloride have quite different Lewis acidities. Consequently their interaction with the non-bonding orbital of the ester carbonyl will differ, which in turn, modifies the n–π^* energy separation and the polarisation of the carbonyl bond. These changes are reflected in the chemical shift tensor.

All three titanium complexes show a single carbonyl resonance suggesting a plane of symmetry connecting the carbonyl groups. In the case of the $TiCl_4$:(diethyl phthalate) complex this is confirmed by the single-crystal X-ray structure.[12] Given the interpretation of the large differences in η between the magnesium and titanium complexes, it is tempting to explain the variations in η found within the titanium complexes in similar terms, *i.e.* because of changes in the Lewis basicity of the dialkyl phthalate. Despite the good fits found to the spinning sideband intensities, it is unrealistic to consider changes in η of <0.1. Having said this the $TiCl_4$:(dicyclohexyl phthalate) complex still appears anomalous with $\eta = 0.91$. A possible interpretation of the weaker interaction between the dicyclohexyl phthalate and titanium is based on the consequence of steric forces. In the crystal structure of $TiCl_4$:(diethyl phthalate), the ethyl groups are turned towards the $TiCl_4$

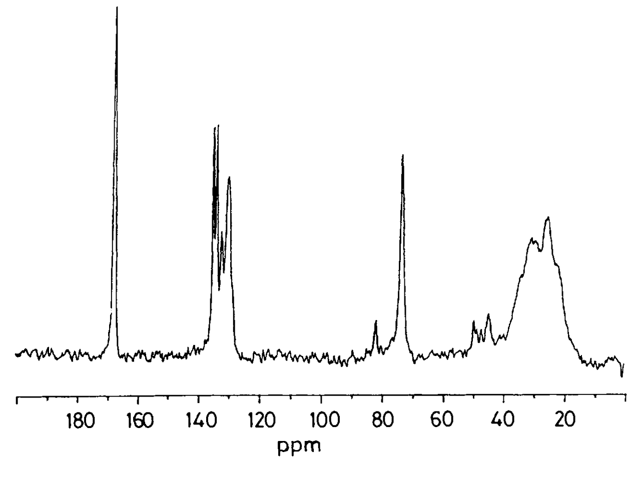

Figure 2. 50.32 MHz ^{13}C CP MAS NMR spectrum of $TiCl_4$: (dicyclohexyl phthalate).

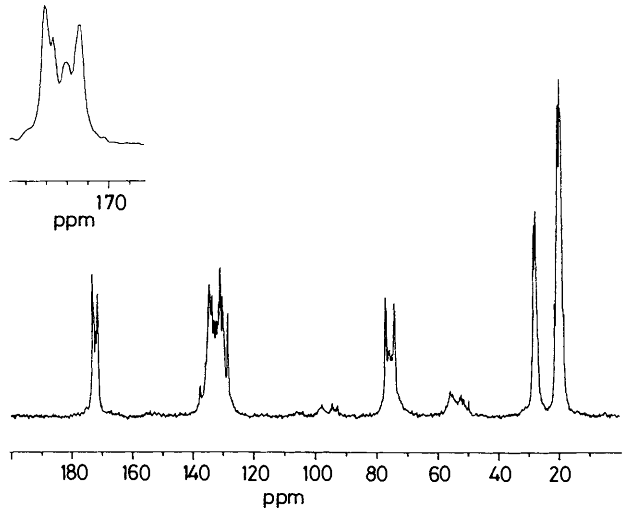

Figure 3. 50.32 MHz ^{13}C CP MAS NMR spectrum of $MgCl_2$:$TiCl_4$: (di-isobutyl phthalate).

fragment; if the same conformation is adopted by the dicyclohexyl phthalate then steric interactions will prevent as close an approach of the carbonyl group to the titanium and hence produce a weaker donor bond, thus we should expect to see an increase in η as the steric bulk of the alkyl group increases. In addition to the high η value, the spectrum of the $TiCl_4$:(dicyclohexyl phthalate) shows an ill-defined set of resonances from the cyclohexyl rings at *ca.* 30 ppm in contrast to the free dicyclohexyl phthalate, see Figure 2. Note this is not a generalised line broadening, as the aromatic resonances are sharp, suggesting that the cyclohexyl group either has an ill-defined conformation or is undergoing a conformational exchange at a fast rate leading to interference with the high power proton decoupling.

In the case of the di-isobutyl and dicyclohexyl phthalate complexes with titanium, it is unclear whether the NMR data are consistent with a bidentate ester interaction with the metal centre. This could be inferred from the presence of a single carbonyl resonance although it is possible that the two carbonyl resonances are coincident in a monodentate complex. To see whether analysis of the spinning sidebands could differentiate between two overlapping resonances with different chemical shift tensors, as might be the case for a monodentate phthalate, or one unique spinning sideband pattern from a bidentate phthalate, test spectral simulations were performed. Taking the extreme case for a monodentate ligand of one carbonyl as in a free phthalate and the other as in the $TiCl_4$:(diethyl phthalate) complex, we can simulate the expected slow-spinning spectrum. The simulated data were then analysed using the SIMPLEX routine. If a monodentate phthalate is to be identified then the two component spinning sideband intensities must give an unacceptably low goodness-of-fit to a unique chemical shift tensor. However, even for the extreme case chosen for a monodentate ligand the goodness-of-fit was found to be just acceptable, $Q = 0.12$. This indicates that an intermediate unique chemical shift tensor can be found which adequately fits the spinning sideband data.

The simulations show that it is unrealistic to expect to be able to distinguish between overlapping resonances in a monodentate and a bidentate complex from a spinning sideband analysis. Since electronic effects will tend to make the carbonyl groups in a monodentate complex more similar it is clear that should the carbonyl resonances overlap then a mono- or bi-dentate phthalate cannot be distinguished. Thus far we have taken the worst possible case, namely that in a monodentate complex the two carbonyl resonances will have the same isotropic chemical shift. Examination of the analogous case of selective hydrogen bonding indicates, however, that we can in fact expect to see small differences in the isotropic chemical shift between a free carbonyl and a carbonyl involved in σ-donation.[13] This means that a sideband analysis can be carried out on the two resonances separately. The test for a monodentate complex is then whether two resonances with similar isotropic chemical shifts have significantly different chemical shift tensors.

A particular example of this is the $MgCl_2$:(diethyl phthalate) complex where two carbonyl resonances are seen, and we would like to know whether this shows the phthalate to be behaving as a monodentate ligand. From the Table it can be seen that the two carbonyl resonances have very similar η values, implying an equal degree of interaction with a magnesium atom. Hence it is reasonable to propose that the diethyl phthalate acts as a bidentate ligand in the magnesium complex.

An interpretation of the number of resonances seen in the carbonyl region for $MgCl_2$:(di-isobutyl phthalate) is not at all clear cut given the range in δ and η. The spectra of different samples are similar but not totally reproducible, little change in the spectrum is seen on treating the sample by Soxhlet extraction in an attempt to remove excess phthalate. Thus it does appear that distinct ester–magnesium structures are being formed, although the sample may well consist of a number of different types of complex. Without placing too much importance on the precise number and intensity of the resonances, the signifcant features are that η is always > 1 and there is a trend for δ to decrease and η to increase towards the free-ester values as the deshielding of the isotropic chemical shift decreases. These changes confirm the hypothesis that magnesium chloride–phthalate complexes only give an η value > 1 and that changes in δ, η, and the isotropic chemical shift occur in a correlated way.

A similar range of resonances is seen in the ^{13}C CP MAS NMR spectrum of $MgCl_2$:$TiCl_4$:(di-isobutyl phthalate) (see Figure 3). By contrast, though, excellent agreement is found between the simulated spinning sideband patterns and those observed experimentally, suggesting the formation of a well-defined complex. No evidence is found for ester complexation to titanium because η lies between 1.09 and 1.25.

In the case of $MgCl_2$:$TiCl_4$:(di-isobutyl phthalate), for all the resonances except the one at 171.3 ppm, η can be considered to be constant within the experimental error, $\eta = 1.12 \pm 0.03$, while δ increases in line with the isotropic chemical shift. This would tend to suggest that the variation in isotropic chemical shift is caused by intermolecular effects, *i.e.* neighbouring groups perturbing the chemical shift tensor, since we have seen that η is sensitive to the metal–carbonyl bonding. Multiplicity of the carbonyl resonance was also seen for [$MgCl_2:TiCl_4(CH_3CO_2Et)_4$], again with a constant η but variable δ.[7] Even the least-perturbed carbonyl resonance in the $MgCl_2:TiCl_4$:(di-isobutyl phthalate) complex is markedly different from a free-phthalate carbonyl, from which we can infer that all the phthalate ester behaves as a bidentate ligand. However, we can not say, on the basis of the NMR results, whether the ester interacts with one magnesium atom or with two as a bridging ligand.

Conclusions

From a study of a series of phthalate ester complexes with magnesium and titanium(IV) chloride, we have been able to show that changes in the chemical shift tensor, similar to those previously reported for ethyl acetate, also occur for dialkyl phthalates. Thus complexes with magnesium and titanium give rise to characteristic changes in the chemical shift tensor of the phthalate carbonyl group, which allows bonding to the metals to be distinguished. Complexes with magnesium give η values > 1 while those with titanium give an $\eta < 1$.

All the chemical shift tensor data are consistent with the phthalate esters acting as bidentate ligands, though bridging or non-bridging behaviour cannot be distinguished. In the case of a mixed magnesium chloride/titanium(IV) chloride complex with di-isobutyl phthalate, no evidence for co-ordination of the ester to titanium was present.

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