Characterisation and Solution Properties of Complexes involving Magnesium Chloride, a Lewis Base, and the Tetrachlorides of Titanium, Zirconium and Tin

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Compounds containing magnesium chloride, an ester or an ether, and a tetrachloride of titanium, zirconium or tin have been obtained as $MgCl_2 \cdot MCl_4 \cdot 4L$ (where M = Ti, Zr or Sn, L = $CH_3COOC_2H_5$ or tetrahydrofuran; M = Ti, L = $HCOOC_2H_5$), $MgCl_2 \cdot TiCl_4 \cdot 2CH_3COOC_2H_5 \cdot 2L$ (L = $HCOOC_2H_5$ or $C_6H_5\text{-}COOC_2H_5$), $MgCl_2 \cdot TiCl_4 \cdot 2CH_3COOC_2H_5$, and $(MgCl_2)_3 \cdot TiCl_4 \cdot (SnCl_4)_2 \cdot 12CH_3COOC_2H_5$. The solution properties of several of these species have been studied through ligand displacement reactions using ^1H n.m.r. spectroscopy, and the stabilities of some metal chloride/ester (metal = Mg or Ti) adducts have been determined.

Introduction

The development of Ziegler–Natta type catalysts for use in the polymerisation of α-alkenes has been well documented [1, 2]. Since the early reports several refinements have been made in the preparation of catalysts, resulting in improved activity and stereo-specificity. Considering one basic component of the catalyst to be a titanium halide, usually $TiCl_4$ or $TiCl_3$, an important modification has been to support the halide on a large surface area solid, especially magnesium chloride [3–8], in the presence of a Lewis base, typically the ester of an aliphatic or aromatic carboxylic acid [3–5, 9–13].

The role of the Lewis base has not yet been defined, and it is also not clear whether the introduction of either the base or the magnesium chloride causes any significant changes in the generally accepted mechanism of polymerisation following Arlman and Cossee [14].

One patent in particular describes several derivatives based on the $MgCl_2/TiCl_4$/ester system [4], and recent reports established the existence and crystal structure of the complex $MgCl_2 \cdot TiCl_4 \cdot 4EtOAc$ (where EtOAc = $CH_3COOC_2H_5$), I [15, 16], and the related bridged adduct $MgCl_2 \cdot TiCl_3 \cdot (OOCCH_2Cl) \cdot (ClCH_2COOC_2H_5)_3$, II [17].

It is also known that the individual components interact with esters, thus $TiCl_4$ forms dimeric com-

(I)

(L = EtOAc)

(II)

(L' = $ClCH_2COOC_2H_5$)
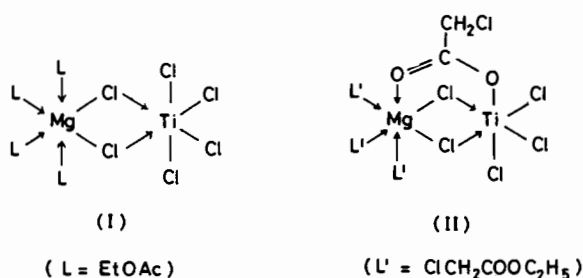
plexes of the type $(TiCl_4 \cdot L)_2$ (L = EtOAc [18–21], $HCOOC_2H_5$ [22, 23], p-ethylanisate [24]), and $TiCl_4 \cdot 2L$ (L = EtOAc [25, 26], $HCOOC_2H_5$ [23]). An unstable solvate of magnesium chloride, $MgCl_2 \cdot 2EtOAc$, has also been reported [27], as has a less well defined complex involving ethyl benzoate, $MgCl_2 \cdot xC_6H_5COOC_2H_5$ (where x = 0.1–2.0) [28].

We now report the preparation and characterisation of several new complexes containing magnesium chloride, coupled with the determination of the properties of some of the compounds in solution, especially with regard to exchange and substitution reactions.

Results and Discussion

Our initial experiments were made using ethyl acetate as the ester ligand. Anhydrous magnesium chloride dissolves slowly in refluxing ethyl acetate, and solutions at room temperature can be about 0.5 *M* concentration before crystalline material deposits on standing. We were unable to isolate a discrete species $MgCl_2 \cdot 2EtOAc$ because the composition of the solid phase varies, depending upon the mode of preparation. Thus pumping down a 0.5 *M* solution to obtain a solid, followed by washing the solid with heptane (2 × 35 cm³), and pumping again for 5 min at room temperature, yields solids of compositions near $MgCl_2 \cdot 2.75EtOAc$. As the time of pumping is increased so the proportion of ethyl acetate decreases as follows: 0.5 h, 25 °C, 1.96 mol EtOAc/mol $MgCl_2$; 3 h, 25 °C, 1.56 mol; 18 h, 25 °C, 0.94

TABLE I. Displacement Reactions with $MgCl_2 \cdot TiCl_4 \cdot 4EtOAc$.[a]

Ligand	Conditions	Product	Remarks
THF	$CDCl_3$ solution in nmr tube and THF added	$MgCl_2 \cdot TiCl_4 \cdot 4THF$	Straightforward displacement takes place, where all EtOAc is replaced by THF. The tin analogue $MgCl_2 \cdot SnCl_4 \cdot 4EtOAc$ acts in a similar way with respect to THF
DMSO	$CDCl_3$ solution in nmr tube and DMSO added	Immediate yellow precipitate	Stronger donor, probably breaks up bridges
Pyridine	Similar to above	Immediate yelllow precipitate	As above for DMSO
CH_3CN	Similar to above	Immediate yellow precipitate	As above for DMSO
$P(OCH_3)_3$	Similar to above	Yellow solution several signals in nmr	Initial displacement, followed by a possible break-up of the complex on addition of excess $P(OMe)_3$
EtOOCPh	Similar to above, and isolation of product on larger scale attempted	Displacement observed though not complete	The solid isolated after addition of excess EtOOCPh still had EtOAc present. After addition of 2 mol of EtOOCPh, 2 mol of EtOAc were displaced, leaving $MgCl_2 \cdot TiCl_4 \cdot 2EtOAc \cdot 2EtOOCPh$
EtOAc	$CDCl_3$ solution in nmr tube	Exchange observed	EtOAc exchange is fast on nmr time scale, only one set of ligand signals
EtOOCH	$CDCl_3$ solution in nmr tube	Displacement observed though not complete	This is similar to the reaction with EtOOCPh. When excess ligand is added to the solid 2 mol of EtOAc are displaced and when 2 mol of EtOOCH are added 2 mol of EtOAc are displaced leaving $MgCl_2 \cdot TiCl_4 \cdot 2EtOAc \cdot 2EtOOCH$

[a]$EtOAc = CH_3COOC_2H_5$, $EtOOCH = HCOOC_2H_5$, $EtOOCPh = C_6H_5COOC_2H_5$.

mol. If a fresh solid sample is pumped at elevated temperatures the composition varies from the starting material $MgCl_2 \cdot 2.75$ EtOAc as: 1 h, 50 °C, 0.84 mol EtOAc; 8 h, 80 °C, 0.56 mol EtOAc.

We have also carried out several t.g.a runs on various samples, and for example when a solid corresponding to $MgCl_2 \cdot 2.75$ EtOAc is heated at 10 °C/min under a stream of nitrogen (100 cm^3/min) a steady loss of ester is observed up to 250 °C when only $MgCl_2$ remains as indicated by the weight loss. The weight then remains constant up to 850 °C when decomposition of the magnesium chloride commences. We did not observe well-defined plateaus in any of the plots corresponding to a stable phase of solvated magnesium chloride, although in some samples a slight break was observed near 100 °C corresponding approximately to a phase $MgCl_2 \cdot 2EtOAc$.

Using a standard $MgCl_2$/EtOAc solution (usually 0.4–0.5 M) a series of complexes involving other metal halides may be prepared. Addition of a yellow solution of $TiCl_4$/EtOAc to the magnesium chloride solution using a molar ratio $TiCl_4:MgCl_2 = 1:1$, followed by heating to 60 °C for 4 hr, and removal of the solvent under vacuum yields the known yellow crystalline complex $MgCl_2 \cdot TiCl_4 \cdot 4EtOAc$, (I). Heating this solid at 80 °C under vacuum yields a pale yellow solid complex, $MgCl_2 \cdot TiCl_4 \cdot 2EtOAc$. Both

solids hydrolyse slowly in air, but are stable indefinitely under dry nitrogen.

The lability of the co-ordinated ethyl acetate in I may be demonstrated by a series of ligand displacement reactions. The ^1H n.m.r. spectrum of I consists of three signals (a triplet, quartet and singlet) arising from the ester ligand protons. The singlet from the acyl methyl group provides a useful indication of ligand binding in that it occurs at $\delta = 2.25$ ppm in I and at 2.05 ppm in free EtOAc. Larger shifts occur as expected in the ^{13}C nmr spectra, but we have used the ^1H nmr spectra for convenience. The addition of EtOAc to I results in a rapid exchange of free and bound ligand, and only one signal from the acyl group protons is observed with its position depending upon the proportions of I and added EtOAc. On the other hand the addition of successive additions of tetrahydrofuran (THF) to I up to a ratio of 4 mol THF: 1 mol I causes a progressive shift of the acyl singlet to 2.05 ppm, and the yellow solid complex $MgCl_2 \cdot TiCl_4 \cdot 4THF$ may be recovered after removal of EtOAc. This complex can also be prepared by mixing $MgCl_2$/$TiCl_4$ in THF solution.

Various other ligands also cause displacement of the EtOAc in I, as indicated from the ^1H nmr spectra, but the new complexes have not been isolated in every case. Trimethyl phosphite is similar to THF

in that initial displacement of the EtOAc occurs, and the phosphite becomes co-ordinated. However, addition of an excess of phosphite [over 4 mol per mol of **I**] causes another signal for the phosphite protons to appear, in addition to the original signal and that due to free phosphite. We tentatively assign this extra signal to be due to cleavage of the complex **I**, with the $P(OMe)_3$ being associated with the separate $MgCl_2$ and $TiCl_4$ fragments. Similar, but more rapid, degradations of the complex **I** apparently occur when pyridine, acetonitrile and dimethyl sulphoxide are added since yellow solids deposit from solution as soon as the new ligand is added.

However, the addition of ethyl formate or ethyl benzoate to **I** in chloroform results in the displacement of only 2 mol of EtOAc, and the new complexes $MgCl_2 \cdot TiCl_4 \cdot 2EtOAc \cdot 2L$ (L = $C_6H_5COOC_2H_5$ or $HCOOC_2H_5$) are obtained as yellow solids with properties similar to those of **I**. In the ^1H nmr spectra addition of the new ester causes the acyl singlet of EtOAc to shift to a position intermediate between 2.25 and 2.05 ppm. The results of the displacement reactions are summarised in Table I.

The studies described above have been extended, and a series of related complexes have been isolated. The complex with ethyl formate, $MgCl_2 \cdot TiCl_4 \cdot 4HCOOC_2H_5$, may be obtained by a similar method to that used for **I**, although magnesium chloride is less soluble in $HCOOC_2H_5$ than in EtOAc. While we have prepared the ethyl benzoate complex with $TiCl_4$ as $TiCl_4 \cdot C_6H_5COOC_2H_5$, we have not yet been able to obtain any complex, other than the mixed complex mentioned above, which contains $MgCl_2$. The lack of solubility of $MgCl_2$ in $C_6H_5COOC_2H_5$ is in part responsible for this difficulty, the relatively weak donor ability of ethyl benzoate obviously does not bring about a breakdown of the magnesium chloride lattice.

Initial attempts to replace the $TiCl_4$ in **I** by $TiCl_2(OPh)_2$ were unsuccessful, and no complex containing both titanium and magnesium was obtained. However, the $TiCl_4$ can be replaced by both $ZrCl_4$, and $SnCl_4$, to yield the corresponding compounds $MgCl_2 \cdot MCl_4 \cdot 4EtOAc$ (M = Zr or Sn). Both compounds are white solids which hydrolyse slowly in air, and while the tin compound forms well defined crystals, the zirconium analogue is usually obtained as an amorphous powder. As with **I**, the corresponding THF adducts $MgCl_2 \cdot MCl_4 \cdot 4THF$ (M = Zr or Sn) can be obtained quantitatively by ligand displacement reactions.

An interesting, well-defined, yellow crystalline complex, $(MgCl_2)_3 \cdot TiCl_4 \cdot (SnCl_4)_2 \cdot 12EtOAc$, **III**, is obtained when the metal halides are mixed in the approximate molar ratios required by the composition of **III**, using EtOAc as the solvent. We have confirmed that this is a discrete molecular complex, and not for example a mixture of 2 mol

of $MgCl_2 \cdot SnCl_4 \cdot 4EtOAc$ and 1 mol of **I** by obtaining single crystals of **III**, and carrying out preliminary X-ray measurements as described below.

All these complexes containing metals in addition to, or instead of, titanium undergo exchange reactions similar to those of **I**, although we have not yet studied their interaction with ethyl benzoate and ethyl formate. In each case THF causes displacement of the co-ordinated EtOAc, and the corresponding THF adducts are obtained. The reaction between the zirconium complex and trimethyl phosphite is more complex than with **I** as indicated from the ^1H nmr spectra; in addition to the signals from the $P(OMe)_3$ there are three sets of signals from EtOAc, and breakdown of the complex appears to be more facile in this case compared with that of **I**. The nmr spectra of the various compounds are given in Table II.

We have made some preliminary studies related to the structures of these derivatives, and it would appear that they are generally isomorphous with **I**. X-ray data on both the tin compound $MgCl_2 \cdot SnCl_4 \cdot 4EtOAc$, and **III**, show that the unit cell dimensions correspond closely with those of **I**. The similarity between the simple tin compound and **I** is not surprising, and even for **III**, which has an overall Mg:M:EtOAc (M = Ti or Sn) ratio of 1:1:4, some relationship might be expected. However, we have not yet determined for **III** whether this arises from random replacement of titanium by tin, or whether there are some other factors influencing the overall composition. From the analytical results carried out on several solids, obtained from reaction solutions containing varying proportions of $MgCl_2/TiCl_4/SnCl_4/EtOAc$, the product which deposits from solution always had the composition corresponding to **III**. The molar proportions have been varied over the ranges $MgCl_2:TiCl_4:SnCl_4$ as 3:1:2 [as required in **III**], 3:2:1, 2:1:1, and 4:1:1.5, but as yet we have been unable to obtain solids with a significantly different composition. We are currently investigating this point further.

The infrared spectra of the various adducts provide evidence for the coordination of the carbonyl group of the ester to the magnesium centre (Table II). Although the spectra often showed more than one absorption in the carbonyl region, the general trend was apparent, namely that the decrease in $\nu(C=O)$ on co-ordination of the ester is dependent upon the metal centre. In free EtOAc the $\nu(C=O)$ stretching mode appears at 1743 cm^{-1}, while in $(TiCl_4 \cdot EtOAc)_2$ it is at 1615 cm^{-1} and in $MgCl_2 \cdot 2.75\text{-}EtOAc$ it occurs near 1700 cm^{-1}; also the band contours are distinctively different in the two cases. There is little doubt therefore that magnesium is the preferred coordination centre for ethyl acetate, and probably for ethyl formate also, although more data is desirable in this case. The

TABLE II. Spectral Properties and Analytical Data of Some Metal Chloride Complexes.

Compound[a]	Infrared		¹H nmr	Analyses (%)[b]				
	νCO (cm⁻¹)	νM–Cl (cm⁻¹)		C	H	Mg	Ti	Sn
MgCl₂(EtOAc)	(1743s), (1720s) (1700s), 1618m	460w, 395w 350w, 290w	1.26t, 2.05s, 4.13q					
MgCl₂(EtOOCH)	1735w, (1680s) 1655w, (1620s)	470m, 365m 310m, 260m	1.30t, 4.25q 8.05s					
(TiCl₄·EtOAc)₂	(1615s), 1580sh	470m, 380s, 265w	1.42t, 2.55s, 4.50q					
TiCl₄·EtOOCH	1625s	400s, 280m	1.48t, 4.59q, 8.60s	13.45 (13.65)	5.20 (5.05)		17.91 (18.16)	
TiCl₄·EtOOCPh	1670s	460s, 350s 290s, 215m	1.50t, 4.72q, 7.50–8.22 aromatics	32.90 (32.73)	3.05 (3.03)		14.50 (15.52)	
MgCl₂·TiCl₄·4EtOAc	1715m, 1725m (1680s), 1615m	460m, 390m 345m, 290m	1.34t, 2.33s, 4.32q	30.10 (30.13)	5.20 (5.05)	3.71 (3.81)	7.52 (7.52)	
MgCl₂·TiCl₄·4EtOOCH	1733m, (1640s) 1620m	350w	1.36t, 4.38q, 8.33s	24.70 (24.78)	4.22 (4.20)	4.23 (4.18)	8.23 (8.24)	
MgCl₂·TiCl₄·4THF	—	360s, 345s, 315m	1.98bs, 3.75bs,	34.22 (33.50)	6.03 (5.59)	4.10 (4.24)	8.86 (8.92)	
MgCl₂·SnCl₄·4EtOAc	1720m, (1685m)	460w, 395w 315s, 285m	1.31t, 2.25s, 4.28q	26.84 (27.12)	4.56 (4.45)	3.48 (3.44)		16.4 (16.7)
MgCl₂·ZrCl₄·4EtOAc	1745s, 1725s (1685s),	460m, 395m 310s, 290s	1.33t, 2.75bs, 4.37bs	27.85 (28.20)	4.78 (4.74)	3.64 (3.57)		
(MgCl₂)₃·TiCl₄·(SnCl₄)₂·12EtOAc	1745m, 1720s (1685s),	460m, 395m, 365s, 350s, 290s	1.30t, 2.25s, 4.28q	27.90 (28.05)	4.76 (4.68)	2.34 (2.33)	3.44 (3.55)	11.1 (11.5)

[a]EtOAC = CH₃COOC₂H₅, EtOOCH = HCOOC₂H₅, EtOOCPh = C₆H₅COOC₂H₅. ν(C=O) for CH₃COOC₂H₅ = 1743 cm⁻¹. [b]Calculated values in parentheses.
b = broad. Major absorptions in carbonyl region are shown in brackets. For nmr data, s = singlet, t = triplet, q = quartet. s = strong, m = medium, w = weak, sh = shoulder.

metal–halogen modes are observed in the 450–250 cm^{-1} region as expected, and appear to be relatively insensitive to the other components present.

These results therefore demonstrate that simple molecular complexes do exist in mixtures which have been claimed to be active in polymerisation reactions. We are now attempting to define the limits on the range of compositions available in such metal halide mixtures, in order to understand better some of the reactions which might occur early on in the polymerisation process.

Experimental

All operations were carried out under dry nitrogen, in conventional Schlenk apparatus, or in a nitrogen-filled glove box. All solvents were dried and distilled prior to use. The esters were dried with P$_2$O$_5$ followed by K$_2$CO$_3$. Petroleum ether (b.p. 60–80 °C) was dried by refluxing for 24 h with Na wire. THF was distilled from Na/benzophenone. Pet. ether (b.p. 180 °C) (E.C. 180), an isomeric mixture of dodecanes, was supplied by Erdolchemie, and dried with Na wire. The metal chlorides, MgCl$_2$, TiCl$_4$, SnCl$_4$, ZrCl$_4$ were used as supplied. (TiCl$_4$·EtOAc)$_2$ was prepared as previously reported [18].

Spectroscopic Techniques

Infrared spectra were obtained as mulls in Nujol between CsI plates using a Perkin-Elmer 580B spectrometer. Hydrogen-1 nmr spectra (220 MHz) were obtained using a Perkin-Elmer R34 spectrometer, and carbon-13 nmr (22.6 MHz) spectra were obtained using a Bruker WH90 spectrometer. All nmr spectra were obtained from solutions in CDCl$_3$. Chemical shifts, δ, are quoted as being positive to the low field of the reference standard tetramethylsilane, SiMe$_4$, which was taken as 0 ppm.

Analysis

Carbon and hydrogen analyses were carried out commercially by Elemental Micro-Analysis Limited, Beaworthy, Devon. Titanium was determined spectrophotometrically using the absorbance at 410 nm of titanium(IV) peroxy species. Magnesium and tin were determined by atomic absorption using a Varian Techtron AA6 atomic absorption spectrophotometer. The t.g.a. runs were conducted using a conventional t.g.a. apparatus with the sample being heated under a blanket of dry nitrogen.

Syntheses of Compounds

MgCl$_2$/EtOAc solution

A standard solution of anhydrous MgCl$_2$ in EtOAc (0.40 M) was prepared by adding EtOAc (500 cm^3)

to solid anhydrous MgCl$_2$ (19.0 g) and refluxing for 12 hours. All the solid dissolved, but on standing for 14 days white needle-like crystals appeared. Attempts to isolate these crystals by pumping to dryness appeared to yield different products depending on the time of pumping.

MgCl$_2$/EtOOCH solution

A standard solution of anhydrous MgCl$_2$ in EtOOCH was prepared exactly as for EtOAc.

MgCl$_2$/EtOOCPh solution

Attempts to dissolve anhydrous MgCl$_2$ in refluxing EtOOCPh proved unsuccessful, even after an extended reaction time of several days.

Preparation of TiCl$_4$·HCOOC$_2$H$_5$

A solution of TiCl$_4$ (2 cm^3, 18.3 mmol) in petroleum ether (b.p. 60–80 °C) (50 cm^3) was prepared by mixing the liquids at 0 °C. The ligand (1.47 cm^3, 18.3 mmol) (ratio TiCl$_4$:HCOOC$_2$H$_5$ = 1:1) was added dropwise, with stirring, and a yellow precipitate formed immediately. The supernatant was removed by syringe, the solid washed with petroleum ether (b.p. 60–80 °C) (2 × 30 cm^3) and dried *in vacuo* for 2 hours to form a yellow powder. Yield: 4.7 g, 98%. The ethyl benzoate adduct TiCl$_4$·C$_6$H$_5$·COOC$_2$H$_5$ was prepared in a similar manner, and recrystallised from pet. ether (b.p. 180 °C), forming large yellow crystals. Yield: 4.5 g, 75%.

Preparation of MgCl$_2$·TiCl$_4$·4CH$_3$COOC$_2$H$_5$

A solution of TiCl$_4$ (2 cm^3, 18.3 mmol) in CH$_3$COOC$_2$H$_5$ was mixed with a solution of MgCl$_2$ in CH$_3$COOC$_2$H$_5$ (45.75 cm^3, 0.4 mol dm^{-3}, 18.3 mmol). The yellow solution was heated to 60 °C, and stirred for 4 hours. After cooling to room temperature the volume of the solution was reduced by pumping, and a yellow solid precipitated. The supernatant was removed, and the solid washed with petroleum ether (b.p. 60–80 °C) (2 × 30 cm^3), and dried *in vacuo* for 2 hours. The solid could be recrystallized from a minimum volume of CH$_3$COOC$_2$H$_5$, to form small yellow crystals. Yield: 10.5 g, 90%. The ^{13}C n.m.r. spectrum showed resonances at δ values of 178.2, 64.8, 22.7, 14.9.

The ethyl formate complex MgCl$_2$·TiCl$_4$·4HCOOC$_2$H$_5$, was prepared similarly, except that the solution had to be pumped to near dryness before the yellow powder precipitated. Yield: 10.4 g, 98%.

Preparation of MgCl$_2$·SnCl$_4$·4CH$_3$COOC$_2$H$_5$

The preparation was identical to that described above, except that crystals formed immediately on mixing of the reactants, but redissolved when the solution was heated to 70 °C. White crystals then

formed as the volume of the solution was reduced. Yield: 11.5 g, 95%.

The zirconium compound, $MgCl_2 \cdot ZrCl_4 \cdot 4CH_3COOC_2H_5$, was also prepared by this method and, after recrystallisation from a minimum volume of $CH_3COOC_2H_5$, was obtained as white crystals.

Preparation of $MgCl_2 \cdot TiCl_4 \cdot 2CH_3COOC_2H_5$

$MgCl_2 \cdot TiCl_4 \cdot 4CH_3COOC_2H_5$ (5.0 g, 7.85 mmol) was heated to 80 °C *in vacuo* for 8 h, when a paler yellow solid resulted. Weight loss (1.40 g, 28%) of $CH_3COOC_2H_5$ indicated that two molecules of ligand are lost from the original compound.

Preparation of $MgCl_2 \cdot TiCl_4 \cdot 4THF$

A solution of $TiCl_4$ (2.0 cm^3, 18.3 mmol) in THF (50 cm^3) was mixed with a solution of $MgCl_2$ in THF (36.6 cm^3, 0.50 mol dm^{-3}, 18.3 mmol) (ratio $TiCl_4$:$MgCl_2$ = 1:1). The resulting yellow solution was heated to 55 °C for 1 hour. The solution was pumped on for 6 hours, when a 'sticky' yellow solid resulted. This was heated to 60 °C *in vacuo* for 4 hours, and a dry yellow powder was produced. Yield: 4.5 g, 98%.

Preparation of $(MgCl_2)_3 \cdot TiCl_4 \cdot (SnCl_4)_2 \cdot 12CH_3COOC_2H_5$

A solution of $TiCl_4$ (2.0 cm^3, 18.3 mmol) in $CH_3COOC_2H_5$ was mixed with a solution of $SnCl_4$ (2.1 cm^3, 18.3 mmol) in $CH_3COOC_2H_5$ and then a solution of $MgCl_2$ in $CH_3COOC_2H_5$ (91.5 cm^3, 0.40 mol dm^{-3}, 36.6 mmol) was added to the mixture [ratio MCl_4:$MgCl_2$ = 1:1 (M = Ti, Sn)]. The resulting yellow solution was heated to 60 °C, and stirred for 4 hours. After cooling and standing at room temperature for 16 hours yellow crystals appeared. The supernatant was removed and the crystals were washed with petroleum ether (b.p. 60–80 °C) (2 × 50 cm^3) and dried *in vacuo* for 4 hours. Yield: 15.6 g, 43%.

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