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Preparation of some carboxylate and alkoxide derivatives of the heterobimetallic species of titanium and magnesium, [TiMgCl$_6$·4EtOAc]

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Abstract

Reaction of the complex [TiMgCl$_6$·4EtOAc] with two moles of acid, RCO$_2$H (R = C$_6$H$_5$, C$_6$H$_5$CHCH, *p*-(CH$_3$)$_3$CC$_6$H$_4$, (CH$_3$)$_2$CCH) leads to the heterobimetallic carboxylates [TiMgCl$_4$(RCO$_2$)$_2$·2EtOAc] while with pivalic acid the derivative [TiMgCl$_4${(CH$_3$)$_3$CCO$_2$}$_2$·1.25EtOAc] is obtained. In corresponding reactions with phenol the complexes [TiMgCl$_5$(OC$_6$H$_5$)·1.25EtOAc] and [TiMg$_2$Cl$_6$(OC$_6$H$_5$)$_2$·2EtOAc] have also been isolated.

Introduction

The role of the early transition metals in the Ziegler–Natta polymerisation of α-alkenes has been the subject of extensive research [1, 2]. Typically the catalyst used consists of a titanium halide, TiCl$_3$ or TiCl$_4$, supported on magnesium chloride with the addition of a Lewis base such as ethyl benzoate [3, 4].

There have been many reports on the interaction of the individual catalyst components with esters, e.g. TiCl$_4$ forms complexes of type [TiCl$_4$·L]$_2$ (L = EtOAc [5–7], HCO$_2$Et [8, 9], *p*-ethyl anisate [10]) and TiCl$_4$·2L (L = EtOAc [11, 12], HCO$_2$Et [9]). The reaction of TiCl$_4$ with various diesters has been investigated more recently, and the structures of [TiCl$_4$·*o*-(CO$_2$Et)$_2$C$_6$H$_4$] [13], [Ti$_2${μ-*m*-(CO$_2$Et)$_2$C$_6$H$_4$}Cl$_8$] [14], [TiCl$_4$·*o*-(CO$_2$CH$_2$CH$_2$Ph)$_2$C$_6$H$_4$] [15], [TiCl$_4$·C$_2$O$_4$(CH$_2$CH$_2$Ph)$_2$] [15], [TiCl$_4$·*o*-(CO$_2$Bu^i)$_2$C$_6$H$_4$]·CH$_2$Cl$_2$ [16], [TiCl$_4$·*p*-(CO$_2$Me)$_2$C$_6$H$_4$] [16] and [Ti$_2$Cl$_6$·{*o*-(CO$_2$Et)$_2$C$_6$H$_4$}$_2$] [17], have been reported. A crystallographic study of the magnesium–ester complex [MgCl$_2$(CH$_3$CO$_2$C$_2$H$_5$)$_2$·0.5(CH$_3$CO$_2$C$_2$H$_5$)] evinced a chloro bridged polymeric structure [18].

Several molecular species are known in which the titanium and magnesium centres are halogen bridged as found for example in the structure of [TiMgCl$_6$·4EtOAc] (I) [19], Fig. 1. The ligand displacement reactions of I have been studied by Gordon and Wallbridge [20] and the complex [TiMgCl$_5$OH·4EtOAc] has also been prepared and structurally characterised [21]. The latter species is unusual in that both OH and Cl ligands coexist on the same titanium centre. Reaction between MgCl$_2$ and TiCl$_4$ in ethyl chloroacetate solution produced the μ-carboxylate species [TiMgCl$_5$(O$_2$CCH$_2$Cl)(ClCH$_2$CO$_2$C$_2$H$_5$)$_3$] [22] and other reported compounds include [TiMgCl$_5$(O$_2$CH)·2EtOAc] [23], [TiMgCl$_5$(O$_2$CC$_6$H$_5$)·2EtOAc] [23], and the bimetallic alkoxide [Ti$_2$(OEt)$_8$Cl]$_2$Mg$_2$(μ-Cl)$_2$ [24].

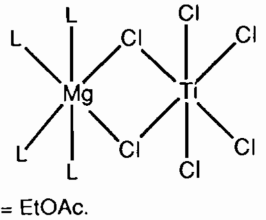

Fig. 1. The structure of [TiMgCl$_6$·4EtOAc].

We now report the preparation and characterisation of several new Ti/Mg complexes containing carboxylate or phenoxy groups.

Experimental

All manipulations were carried out under an inert atmosphere of nitrogen using Schlenk apparatus or a glove box. All solvents were dried before use by distillation from CaH$_2$. The metal chlorides and organic acids were used as supplied.

Spectroscopic techniques

IR spectra were run as Nujol mulls between CsI plates on a Perkin-Elmer 580B spectrometer. ^{1}H NMR spectra (220 MHz) were recorded on a Perkin-Elmer

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R34 spectrometer. All NMR spectra were obtained in $CDCl_3$ solution using $SiMe_4$ as the internal standard.

Analysis

Carbon, hydrogen and magnesium analyses were carried out by Butterworth Laboratories Ltd., Teddington. Titanium was determined spectrophotometrically using the absorbance of the titanium(IV) peroxy species at 410 nm. Chlorine was determined by the Volhard method.

Preparation of [TiMgCl$_6$·4EtOAc]

This was prepared by the literature method [19, 20].

Preparation of [TiMgCl$_4$(C$_6$H$_5$CO$_2$)$_2$·2EtOAc]

[$TiMgCl_6$·4EtOAc] (2.04 g, 3.2 mmol) was dissolved in CH_2Cl_2 (30 cm^3) and benzoic acid (0.8 g, 6.5 mmol) added against a stream of nitrogen. The yellow solution was then warmed to 35 °C for 1.5 h. On cooling to room temperature the solvent was removed at the pump. A yellow 'foam' was produced which was broken down to a solid and stirred with hexane (60 cm^3) before being filtered off and dried *in vacuo* for 2 h. Yield = 1.05 g, 51% based on Ti content. *Anal.* Calc. for $C_{22}H_{26}O_8Cl_4MgTi$: C, 41.76; H, 4.11; Cl, 22.52; Mg, 3.85; Ti, 7.61. Found: C, 41.65; H, 4.39; Cl, 22.41; Mg, 3.55; Ti, 8.31%.

Preparation of [TiMgCl$_4$(RCO$_2$)$_2$·2EtOAc] (R = C$_6$H$_5$CHCH, (CH$_3$)$_3$CC$_6$H$_4$, (CH$_3$)$_2$CCH)

The method used was as given above. Yellow powders were produced in 48, 58 and 98% yields for C_6H_5CHCH, $(CH_3)_3CC_6H_4$ and $(CH_3)_2CCH$, respectively. The compounds were identified from both analytical and NMR data. The derivative with 3,3-dimethylacrylic acid is less well characterised from analytical data, although the NMR data are fully consistent with the formulation given. Analytical data for the three compounds in the order given above are as follows. *Anal.* Calc. for $C_{26}H_{30}O_8Cl_4MgTi$: C, 45.58; H, 3.88; Cl, 24.41; Mg, 3.55; Ti, 7.01. Found: C, 45.81; H, 4.66; Cl, 24.91; Mg, 3.54; Ti, 7.95%. Calc. for $C_{30}H_{42}O_8Cl_4MgTi$: C, 48.39; H, 5.64; Mg, 3.27. Found: C, 47.36; H, 5.66; Mg, 3.54%. Calc. for $C_{18}H_{30}O_8Cl_4MgTi$: Cl, 20.75; Ti, 8.13. Found: Cl, 20.67; Ti, 8.91%.

Preparation of [TiMgCl$_4${(CH$_3$)$_3$CCO$_2$}$_2$·1.25EtOAc]

Pivalic acid (0.86 g, 8.39 mmol) was added to a stirred suspension of [$TiMgCl_6$·4EtOAc] (1.66 g, 4.20 mmol) in CCl_4 (50 cm^3). The mixture was left to stir for 2 h before heating to 70 °C for 1 h. A pale yellow solution was obtained. After cooling to room temperature the solvent was removed at the pump until a cream yellow precipitate formed. This was filtered off, washed with hexane (2×20 cm^3) and dried *in vacuo* for 2 h. Yield = 1.04 g, 47%. *Anal.* Calc. for $C_{15}H_{28}O_{6.5}Cl_4MgTi$: C, 34.22; H, 5.36; Cl, 26.90; Mg, 4.62; Ti, 9.09. Found: C, 34.54; H, 5.51; Cl, 25.30; Mg, 4.86; Ti, 9.77%.

Preparation of [TiMg$_2$Cl$_6$(OC$_6$H$_5$)$_2$·2EtOAc]

[$TiMgCl_6$·4EtOAc] (3.05 g, 4.8 mmol) was stirred in hexane (50 cm^3) and phenol (0.9 g, 9.5 mmol) was added under nitrogen with cooling. An orange precipitate was produced which slowly turned to a purple paste on warming to room temperature. The mixture was stirred at room temperature for 30 min and the solvent then removed at the pump. The solid left was broken up and dissolved in a dichloromethane/hexane mixture. The solvent was then slowly removed until precipitation occurred. The precipitate was filtered off, washed with hexane (3×20 cm^3) and dried *in vacuo* for 2 h. A purple solid was produced, yield = 0.34 g, 21%. *Anal.* Calc. for $C_{20}H_{26}O_6Cl_6Mg_2Ti$: C, 35.75; H, 3.90; Mg, 7.24. Found: C, 34.69, H, 4.16; Mg, 7.20%.

Preparation of [TiMgCl$_5$(OC$_6$H$_5$)·1.25EtOAc]

[$TiMgCl_6$·4EtOAc] (3.96 g, 6.21 mmol) was stirred in CCl_4 (40 cm^3) and phenol (0.59 g, 6.62 mmol) added under nitrogen with cooling to 0 °C. The mixture was allowed to warm to room temperature and stirred for 1 h. The solvent was then removed at the pump and the purple solid produced was dissolved in a dichloromethane/hexane mixture and reprecipitated by pumping. The solid was then washed with hexane (3×20 cm^3) and dried *in vacuo* for 2 h. A maroon red solid was produced, yield = 1.28 g, 46%. *Anal.* Calc. for $C_{11}H_{15}O_{3.5}Cl_5MgTi$: C, 29.50; H, 4.01; Mg, 5.40. Found: C, 29.18; H, 3.34; Mg, 5.50%.

Results and discussion

Reaction of [$TiMgCl_6$·4EtOAc] with a variety of alkyl and aryl carboxylic acids in a suitable solvent such as dichloromethane leads to the evolution of HCl gas and the formation of the carboxylate species [$TiMgCl_4(RCO_2)_2$·2EtOAc] (R = C_6H_5, C_6H_5CHCH, $(CH_3)_3CC_6H_4$, $(CH_3)_2CCH$) as yellow–orange solids in moderate to good yields.

$$[TiMgCl_6\cdot 4EtOAc] + 2RCO_2H \longrightarrow$$

$$[TiMgCl_4(RCO_2)_2\cdot 2EtOAc] + 2HCl\uparrow + 2EtOAc \quad (1)$$

IR and ^{1}H NMR data are presented in Tables 1 and 2, respectively. The band in the 1700–1680 cm^{-1} region is characteristic of ν(C=O) of the coordinated ethyl acetate ligand, and although two bands would be expected in this region from the coordinated ester we have been unable to resolve the rather broad band

TABLE 1. IR data of the complexes (cm^{-1})

Compound[a]	ν(C=O) (EtOAc)	$\nu(CO_2^-)$asym.	$\nu(CO_2^-)$sym.	Δ[b]	ν(m–Cl)
$[TiMgCl_4(C_6H_5CO_2)_2 \cdot 2EtOAc]$	1690(s)	1530(m)	1410(sh)	120	485(s) 375(s), 360(s)
$[TiMgCl_4(C_6H_5CHCHCO_2)_2 \cdot 2EtOAc]$	1695(s)	1520(sh)			340(s), 380(s) 440(s), 460(s)
$[TiMgCl_4((CH_3)_3CC_6H_4CO_2)_2 \cdot 2EtOAc]$	1695(s)	1530(m)	1415(sh)	115	400(s)
$[TiMgCl_4((CH_3)_2CCHCO_2)_2 \cdot 2EtOAc]$	1690(s)	1520(s)	1410(sh)	110	350(sh), 380(m) 470(m)
$[TiMgCl_4((CH_3)_3CCO_2)_2 \cdot 1.25EtOAc]$	1700(s)	1558(m)	1405(m)	153	470(m) 395(s), 330(w)
$[TiMgCl_5(OC_6H_5) \cdot 1.25EtOAc]$	1685(s)				400(m), 370(s) 300(m), 260(m)
$[TiMg_2Cl_6(OC_6H_5)_2 \cdot 2EtOAc]$	1680(s)				390(s), 370(s) 330(s), 260(m)

[a] EtOAc = $CH_3COOC_2H_5$, s = strong, m = medium, w = weak, sh = shoulder. [b] $\Delta = \nu(CO_2$ asym.) $- \nu(CO_2$ sym.).

TABLE 2. ^1H NMR data for complexes ($CDCl_3$, $SiMe_4$)

Compound	δ (ppm)[b]	Relative intensity
$[TiMgCl_4(C_6H_5CO_2)_2 \cdot 2EtOAc]$	8.20–7.50(m), 4.30(q), 2.25(s), 1.30(t)	5:2:3:3
$[TiMgCl_4(C_6H_5CHCHCO_2)_2 \cdot 2EtOAc]$[a]	7.90–7.40(m), 4.45(q), 2.30(s), 1.40(t)	5:2:3:3
$[TiMgCl_4((CH_3)_3CC_6H_4CO_2)_2 \cdot 2EtOAc]$	8.40–7.40(m), 4.30(q), 2.20(s), 1.30(m)	4:2:3:12
$[TiMgCl_4((CH_3)_2CCHCO_2)_2 \cdot 2EtOAc]$	5.90(m), 4.35(q), 2.34(m), 2.05(s), 1.35(t)	1:2:6:3:3
$[TiMgCl_4((CH_3)_3CCO_2)_2 \cdot 1.25EtOAc]$	4.30(q), 2.25(s), 1.35(m)	2:3:17 (to nearest integer)
$[TiMg_2Cl_6(OC_6H_5)_2 \cdot 2EtOAc]$	7.6–7.2(m), 4.50(q), 2.40(s), 1.50(t)	5:2:3:3
$[TiMgCl_5(OC_6H_5) \cdot 1.25EtOAc]$	7.10–7.60(m), 4.35(q), 2.33(s), 1.30(t)	5:2.5:3.75:3.75

[a] A very weak signal due to the CH proton being assigned at 6.5 ppm. This appeared to be unusually broad. [b] m = multiplet, q = quartet, t = triplet, s = singlet.

observed in this study. The position of the band also indicates that the EtOAc is bound to the magnesium and not the titanium centre in these compounds, since for bonding to the latter element a ν(C=O) would be expected to be visible at ~1600 cm^{-1} yet no such band is present. The observed values of Δ ($\Delta = \nu(CO_2$ asym.) $- \nu(CO_2$ sym.)) (Table 1) between 100 and 120 cm^{-1} are consistent with the presence of bidentate chelating and/or bridging carboxylate groups between the Ti and Mg atoms. In addition the proton NMR data shows the presence of EtOAc: carboxylate residues in a 1:1 ratio. The precise nature of the structures of these compounds remains uncertain due to the lack of suitable single crystals for an X-ray diffraction investigation. Nevertheless some comments consistent with the cited spectroscopic data can be made. The single binuclear structure shown in Fig. 2(a) is plausible but rather unlikely since it contains a bridge system consisting of two carboxylate groups and two chlorine atoms. Previous studies have found that in the species $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ (R = CH_3CHCH, p-ClC_6H_4) [25] and $[TiMgCl_5(O_2CCH_2Cl)(CH_2ClCO_2C_2H_5)_3]$ [22] the presence of a single bridging carboxylate considerably distorts the $M(\mu\text{-}Cl)_2M'$ (M,M′ = Ti,Ti or Ti,Mg) unit making it very difficult for a further bridging carboxylate ligand to be accommodated. Therefore, despite being in accord with the spectroscopic data we are at present sceptical of the structure shown in Fig. 2(a). An alternative structure which avoids this problem by postulating the presence of a chelating carboxylate group is shown in Fig. 2(b). However, since two sets of carboxylate stretching modes (bridging and chelating) would now be expected to be observed instead of the single set found at around 1530 and 1410 cm^{-1}, this type of structure also seems unlikely. This conclusion is further reinforced by the fact that we have also found, from results on compounds of the type $[TiCl_2(O_2CRCO_2)]$ (e.g. R = 1,4-cyclohexane) which contain a bidentate chelating carboxylate group, that in these cases the $\nu(CO_2^-)$ asym. stretch of the chelating group occurs near 1650 cm^{-1}, yet no such band is observed in the present cases. We suggest therefore that the compounds are structurally more complex than the simple monomeric formulations shown in Fig. 2, and more precise structural data are clearly desirable. When the reaction between pivalic acid and $[TiMgCl_6 \cdot 4EtOAc]$ was carried out under similar conditions to those given above, a cream solid $[TiMgCl_4((CH_3)_3CCO_2)_2 \cdot 1.25EtOAc]$ was isolated.

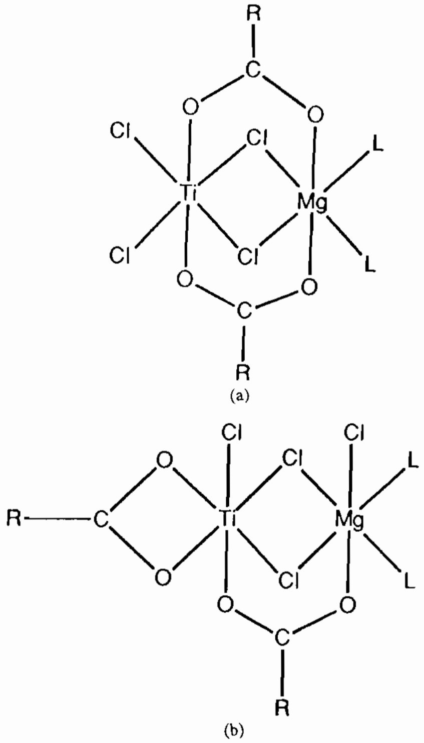

Fig. 2. Postulated structures of $[TiMgCl_4(RCO_2)_2 \cdot 2EtOAc]$ type species.

$$4[TiMgCl_6 \cdot 4EtOAc] + 8(CH_3)_3CCO_2H \longrightarrow 4[TiMgCl_4((CH_3)_3CCO_2)_2 \cdot 1.25EtOAc] + 8HCl\uparrow + 11EtOAc \quad (2)$$

As before the ethyl acetate is bound to the magnesium atom with $\nu(C{=}O)$ appearing as a strong band at 1700 cm^{-1}. A Δ value of 153 cm^{-1} is observed, consistent with the presence of bridging and/or bidentate chelating carboxylate groups. Both the proton NMR and elemental analysis indicate the ratio of carboxylate to ethyl acetate ligand is 2:1.25. Addition of phenol to $[TiMgCl_6 \cdot 4EtOAc]$ in a 2:1 molar ratio in hexane produced a maroon–red solid that analysed as $[TiMg_2Cl_6(C_6H_5O)_2 \cdot 2EtOAc]$. A strong band at 1680 cm^{-1} in the IR spectrum of this compound is assigned to $\nu(C{=}O)$ of the ethyl acetate ligand indicating that, as in the carboxylate species previously discussed, the ester is bound to the magnesium atom. A band at 980 cm^{-1} is assigned to $\nu(CO)$ of the phenoxide ligand. The ^1H NMR corroborates the postulated phenoxide:ethyl acetate ratio as 1:1. A possible reaction is therefore

$$2[TiMgCl_6 \cdot 4EtOAc] + 4C_6H_5OH \longrightarrow [TiMg_2Cl_6(OC_6H_5)_2 \cdot 2EtOAc] + 4HCl\uparrow + 6EtOAc + [Cl_2Ti(OC_6H_5)_2] \quad (3)$$

The bisphenoxide was not isolated and, in the presence of ethyl acetate, an adduct(s) might be expected to form. Reaction between phenol and $[TiMgCl_6 \cdot 4EtOAc]$ in a 1:1 molar ratio using a similar method to that used to prepare $[TiMg_2Cl_6(OC_6H_5)_2 \cdot 2EtOAc]$ led to the isolation of a reddish purple solid formulated as $[TiMgCl_5(OC_6H_5) \cdot 1.25EtOAc]$.

$$4[TiMgCl_6 \cdot 4EtOAc] + 4C_6H_5OH \longrightarrow 4[TiMgCl_6(OC_6H_5) \cdot 1.25EtOAc] + 4HCl\uparrow + 11EtOAc \quad (4)$$

The IR spectrum again indicates that the ester is bound to the magnesium atom with no evidence being seen for the presence of any uncoordinated ethyl acetate. Clearly then the bimetallic species $[TiMgCl_6 \cdot 4EtOAc]$ is a useful precursor to novel metal carboxylates or alkoxides and work is currently in progress both to define structurally these species more closely and to extend the range of materials prepared.

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