REACTION BETWEEN THE [MgCL]²⁻ ANION AND TITANIUM CHLORIDES. THE CRYSTAL STRUCTURE OF [NBu_][trans-TiCL_(THF)2] • THF*

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Abstract—The reaction between $[TiCl_4(THF)_2]$ and $[NBu_4]_2[MgCl_4]$ in tetrahydrofuran (THF) gave the compound $[NBu_4]_2[TiCl_6]$ (I). Under the influence of light in THF solution, the compound undergoes reduction to $[NBu_4][trans-TiCl_4(THF)_2]$ •THF (II). Compound II was also obtained by the direct reaction between $[TiCl_3(THF)_3]$ and $[MgCl_4]^{2-}$ ions. Crystals of II are orthorhombic, space group $P2_12_12_1$ with a = 12.18(1), b = 17.09(1) and c = 18.57(2) Å; Z = 4. The structure was refined by full-matrix least-squares methods to R = 0.064 for 1569 independent non-zero reflections.

Reactions between MgCl₂ and TiCl₄ in THF, depending on molar ratio, produce the following compounds:^{1,2} [Mg(THF)₆][TiCl₅(THF)]₂, [(THF)₄ Mg(μ -Cl)₂TiCl₄] and [Mg₂(μ -Cl)₃(THF)₆][TiCl₅ (THF)]. These compounds are used in the ethylene polymerization process.³ However, MgCl₂ and TiCl₃ in THF do not react mutually, because, in the simplest sense, the acid–base properties of MgCl₂ and TiCl₃ are similar. Instead, MgCl₂ on reaction with [NBu₄][BF₄] yields [MgCl₄]²⁻ and [MgCl(THF)₅]⁺ ions:^{4,5}

 $3[MgCl_{2}(THF)_{2}] + 2[NBu_{4}][BF_{4}] \xrightarrow{THF} [NBu_{4}]_{2}[MgCl_{4}] \cdot 2THF + 2[MgCl(THF)_{5}][BF_{4}]. \quad (1)$

The reactivity of the $[MgCl_4]^{2-}$ anion was unknown until now. It was expected that $[MgCl_4]^{2-}$ and TiCl₄ or TiCl₃ would react mutually to produce new products which should bear useful relations between the structure and mechanism involved in some Ziegler– Natta polymerization systems.

EXPERIMENTAL

All reactions were carried out under N_2 using dried solvents and Schlenk-tube techniques. [TiCl₄

 $(THF)_2]_{1}[TiCl_{3}(THF)_{3}]$ and $[NBu_{4}]_{2}[MgCl_{4}] \cdot 2THF$ were obtained by literature methods.^{4,6} The crystalline $[NBu_{4}]_{2}[MgCl_{4}] \cdot 2THF$ under vacuum, liberates two THF molecules from the crystal lattice and yields $[NBu_{4}]_{2}[MgCl_{4}]$. Microanalyses were performed at the University of Wrocław. ESR spectra were obtained on a Varian E9 spectrometer and solid-state magnetic moments were determined by the Gouy method. IR spectra were obtained using a Perkin–Elmer 180 spectrometer.

Bis(tetra - n - butylammonium)hexachlorotitanate(IV) (I)

[TiCl₄(THF)₂] (1.5 g, 4.5 mmol) and [NBu₄]₂ [MgCl₄] (1.8 g, 2.76 mmol) were dissolved separately in 30 and 40 cm³ of THF, respectively. The solutions were mixed and the stirring was continued until the compounds dissolved. The solution was filtered off and the volume was reduced *in* vacuo to ca 20 cm³. After 24 h, the yellow compound was filtered off, washed with *n*-pentane (3×10 cm³) and dried *in vacuo*. Yield ca 1.9 g; 57%. Found: N, 3.7; Cl, 31.1; Ti, 6.6. C₃₂H₇₂N₂Cl₆Ti requires N, 3.8; Cl, 28.5; Ti, 6.4%. Density 1.28 g cm⁻³.

Tetra-n-butylammonium tetrachlorobis(tetrahydrofuran)titanate(III) tetrahydrofuran (II)

(a) $[NBu_4]_2[TiCl_6]$ (1.5 g, 2 mmol) was dissolved in 50 cm³ of THF and during slow diffusion of *n*pentane, yellow crystals appeared. The yellow crys-

^{*} Tetra-*n*-butylammonium tetrachlorobis(tetrahydrofuran)titanate(III) tetrahydrofuran.

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tals, in the same solution, under the influence of light (near a window), very slowly (1 month) changed colour to blue and simultaneously a white $[NBu_4][Cl]$ salt precipitated. The compound was separated mechanically. The blue crystals were identified by X-ray crystallography as the ionic salt $[NBu_4][trans-TiCl_4(THF)_2]$. THF. The formation of $[NBu_4][Cl]$ was proved by elementary analysis.

(b) $[\text{TiCl}_3(\text{THF})_3]$ (3.2 g, 8.7 mmol) and $[\text{NBu}_4]_2[\text{MgCl}_4]$ (3.4 g, 5.2 mmol) were suspended in 75 and 65 cm³ of THF, respectively, and stirred until the solution became light-blue. The solution was filtered off and its volume was reduced to 25 cm³ and this was left in a refrigerator until crystallization occurred. After 12 h, the crystals were filtered off, washed with THF (2 × 5 cm³) and dried *in vacuo*. Yield 3.1 g; 55%. Found: N, 2.3; Cl, 23.5; Ti, 6.7. Calc. for C₂₈H₆₀Cl₄NO₃Ti: N, 2.2; Cl, 21.9; Ti, 7.4%.

The good quality, multi-faced crystals for X-ray examination were taken directly from the postreaction mixture obtained by method (a). The same crystals may be obtained by slow diffusion of *n*-pentane into the compound obtained by method (b) dissolved in THF. The density was measured by flotation in a mixture of *n*-C₄H₉Cl and 1,1-dichloroethane. Crystal data. [N(C₄H₉)₄]⁺ [(C₄H₈O)₂Cl₄Ti]⁻·C₄H₈O; M = 648.5, orthorhombic, a = 12.18(1), b = 17.09(1), c = 18.57(2)Å; U = 3865(6) Å³, Z = 4, $D_c = 1.114(2)$ g cm⁻³, $D_m = 1.084$ g cm⁻³, space group $P2_12_12_1$, Mo-K_a radiation $\lambda = 0.71069$ Å, $\mu = 5.3$ cm⁻¹.

A specimen, $0.8 \times 0.7 \times 0.6$ mm, was cut from a large crystal and sealed in a capillary. A Syntex $P2_1$ diffractometer, $Mo-K_{\alpha}$ radiation and a graphite monochromator were used for lattice parameters and intensity measurements at T = 300(2) K. Intensities were measured by the $2\theta - \omega$ scan technique up to $2\theta = 48^{\circ}$. From 3425 measured reflections, 1569 with $I > 3\sigma(I)$ were used for structure determination. The structure was solved by the heavyatom method and refined using SHELX-76.7 The thermal parameters of the atoms in the non-bonded THF molecules and some of the carbon atoms in the $[NBu_4]^+$ cations were very high and some of the interatomic distances were rather unrealistic. For that reason, calculations were continued with constraints for non-bonded THF molecules and methyl carbon atoms of the [NBu₄]⁺ cations. All methylene hydrogen atoms were introduced in calculated positions with d(C-H) = 1.08 Å and were not refined. The refinement was completed by using anisotropic thermal parameters for all non-hydrogen atoms and gave final R = 0.064 and $R_w = 0.058$ (the refinement of the parameters for the inverted structure gave R = 0.065 and $R_w = 0.059$). Residual electron

density in the final difference Fourier map was within -0.25 and 0.25 e Å⁻³. Attempts to measure data at liquid nitrogen temperature failed because the crystal probably undergoes a phase transition.

Atomic coordinates, displacement factor coefficients and a list of F_o/F_c values have been deposited as supplementary data with the Editor, from whom copies are available on request. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

The addition of the $[NBu_4]_2[MgCl_4]$ salt to $[TiCl_4(THF)_2]$ (1:1 molar ratio) in THF, gave a yellow precipitate of $[NBu_4]_2[TiCl_6]$ (I):

$$[TiCl_{4}(THF)_{2}] + [NBu_{4}]_{2}[MgCl_{4}] \longrightarrow$$

$$[NBu_{4}]_{2}[TiCl_{6}] + [MgCl_{2}(THF)_{2}]. \quad (2)$$
(I)

The IR spectrum of compound I presents the v(Ti-Cl) stretching mode at 385 cm⁻¹, which is typical for $[\text{TiCl}_6]^{2-}$ anions e.g. in M₂TiCl₆ (M = K, Rb or Cs).⁸

The yellow crystals in THF solution in light under N_2 , slowly (1 month) changed their colour from yellow to blue, and simultaneously a white $[NBu_4]$ [Cl] salt precipitated :



Fig. 1. The overall view of the $[trans-TiCl_4(THF)_2]^$ anion.

Reaction of $[MgCl_4]^{2-}$ and titanium chlorides

Bond lengths				
TiCl(1)	2.387(5)	TiCl(2)	2.408(4)	
Ti-Cl(3)	2.392(5)	Ti-Cl(4)	2.392(4)	
Ti—O(1)	2.083(10)	Ti—O(2)	ſi—O(2) 2.115(10)	
Interbond angles				
Cl(1)— Ti — $Cl(2)$	91.2(2)	Cl(1)— Ti — $Cl(3)$	178.8(2)	
Cl(1)— Ti — $Cl(4)$	91.7(2)	Cl(2)— Ti — $Cl(3)$	89.8(2)	
Cl(2)— Ti — $Cl(4)$	177.1(2)	Cl(3)—Ti—Cl(4)	87.3(2)	
Cl(1)— Ti — $O(1)$	89.5(3)	Cl(1)—Ti—O(2)	90.0(3)	
Cl(2) - Ti - O(1)	90.8(3)	Cl(2)—Ti—O(2)	88.8(3)	
Cl(3)-Ti-O(1)	91.2(3)	Cl(3)— Ti — $O(2)$	89.3(3)	
Cl(4)— Ti — $O(1)$	89.0(3)	Cl(4)—Ti—O(2)	91.5(3)	
O(1)—Ti—O(2)	179.3(4)			

Table 1.	Principal bond	lengths (A) an	d angles (°) ir	n the [trans-TiC	l₄(THF)2j [−]
		an	ion		

 $[NBu_4]_2[TiCl_6] \xrightarrow{hv}_{THF}$

[NBu₄][*trans*-TiCl₄(THF)₂] • THF (II)

+[NBu₄][Cl]+1/2HCl+C₄H₇OCl. (3)

Blue $[NBu_4][trans-TiCl_4(THF)_2] \cdot THF$ (II) is also formed in the direct reaction between $[TiCl_3(THF)_3]$ and $[MgCl_4]^{2-}$ ions:

 $2[TiCl_3(THF)_3] + [NBu_4]_2[MgCl_4] \longrightarrow$

 $+[MgCl_2(THF)_2].$ (4)

Compound II is paramagnetic, with $\mu_{eff} = 1.6$ at room temperature. The ESR spectra in the solid state and in CH₂Cl₂ are broad and typical for Ti³⁺. In [NBu₄][*trans*-TiCl₄(THF)₂] • THF, the titanium atom exists as Ti³⁺, and the reduction of Ti⁴⁺ (in I) to Ti³⁺ (in II) is caused by the influence of light in THF. The post-reaction mixture revealed (MS– GL) the presence of HCl and C₄H₇OCl. The mechanism of these reactions has not yet been explained.

The geometry of the $[trans-TiCl_4(THF)_2]^-$ anion is presented in Fig. 1. Selected bond lengths and angles are summarized in Table 1. The titanium atom is six-coordinate with four square-planar chlorine atoms and two *trans*-THF molecules.



Fig. 2. The packing of the [NBu₄][*trans*-TiCl₄(THF)₂] • THF crystal. The hydrogen atoms are omitted for clarity.

The TiCl₄O₂ unit forms a distorted octahedron. The average Ti—Cl and Ti—O bond lengths are equal, 2.395(9) and 2.10(1) Å, and are similar to 2.352(3) and 2.118(7) Å in [TiCl₃(THF)₃].¹⁰ The structure of [*trans*-TiCl₄(THF)₂]⁻ is similar to that of the [*trans*-MoCl₄(THF)₂]⁻ anion.¹¹ The parameters presented for the coordinated THF are close to those in [TiCl₃(THF)₃] and the [*trans*-TiCl₂(THF)₄]⁺ cation.⁹ The [NBu₄]⁺ cation has the *cis*-carbon-chain configuration and differs from the *trans* conformation observed earlier^{4,12} (see Fig. 2).

The $[MgCl_4]^{2-}$ anion was shown to react easily with TiCl₄ and TiCl₃, to form the anions $[TiCl_6]^{2-}$ and $[trans-TiCl_4(THF)_2]^-$, respectively. In our opinion, MgCl₂ as a support could react directly with TiCl₄ to form the ionic or molecular compounds presented at the beginning of the paper, or undergo ionization under the influence of polar solvents (THF, esters, etc.) to form $[Mg(solvent)_6]^{2+}$, $[MgCl(solvent)_5]^+$ cations and $[MgCl_4]^{2-}$ anions, which would react further with titanium compounds to form the pre-catalyst.

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