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[Ti$(MgCl)_2 \cdot x$THF]$_q$: a reagent for the McMurry reaction and a novel inorganic Grignard complex *

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Abstract

The stepwise formation of two distinct bimetallic titanium/magnesium complexes during the reduction of $TiCl_3$ (or $TiCl_4$) by magnesium in tetrahydrofuran (THF) has been identified. [$TiMgCl_2 \cdot x$THF] (**1**) is produced in a first stage, but reacts further with excess Mg to give [Ti$(MgCl)_2 \cdot x$THF] (**2**). The reaction is reversible in the presence of excess $TiCl_3$. X-ray absorption spectroscopy has been used to identify the local environment in **2**. The most striking feature is the existence of the shortest Ti–Mg interatomic distance yet observed. The Ti–Mg bond length, 2.72(1) Å, is close to the sum of the Pauling single bond metallic radii (2.69 Å) and the complex is termed an inorganic Grignard reagent by analogy with other complexes containing direct transition metal–magnesium bonds. Overall, a dimeric model is compatible with the EXAFS-derived structural parameters and solubility characteristics. The titanium atoms are linked through two bridging $MgCl_2Mg$ units and their coordination shells are completed by THF ligands. The structure of **2**, and the existence of intermediate **1**, can be used to rationalize the known catalytic activity of the $TiCl_3$/Mg/THF system with respect to ether cleavage.

1. Introduction

Low valent titanium species prepared through the reduction of $TiCl_3$ or $TiCl_4$ with various metals (Mg, Li, K, Zn and ZnCu) or metal hydrides ($LiAlH_4$, LiH) have been exploited extensively as reagents in organic synthesis especially for the reductive coupling of carbonyl compounds to give olefins (the McMurry reaction) [1]. The reaction of titanium tri- or tetrachloride with magnesium in tetrahydrofuran (THF) proceeds with the formation of $MgCl_2$ and a black solution containing a reactive bimetallic chloride system [1a,2]. This system has proven to be an active catalyst or reagent for a wide range of reactions including ether cleavage [3] and hydrogen transfer to substrates like olefins [4] or to magnesium [4,5] (i.e. formation of MgH_2). Very little is known about the structure of this system, and even with respect to stoichiometry, the literature contains seemingly conflicting information.

Geise *et al.* [6] have reported an optimal $TiCl_3$ to magnesium molar ratio of 1 : 1.7 for the induced reductive coupling of ketones and have suggested that the resulting titanium species exists as finely divided Ti^0 particles with magnesium, chlorine, and THF adsorbed onto the surface. Yamamoto *et al.* [2a] have shown that 2.5 mol of magnesium per mol of titanium are consumed during the reduction of $TiCl_3$ in THF. Furthermore Sobota *et al.* [4,7] have reported a 1 : 2 : 2 (Ti : Mg : Cl) stoichiometry for the bimetallic chloride system and have proposed that it exists as the dimeric species shown below in which magnesium is directly bonded to titanium, although this model suffers from the inclusion of highly improbable one- and two-coordinate magnesium atoms. Furthermore, such Mg–Ti bonds have not, up to now, been structurally characterized.

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* Dedicated to Prof. E.O. Fischer on the occasion of his 75th Birthday.

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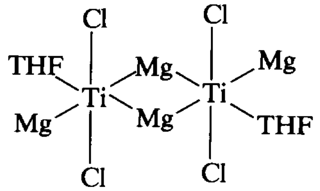


The interaction between titanium chloride and magnesium plays an important role in the catalytic production of active magnesium hydride [5] and, as part of a wider-ranging study of the reaction of magnesium with transition metal halides, we have reinvestigated the chemistry of this system. We report here the existence of two distinct complexes in the titanium chloride–magnesium–THF system, $[TiMgCl_2 \cdot xTHF]$ (**1**) and $[Ti(MgCl)_2 \cdot xTHF]$ (**2**) and describe the local structural arrangement around titanium in the more reduced species **2** obtained from an X-ray absorption spectroscopic study. This study has allowed $[Ti(MgCl)_2 \cdot xTHF]$ to be described as a novel inorganic Grignard compound.

2. Experimental details

THF was refluxed over Mg anthracene and distilled under argon. Mg turnings (99%, Enichem Sintesi), Mg powder (270 mesh, 97%, Eckart Werke Fürth) and α-$TiCl_3$ (99%, Aldrich, corrosive pyrophoric solid!) were used without further purification. Saturated solutions of anhydrous $MgCl_2$ in THF were prepared by reacting Mg powder with 1,2-dichloroethane in THF. $TiCl_2(TMEDA)_2$ was synthesized according to the published procedure [8]. All experimental procedures were performed under argon atmosphere.

2.1. $[TiMgCl_2 \cdot xTHF]$ (1)

2.09 g (13.5 mmol) of α-$TiCl_3$ in 100 ml THF were stirred together with an excess amount, 2.43 g (100 mmol), of Mg turnings at room temperature (RT). At defined time intervals, the stirring was interrupted for 30 min, and a sample of the supernatant was removed, hydrolyzed and analyzed for Mg^{2+} (compleximetric), Ti^{4+} (photometric) and Cl^- (Volhardt method). After *ca.* 20 h the titanium concentration in solution reached 90–95% of the concentration expected, based on the initial mass of α-$TiCl_3$, and the Mg/Ti ratio in solution reached a value of 1.5 (Fig. 1, -■-). After an additional 49 h of stirring, the concentrations of Ti, Mg and Cl in solution were 0.125, 0.183 and 0.361 mol l^{-1} respectively, and the hydrolysis (4 N H_2SO_4) of an aliquot of the reaction solution delivered 1.58 H_2/Ti.

2.2. $[Ti(MgCl)_2 \cdot xTHF]$ (2)

The reaction described above was stirred for an additional 7 days to allow further reaction with excess magnesium in the system. The Mg/Ti ratio in solution reached a value of 2.5 (Fig. 1, -■-); hydrolysis of an aliquot of the solution yielded 2.5 H_2/Ti.

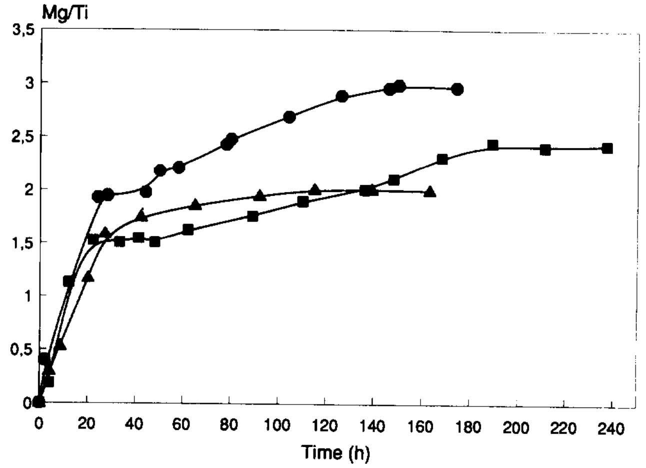


Fig. 1. The ratio of magnesium to titanium in solution over the course of the reaction between α-$TiCl_3$ (-■-) or $TiCl_4$ (-●-) or $TiCl_2(TMEDA)_2$ (-▲-) and magnesium in THF.

It is well known that magnesium cleaves THF at reflux (66°C) to give oxymagnesium cyclohexane and this reaction is catalyzed by **2**. However at RT ether cleavage remains insignificant. The amount of n-butanol (formed through the protolysis of the cyclic magnesium hydrocarbon) found in the hydrolyzed sample taken after 10 days of reaction was very low, corresponding to 1–2% of the initial mass of Mg.

2.3. Formation of $MgCl_2$

To determine whether $MgCl_2$ was produced during the reduction, a reaction consisting of 3.030 g (19.6 mmol) α-$TiCl_3$ and 2.425 g (99.8 mmol) Mg powder was performed in a $MgCl_2$ saturated THF solution (195 ml, 0.503 M) at 20°C. After 8 h a white solid began to precipitate from the reaction solution. After 48 h the reaction suspension was filtered. The filtrate (189 ml) was analyzed and contained 18.7 mmol Ti, 117.9 mmol Mg and 229.6 mmol Cl. The solid isolated during the filtration consisted of excess, unreacted Mg, the white precipitate ($MgCl_2$), and a residual amount of the reaction solution (*ca.* 6 ml). The solid was thoroughly washed with fresh THF to separate the THF-soluble $MgCl_2$ from Mg. The resulting solution was analyzed and found to contain 0.4 mmol Ti, 12.4 mmol Mg and 24.6 mmol Cl. The Ti and a small proportion of the Mg and Cl found in the wash solution correspond to the $TiMgCl_2$ complex and the $MgCl_2$ present in the residual amount of reaction solution left in the solid after filtration. After taking this into account, the amount of $MgCl_2$ which precipitated during the reduction can be computed to be near 9 mmol, corresponding to approximately 0.5 mol of $MgCl_2$ per mol Ti.

Thus the reduction of α-$TiCl_3$ proceeds over two steps as illustrated in Scheme 1(a) whereby **1** and magnesium chloride are formed in the first step in a 2 to 1 molar ratio, and **1** reacts further with magnesium to yield **2** in the second step.

2.4. *1 from 2*

1.65 g (10.7 mmol) of α-$TiCl_3$ was stirred together with 5.3 mmol (based on Ti) of $[\mathbf{2} + 0.5\ MgCl_2 \cdot 2THF]$ in 75 ml THF, and as a control reaction, 1.64 g (10.6 mmol) of α-$TiCl_3$ were stirred in 75 ml THF. After three days, both suspensions were filtered, and the residual solid and filtrate were analyzed for Ti content. In the control reaction, 5.7% of the total Ti was found in solution as $TiCl_3(THF)_3$. In the other reaction, 6.5 mmol Ti remained as solid, unreacted α-$TiCl_3$, and in solution a total of 9.4 mmol Ti was found corresponding, by comparison with the control reaction, to 0.6 mmol $TiCl_3(THF)_3$ and 8.8 mmol **1** (verified through hydrolysis). Thus α-$TiCl_3$ reacted with **2** in a molar ratio of 0.66 to 1 (3.5 mmol/5.3 mmol) according to the equation given in Scheme 1(a).

2.5. *$[Ti(MgCl)_2 \cdot x(TMEDA, THF)]$ (2a)*

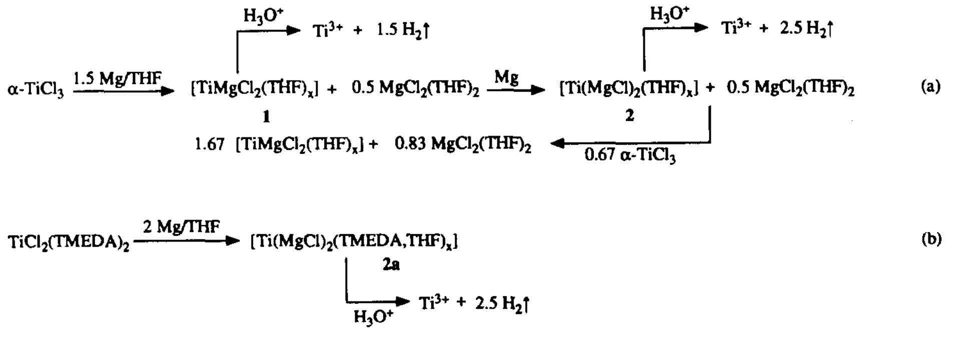
2.98 g (8.5 mmol) of $TiCl_2(TMEDA)_2$ together with 2.05 g (84 mmol) Mg powder were stirred in 200 ml THF at RT. Mg-, Ti- and Cl-analyses were performed during the course of the reaction as described for **1**. After 6 days of stirring, the Mg/Ti ratio in solution leveled off at 2.0 (Fig. 1, -▲-). Hydrolysis of an aliquot of the product solution gave 2.49 H_2/Ti. The reaction can be accelerated by ultrasonic treatment. For example, the reaction of 2.77 g (7.9 mmol) $TiCl_2(TMEDA)_2$ with 2.40 g (99 mmol) Mg powder in 200 ml THF in an ultrasonic bath maintained at 10°C is completed within 24 h.

2.6. *X-ray absorption spectroscopy and data analysis for 2*

X-ray absorption spectra were recorded at the titanium K-edge (4965 eV) on the EXAFS 3 spectrometer at the French synchrotron facility, DCI at Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, running at 1.85 GeV and approximately 300 mA. The X-ray beam was monochromatized with a double Si [111] crystal slightly detuned for harmonic rejection. The spectrometer was calibrated by assigning the first maximum in the absorption edge of a 5 μm titanium foil as 4965 eV. Measurements were performed in transmission mode and spectra recorded from, in general, 100 eV before the edge to 900 eV after the edge (step size 2 eV). Helium-filled ionization chambers were used to measure the incident and transmitted X-ray flux.

$[\mathbf{2} + 0.5MgCl_2 \cdot 2THF]$ was examined as both a solution and a dried solid, while solid α-$TiCl_3$ and $TiCl_3(THF)_3$ were used as reference compounds. In each case, sampling was carried out, under argon, immediately prior to recording the EXAFS spectrum to avoid any deterioration. Solids were mulled with paraffin oil stored over molecular sieves, and then loaded and pressed between the parafilm window of stainless steel sample holders to form homogeneous films free from pinholes or cracks. The solution was loaded into a cell with mylar windows and of adjustable path length. In each case at least five spectra were recorded at 77 K for the solids and at RT for the solution.

Reduction and analysis of all data were carried out using the programs developed by A. Michalowicz, "EXAFS pour le MAC" [9]. The X-ray absorption spectra were subjected to background removal and normalization using standard techniques (linear pre-edge function, removal of the background curvature using a high (5th–6th) order polynomial or a spline polynomial with division of the absorption spectrum into manually selected zones) and the resulting EX-



Scheme 1.

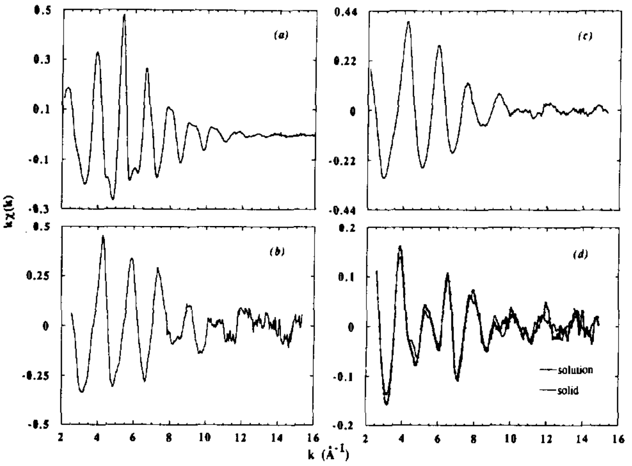


Fig. 2. Background subtracted and normalized EXAFS data for (a) Ti metal, (b) α-$TiCl_3$, (c) $TiCl_3(THF)_3$, and (d) **2** in solution (-•-) and in solid state (———).

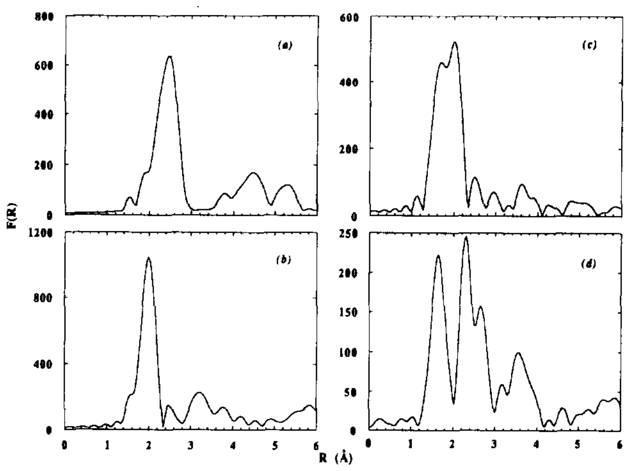


Fig. 3. Fourier transformed EXAFS spectrum of (a) Ti metal, (b) α-$TiCl_3$, (c) $TiCl_3(THF)_3$, and (d) **2** in solid state; phase shift not corrected.

AFS spectra were selectively summed to give the best signal-to-noise ratio and minimum mean standard deviation. The resulting average spectra $\chi(k)$ *vs.* k are represented in Fig. 2. Fourier transformation was carried out over a range typically 2.5–15 $Å^{-1}$ using a Hamming window and k^3 weighting (Fig. 3). Quantitative analysis using curve-fitting procedures was performed on Fourier-filtered spectra, back-transformed to reciprocal space, by systematically varying the coordination number N_i (this was however fixed at crystallographic values for the reference compounds), the Debye–Waller factor σ_i, and R_i, the distance of the ith shell of atoms from the absorber.

For the model compounds Ti, α-$TiCl_3$ and $TiCl_3(THF)_3$, the phase and amplitude functions utilized were the *ab initio* calculated values of McKale using spherical wave approximation [10]. These gave satisfactory agreement with the known structures when allowance was made for changes in the energy origin E_0 and for the variations in the path γ parameter (used to compute the photoelectron mean free path, $\lambda = k/\gamma$) for each type of atom shell Ti–Ti, Ti–O, Ti–Cl (see Table 1). The values of the latter parameter so determined were used in least squares refinement cycles of $Ti(MgCl)_2 \cdot xTHF$. The γ value found for the Ti–O shell was also applied to the Ti–C shell. No model compound containing a Ti–Mg interaction could be found in the literature, thus precluding the determination of a typical value of γ for this shell. γ was therefore held equal to a value of 1.

3. Results and discussion

3.1. Reaction of titanium chlorides with magnesium

The reduction of α-$TiCl_3$ (or $TiCl_4$) with excess magnesium in THF at RT proceeds in two steps. Until now, the occurrence of a two-step reaction has remained unrecognized which may be the source of the confusion in literature with respect to the stoichiome-

TABLE 1. Structural parameters derived from EXAFS spectroscopy for Ti foil, α-$TiCl_3$, $TiCl_3(THF)_3$, and $[Ti(MgCl)_2 \cdot xTHF]$ (**2**) [a]

	Shell	N	σ, Å	γ	R_{exp}, Å	R_{th}, Å [b]	ΔE_0, eV	Res, %
Ti	Ti	12	0.10(1)	0.60(10)	2.93(1)	2.926	−6	1
α-$TiCl_3$	Cl	6	0.06(1)	0.60(10)	2.40(1)	2.460	−3	2
$TiCl_3(THF)_3$	O	3	0.06(2)	0.76(10)	2.10(2)	2.126	−4	
	Cl	3	0.06(1)	0.60(10)	2.39(2)	2.346	3	5
$[Ti(MgCl)_2 \cdot xTHF]$	O	1.4(4)	0.03(5)	0.76	2.03(1)		−10	
	Mg	2.2(4)	0.05(2)	1.00	2.72(2)		−14	
	C	5(2)	0.04(3)	0.76	3.02(2)		3	4
	Cl	3.6(7)	0.08(2)	0.60	4.05(7)		−7	2

[a] N: number of atoms in the shell; σ: Debye–Waller factor; γ: parameter for photoelectron mean free path; R: distance from the Ti absorber; ΔE_0; shift in the energy origin; and Res = $\Sigma_k(k[\chi_{exp}(k)] - k[\chi_{th}(k)]^2 k^3 / \Sigma_k(k[\chi_{exp}(k)]^2)k^3$. [b] Mean distance from the Ti absorber as calculated from single crystal diffraction data.

try of the ensuing bimetallic system(s). During the course of the reaction, the Mg/Ti ratio in solution initially levels off at 1.5 (or 2.0 when $TiCl_4$ is used as the titanium source) as shown in Fig. 1. Protolysis of the black solution delivers $1.5H_2$/Ti. This observation, together with the fact that low valent titanium is oxidized to Ti^{3+} during protolysis [11], indicates that a Ti^0 system exists in solution. By performing the reduction in a saturated $MgCl_2$/THF solution, it can be shown that 0.5 mol of $MgCl_2$ per mol Ti are generated during this step. Thus one mol of a complex with the formula [$TiMgCl_2 \cdot x$THF] (**1**) plus 0.5 mol of $MgCl_2 \cdot 2$THF are produced, as summarized in Scheme 1(a). The reactant molar ratio of $TiCl_3$ to magnesium in the first step, *i.e.* 1 : 1.5, is quite close to that reported by Geise *et al.* [6] as the optimum ratio (1 : 1.7) for the reagent utilized in the McMurry reaction. Thus the reagent described by Geise *et al.* [6] as being finely divided titanium may indeed be the bimetallic chloride complex **1**.

Over a longer reaction time, the system slowly reacts further with excess magnesium to give a final Mg/Ti ratio of 2.5 in solution (Fig. 1). This confirms the work of Yamamoto *et al.* [2a], who report that 2.5 mol of Mg are consumed per mol of Ti during the reduction of $TiCl_3$ in THF. As illustrated in Scheme 1(a), the second step corresponds to the uptake of one additional mol of Mg per mol of Ti. Since there is still 0.5 mol of $MgCl_2$ per mol Ti in solution, the resulting bimetallic complex can be identified as [$Ti(MgCl)_2 \cdot x$THF] (**2**). Thus in the final bimetallic system, the Ti : Mg : Cl ratio is 1 : 2 : 2, as previously reported by Sobota *et al.* [7]. The existence of the highly reduced complex **2** is further confirmed through protolysis of the final solution; 2.5 mol of H_2 per mol Ti were evolved. The second reaction step appears to be reversible; 0.67 mol of THF-insoluble α-$TiCl_3$ react within 72 h with the [**2** + $0.5MgCl_2 \cdot 2$THF] system to yield a solution of **1** plus $MgCl_2 \cdot 2$THF.

To confirm the stoichiometries of the resulting bimetallic complexes, an alternative synthetic route was explored, *i.e.* the reaction of $TiCl_2(TMEDA)_2$ [8] with magnesium. This reaction is particularly advantageous for the verification of the Ti : Mg : Cl ratio in the bimetallic chlorides because $MgCl_2$ is not generated as a by-product. Surprisingly, the reduction of $TiCl_2$ $(TMEDA)_2$ in THF takes place in a single step as shown in Fig. 1 (-▲-). The Mg/Ti content in the reaction solution reaches a plateau at a value of 2.0 which, as described in Scheme 1(b), points to the formation of a bimetallic complex with the general formula [$Ti(MgCl)_2 \cdot x$(TMEDA, THF)] (**2a**). 2.5 mol of H_2 per mol Ti are released upon protolysis of **2a**.

These complexes exist either in solution or, after evaporation of THF, as dried, amorphous powders, and structural characterization through traditional X-ray diffraction techniques is not possible. Thus, the environment about Ti in **2** was investigated using X-ray absorption spectroscopy.

3.2. X-ray absorption spectroscopic study and structural characterization of 2

Figure 2(d) illustrates that the EXAFS spectra for **2** in the solid state and in solution are practically identical. This may be an indication that the solution is, in fact, a colloidal suspension of the bimetallic complex, a possibility that is presently being explored. The structural parameters derived from the EXAFS spectrum of **2** in solution are essentially the same as those derived from that of the solid and, for simplicity, the discussion here will be limited to the results obtained from the solid sample.

The Fourier-transformed EXAFS spectrum of **2** is represented in Fig. 3(d) and, in a first qualitative appraisal, reveals five shells of atoms with distances from the Ti absorber of *ca.* 1.6, 2.3, 2.7, 3.2 and 3.6 Å before phase correction. Quantitative analysis (Table 1 and Figure 4) was initally performed on three separate Fourier-filtered, back-transformed EXAFS spectra: the

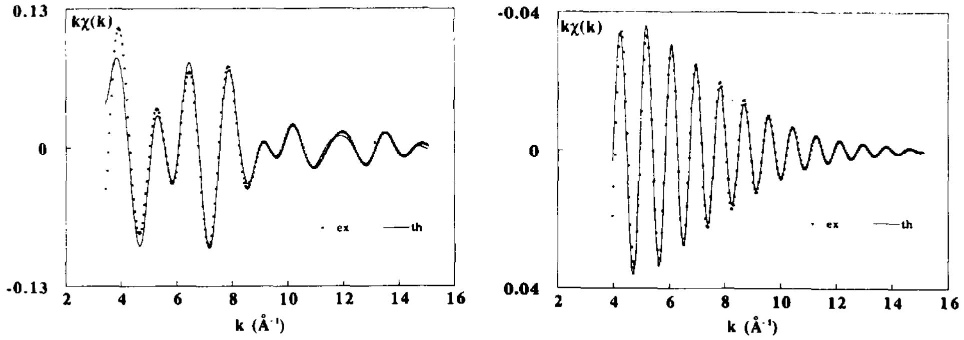


Fig. 4. Fits of the backtransforms of (a) the first three shells (Ti–O, Ti–Mg, Ti–C) and (b) the Ti–Cl shell of the FT of **2**. ×, experimental; ———, calculated.

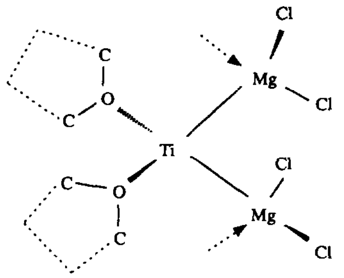


Fig. 5. The environment about titanium in 2 as projected from the EXAFS results.

first peak filtered from 1.25 to 2.03 Å in the Fourier transform (FT), the second composite shell from 1.89 to 3.02 Å, and the last shell from 3.20 to 4.20 Å. In a second stage, a broader filter envelope allowed a global refinement of the structural parameters of the first 3 atom shells.

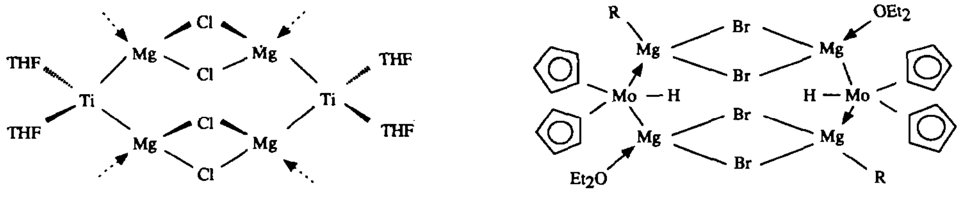
The results of the fitting for the first three shells include 1.4(4) oxygen atoms at a distance of 2.03(1) Å from the titanium absorber, 2.2(4) Mg atoms at 2.72(2) Å, and 5(2) C atoms at 3.02(2) Å. The oxygen and carbon shells can be attributed to the oxygen and α-carbon atoms of THF-ligands bound to titanium. $Ti-O_{THF}$ distances in $TiCl_3(THF)_3$, as determined by single crystal X-ray diffraction, range from 2.08 to 2.18 Å. The number of neighbouring oxygen and carbon atoms suggests that the titanium is coordinated by two THF ligands.

Since there are no known compounds with Ti–Mg bonds, to assess whether the short Ti–Mg distance found here is reasonable, a comparison with other compounds containing transition metal–magnesium bonds is necessary. A series of such compounds, so-called inorganic Grignard complexes, is known and several have been structurally characterized, for example $[CpFe(diphos)MgBr(THF)_2]$ [12]; $[Cp_2Mo(H)MgBr(THF)_2]$ [13]; and $[CpCo(\eta^3\text{-}C_3H_5)MgBr(THF)_2]$ [14]. In these complexes the transition metal–magnesium bond is considered covalent and the observed bond length is near the sum of the single-bond metallic radii of Pauling [15]: an observed Mg–Co bond length of 2.480 Å *vs.* a radii sum of 2.526 Å (1.364 + 1.162); Mg–Fe, 2.593 Å *vs.* 2.529 Å (1.364 + 1.165); and Mg–Mo, 2.732 Å *vs.* 2.660 Å (1.364 + 1.126). Extending this reasoning to the titanium–magnesium system, a covalent Mg–Ti bond length would be expected to be around 2.688 Å (1.364 + 1.324), a value quite close to the distance determined in this work by X-ray absorption spectroscopy, 2.72 Å.

The last major peak in the FT of 2 was successfully identified as resulting from backscattering from chlorine atoms at a distance of 4.05(7) Å from titanium. This distance does not correspond to a direct Ti–Cl bond and the model proposed for 2 by Sobota *et al.* [4,7] would therefore seem to be incompatible with the EXAFS results. These Cl atoms are however bonded to magnesium. Assuming Mg is also coordinated by THF, the fourth peak in the FT of 2 at *ca.* 3.6 Å after phase correction could arise from oxygen of THF ligands bound to magnesium and/or the β-carbons of the THF ligands on titanium. Due to the uncertainty in the origin and the identity of this shell, it was not fitted.

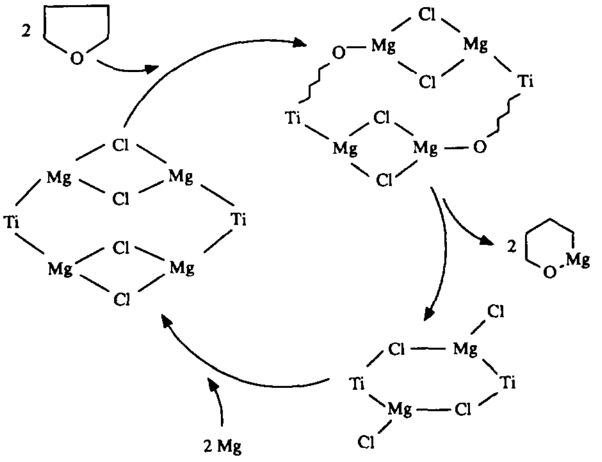
The results indicate that the environment about titanium in 2 includes two THF ligands and two Mg atoms, which are bonded Cl atoms, as represented diagramatically in Fig. 5. To maintain the appropriate stoichiometry and to account for the number of nearest neighbors, an oligomeric structure is dictated. The simplest structural model which would fulfill both of these requirements is a dimer in which the two Ti-centred entities are bridged over the chlorine atoms as shown in Fig. 6(a). Cyclic structures of higher nuclearity can also be formed through analogous bridging whereby each Ti unit is bridged to two neighboring Ti units rather than to one. A polymeric structure based on an alternative bridging scheme can also be constructed. However, considering the observed high solubility of 2 in THF, a low nuclear complex, such as the dimer, is more plausible.

Such an arrangement based on bridging halogen atoms was observed previously in another inorganic Grignard complex, $[Cp_2Mo(H)MgBr(OEt_2)MgBr(C_6$



(a) (b)

Fig. 6. (a) Dimeric structural model for 2 based on both chemical and spectroscopic findings in comparison to (b) the structural arrangement observed in a previously reported inorganic Grignard complex, $[Cp_2Mo(H)MgBr(OEt_2)MgBr(C_6H_{11})]_2$ [16].



Scheme 2.

$H_{11})]_2$ [16] (Fig. 6(b)), the structure of which has been determined by single crystal X-ray diffraction. The nature of the environment of the metallic core as identified by EXAFS in $[Ti(MgCl)_2 \cdot x THF]_q$ is entirely comparable to that around molybdenum in the above molybdenum complex, apart from the tetrahedral arrangement around titanium. Moreover, the identical metal : magnesium : halogen atom ratio as that in **2** (1 : 2 : 2) further supports the proposal that the Mg–Ti complex may exist as a dimer.

4. Concluding remarks

2 represents a novel inorganic Grignard complex with Mg–Ti bonds. These are the first Mg–Ti covalent interactions to be characterized. Taking the existence of this type of intermetallic bonding into consideration, the catalytic effect of the Mg–Ti complex in a wide variety of reactions may now be easier to understand. For example, it is well known that $[Ti(MgCl)_2 \cdot x THF]_q$ catalyzes the cleavage of ethers by activated magnesium [3]. Magnesium inserts into a C–O bond of the ether to form a cyclic magnesium alkoxyl alkyl compound. Given the proposed structure of $[Ti(MgCl)_2 \cdot x THF]_q$, the catalytic cycle originally suggested by Bartmann [3a] can be expanded, whereby a C–O bond of the ether adds over a Mg–Ti bond, the cyclic magnesium hydrocarbon splits off leaving a [TiClMgCl] fragment which can incorporate an additional Mg atom to regenerate $[Ti(MgCl)_2 \cdot x THF]_q$ and thus complete the cycle. The bimetallic intermediate may indeed be the initial Mg–Ti complex, $[TiMgCl_2 \cdot x THF]$ (**1**), observed during the reduction of α-$TiCl_3$ with magnesium. In order to gain some insight on the structural relationship between the two Mg–Ti complexes, an EXAFS study of **1** is also being performed.

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References

1 (a) S. Tyrlik and I. Wolochowicz, *Bull. Soc. Chim. Fr.*, (1973) 2147; (b) T. Mukaiyama, T. Sato and J. Hanna, *Chem. Lett.*, (1973) 1041; (c) J.E. McMurry and M.P. Fleming, *J. Am. Chem. Soc.*, *96* (1974) 4708. Recent reviews: (d) B.E. Kahn and R.D. Rieke, *Chem. Rev.*, *88* (1988) 733; (e) J.-M. Pons and M. Santelli, *Tetrahedron*, *44* (1988) 4295; (f) D. Lenior, *Synthesis*, (1989) 883; (g) Y. Dang and H.J. Geise, *Janssen Chim. Acta*, *7* (1989) 3; (h) C. Betschart and D. Seebach, *Chimia*, *43* (1989) 39; (i) J.E. McMurry, *Chem. Rev.*, *89* (1989) 1513; (j) A. Fürstner, *Angew. Chem.*, *105* (1993) 171; *Angew. Chem., Int. Ed. Engl.*, *32* (1993) 164.

2 (a) A. Yamamoto, S. Go, M. Ookawa, M. Takahashi, S. Ikeda and T. Keii, *Bull. Chem. Soc. Jpn.*, *45* (1972) 3110; (b) P. Sobota, T. Pluzinski, B. Jezowska-Trzebiatowska and S. Rummel, *J. Organomet. Chem.*, *185* (1980) 69.

3 (a) E. Bartmann, *J. Organomet. Chem.*, *284* (1985) 149; (b) S.M. Kadam, S.K. Nayak and A. Banerji, *Tetrahedron Lett.*, *33* (1992) 5129.

4 P. Sobota and B. Jezowska-Trzebiatowska, *Coord. Chem. Rev.*, *26* (1978) 71.

5 B. Bogdanović, S. Liao, M. Schwickardi, P. Sikorsky and B. Spliethoff, *Angew. Chem.*, *92* (1980) 845; *Angew. Chem., Int. Ed. Engl.*, *19* (1980) 818.

6 R. Dams, M. Malinowski, I. Westdorp and H.J. Geise, *J. Org. Chem.*, *47* (1982) 248.

7 (a) B. Jezowska-Trzebiatowska and P. Sobota, *J. Organomet. Chem.*, *76* (1974) 43; (b) P. Sobota, B. Jezowska-Trzebiatowska and J. Wroblewski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, *28* (1980) 679.

8 J.J.H. Edema, R. Duchateau, S. Gambarotta, R. Hynes and E. Gabe, *Inorg. Chem.*, *30* (1991) 154.

9 A. Michalowicz, in Société Française de Chimie (ed.), *Logiciels pour la Chimie*, Paris, 1991, pp. 102–103.

10 A.G. McKale, *J. Am. Chem. Soc.*, *110* (1988) 3703.

11 H. Martin and J. Stedefeder, *Liebigs Ann. Chem.*, *618* (1958) 17.

12 H. Felkin, P.J. Knowles, B. Meunier, A. Mitschler, L. Ricard and R. Weiss, *J. Chem. Soc., Chem. Commun.*, (1974) 44.

13 S.G. Davies, M.L.H. Green, K. Prout, A. Coda and V. Tazzoli, *J. Chem. Soc., Chem. Commun.*, (1977) 135.

14 K. Jonas, G. Koepe and C. Krüger, *Angew. Chem.*, *98* (1986) 901; *Angew. Chem., Int. Ed. Engl.*, *25* (1986) 923.

15 L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*, 3rd Ed., Cornell University Press, 1960.

16 (a) M.L.H. Green, G.A. Moser, I. Packer, F. Petit, R.A. Forder and K. Prout, *J. Chem. Soc., Chem. Commun.*, (1974) 839; (b) K. Prout and R.A. Forder, *Acta Crystallogr.*, *B31* (1975) 852.