

MgCl₂ – ONE OF THE FACTORS CONTROLLING THE MECHANISM OF THE REACTION BETWEEN GRIGNARD REAGENTS AND TITANIUM OR ZIRCONIUM TETRACHLORIDE. II *

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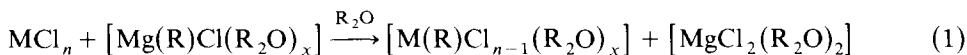
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Summary

Treatment of a Grignard reagent or [MgR₂(THF)₂] with zirconium or titanium tetrachloride gives [MgCl₂(THF)₂], which when treated with [MCl₄(THF)₂] (M = Ti or Zr) yields the compounds: [Mg(THF)₆][ZrCl₆] (I), [Mg(THF)₆][ZrCl₅(THF)]₂ (II), [Mg(THF)₆][TiCl₅(THF)]₂ (IV), [(THF)₄Mg(μ-Cl)₂TiCl₄] (V) and [Mg₂(μ-Cl)₃(THF)₆][TiCl₅(THF)] (VI), along with MR₄. The zirconium compounds I and II are insoluble in THF, which results in a decrease of the ZrR₄ yield. The titanium compounds IV, V and VI are transient intermediates in the formation of TiR₄.

In the synthesis of compounds of transition metals in low oxidation states, the most frequently used initial substrates are the transition metal chlorides MCl_n, while the Main Group I–III metals of the periodic system or their organometallic compounds are the reducing agents. Ether or other polar compounds are used as solvents e.g.:



Depending on the substrate molar ratio, different products can be obtained. In reaction 1, besides the transition metal compound, [MgCl₂(R₂O)₂] is also formed. Such inorganic compounds were thought to be side-products, and not involved in the reaction. So the question arose; whether an inorganic salt formed in reaction 1 and in analogous reactions, is chemically neutral or whether it reacts with either the substrate or the products or both. If the answers were affirmative, such a salt could essentially influence the reaction mechanism and the constitution of its products. To answer this question, we examined well-known reactions between zirconium or titanium tetrachloride with the Grignard reagent and the reaction of [TiCl₄(THF)₂] or [ZrCl₄(THF)₂] with [MgCl₂(THF)₂] in tetrahydrofuran (THF).

* For Part I see Ref. 1.

Results and discussion

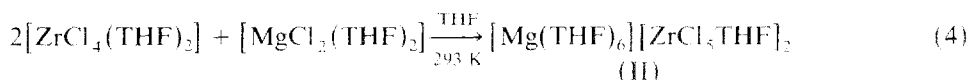
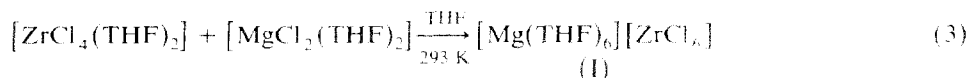
It is well known that in the reaction between a Grignard reagent and $[\text{MCl}_4(\text{THF})_2]$ organometallic zirconium or titanium compounds (MR_3) are formed, along with magnesium dichloride [2–4] (eq. 2).



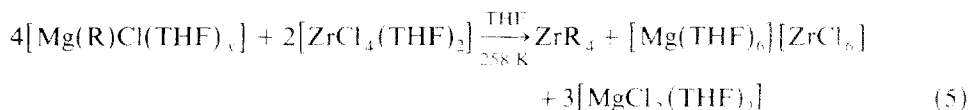
($\text{R} = \text{CH}_2\text{C}_6\text{H}_5$)

When the Grignard reagent is slowly added to $[\text{ZrCl}_4(\text{THF})_2]$ at a 4/1 molar ratio in THF a white compound (I) (58% yield) separates out. Elemental analysis allowed us to formulate this compound as $\text{ZrCl}_4 \cdot \text{MgCl}_2 \cdot 6\text{THF}$. It was assigned the $[\text{Mg}(\text{THF})_6][\text{ZrCl}_6]$ ionic structure as it was analogous to $[\text{Mg}(\text{THF})_6][\text{MoOCl}_4(\text{THF})_2]$, whose X-ray structure had been resolved [5]. When, however, the $[\text{ZrCl}_4(\text{THF})_2]$ was added to the Grignard reagent, compound I was formed in 42% yield.

The composition of $[\text{Mg}(\text{THF})_6][\text{ZrCl}_6]$ suggests that its formation is by a secondary reaction between the substrate $[\text{ZrCl}_4(\text{THF})_2]$ and the product $[\text{MgCl}_2(\text{THF})_2]$. This reaction was found to proceed easily (eqs. 3 and 4).

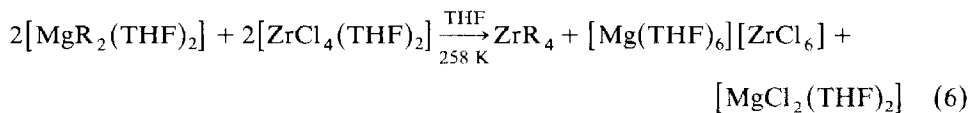


Depending on the molar ratio of the substrates, two different compounds I and II, are formed. In both reactions, the zirconium atom is the Lewis acid and takes chlorine atoms from the magnesium atom, to give the $[\text{Mg}(\text{THF})_6]^{2+}$ cation, and the $[\text{ZrCl}_6]^{2-}$ and $[\text{ZrCl}_5(\text{THF})]^{-}$ anions. It follows then, that eq. 2 describes only the first stage of the reaction between the Grignard reagent and $[\text{ZrCl}_4(\text{THF})_2]$ but does not include the formation of I. When the yield of compound I is taken into account, the reaction can be written as eq. 5.



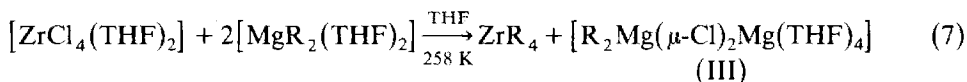
Thus only half of the zirconium used, produced ZrR_4 . Beside compound I, an excess of unreacted magnesium dichloride remained in the reaction mixture. The yield of I and the course of eq. 5 depend on the sequence of addition of substrate. When the Grignard reagent is added to zirconium tetrachloride in THF the yield of I is higher (58%) because of the presence in the reaction medium of the excess $[\text{ZrCl}_4(\text{THF})_2]$, which reacts immediately with the magnesium dichloride formed. In contrast, when zirconium tetrachloride is added to the Grignard reagent, the $[\text{MgCl}_2(\text{THF})_2]$ formed initially has nothing with which to react, but as the magnesium dichloride concentration in the reaction mixture increases, two competitive reactions begin simultaneously, i.e. formation of ZrR_4 and compound I (yield 42%).

When the Grignard reagent is replaced by $[\text{MgR}_2(\text{THF})_2]$ in the reaction, I is formed in 54% yield, only when $[\text{MgR}_2(\text{THF})_2]$ is added to $[\text{ZrCl}_4(\text{THF})_2]$ (eq. 6).



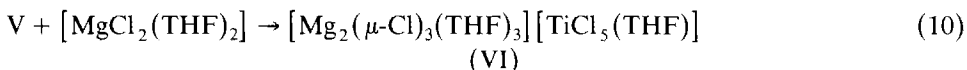
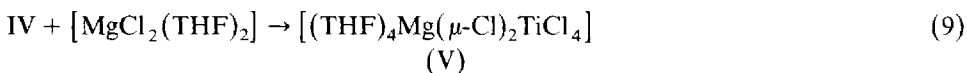
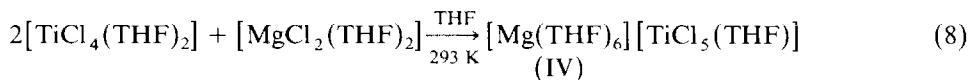
(R = $\text{CH}_2\text{C}_6\text{H}_5$)

However, when, zirconium tetrachloride is added to the $[\text{MgR}_2(\text{THF})_2]$ ZrR_4 , is formed and compound I is not, (eq. 7).



This is probably owing to the fact that $[\text{MgCl}_2(\text{THF})_2]$ formed in this reaction, reacts immediately with $[\text{MgR}_2(\text{THF})_2]$ to produce compound III. This compound has not been isolated in the pure state although its formulation has been postulated [6]. The structure of $[\text{R}_2\text{Mg}(\mu\text{-Cl})_2\text{Mg}(\text{THF})_4]$ as postulated is substantiated by that of $[(\text{THF})_4\text{Mg}(\mu\text{-Cl})_2\text{FeCl}_2]$ as given in ref. 7. Compound III is unstable in solution and undergoes subsequent changes.

Investigation of the course of reaction between $[\text{TiCl}_4(\text{THF})_2]$ and $[\text{Mg}(\text{R})\text{Cl}(\text{THF})_x]$ is difficult, as all products are soluble. For that reason the direct reaction between the titanium tetrachloride and magnesium dichloride was performed and scrutinized. Three different complexes can be obtained, depending on the molar ratio of the substrates (eqs. 8, 9, 10).



Equation 8, with $\text{TiCl}_4/\text{MgCl}_2$ 2/1 gives compound IV. The titanium atom exhibits the acidic properties because it removes chlorine atoms from $[\text{MgCl}_2(\text{THF})_2]$ to give the $[\text{Mg}(\text{THF})_6]^{2+}$ cation and $[\text{TiCl}_5(\text{THF})]^-$ anions. The compound $[(\text{THF})_4\text{Mg}(\mu\text{-Cl})_2\text{TiCl}_4]$ (V) is formed in reaction 9, where $[\text{MgCl}_2(\text{THF})_2]$ is also the Cl^- donor. The sixth chlorine atom, coordinated to the titanium atom causes such an accumulation of negative charge around the Ti^{4+} atom that its acidic properties decrease. Consequently, the chlorine atoms become more basic and dislodge the THF molecules from the coordination sphere of the magnesium atom. This allows the formation of a heterobimetallic molecular compound (V). In this context the acidic and basic properties of both metal atoms in V have to be similar. In eq. 10, where compound V reacts with $[\text{MgCl}_2(\text{THF})_2]$; magnesium dichloride also has basic properties because it takes the MgCl^+ cation from $[(\text{THF})_4\text{Mg}(\mu\text{-Cl})_2\text{TiCl}_4]$ to produce the bimagnesium $[\text{Mg}_2(\mu\text{-Cl})_3(\text{THF})_6]^+$ cation and the $[\text{TiCl}_5(\text{THF})]^-$ anion. Structures of V and VI has been resolved using X-ray crystallography [8,9].

The course of the reactions 8–10 indicates that as the concentration of $[\text{MgCl}_2(\text{THF})_2]$ in the reaction mixture increases the compounds, IV, V, and VI are produced in that order, because MgCl_2 is the Cl⁻ donor, and MgCl^+ the acceptor.

It could be suggested that compounds IV, V and VI are formed as intermediates in the reaction of the Grignard reagent with $[\text{TiCl}_4(\text{THF})_2]$ (eq. 11).



These compounds are readily soluble in THF and for that reason the reaction follows the pattern of eq. 11.

The results presented here reveal the complicated course of the substitution of chlorine atoms in titanium or zirconium tetrachloride by alkyl or aryl groups. The MR_4 compounds, i.e. the final reaction products, probably arise from side reactions, owing to the presence of $[\text{MgCl}_2(\text{THF})_2]$ in the reaction mixture. The mechanisms of these reactions are the subject of our continued investigations.

Experimental

All reactions were carried out under N_2 using dried THF and conventional Schlenk apparatus. Tetrahydrofuran was distilled under N_2 from sodium and benzophenone. $[\text{TiCl}_4(\text{THF})_2]$, $[\text{ZrCl}_4(\text{THF})_2]$ and $[\text{MgCl}_2(\text{THF})_2]$ were obtained by literature methods [10,11]. Microanalyses were performed at the University of Wrocław.

Reactions of $[\text{Mg}(\text{R})\text{Cl}(\text{THF})_3]$ with $[\text{ZrCl}_4(\text{THF})_2]$

$[\text{ZrCl}_4(\text{THF})_2]$, 2.2 g (5.6 mmol), was dissolved in THF (50 cm³) and cooled to 258 K, a solution of $[\text{Mg}(\text{CH}_2\text{C}_6\text{H}_5)\text{Cl}(\text{THF})_3]$ (28.2 mmol) in THF was slowly added dropwise. The white precipitate was allowed to settle and was filtered off, washed in 3×5 cm³ THF and dried in vacuo. Yield: 2.5 g (58%). Found: C, 37.53; H, 6.01; Cl, 27.63; Mg, 3.27; Zr, 11.87. $\text{C}_{24}\text{H}_{48}\text{Cl}_6\text{MgO}_6\text{Zr}$ calcd.: C, 37.88; H, 6.13; Cl, 27.98; Mg, 3.20; Zr, 12.00%.

$[\text{Mg}(\text{THF})_6][\text{ZrCl}_6]$ (I). 7.2 g (9.5 mmol) of $[\text{ZrCl}_4(\text{THF})_2]$ and 14.0 g (58.5 mmol) of $[\text{MgCl}_2(\text{THF})_2]$ and 220 cm³ THF were added to the reaction flask and heated under reflux for 10 h to complete dissolution of compound and was left to stand. After 24 h white crystals were filtered off and washed with THF (3×5 cm³) and dried in vacuo. Yield: 14.9 g (95%). Found: C, 37.42; H, 5.97; Cl, 27.71; Mg, 3.15; Zr, 11.73. $\text{C}_{24}\text{H}_{48}\text{Cl}_6\text{MgO}_6\text{Zr}$ calcd.: C, 37.88; H, 6.13; Cl, 27.98; Mg, 3.20; Zr, 12.00%.

$[\text{Mg}(\text{THF})_6][\text{ZrCl}_5(\text{THF})_2]$ (II). 1.8 g (4.7 mmol) of $[\text{ZrCl}_4(\text{THF})_2]$ and 2.3 g of $[\text{MgCl}_2(\text{THF})_2]$ were dissolved in hot THF (343 K) (50 and 40 cm³, respectively) and cooled to room temperature, the solution was stirred and left to stand. After 24 h white crystals were filtered off and washed with THF (3×5 cm³). Yield: 2.4 g (87%). Found: C, 33.54; H, 6.54; Cl, 31.33; Mg, 2.03; Zr, 15.73. $\text{C}_{32}\text{H}_{64}\text{Cl}_{10}\text{MgO}_8\text{Zr}_2$ calcd.: C, 33.76; H, 5.63; Cl, 31.17; Mg, 2.14; Zr, 16.04%.

Reactions of [TiCl₄(THF)₂] with [MgCl₂(THF)₂]

[Mg(THF)₆][TiCl₅(THF)]₂ (IV). [TiCl₄(THF)₂] (2.1 g) and [MgCl₂(THF)₂] (0.74 g) were dissolved separately in THF (25 and 20 cm³, respectively). The two solutions were filtered, stirred, and left to stand. After 24 h yellow crystals separated, these were filtered off and washed with THF (3 × 5 cm³). Yield: 2.6 g (80%). Found: C, 36.41; H, 5.87; Cl, 33.91; Mg, 2.26; Ti, 8.96. C₃₂H₆₄Cl₁₀MgO₈Ti₂ calcd.: C, 36.55; H, 6.09; Cl, 33.74; Mg, 2.31; Ti, 9.12%.

[(THF)₄Mg(μ-Cl)₂TiCl₄] (V). 3.6 g (10.7 mmol) of [TiCl₄(THF)₂] and 2.5 g (10.7 mmol) of [MgCl₂(THF)₂] were dissolved in hot THF (343 K) (50 and 30 cm³, respectively), and cooled to room temperature, the solution was stirred and left to stand. After 24 h yellow crystals separated, these were filtered off, washed with THF (3 × 5 cm³), and dried in vacuo. Yield 4.9 g (79%). Found: C, 24.19; H, 4.11; Cl, 26.68; Mg, 2.96; Ti, 5.81. C₁₆H₃₂Cl₆MgO₄Ti calcd.: C, 24.42; H, 4.03; Cl, 26.78; Mg, 3.06; Ti, 6.03%.

[Mg₂(μ-Cl)₃(THF)₆][TiCl₅(THF)] (VI). [TiCl₄(THF)₂] 2.1 g (6.2 mmol) and [MgCl₂(THF)₂] 2.9 g (12.4 mmol) were dissolved separately in THF (25 and 35 cm³, respectively). The solutions were filtered, mixed, and left to stand. After 24 h yellow crystals precipitated, which were filtered off and washed with THF (3 × 5 cm³). Yield: 3.9 g (69%). Found: C, 30.03; H, 6.39; Cl, 31.98; Mg, 5.52; Ti, 5.51. C₂₈H₅₆Cl₈Mg₂O₇Ti calcd.: C, 37.97; H, 6.33; Cl, 32.65; Mg, 5.49; Ti, 5.41%.

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