Journal of Organometallic Chemistry, 332 (1987) 239–245
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Influence of $MgCl_2$ on Grignard reagent composition in tetrahydrofuran. III *

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(Received March 15th, 1987)

Abstract

Reaction of $[MgCl_2(THF)_2]$ with $[NBu_4][BF_4]$ yields the compounds $[NBu_4][MgCl_4]$ (IV) and $[Mg(THF)_6][BF_4]_2$ (V). After addition of dioxane the reaction equilibrium shifts in the opposite direction. The formation of $[MgCl_2(C_4H_8O_2)_2]$ in solution does not require the presence of $MgCl_2$. This compound may be formed in the reaction of dioxane with the ionic or molecular species formed by the magnesium atom in solution. The $[NBu_4][BF_4]$ salt also reacts with the Grignard reagent to produce compound IV which confirms that there is a new equilibrium between $[Mg(R)X(THF)_n]$ and $[MgR_2(THF)_2]$, $[MgCl_4]^{2-}$ and $[Mg(THF)_6]^{2+}$. Bis(tetrahydrofuran)magnesium dichloride, because of its reactivity is only stable in Grignard reagent. For that reason the composition of the Grignard reagent in solution is best described as an equilibrium between $[Mg(R)X(THF)_n]$ and $[(THF)_4Mg(\mu\text{-}Cl)_2MgR_2]$ and $[RMg_2(\mu\text{-}Cl)_3(THF)_5]$ rather than as a Schlenk equilibrium.

The nature of the Grignard reagents "RMgX" in solution is not simple. They exist in an equilibrium mixture which may involve various mono-, bi- and polynuclear solvated compounds [1–3]. The primary equilibrium, known generally as the Schlenk equilibrium [4], (e.g. in tetrahydrofuran (THF)) is expressed simply as:

$$2[Mg(R)X(THF)_n] \overset{THF}{\rightleftharpoons} [MgR_2(THF)_2] + [MgX_2(THF)_2] \quad (1)$$

This was initially proposed on the basis of dioxane precipitation of MgX_2. To precipitate MgX_2, diglyme [5] and pyridine [6] have also been used. We have discovered previously that $[MgCl_2(THF)_2]$, being a component of the Grignard reagent, exhibited great reactivity and had a marked influence on the reaction mechanism and composition of the products formed between "RMgX" and various

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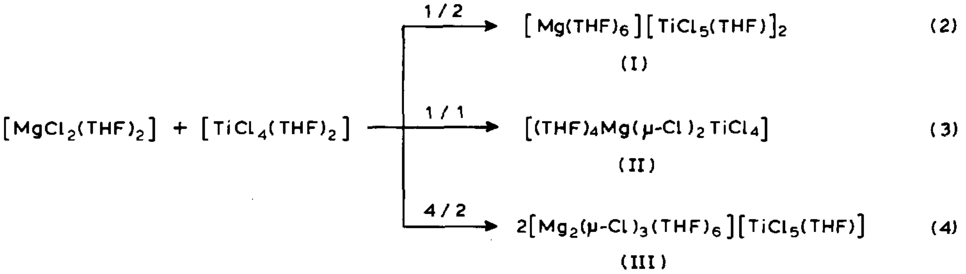
* For Part II see Ref. 7.

0022-328X/87/$03.50

substrates. $[MgCl_2(THF)_2]$ reacts readily with Lewis acids to produce different compounds, depending on the $MgCl_2/MCl_n$ molar ratio, with M = Ti or Zr.



$$[MgCl_2(THF)_2] + [TiCl_4(THF)_2] \xrightarrow{1/2} [Mg(THF)_6][TiCl_5(THF)]_2 \quad \text{(I)} \qquad (2)$$

$$\xrightarrow{1/1} [(THF)_4Mg(\mu\text{-}Cl)_2TiCl_4] \quad \text{(II)} \qquad (3)$$

$$\xrightarrow{4/2} 2[Mg_2(\mu\text{-}Cl)_3(THF)_6][TiCl_5(THF)] \quad \text{(III)} \qquad (4)$$

The reaction of MCl_n with Grignard reagent yields compounds I–III, which are intermediates in the synthesis of MR_4 [7]. These compounds are also catalyst precursors in ethylene polymerization. Bis(tetrahydrofuran)magnesium dichloride reacts not only with Lewis acids, but also with cations, such as $[NBu_4]^+$:

$$2[MgCl_2(THF)_2] + 2[NBu_4][BF_4] \rightarrow \underset{(IV)}{[NBu_4]_2[MgCl_4]} + \underset{(V)}{[Mg(THF)_6][BF_4]_2} \qquad (5)$$

In this reaction the magnesium atom exhibits amphoteric behaviour, since $[MgCl_2(THF)_2]$ is both donor and acceptor of Cl^- and the $[Mg(THF)_6]^{2+}$ and $[MgCl_4]^{2-}$ ions are formed [8].

Ease of formation of $[Mg(THF)_6]^{2+}$, $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+$ and $[MgCl_4]^{2-}$ ions from $[MgCl_2(THF)_2]$ by the action of acids in THF and by the action of molecular compounds II or $[(THF)_4Mg(\mu\text{-}Cl)_2FeCl_2]$ (VI) [9], suggests that such species could also be formed by reaction of Grignard reagent with other substrates leading to the intermediates in the formation of MgX_2 (eq. 1). It was interesting to see whether $[MgCl_2(THF)_2]$ in Grignard reagent undergoes ionisation and thus behaves as in reaction 5, and whether the Schlenk equilibrium 1 could be shifted by $[NBu_4][BF_4]$ and whether dioxane affects the reaction equilibria 2–5.

Results and discussion

It was expected that addition of $[NBu_4][BF_4]$ to the Grignard reagent in THF would result in liberation of compound $[NBu_4]_2[MgCl_4]$ IV, and that only $[MgR_2(THF)_2]$ and $[Mg(THF)_6][BF_4]_2$ (V) would remain in the post-reaction mixture

$$\begin{array}{l} 4[Mg(R)X(THF)_n] \rightleftharpoons 2[MgR_2(THF)_2] + 2[MgCl_2(THF)_2] \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow 2[NBu_4][BF_4] \\ \qquad 2[MgR_2(THF)_2] + [NBu_4]_2[MgCl_4] + [Mg(THF)_6][BF_4]_2 \end{array} \qquad (6)$$

The stoichiometry shows that when $[Mg(R)X(THF)_n]$ is mixed with $[NBu_4]^+$ in a 2/1 molar ratio, 1/4 of the initial amount of magnesium should have been liberated as compound IV. It was found, however, that only compound IV was formed with yield 36% (reaction 6). However, when $[NBu_4][BF_4]$ was used for the reaction, in a molar ratio 1/1 and higher, the yield of IV increased to 90%. The question then arose, why the double excess of $[NBu_4][BF_4]$ was required to isolate IV from Grignard reagent. At present there is no immediate answer. The $[NBu_4][BF_4]$ salt in solution exists in the ionic form and could also be "utilized" to stabilize ions produced by the dissociation of $[MgR_2(THF)_2]$:

$$2[MgR_2(THF)_2] \overset{THF}{\rightleftharpoons} [MgR(THF)_5]^+ + [MgR_3]^- \qquad (7)$$

$[MgR_2(THF)_2]$ in THF is monomeric [10]. Its ionization state is small [1]. However, the number of ions in solution can be increased by addition of 2,2,1-cryptand, which results in formation of $[MgR(cryptand)][R_2Mg(\mu\text{-}R_2)MgR_2]$ when $R = C_2H_5$. However, when R = neopentyl (Np), the $[MgNp(cryptand)]^+$ and $[MgNp_3]^-$ ions result [11,12]. $[MgR_3]^-$ either dimerizes to give $[R_2Mg(\mu\text{-}R)_2MgR_2]^-$ anion, or associates with $[MgR_2(THF)_2]$ to give $[Mg_2R_5]^-$ anion.

The reaction of $[NBu_4][BF_4]$ with $[MgCl_2(THF)_2]$ gave the compound $[NBu_4]_2[MgCl_4]$ (IV) (eq. 5) which was isolated from the post-reaction mixture in 70% yield at 243 K. Its structure was determined by X-ray crystallography [8]. The studies revealed that the compound IV crystallized with two solvate THF molecules: $[NBu_4]_2[MgCl_4] \cdot 2THF$. From the stoichiometry of eq. 5 it follows that besides IV $[Mg(THF)_6][BF_4]_2$ should also be formed. The ease of reaction raises the question; what is the driving force behind this reaction? $[NBu_4]^+$ cation exists only in the ionic form and its direct interaction with bis(tetrahydrofuran)magnesium dichloride was not expected. Theoretically, the $[BF_4]^-$ anion could form different compounds with Mg^{2+}, e.g. $[(THF)_4Mg(\mu\text{-}Cl)_2BF_2]$, etc. Such a possibility, however, was excluded by ^{19}F NMR spectroscopy. The spectrum shows only one signal from free $[BF_4]^-$ anion, and another weaker one most likely from its interaction with THF [13]. This indicates that the course of reaction 5 can thus be explained only as the ionization of $[MgCl_2(THF)_2]$ in THF. Analogous to $[MgR_2(THF)_2]$ that process can be written as follows:

$$2[MgCl_2(THF)_2] \rightleftharpoons [MgCl(THF)_5]^+ + [MgCl_3]^- \rightleftharpoons [Mg(THF)_6]^{2+} + [MgCl_4]^{2-} \qquad (8)$$

The conductivity of $[MgCl_2(THF)_2]$ in THF is low and equal to 0.5 μS. This is indicative of a small amount of ion in solution. Addition to bis(tetrahydrofuran)magnesium dichloride $[NBu_4][BF_4]$ in THF results in precipitation of the least soluble ionic compound $[NBu_4]_2[MgCl_4]$ (IV) followed by a shift in equilibrium of reactions 5 and 8 to the right. Equation 8 shows the simplified situation. The ions which remain in solution would then react mutually and/or with substrate [7,14].

$$\left.\begin{array}{l} [Mg(THF)_6]^{2+} + 3[MgCl_2(THF)_2] \\ 2[MgCl(THF)_5]^+ + 2[MgCl_2(THF)_2] \\ 2[Mg(THF)_6]^{2+} + 2[MgCl_3]^- \end{array}\right] \longrightarrow 2[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+ \qquad (9)$$

To find out whether reaction 5 is reversible, dioxane was added with stirring to the post-reaction mixture containing the precipitate, compound IV. A stoichiometric amount of $[MgCl_2(C_4H_8O_2)]_2$ was obtained, i.e. the effect of dioxane was such that the equilibrium of reaction 5 was shifted completely to the left. However, when $[NBu_4]_2[MgCl_4] \cdot 2THF$ (70%) was isolated from the reaction mixture first and then dioxane added, the remaining 30% of compound formed $[MgCl_2(C_4H_8O_2)_2]$. That compound IV was obtained only in 70% yield could indicate that $[MgCl_4]^{2-}$ and $[Mg(THF)_6]^{2+}$ ions in solution interact mutually and produce another species. Cyclic voltammetric studies of $[MgCl_2(THF)_2]/[NBu_4][BF_4]$ solution in THF show two irreversible cathodic waves of about −2.0 and −0.48 V [13]. The former corresponds most likely to the reduction of $[MgCl_4]^{2-}$, however the latter does not correspond to $[Mg(THF)_6]^{2+}$, this follows from a comparison of the $E_{1/2}^{red}$ values obtained for complex I and $[Mg(THF)_6][MoOCl_4(THF)]_2$ [14]. These studies confirm the existence of the other magnesium species in solution, besides that of $[MgCl_4]^{2-}$. These species, as indicated by comparison of the obtained $E_{1/2}$ values should be different from those reported here. So the $[Mg(THF)_6]^{2+}$ cation is formed after addition of dioxane to the post-reaction mixture, and after IV has been separated off. The ^1H NMR results reveal that the THF molecules in $[Mg(THF)_6]^{2+}$ cation do not undergo substitution with dioxane. This is consistent with their donor number values, for dioxane it is 14.8 – somewhat lower than that for tetrahydrofuran 20.0 [15]. The results of the reaction with dioxane support the existence of the equilibrium given by eqs. 5 and 8. The compound $[MgCl_2(C_4H_8O_2)]_2$ which is less soluble than IV, separates from the solution causing a complete shift of the reaction equilibrium to the left. Formation of $[MgCl_2(C_4H_8O_2)_2]$ means that some replacement of THF by dioxane has occurred in bis(tetrahydrofuran)magnesium dichloride.

$$[MgCl_2(THF)_2] + 2\ C_4H_8O_2 \rightarrow [MgCl_2(C_4H_8O_2)_2] + 2THF \qquad (10)$$

The addition of dioxane always results in formation of the bis(dioxane)magnesium dichloride, which is independent of the environment of magnesium atom (eq. 11).

$$\text{I (II or III)} + 2C_4H_8O_2 \xrightarrow{THF} [TiCl_4(THF)_2] + [MgCl_2(C_4H_8O_2)_2] \qquad (11)$$

These reactions were found to produce $[TiCl_4(THF)_2]$ as well. It did not contain coordinated dioxane molecules, as was deduced from ^1H NMR spectroscopy. The course of reaction 11 revealed that formation of $[MgCl_2(C_4H_8O_2)_2]$ in solution does not require the presence of $MgCl_2$. That conclusion in our opinion is most important for a greater understanding of Grignard reagent composition and the existence of a Schlenk equilibrium. Up to now studies on Grignard reagents were focused on attempts to show the existence of Mg(R)X, its degree of association, and the existence of a Schlenk equilibrium, by mixing MgX_2 with MgR_2 [1–3].

The data reported here tend to refute the idea of the "Schlenk equilibrium". That idea is, in our opinion, erroneous because it suggests the simultaneous existence of MgR_2 and MgX_2 in solution. However, results of studies on $[MgCl_2(THF)_2]$ reactivity in THF did not show the existence of that compound in the presence of Lewis acid or $[NBu_4]^+$ cation. With the transition metal chlorides it forms compounds I–III, VI and other compounds [7,14]. In all these reactions bis(tetrahydrofuran)magnesium dichloride is the Cl^- donor, and $MgCl^+$ the acceptor. Evidence for the existence of the Schlenk equilibrium is given by the reaction with dioxane leading to the formation of $[MgCl_2(C_4H_8O_2)_2]$, together with $[MgR_2(THF)_2]$. Furthermore reaction 11 also reveals that $MgCl_2$ in solution is not necessary for the formation of $[MgCl_2(C_4H_8O_2)_2]$. The reaction with $[NBu_4][BF_4]$ salt could also confirm the equilibrium in the Grignard reagent (eq. 12):

$$4[Mg(R)X(THF)_n] \rightleftharpoons 2[MgR_2(THF)_2] + [MgCl_4]^{2-} + [Mg(THF)_6]^{2+} \quad (12)$$

It seems rather impossible that $[MgCl_2(THF)_2]$ should exist in the Grignard reagent as the free species, because of its reactivity. Rather, it should react with $[Mg(R)X(THF)_n]$ and with $[MgR_2(THF)_2]$, and for that reason we believe that the Grignard reagent constitution would be better described by eq. 13:

$$4[Mg(R)X(THF)_n] \rightleftharpoons [(THF)_4Mg(\mu\text{-}Cl)_2MgR_2] + [RMg_2(\mu\text{-}Cl)_3(THF)_5] \quad (13)$$

The supposition that $[MgR_2(THF)_2]$ with $[MgCl_2(THF)_2]$ should produce the $[(THF)_4Mg(\mu\text{-}Cl)_2MgR_2]$ type compound, was supported by the structure of $[(THF)_4Mg(\mu\text{-}Cl)_2FeCl_2]$ [9] and $[(THF)_4Mg(\mu\text{-}Cl)_2TiCl_4]$, [7] obtained by reaction of bis(tetrahydrofuran)magnesium dichloride with the appropriate iron and titanium chlorides. Similar structures have been postulated elsewhere [1–3]. The existence of the $[RMg_2(\mu\text{-}Cl)_3(THF)_5]$ adduct is accounted for by the readiness of formation of the $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+$ cation. In the past four years four compounds containing the latter have been reported [7,16–18]. The cation tri-μ-chlorohexakis(tetrahydrofuran)dimagnesium(II) is also formed in the reaction of the Grignard reagent, $[TiCl_3(THF)_3]$ and diphenylacetylene [17]. $[RMg_2(\mu\text{-}Cl)_3(THF)_5]$ probably undergoes dimerization to yield $[EtMg_2Cl_3(THF)_3]_2$ [19,20].

The equilibrium in eq. 13 comprises only the main compounds in solution. Each of them undergoes ionization, which was indicated by conductivity measurements of the Grignard reagents.

The equilibrium attained in solution would depend upon the least soluble species formed in solution with a given substrate.

All results presented here were obtained exclusively for $X = Cl$ in MgX_2 in THF solutions. So then the question arose, whether the conclusions should apply to the diethyl ether solutions and for $X = Br$. Up to now we have stated that $[MgBr_2(THF)_2]$ formed the $AlMgBr_5(THF)_6$, and a similar compound in Et_2O. Hence it follows that $MgBr_2$ present in the Grignard reagent undergoes subsequent reactions, which are the subject of our present investigations.

Experimental

All reactions were carried out under dinitrogen using dry solvent and conventional Schlenk techniques. Tetrahydrofuran was distilled under N_2 from sodium and benzophenone. $[MgCl_2(THF)_2]$, $[TiCl_4(THF)_2]$ and compounds I, II and III were prepared by published procedures [21,22,7]. ^1H and ^{19}F NMR measurements were recorded on a JEOL JNM-PS-100 spectrometer in $CDCl_3$ and THF-d_8. Microanalyses were performed at the University of Wrocław.

Reaction of bis(tetrahydrofuran)magnesium dichloride with tetra-n-butylammonium tetrafluoboride. Preparation of $[NBu_4]_2[MgCl_4] \cdot 2THF$

$[MgCl_2(THF)_2]$, 2.5 g (10 mmol) was dissolved under N_2 in 40 cm^3 THF and mixed with $[NBu_4][BF_4]$, 3.3 g (10 mmol) dissolved in 20 cm^3 THF, and stirred for 1 h. Next the solution was placed in a freezer (243 K). After 24 h the colourless crystals were filtered off. Yield: 2.8 g (70%).

Reaction of Grignard reagent with tetra-n-butylammonium tetrafluoroboride

A mixture of 3 g magnesium turnings (0.12 mmol) and 5.5 cm^3 PrCl in 100 cm^3 THF was boiled under reflux. After 4 h the solution was decanted, 20.5 g $[NBu_4][BF_4]$ was added under N_2 and then stirred for 1 h and placed in a freezer (243 K). After 24 h the colourless crystals which separated were filtered off.

Yield 8.2 g (90%). Results of elemental analysis and properties of the compound obtained are identical to those of $[NBu_4]_2[MgCl_4] \cdot 2THF$, whose crystallographic structure is described in ref. 8. Results identical to PrCl were obtained with EtCl and BuCl.

Reactions with dioxane

(a) A mixture of $[MgCl_2(THF)_2]$, 2.5 g (10 mmol) and $[NBu_4][BF_4]$, 3.3 g (10 mmol) was dissolved in 60 cm^3 THF. After 24 h, when the $[NBu_4]_2[MgCl_4] \cdot 2THF$ had precipitated, an excess of dioxane was added to the solution and stirred. The white precipitate which settled was dried, and washed (3×15 cm^3) with THF and identified as $[MgCl_2(C_4H_8O_2)_2]$ from elemental analysis.

(b) A mixture of $[MgCl_2(THF)_2]$, 2.5 g (10 mmol) and $[NBu_4][BF_4]$, 3.3 g (10 mmol) dissolved in 60 cm^3 THF was placed in a freezer (243 K). After 24 h the precipitate was filtered off. (Yield 2.8 g (70%)). To the filtrate was added an excess of dioxane. The white precipitate which immediately settled was formulated as $[MgCl_2(dioxane)_2]$. Yield 1.2 g (30%). The filtrate was evaporated under vacuo to dryness, then dissolved in $CDCl_3$ and examined by ^1H NMR spectroscopy.

(c) The compounds I, II or III (10 mmol) were treated individually with an excess of dioxane in 50 cm^3 THF. The white precipitate which formed was filtered off and washed with THF (3×15 cm^3). In all cases the elemental analysis showed it to be $[MgCl_2(C_4H_8O_2)_2]$. The filtrate was evaporated under vacuo to dryness. The residue was treated with $CDCl_3$ and examined by ^1H NMR spectroscopy.

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