

### Preliminary communication

---

## REACTION OF GRIGNARD REAGENT WITH TETRA-N-BUTYLAMMONIUM CATION. THE FORMATION OF $[\text{Mg}(\text{THF})_6]^{2+}$ , $[\text{Mg}_2(\mu\text{-Cl})_3(\text{THF})_6]^+$ AND $[\text{MgCl}_4]^{2-}$ IONS

PIOTR SOBOTA

*Institute of Chemistry, University of Wrocław, 14, Joliot-Curie, 50-383 Wrocław (Poland)*

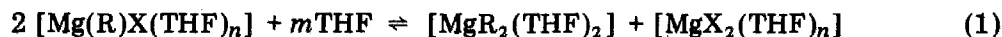
(Received April 23rd, 1985)

### Summary

Bis(tetrahydrofuran)magnesium dichloride  $[\text{MgCl}_2(\text{THF})_2]$ , the component of the Grignard reagent, reacts with  $[\text{NBu}_4]^+$  to produce  $[\text{MgR}_2(\text{THF})_2]$ ,  $[\text{NBu}_4]_2[\text{MgCl}_4] \cdot 2\text{THF}$  and  $[\text{Mg}(\text{THF})_6]^{2+}$  cations. The results indicate that the  $[\text{Mg}_2(\mu\text{-Cl})_3(\text{THF})_6]^+$  cation was the intermediate product in the formation process of hexakis(tetrahydrofuran)magnesium(II) and tetrachloromagnesium(II).

---

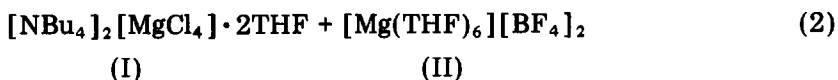
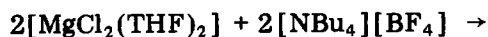
The nature of Grignard reagents in solution is not simple. They exist in an equilibrium mixture which may involve various mono-, bi- and poly-nuclear solvated compounds [1,2]. The primary equilibrium, known generally as the Schlenk equilibrium [3] is expressed simply, e.g. in tetrahydrofuran (THF), eq. 1 [4].



(where  $n = 2-3$ , and  $m = 0-2$ )

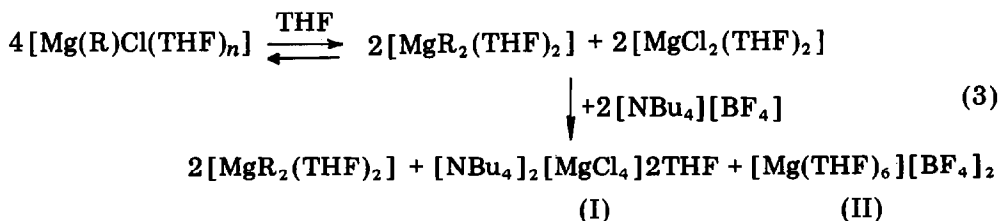
This was initially proposed on the basis of dioxane precipitation of  $\text{MgX}_2$ . To precipitate  $\text{MgX}_2$ , diglyme [5] and pyridine [6] have also been used. Hence, it is possible to use this method, via Schlenk equilibrium, as a synthetic route for  $\text{MgR}_2$ . For this reason it was interesting to examine the behaviour of  $\text{MgX}_2$  in ethers. Recent studies indicate that  $[\text{MgCl}_2(\text{THF})_2]$  in THF reacts easily with compounds which exhibit Lewis acid properties, e.g.  $\text{MCl}_n$  ( $M = \text{transition metal}$ ). Such reactions produce the complexes of molecular formulae  $[\text{Cl}_2\text{Fe}(\mu\text{-Cl})_2\text{Mg}(\text{THF})_4]$  [7],  $[\text{Cl}_4\text{Ti}(\mu\text{-Cl})_2\text{Mg}(\text{THF})_4]$  [8], and ionic  $[\text{Mg}_2(\mu\text{-Cl})_3(\text{THF})_6][\text{TiCl}_5\text{THF}]$  [9],  $[\text{Mg}_2(\mu\text{-Cl})_3(\text{THF})_6][\text{MoOCl}_4\text{THF}]$  [10] and  $[\text{Mg}(\text{THF})_6][\text{MoOCl}_4\text{THF}]_2$  [10]. Bis(tetrahydro-

furan)magnesium dichloride reacts not only with the Lewis acids, but also with cations [11], e.g.  $[\text{NBu}_4]^+$  eq. 2,



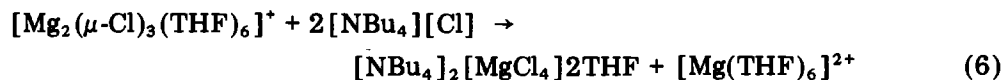
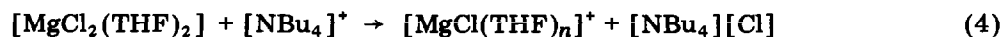
In this reaction the magnesium atom exhibits amphoteric behaviour, since  $[\text{MgCl}_2(\text{THF})_2]$  is both donor and acceptor of  $\text{Cl}^-$  and the  $[\text{Mg}(\text{THF})_6]^{2+}$  and  $[\text{MgCl}_4]^{2-}$  ions are formed.

It was interesting to find out whether  $[\text{MgCl}_2(\text{THF})_2]$  in Grignard reagent would behave as in reaction 2, and whether the Schlenk equilibrium could be shifted by means of  $[\text{NBu}_4][\text{BF}_4]$ . It was expected that addition of  $[\text{NBu}_4][\text{BF}_4]$  to the Grignard reagent would result in liberation of compound I and only  $[\text{MgR}_2(\text{THF})_2]$  and compound II would remain in the post-reaction mixture, eq. 3:



The equation's stoichiometry shows that upon mixing  $[\text{Mg}(\text{R})\text{Cl}(\text{THF})_n]$  with  $[\text{NBu}_4]^+$  in a 2/1 molar ratio, 1/4 of the initial amount of magnesium in  $[\text{Mg}(\text{R})\text{Cl}(\text{THF})_n]$  will be liberated as compound I.

As a result of reaction 3 it was found that in such conditions the yield of compound I was 36% [12]. However, when  $[\text{NBu}_4][\text{BF}_4]$  was used for the reaction, in a molar ratio of 1/1 and higher, the yield of I increased to 95%. Solubility of compound I in THF is low. This compound could also be isolated from the products of reaction 2 with 95% yield at 243 K [11]. It is evident, that at high  $[\text{NBu}_4]^+$  excess the equilibrium was shifted to the right. We failed to isolate pure  $[\text{MgR}_2(\text{THF})_2]$  from the post-reaction mixture of reaction 3. When the post-reaction remains were evaporated to dryness and extracted with benzene, traces of  $[\text{Mg}(\text{R})\text{Cl}(\text{THF})_n]$  and compound II were found in solution as well as  $[\text{MgR}_2(\text{THF})_2]$ . Formation of compounds I and II during reactions 2 and 3, together with the results of our previous investigations [10] suggest the following reaction pathways, eqs. 4, 5 and 6:



(I)

The tri- $\mu$ -chlorohexakis(tetrahydrofuran)dimagnesium(II) cation is also formed in the reaction of the hexakis(tetrahydrofuran)magnesium(II) cation with bis(tetrahydrofuran)magnesium dichloride eq. 7, [10].



The structure of the  $[\text{Mg}(\text{THF})_6]^{2+}$ ,  $[\text{Mg}_2(\mu\text{-Cl})_3(\text{THF})_6]^+$  cations and the  $[\text{MgCl}_4]^{2-}$  anion was confirmed crystallographically [10,11].

Attempts to prove the presence of the  $[\text{MgCl}(\text{THF})_n]^+$  cation failed, nevertheless, further attempts were undertaken. Non-published crystallographic studies of the compound of general formula  $\text{MgCl}(\text{THF})_6$  show that  $[\text{Mg}(\text{THF})_6]^{2+}$  cations are building blocks of the compound. The overall packing is of the fluorite type structure. The  $\text{Cl}^-$  and  $\Gamma^-$  anions are irregularly distributed in the lattice and for that reason the problem was not definitely settled [13]. The structure of the postulated  $[\text{MgCl}(\text{THF})_n]^+$  cation requires further investigations. It is possible that the cation could have the structure  $[\text{Mg}(\text{THF})_6]\text{Cl}^+$ .

$[\text{MgX}_2(\text{THF})_2]$  (when  $X = \text{Br}$  or  $\text{I}$ ) does not react with  $[\text{NBu}_4]^+$ , probably due to the stronger covalent character of the  $\text{Mg}-\text{Br}$  and  $\text{Mg}-\text{I}$  bonds, than of the  $\text{Mg}-\text{Cl}$  bond. For that reason reactions according to eq. 3, for  $[\text{Mg}(\text{R})\text{X}(\text{THF})_n]$  ( $X = \text{Br}, \text{I}$ ), proceed in a different way.

## References

- 1 E.C. Ashby, *Quart. Rev.*, 21 (1967) 259.
- 2 W.E. Lindsell, 'Comprehensive Organometallic Chemistry' Vol. 1 Pergamon Press 1982.
- 3 W. Schlenk and W. Schlenk, *Chem. Ber.*, 62 (1929) 920.
- 4 R. Petlaud, P. Claudy and Q.T. Pham, *Eur. Polym. J.*, 12 (1976) 441.
- 5 K. Nutzel and Houben-Weyl, 'Methoden der Organische Chemie Vol. 13/2a, Metallorganische Verbindungen Be, Mg, Ca, Sr, Ba, Zn, Cd' Thieme Verlag, Stuttgart, 1973.
- 6 G.J. Dubsy and A. Jacot-Guillarmod, *Helv. Chim. Acta*, 52 (1969) 1735.
- 7 P. Sobota, T. Pluziński and Lis, *Polyhedron* 3 (1984) 45.
- 8 J.C.J. Bart, I.W. Bassi, M. Calcaterra, E. Albizzati, U. Giannini and S. Parodi, *Z. Anorg. Allg. Chem.*, 482 (1981) 121; 496 (1983) 205, P. Sobota and Z. Janas, *J. Organomet. Chem.*, 276 (1984) 171.
- 9 P. Sobota, J. Utko and T. Lis, *J. Chem. Soc. Dalton Trans.*, (1984) 2077.
- 10 P. Sobota, T. Pluziński and T. Lis, *J. Chem. Soc. Dalton Trans.*, in press.
- 11 P. Sobota, T. Pluziński and T. Lis, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.*, in press.
- 12 3 g magnesium turnings, 5.5 cm<sup>3</sup>  $\text{PrCl}$  in 100 cm<sup>3</sup> THF were boiled under reflux. After 4 h the solution was decanted, 20.5 g  $[\text{NBu}_4][\text{BF}_4]$  was added under  $\text{N}_2$ , and stirred for 1 h. Next the solution was placed in a freezer (243 K). After 24 hrs the colourless crystals were filtered off (8.6 g yield 95%). Results of elemental analysis and properties of the compound obtained are identical to those of  $[\text{NBu}_4]_2[\text{MgCl}_4]_2\text{THF}$ , whose crystallographic structure was described in Ref. 11. Identical results to  $\text{PrCl}$  were obtained with  $\text{EtCl}$  and  $\text{BuCl}$ .
- 13 P. Sobota and G. Huttner, unpublished results.