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Constitution of Grignard Reagent RMgCl in Tetrahydrofuran

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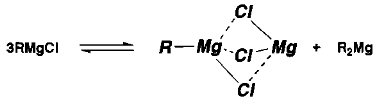
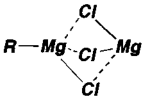
ABSTRACT



The constitution of Grignard reagent, RMgCl (R = Me, *t*Bu, Ph or benzyl), was investigated in the solid state by means of X-ray crystallography and in THF by coldspray ionization mass spectrometry (CSI-MS). Three types of crystal structures, (a) $[Mg_2(\mu\text{-}Cl_3)(THF)_6]^+\cdot[RMgCl_2(THF)]^-$, (b) $R_2Mg_4Cl_6(THF)_6$, and (c) $[2Mg_2(\mu\text{-}Cl_3)(THF)_6]^+\cdot[R_4Mg_2Cl_2]^{2-}$, were identified, and $MeMg_2(\mu\text{-}Cl_3)(THF)_{4-6}$ were detected as major species of MeMgCl in solution.

Investigation of the constitution of Grignard reagents[1] in solution has been extremely challenging. Although the Schlenk equilibrium[2] is generally accepted to interpret the structure of RMgX, our knowledge of the real species in solution is still limited. In this paper, we present evidence suggesting that $RMg_2(\mu\text{-}Cl_3)$ is the dominant species in the case of RMgCl in THF solution.



$RMg_2(\mu\text{-}Cl_3)$

In 1963, Ashby and Becker suggested this constitution on the basis of a gas evolution analysis.[3a] Tony and Stucky also predicted the existence of this structure in solution from X-ray diffraction data in 1971.[4] A crystallographic study involving $Mg_2(\mu\text{-}Cl_3)$ species was reported by Sobota and Duda in 1987.[5] However, in all cases the evidence was rather indirect. Therefore, we have precisely investigated the constitution of RMgCl by means of X-ray crystallography and coldspray ionization mass spectrometry (CSI-MS),[6] a variant of electrospray (ESI)[7] MS operating at low temperature, which has been used to characterize solution structures of various self-assembling metal complexes.[8]

Three types of crystal structures were characterized by X-ray analysis[9] (Figure 1): (a) $[Mg_2(\mu\text{-}Cl_3)(THF)_6]^+\cdot[RMgCl_2\text{-}(THF)]^-$ (R = *t*Bu and Ph) obtained from *t*BuMgCl(THF) and PhMgCl(THF), (b) $R_2Mg_4Cl_6(THF)_6$ (R = Me, *t*Bu, and benzyl) from MeMgCl(THF), *t*BuMgCl(THF), and benzylMgCl(THF), and (c) $[2Mg_2(\mu\text{-}Cl_3)(THF)_6]^+\cdot[R_4Mg_2Cl_2]^{2-}$ (R = Ph) obtained from PhMgCl(THF).

The crystal structure of (a) consists of a pair of ionic species. The cationic species contains three Cl atoms bridging

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(1) (a) Wakefield, B. J. *Organomagnesium Methods in Organic Synthesis*; Academic Press: London, 1995. (b) Silverman, G. S.; Rakita, P. E. *Handbook of Grignard Reagents*; Marcel Dekker: New York, 1996.

(2) Schlenk, W.; Schlenk, W., Jr. *Ber. Dtsch. Chem. Ges*. **1929**, *62*, 920−924.

(3) (a) Ashby, E. C.; Becker, W. E. *J. Am. Chem. Soc.* **1963**, *85*, 118−119. (b) Ashby, E. C.; Smith, M. B. *J. Am. Chem. Soc.* **1964**, *86*, 4363−4370.

(4) Tony, J.; Stucky, G. D. *J. Organomet. Chem.* **1971**, *28*, 5−20.

(5) Sobota, P.; Duda, B. *J. Organomet. Chem.* **1987**, *332*, 239−245.

(6) Sakamoto, S.; Fujita, M.; Kim, K.; Yamaguchi, K. *Tetrahedron* **2000**, *56*, 955−964.

(7) (a) Yamashita, M.; Fenn, J. B. *J. Phys. Chem.* **1984**, *88*, 4451−4459. (b) Fenn, J. B.; Mann, M.; Meng, K.; Wong, S. F.; Whitehouse, C. M. *Science* **1989**, *246*, 64−71. (c) Kebarle, P.; Tang, L. *Anal. Chem.* **1993**, *65*, 972A−986A. (c) Bruins, A. P. *J. Chromatogr. A* **1998**, *794*, 345−357.

(8) (a) Ikeda, A.; Ayabe, M.; Shinkai, S.; Sakamoto, S.; Yamaguchi, K. *Org. Lett.* **2000**, *2*, 3707−3710. (b)Yamanoi, Y.; Sakamoto, Y.; Kusukawa, T.; Fujita, M.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **2001**, *123*, 980−981. (c) Zhong, Z.; Ikeda, A.; Ayabe, M.; Shinkai, S. Sakamoto, S.; Yamaguchi, K. *J. Org. Chem.* **2001**, *66*, 1002−1008.

(9) Single crystals were obtained from MeMgCl, *t*BuMgCl, PhMgCl, and benzylMgCl in THF by addition of dry hexane (10% vol) to a 4−5 M solution under argon in a Schlenk tube. These single crystals were enclosed in a capillary tube under nitrogen in a glovebox. A Bruker SMART CCD diffractometer or Rigaku RAXISIIC imaging plate diffractometer was used.

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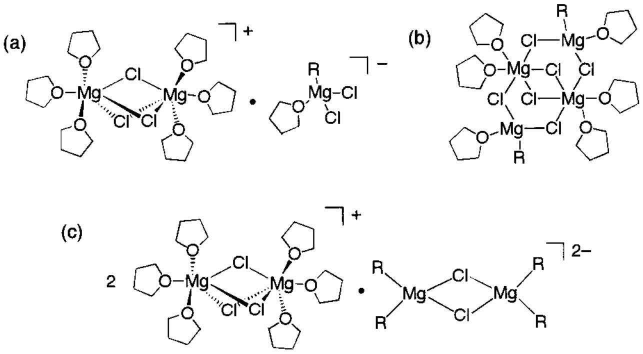

Figure 1. Crystal structures of (a) $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+\cdot[RMgCl_2(THF)]^-$, (b) $R_2Mg_4Cl_6(THF)_6$, and (c) $[2Mg_2(\mu\text{-}Cl)_3(THF)_6]^+\cdot[R_4Mg_2Cl_2]^{2-}$.

two Mg atoms and three THF molecules coordinated to each Mg atom via oxygen.[10] As the anionic species, a quaternary coordinated Mg atom with an alkyl or aryl (R = *t*Bu[11] and Ph[12]) moiety, two Cl atoms, and a THF oxygen was observed.

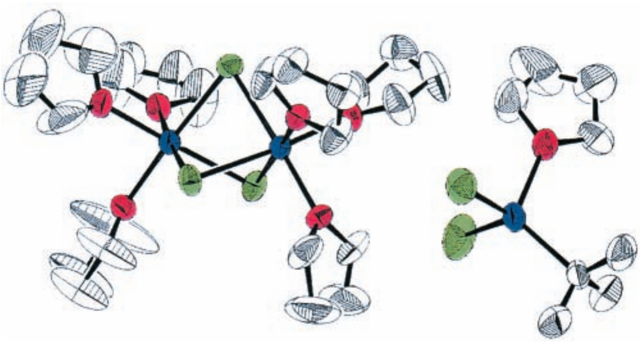

Figure 2. ORTEP drawing of $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+\cdot[t\text{Bu}MgCl_2(THF)]^-$: Mg, blue; Cl, green; and O, red.

The unit crystal structure of (b) includes four Mg atoms. Two quaternary coordinated Mg atoms with an alkyl or aryl (R = Me,[13] *t*Bu[14], and benzyl[15]) moiety, two Cl atoms, and a THF oxygen were observed, together with two hexacoordinated Mg atoms bearing four Cl atoms and two THF oxygens.[16] The crystal structure of (c) contains a cationic species identical with that of (a),[17] $[Mg_2(\mu\text{-}Cl_3)(THF)_6]^+\cdot[RMgCl_2]^-$, and a dianionic species with two Cl atoms bridging two Mg atoms and two phenyl groups coordinated with each Mg atom. No solvent molecules were seen in this case.[18]

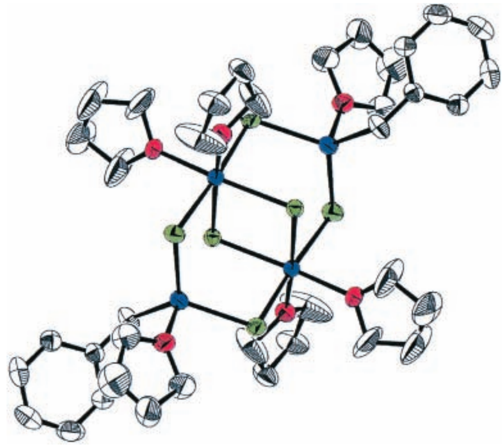

Figure 3. ORTEP drawing of $\text{benzyl}_2Mg_4Cl_6(THF)_6$: Mg, blue; Cl, green; and O, red.

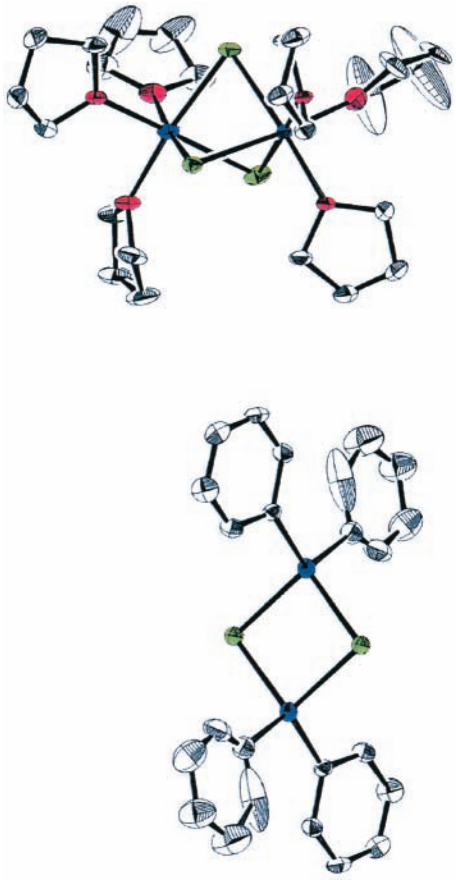

Figure 4. ORTEP drawing of $[2Mg_2(\mu\text{-}Cl)_3(THF)_6]^+\cdot[Ph_4Mg_2Cl_2]^{2-}$: Mg, blue; Cl, green; and O, red.

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[10] The Mg−Mg distances are 3.169(3) and 3.192(6) Å in the cases of *t*BuMgCl and PhMgCl, respectively. These distances are significantly shorter than the sum of two magnesium radii (3.46 Å), even though these Mg atoms probably repel each other owing to their positive charges.

[11] Crystal data of $[Mg_2(\mu\text{-}Cl_3)(THF)_6]^+\cdot[t\text{Bu}MgCl_2(THF)]^-$: MW = 812.04, triclinic, $P\bar{1}$; $a = 9.8522(7)$ Å, $b = 14.8274(11)$ Å, $c = 16.0742(11)$ Å; $\alpha = 92.6460(10)°$, $\beta = 96.0950(10)°$, $\gamma = 104.7020(10)°$; $V = 2252.6(3)$ Å^3, $Z = 2$, $d_{calc} = 1.197$ g cm^{-3}, $T = 296$ K, μ(Mo Kα) = 4.01 cm^{-1}, 4887 observed reflections ($I > 2.0\sigma(I)$), 455 variables, $R = 0.089$, $R_w = 0.124$.

[12] Crystal data of $[Mg_2(\mu\text{-}Cl_3)(THF)_6]^+\cdot[PhMgCl_2(THF)]^-$: MW = 832.03, triclinic, $P\bar{1}$; $a = 9.462(3)$ Å, $b = 13.537(4)$ Å, $c = 18.129(5)$ Å; $\alpha = 104.975(4)°$, $\beta = 91.272(4)°$, $\gamma = 90.973(4)°$, $V = 2242.0(9)$ Å^3, $Z = 2$, $d_{calc} = 1.232$ g cm^{-3}, $T = 296$ K, μ(Mo Kα) = 4.05 cm^{-1}, 2439 observed reflections ($I > 3.0\sigma(I)$), 442 variables, $R = 0.109$, R_w =0.145.

These crystal structures do not necessarily reflect the state in solution, because *n*-hexane was added to the solution in order to obtain the single crystals. However, it is reasonable to presume that the cation, $Mg_2(\mu\text{-}Cl_3)$, observed in three crystals, is a key player.[19] This would be consistent with the existence of $RMg_2(\mu\text{-}Cl_3)(THF)_5$ as the major component of RMgCl in THF, as predicted by Ashby and Becker,[3] Tony and Stucky,[4] and Sobota and Duda.[5]

This idea was supported by the result of CSI-MS, which made it possible to elucidate dynamic solution structure as observed in NMR.[8b] In the mass spectrum of MeMgCl in THF solution (10 mM),[20] three major ion peaks, *m*/*z* 457, 529, and 601, were clearly observed (Figure 5). We examined the compositions of these ions, using tandem mass spectrometry (MS/MS) and compared the calculated and observed isotopic patterns. It is apparent that these species include plural solvent molecules and a Mg_2Cl_3 component. Therefore, the ions *m*/*z* 457, 529, and 601 obtained from MeMgCl were assigned as $[MeMg_2Cl_3(THF)_4\text{-}H]^+$, $[MeMg_2Cl_3(THF)_5\text{-}H]^+$ and $[MeMg_2Cl_3(THF)_6\text{-}H]^+$, respectively, pointing to the involvement of $MeMg_2(\mu\text{-}Cl_3)(THF)_{4-6}$. This supports the idea that $RMg_2(\mu\text{-}Cl_3)$ is a major species in the case of RMgCl in THF.

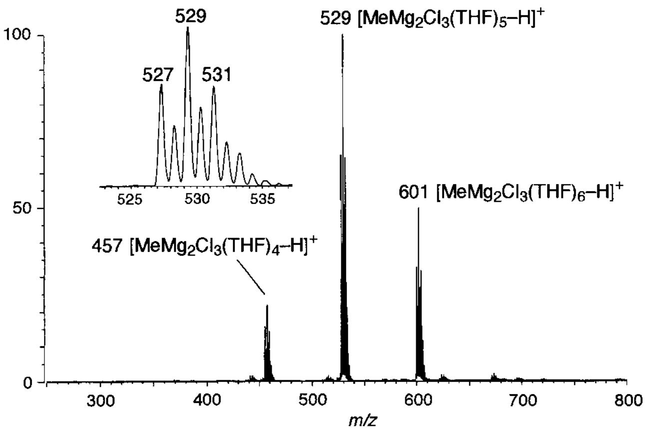

Figure 5. CSI-MS spectrum of MeMgCl in THF solution.

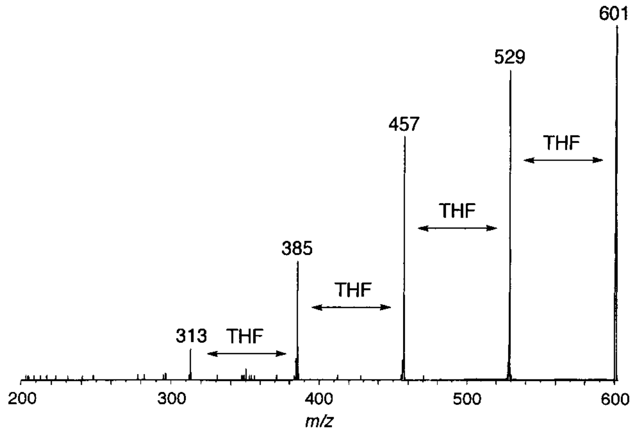

Figure 6. Product ion spectrum of *m*/*z* 601.

In summary, we investigated the constitution of RMgCl (R = Me, *t*Bu, Ph, and benzyl) in THF by means of X-ray crystallography. The cation $Mg_2(\mu\text{-}Cl_3)$ was directly observed in three crystals, suggesting that $RMg_2(\mu\text{-}Cl_3)(THF)_5$ might be a major species in solution. Direct CSI-MS measurement of MeMgCl in THF confirmed the presence of $MeMg_2(\mu\text{-}Cl_3)(THF)_{4-6}$.

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Supporting Information Available: CIF data for six compounds, and three ORTEP images, $[Mg_2(\mu\text{-}Cl_3)(THF)_6]^+\cdot[PhMgCl_2(THF)]^-$, $Me_2Mg_4Cl_6(THF)_6$ and $t\text{Bu}_2Mg_4Cl_6(THF)_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Crystal data of $Me_2Mg_4Cl_6(THF)_6$: MW = 772.65, triclinic, $P\bar{1}$; $a = 10.077(2)$ Å, $b = 10.782(2)$ Å, $c = 10.903(2)$ Å; $\alpha = 62.699(2)°$, $\beta = 78.682(3)°$, $\gamma = 75.456(3)°$; $V = 1014.3(2)$ Å^3, $Z = 1$, $d_{calc} = 1.265$ g cm^{-3}, $T = 296$ K, μ(Mo Kα) = 5.18 cm^{-1}, 2396 observed reflections ($I > 3.0\sigma(I)$), 191 variables $R = 0.074$, $R_w = 0.097$.

(14) Crystal data of $t\text{Bu}_2Mg_4Cl_6(THF)_6$: MW = 856.80, monoclinic, $P2_1/a$; $a = 10.919(8)$ Å, $b = 16.698(6)$ Å, $c = 12.615(4)$ Å; $\beta = 90.87(2)°$, $V = 2299(1)$ Å^3, $Z = 2$, $d_{calc} = 1.237$ g cm^{-3}, $T = 296$ K, μ(Mo Kα) = 4.63 cm^{-1}, 2721 observed reflections ($I > 3.0\sigma(I)$), 218 variables, $R = 0.097$, $R_w = 0.146$.

(15) Crystal data of benzyl$_2Mg_4Cl_6(THF)_6$: MW = 924.84, monoclinic, $P2_1/c$; $a = 13.821(2)$ Å, $b = 10.8321(12)$ Å, $c = 17.068(2)$ Å; $\beta = 107.825(2)°$, $V = 2432.6(4)$ Å^3, $Z = 2$, $d_{calc} = 1.263$ g cm^{-3}, $T = 296$ K, μ(MoKα) = 4.43 cm^{-1}, 2922 observed reflections ($I > 2.5\sigma(I)$), 245 variables, $R = 0.056$, $R_w = 0.074$.

(16) This is similar to $Et_2Mg_4Cl_6(THF)_6$ obtained from EtMgCl, which was previously analyzed by Tony and Stucky.

(17) The Mg−Mg distance was 3.151(3) Å.

(18) Crystal data of $[2Mg_2(\mu\text{-}Cl_3)(THF)_6]^+\cdot[Ph_4Mg_2Cl_2]^{2-}$: MW = 1603.16, triclinic, $P\bar{1}$; $a = 13.231(1)$ Å, $b = 13.263(1)$ Å, $c = 13.435(1)$ Å; $\alpha = 86.139(2)°$, $\beta = 70.006(2)°$, $\gamma = 67.025(2)°$; $V = 2033.8(3)$ Å^3, $Z = 1$, $d_{calc} = 1.309$ g cm^{-3}, $T = 123$ K, μ(Mo Kα) = 3.78 cm^{-1}, 4961 observed reflections ($I > 3.0\sigma(I)$), 443 variables $R = 0.081$, $R_w = 0.110$.

(19) The structures of three other crystals represented by the formulae $Me_2Mg_4Cl_6(THF)_6$, $t\text{Bu}_2Mg_4Cl_6(THF)_6$ and benzyl$_2Mg_4Cl_6(THF)_6$ suggest a dimeric form of $RMg_2(\mu\text{-}Cl_3)$.

(20) CSI-MS spectrum measurement was performed with a four-sector (BE/BE) tandem mass spectrometer (JMS-700T, JEOL) equipped with the CSI source. Typical measurement conditions are as follows: (CSI-MS) acceleration voltage, 5.0 kV; needle voltage, 2.8 kV; needle current, 300−700 nA; orifice voltage, 50 V; resolution (10% valley definition), 1000; sample flow, 33 μL/min; solvent, dry THF; concentration, 10 mmol/L; spray temperature, −20 °C; ion source temperature, 10 °C. (MS/MS) acceleration voltage, 5.0 kV; collision gas, Xe; collision cell voltage, 0 V.