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Access to the structures of fluoromagnesium compounds: synthesis and structural characterization of the β-diketiminato magnesium fluoride $[\{CH(CMeNAr)_2\}Mg(\mu\text{-}F)(THF)]_2\cdot toluene$

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Dedicated to Professor Wei-Yuang Huang on the occasion of his 80th birthday.

Abstract

β-Diketiminato magnesium fluoride $[\{CH(CMeNAr)_2\}Mg(\mu\text{-}F)(THF)]_2\cdot toluene$ (Ar = 2,6-i-$Pr_2C_6H_3$, **2**·toluene) was synthesized. The molecular structure of **2** revealed for the first time, the double fluoro bridge feature between the two magnesium atoms with a typical Mg–F bond length (average 1.95 Å). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Magnesium; Fluorides; β-Diketiminato ligands; Bischelating ligands

1. Introduction

Grignard reagents became indispensable for synthetic chemistry soon after they were reported in 1900. Throughout the past century numerous magnesium halide compounds LMgX (L = various organic substituents; X = Cl, Br, and I) have been synthesized, structurally characterized and used as active intermediates for diverse transformations. Nevertheless, it was nearly seven decades after the discovery of Grignard reagents that Ashby and co-workers managed to prepare fluoride congeners [1,2]. By spectroscopic investigation, Ashby and Yu deduced that the mobile Schlenk equilibrium used to describe organomagnesium chlorides, bromides and iodides in solution does not exist in the case of alkylmagnesium fluorides due to the unusual stability of Mg–F–Mg bridge bonds [3]. Accordingly, alkylmagnesium fluorides were believed to exist in either THF or diethyl ether as discrete dimers bound by a double fluoro bridge. Since then, little work related to fluoromagnesium compounds has been reported. As a structure-directing element [4], fluorine was instrumental in constructing several magnesium-containing bimetallic conglomerates, namely $[(MesInF_2)_{10}\text{-}MgF\cdot 5toluene]$ (Mes = 2,4,6-trimethylphenyl, **I**) [5], $K_x(Mg_xIn_{1-x})F_3$ ($x = 0.38$, **II**) [6], $[Cp^*_4Ti_4Mg_2F_{12}\cdot 7THF]$ ($Cp^* = C_5Me_5$, **III**) [7], and $[Na_3Mg(O_3PCH_2PO_3)(\mu\text{-}F)\cdot H_2O]$ (**IV**) [8]. However, unlike LMgX which had been intensively investigated by X-ray single crystal analysis, the solid structures of fluoride congeners, LMgF, were still beyond our discernment due mainly to the relatively inconvenient synthetic method and the difficulties to crystallize them. Herein, we report the synthesis and structural investigation of the β-diketiminato magnesium fluoride $[\{CH(CMeNAr)_2\}Mg(\mu\text{-}F)(THF)]_2\cdot toluene$ (Ar = 2,6-i-$Pr_2C_6H_3$), which gives an insight into the structures of LMgF type compounds.

2. Results and discussion

In the absence of coordinative solvents like THF or diethyl ether, the starting materials, alkylmagnesium β-diketiminates, $[\{HC(CMeNAr)_2\}MgR]_2$ (Ar = 2,6-i-Pr_2-C_6H_3 or 2,6-$Me_2C_6H_3$, R = Me or n-Bu) are preferentially dimeric as represented by $[\{CH(CMeNAr)_2\}Mg(\mu\text{-}\eta^1\text{-}Bu)]_2$ (Ar = 2,6-$Me_2C_6H_3$, **1**). Compound **1** was conventionally prepared from the reaction of [ArN = CMeCH = CMeNHAr] (Ar = 2,6-$Me_2C_6H_3$, **V**) with Bu_2Mg. The solubility of **1** in toluene is much lower than that of **V**. Therefore, crystalline **1** can be readily obtained by simply cooling slowly the hot toluene solution of **1** to room temperature. The crystal structure of **1** is shown in Fig. 1 and the bond lengths and

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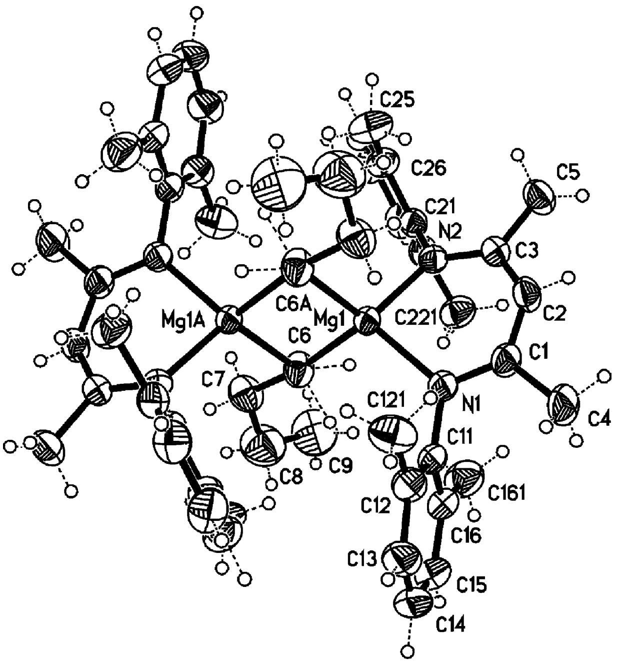


Fig. 1. Crystal structure of **1**.

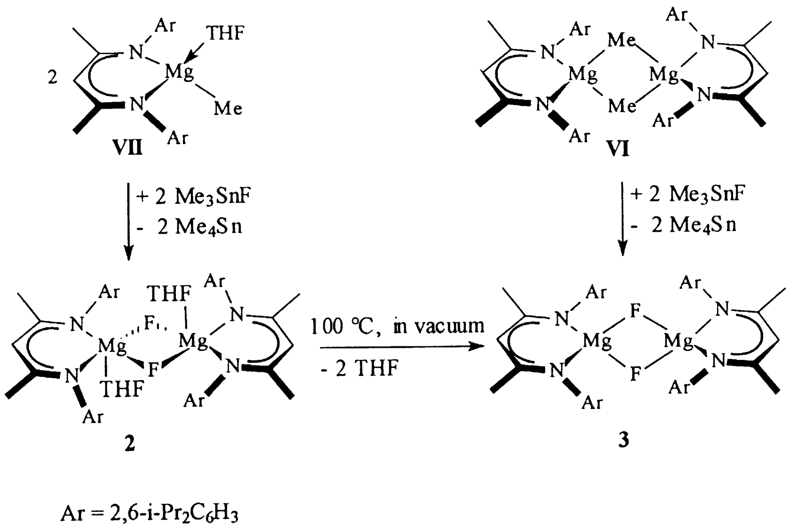
angles given in Table 1. The molecule of compound **1** is centrosymmetric with distortions from tetrahedral coordination at each magnesium center (angles in the range 93.52(9)–114.84(10)°, the most acute angle being associated with the bite of the β-diketiminato ligand). The average Mg–N bond length (2.05 Å) is comparable to these in $[\{HC(CMeNAr)_2\}Mg(\mu\text{-}Me)]_2$ (**VI**) and $[\{HC(CMeNAr)_2\}MgMe(THF)]$ (**VII**) (Ar = 2,6-i-$Pr_2C_6H_3$; Mg–N bond length: average 2.09 and 2.06 Å, respectively) [9,10], with a typical bond delocalization in the β-diketiminato backbone (N(1)–C(1) 1.333(3) Å, C(1)–C(2) 1.405(3) Å). The butyl groups bridge the two magnesium atoms in an η^1 fashion. The average Mg–C bond length (2.25 Å) is quite close to that in **VI** (2.24 Å). There is a large C–C–C angle deviation at C(7) and C(8) from the ideal sp^3 hybridization angle (C(8)–C(7)–C(6): 118.9(3)°; C(9)–C(8)–C(7): 119.8(4)°). While the bond lengths of C(6)–C(7) (1.531(4) Å) and C(7)–C(8) (1.511(5) Å) are typical for a C–C single bond, the C(8)–C(9) (1.420(6) Å) bond length is much shorter probably because the terminal C(9) methyl group is slightly disordered. The ^1H NMR spectrum supports fully the presence of the μ-Bu groups in **1**. The non-bonding Mg···Mg distance (2.7248(16) Å) is shorter than that in **VI** (2.8777(12) Å). The Mg–C–Mg and C–Mg–C angles are 74.45(9) and 105.56(9)°, respectively.

Table 1
Selected bond lengths (Å) and angles (°) for **1**

Mg(1)–N(2)	2.046(2)
Mg(1)–N(1)	2.054(2)
Mg(1)–C(6A)	2.251(3)
Mg(1)–C(6)	2.253(3)
Mg(1)–Mg(1A)	2.7248(16)
Mg(1)–C(7A)	2.858(3)
N(1)–C(1)	1.333(3)
N(1)–C(11)	1.444(3)
N(2)–C(3)	1.340(3)
N(2)–C(21)	1.439(3)
C(1)–C(2)	1.405(3)
C(2)–C(3)	1.403(4)
C(6)–C(7)	1.531(4)
C(7)–C8)	1.511(5)
C(8)–C(9)	1.420(6)
C(8)–C(7)–C(6)	118.9(3)
C(9)–C(8)–C(7)	119.8(4)
N(1)–Mg(1)–C(6A)	118.70(10)
N(2)–Mg(1)–N(1)	93.52(9)
N(2)–Mg(1)–C(6A)	114.94(10)
N(2)–Mg(1)–C(6)	111.47(10)
N(1)–Mg(1)–C(6)	112.58(10)
C(6A)–Mg(1)–C(6)	105.56(9)
Mg(1A)–C(6)–Mg(1)	74.45(9)
C(7)–C(6)–Mg(1)	170.4(2)
C(1)–C(2)–C(3)	129.3(2)

The alkyl metal complexes ligated by nitrogen donor ligands can serve as precursors to access some unprecedented fluorine compounds, as we showed in the case of molybdenum [11] and zinc [12]. The reaction of methyl magnesium diketiminate with Me_3SnF in toluene at room temperature for 48 h followed by concentration and crystallization from toluene afforded colorless crystals of $[\{CH(CMeNAr)_2\}Mg(\mu\text{-}F)(THF)]_2\cdot$toluene (Ar = 2,6-i-$Pr_2C_6H_3$, **2**·toluene), which were characterized by elemental analysis, EIMS, ^1H and ^{19}F NMR. Heating of **2**·toluene at 100 °C in vacuum for 4 h resulted in the elimination of the coordinated THF and the lattice toluene; this is indicated by ^1H NMR, and the change to the white powder $[\{CH(CMeNAr)_2\}Mg(\mu\text{-}F)]_2$ (**3**) (Scheme 1). The ^{19}F NMR resonance of **3** (−26 ppm) is comparable to that of **2** (−25 ppm), suggesting that coordinated THF had no substantial influence on the Mg–F bonding fashion in toluene solution. The EIMS spectra of **2** and **3** are similar. Both of them showed the peaks near 921, which were recognized as the molecular ion peaks of **3** by comparing with the computed isotope patterns. Compound **3** also can be readily synthesized from the fluorination reaction of **VI** with Me_3SnF in toluene (Scheme 1). The structure of **2** has been revealed by the X-ray single crystal analysis (Fig. 2). Selected bond lengths and angles are given in Table 2.

The structure of **2** shows that the centrosymmetric molecule adopts a distorted pyramidal geometry around magnesium. Oxygen is arranged at the top vertex with Mg(1)–O(30) bond length of 2.078(2) Å. The equatorial square is essentially planar formed by N(1), N(2), F(1) and F(1A) atoms, out of which the magnesium center is displaced by 0.03 Å. The Mg–N bond lengths (average 2.15 Å) in **2** are longer than that in **1** (average 2.05 Å), **VI** (average 2.09 Å) and **VII** (average 2.06 Å) [9,10], supposed to be a result of the strong electronegativity of fluorine. However, the Mg–F bond lengths (1.95 Å) are in the range of those reported in bimetallic clusters (1.90–2.03 Å) [5–8]. The Mg–O bond



Scheme 1.

oriented almost perpendicular to the plane defined by F(1)–F(1A)–N(1)–N(1A) as indicated by the Mg(1A)–Mg(1)–O(30) angle (99.82(7)°).

In conclusion, we have accomplished the synthesis of fluoromagnesium β-diketiminate **2**. For the first time, the double fluorine bridge feature between the two magnesium atoms was revealed by the molecular structure of **2**. Having observed the interesting transformation of the zinc analogue [12] and due to the similarities of zinc and magnesium, we are conducting investigation of the reactivity of **2** and **3**.

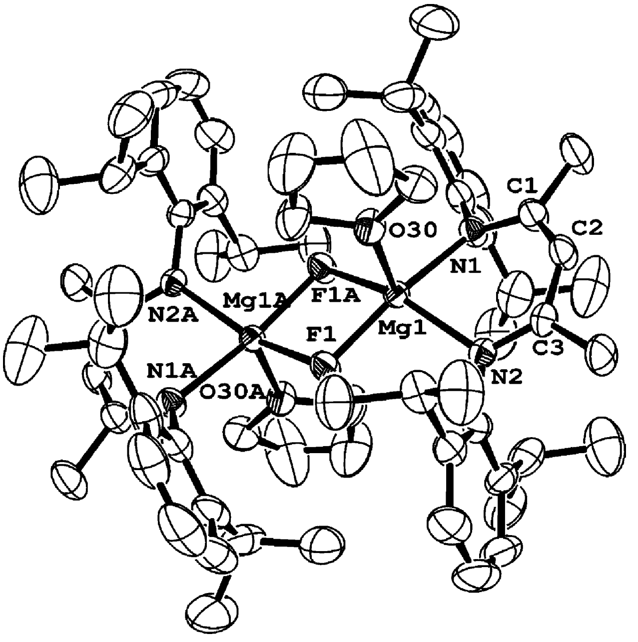


Fig. 2. Crystal structure of **2**. Toluene molecule and hydrogen atoms are omitted for clarity.

3. Experimental

All experiments were carried out under an atmosphere of dry dinitrogen using standard Schlenk techniques. All solvents were dried by common methods and freshly distilled prior to use. The toluene solution of dibutyl magnesium was purchased commercially. Starting materials **V** [13], **VI**, **VII** [9], and Me_3SnF [14] were prepared according to the literature methods. ^1H and ^{19}F NMR spectra were recorded on Bruker AS-250 or Bruker AM-200 spectrometers with

Table 2
Selected bond lengths (Å) and angles (°) for **2**

Mg(1)–F(1)	1.9507(17)
Mg(1)–F(1A)	1.9505(17)
Mg(1)–O(30)	2.078(2)
Mg(1)–N(1)	2.144(2)
Mg(1)–N(2)	2.147(2)
Mg(1)–Mg(1A)	3.0640(17)
N(1)–C(1)	1.334(4)
N(1)–C(11)	1.449(3)
N(2)–C(3)	1.330(3)
N(2)–C(21)	1.443(3)
C(1)–C(2)	1.399(4)
C(1)–C(4)	1.522(4)
C(2)–C(3)	1.397(4)
C(3)–C(5)	1.525(4)
F(1)–Mg(1)–F(1A)	76.49(7)
F(1)–Mg(1)–O(30)	97.72(8)
F(1A)–Mg(1)–O(30)	97.68(8)
F(1)–Mg(1)–N(1)	161.72(9)
F(1A)–Mg(1)–N(1)	95.63(8)
O(30)–Mg(1)–N(1)	99.69(9)
F(1)–Mg(1)–N(2)	95.43(8)
F(1A)–Mg(1)–N(2)	162.35(9)
O(30)–Mg(1)–N(2)	98.95(9)
N(1)–Mg(1)–N(2)	87.35(9)
Mg(1)–F(1)–Mg(1A)	103.52(7)
Mg(1A)–Mg(1)–O(30)	99.82(7)

references to external Me_4Si and $BF_3{\cdot}OEt_2$, respectively. EI-mass spectra were obtained on Finnigan MAT8230 and Varian MAT CH5 spectrometers.

1: To a solution of $MgBu_2$ (20 ml of a 1 M solution in n-heptane) in toluene (20 ml), a solution of **V** (6.1 g, 20 mmol) in toluene (20 ml) was added dropwise at −78 °C. After the addition, the resulting reaction mixture was warmed slowly to ambient temperature and continuously stirred at room temperature for 20 h. A large amount of a white precipitate formed. Heating the suspension to dissolve the precipitate and cooling it slowly to room temperature, afforded colorless crystals. Yield: 5.4 g (70%); mp 238–241 °C; ^{1}H NMR (200.13 MHz, C_6D_6): δ 7.15–6.85 (m, 12H, Ar-H), 4.80 (s, 2H, γ-H), 1.98 (s, 24H, Ar-*Me*), 1.44 (s, 12H, β-H), 1.00–0.80 (m, 14H, $CH_2C_3H_7$), −0.40 (t, 4H, $J = 8.8$ Hz, $CH_2C_3H_7$); EIMS (probe) 70 eV, *m*/*z* (rel. int.): 715 $[M - Bu]^+$ (5), 692 $[M - MgBu]^+$ (24), 146 $[ArNCCH_3]^+$ (100).

2: Toluene: A mixture of **VII** (1.72 g, 3.25 mmol) and Me_3SnF (0.60 g, 3.3 mmol) in toluene (20 ml) was stirred at room temperature for 48 h. After the removal of all volatiles in vacuum at room temperature the residue was re-dissolved in toluene (20 ml) and stored at 0 °C in a refrigerator for 16 h to afford colorless crystals. Yield: 0.87 g (22%); mp 240–245 °C; ^{1}H NMR (200.13 MHz, C_6D_6): δ 7.10–6.90 (m, 17H, i-$Pr_2C_6H_3$ and $C_6H_5CH_3$), 4.82 (s, 2H, γ-*H*), 3.52 (br, 8H, THF), 3.05 (sept, 4H, $J = 6.8$ Hz, C*H*Me_2), 2.10 (s, 3H, $C_6H_5Me_3$), 1.50 (s, 6H, β-Me), 1.19 (m, 8H, THF) 1.10 (d, 12H, $J = 6.8$ Hz, CHMe_2), 0.96 (d, 12H, $J = 6.8$ Hz, CHMe_2); ^{19}F NMR (C_6D_6, 188 MHz): δ −25; EIMS (probe) 70 eV, *m*/*z* (rel. int.): 921 $[M{-}2THF]^+$ (75), 503 $[M{-}2THF - C_{29}H_{42}N_2]^+$ (100); Anal. Calcd. for $C_{73}H_{106}F_2Mg_2N_4O_2$: C, 75.70; H, 9.22; N, 4.85. Found: C, 75.53; H, 9.10; N, 4.91.

3: The reaction of **VI** (1.00 g, 1.1 mmol) and Me_3SnF (0.40 g, 2.2 mmol) in toluene (20 ml) at room temperature for 48 h resulted in a clear solution. After removal of all volatiles the residue was washed with n-pentane (15 ml) and then dried in vacuo for 2 h affording a white powder. Yield: 0.67 g (66%); mp 240–247 °C; ^{1}H NMR (200.13 MHz, C_6D_6): δ 7.10–6.90 (m, 12H, i-$Pr_2C_6H_3$), 4.83 (s, 2H, γ-*H*), 3.00 (sept, 8H, $J = 6.9$, C*H*Me_2), 1.47 (s, 12 H, *Me*), 1.09 (d, 24H, $J = 6.9$, CHMe_2), 0.95 (d, 24H, $J = 6.9$, CHMe_2); ^{19}F NMR (188.28 MHz, C_6D_6): δ −26; EIMS (probe) 70 eV, *m*/*z* (rel. int.): 921$[M]^+$ (90), 503 $[M - C_{29}H_{42}N_2]^+$ (100); Anal. Calcd. for $C_{58}H_{82}F_2Mg_2N_4$: C, 75.56; H, 8.97; N, 6.08. Found: C, 76.14; H, 9.02; N, 6.21.

3.1. X-ray single crystal analysis

Single crystals of **1** and **2** were taken from the flask under nitrogen gas and mounted on a glass fiber in a rapidly cooled perfluoropolyether [15]. Diffraction data for **1** and **2** were collected on a Stoe–Siemens–Huber four-circle diffractometer coupled to a Siemens CCD area detector at 200(2) K with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The single crystals of **1** and **2** are monoclinic, space group $P2_1/n$. The structures were solved by direct methods (SHELXS-96) [16] and refined against F^2 using SHELXL-97 [17]. All non-hydrogen atoms were refined anisotropically with similarity and rigid bond restraints. All hydrogen atoms were included in the refinement in geometrically ideal positions. Crystallographic data

Table 3
Crystallographic data for compounds **1** and **2**

	Compound **1**	Compound **2**
Empirical formula	$C_{50}H_{68}Mg_2N_4$	$C_{73}H_{106}F_2Mg_2N_4O_2$ (including one toluene molecule)
Formula weight	773.72	1158.24
Unit cell dimensions	$a = 11.3587(15)$ Å $b = 13.174(3)$ Å $c = 15.463(2)$ Å $\beta = 97.426(13)°$	$a = 12.6483(18)$ Å $b = 14.298(3)$ Å $c = 19.117(3)$ Å $\beta = 95.493(17)°$
Volume, *Z*	2294.4(6) Å^3, 2	3441.4(9) Å^3, 4
Density (calculated)	1.120 mg/m^3	1.118 mg/m^3
Absorption coefficient	0.089 mm^{-1}	0.086 mm^{-1}
F(0 0 0)	840	1260
Crystal size	0.90 mm × 0.60 mm × 0.40 mm	0.60 mm × 0.50 mm × 0.50 mm
θ range for data collection	3.58–25.02°	3.51–25.02°
Index ranges	$-13 \leq h \leq 13$, $-15 \leq k \leq 15$, $-18 \leq l \leq 18$	$-15 \leq h \leq 15$, $-17 \leq k \leq 17$, $-22 \leq l \leq 22$
Reflections collected	8088	10081
Independent reflections	4044 (R(int) = 0.0340)	6053 (R(int) = 0.0386)
Completeness to $\theta = 25.02°$	99.7%	99.7%
Data/restraints/parameters	4044/6/260	6053/379/395
Goodness-of-fit on F^2	1.037	1.308
Final *R* indices ($I > 2\sigma(I)$)	$R1 = 0.0585$, $wR2 = 0.1620$	$R1 = 0.0689$, $wR2 = 0.1910$
R indices (all data)	$R1 = 0.0753$, $wR2 = 0.1774$	$R1 = 0.0939$, $wR2 = 0.2148$
Largest diffraction peak and hole	0.661 and −0.433 e/Å^3	0.653 and −0.966 e/Å^3

for **1** and **2** are given in Table 3. The toluene solvate molecules in **2** are highly disordered.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-173485 and CCDC-173486. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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