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Synthesis and Characterization of an Unsolvated Dimeric Diarylmagnesium Compound and Its Magnesium Iodide Byproducts

Rudolf. J. Wehmschulte,*,[†] Brendan Twamley,[‡] and Masood A. Khan[†]

Department of Chemistry and Biochemistry, University of Oklahoma, 620 Parrington Oval, Room 208,
Norman, Oklahoma 73019, and University Research Office, University of Idaho, PO Box 443010,
Moscow, Idaho 83844-3010

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The Grignard reagent 2,6-$Et_2C_6H_3MgI(THF)_n$, **1**, undergoes rapid aryl exchange in THF solution at room temperature to afford the diorganomagnesium compound (2,6-$Et_2C_6H_3)_2Mg(THF)_n$, **2**, and the sparingly soluble salt $Mg(THF)_6I_2$, **5**. Removal of the coordinated THF in **2** under reduced pressure and elevated temperature affords the unique diorganomagnesium species [2,6-$Et_2C_6H_3Mg(\mu$-$C_6H_3Et_2$-2,6)$]_2$, **3**, which features three-coordinate magnesium. Compound **3** is fluxional in benzene or toluene solution at room temperature and dissociates into monomeric (2,6-$Et_2C_6H_3)_2Mg$ around 115 °C. Recrystallization of crude **5** from benzene solution gave large well-shaped crystals of $MgI_2(THF)_3$, **4**, and **5**. Benzene solutions of **4** and **5** are remarkably easily oxidized by laboratory air to $MgI(THF)_5I_3$, **6**. Coumpound **3** has been characterized by variable-temperature ^{1}H NMR spectroscopy and X-ray crystallography, and compounds **4**−**6** have been characterized by X-ray crystallography.

Introduction

Grignard compounds RMgX are among the most common organometallic reagents used in organic synthesis.[1−5] In cases in which the presence of a halide could be detrimental or a higher reactivity is required, diorganomagnesium compounds R_2Mg may be employed. There are numerous methods available for the synthesis of these R_2Mg compounds, but they are generally obtained by exploiting the Schlenk equilibrium using 1,4-dioxane, which forms an essentially insoluble, polymeric magnesium halide dioxane complex, MgX_2(1,4-dioxane)$_2$ (eqs 1 and 2).[2,3]

$$2\ \mathrm{RMgX(L)}_n \rightleftharpoons \mathrm{R_2Mg(L)}_n + \mathrm{MgX_2(L)}_n \tag{1}$$

$$\mathrm{MgX_2(L)}_n + 2\ \text{1,4-dioxane} \rightarrow \mathrm{MgX_2(\text{1,4-dioxane})_2}\downarrow \ + n\mathrm{L} \tag{2}$$

$$\begin{aligned}\mathrm{R} &= \text{alkyl, aryl}\\ \mathrm{X} &= \mathrm{Cl, Br}\\ \mathrm{L} &= \mathrm{Et_2O}, \text{THF, etc.}\end{aligned}$$

In many cases, the donor solvent can be removed by heating under reduced pressure to give the unsolvated, often oligomeric, diorganomagnesium compounds $(R_2Mg)_n$. An alternative method involves the reaction of diorganomercury compounds R_2Hg with magnesium powder, and this reaction can also be performed in the absence of coordinating solvents.[6] A third, apparently little known, method utilizes the low solubility of $MgI_2(THF)_6$ in THF as the driving force for the formation of $R_2Mg(THF)_n$ from solutions of Grignard reagents, $RMgI(THF)_n$, derived from the reaction of organic iodides RI with magnesium.[7]

The continued success of "single-site" olefin polymerization catalysts has spawned numerous research projects involving low-coordinate neutral and cationic species.[8−10] Recently, two groups reported the syntheses of rare three-coordinate alkylmagnesium compounds. Oligomerization was avoided due to the use of bulky β-diketiminate ligands $[(DippNCR)_2CH]^-$ (Dipp = 2,6-*i*-$Pr_2C_6H_3$, R = Me, *t*-Bu).[11,12]

During our work with bulky *m*-terphenyl-substituted boron and phosphorus compounds for the development of unsymmetrical boroles[13] and phospholes,[14] we prepared the Grignard reagent 2,6-$Et_2C_6H_3MgI(THF)_n$, **1**, as precursor for the new *m*-terphenyl substituent 2,6-(2,6-$Et_2C_6H_3)_2C_6H_3$. The 2,6-$Et_2C_6H_3$ substituent is intermediate in size between 2,4,6-$Me_3C_6H_2$ and 2,4,6-*i*-$Pr_3C_6H_2$ and has been employed success-

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* To whom correspondence should be addressed. Fax: +1 405 325 6111. E-mail: rjwehmschulte@ou.edu.

[†] University of Oklahoma.

[‡] University of Idaho.

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fully in the stabilization of disilenes[15] and phosphasilenes.[16] Here we report (i) the rapid conversion of **1** to $(2,6\text{-}Et_2C_6H_3)_2Mg(THF)_n$, **2**, (ii) its desolvation to the unique three-coordinate diarylmagnesium species $[(2,6\text{-}Et_2C_6H_3)_2Mg]_2$, **3**, (iii) the structures of two THF solvated magnesium iodide compounds, and (iv) the unexpected air and moisture sensitivity of benzene solutions of $MgI_2(THF)_n$.

Experimental Section

General Procedures. All work was performed under anaerobic and anhydrous conditions by using either modified Schlenk techniques or an Innovative Technologies drybox. Solvents were freshly distilled under N_2 from Na/K alloy and degassed twice prior to use. 2,6-Diethylaniline was obtained from a commercial supplier and used as received. 2,6-Diethyliodobenzene was synthesized according to the literature method.[17] ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 MHz, a Varian Unity Plus 400 MHz, or a Varian VXR-500S spectrometer, and ^1H NMR chemical shift values were determined relative to the residual protons in C_6D_6 or C_7D_8 as internal reference ($\delta = 7.15$ or 2.09 ppm). ^{13}C NMR spectra were referenced to the solvent signal ($\delta = 20.4$ ppm). Electrospray mass spectra were measured with a Micromass Q-ToF spectrometer. Melting points were determined in Pyrex capillary tubes (sealed under nitrogen where appropriate) with a Mel-Temp apparatus and are uncorrected.

$[(2,6\text{-}Et_2C_6H_3)_2Mg]_2$, 3. A solution of 2,6-diethyliodobenzene (34.6 g, 133 mmol) in THF (200 mL) was added slowly to magnesium turnings (3.65 g, 150 mmol), which had been activated by grinding in a mortar and stirring in vacuo for 2 h. The reaction was started by heating the mixture with a heatgun after 20 mL of the 2,6-diethyliodobenzene were added. After 12 h, a thick gray slurry had formed, which was diluted with THF (150 mL) and stirred for an additional 24 h. The grayish precipitate was collected on a glass frit and dried under reduced pressure (28.16 g yield). The solvent was removed from the pale yellow filtrate under reduced pressure, and the remaining yellow oil was distilled under reduced pressure (0.05 Torr). Fraction 1 (70 °C, probably overheated 2 mL) was identified as impure 2,6-diethyliodobenzene, and fraction 2 (60−70 °C, 10 mL) was pure unreacted 2,6-diethyliodobenzene (^1H NMR and GC/MS). The flask was heated to a temperature of 130 °C, leaving a viscous yellow oil (ca. 10 mL) in the flask. This oil partially solidified after 5 days at room temperature. Recrystallization of this sticky solid from concentrated benzene or hexane solution was unsuccessful, but thin needles of sufficient quality for X-ray diffraction were obtained after removal of the solvent and slow solidification of the remaining oil at room temperature for 3 days. Attempts to purify the sticky crystals by washing with cold hexanes (0 °C) to remove unreacted 2,6-diethyliodobenzene were only marginally successful. Crystals used for the NMR studies contained ca. 33% 2,6-diethyl iodobenzene and 17% 1,3-diethylbenzene. ^1H NMR (C_7D_8, −80 °C, 500 MHz): 7.31 (t, *p*-H, 2H, $J = 5.8$ Hz), 7.26 (t, *p*-H, 2H, $J = 6.4$ Hz), 7.06 (d, *m*-H, 4H, $J = 5.8$ Hz), 6.84 (d, *m*-H, 4H, $J = 6.4$ Hz), 2.72 (q, CH_2, 8H, $J = 5.6$ Hz), 2.13 (q, CH_2, 8H, $J = 5.6$ Hz), 1.14 (t, CH_3, 12H, $J = 5.6$ Hz), 0.86 (t, CH_3, 12H, $J = 5.6$ Hz). ^1H NMR (C_7D_8, 20 °C): 7.19 (s, broad, *p*-H, 4H), 6.93 (d, broad, *m*-H, 8H, $J = 6.4$ Hz), 2.82 (s, broad, CH_2, 8H), 2.05 (s, broad, CH_2, 8H), 1.18 (s, broad, CH_3, 12H), 0.89 (s, broad, CH_3, 12H). ^{13}C NMR (C_7D_8, −80 °C, 75.45 MHz): 158.4, 156.5, 153.3, 147.3, 133.4, 125.4 (*m*-C), 123.2 (*m*-C), 36.6 (CH_2), 35.8 (CH_2), 18.6 (CH_3), 15.9 (CH_3).

$MgI_2(THF)_3$, 4. A sample of the grayish solid from the above reaction (1.83 g) was dissolved in benzene (40 mL), and the supernatant liquid was decanted off to leave behind unreacted Mg turnings. The clear colorless solution was concentrated to ca. 3 mL and left standing at room temperature for 1 day. Shaking of the flask induced rapid crystallization. The colorless needles, which formed initially, developed into big plates and blocks (ca 1 mm) after another day at room temperature.

$Mg(THF)_6I_2$, 5. The remainder of the grayish solid from the synthesis of **3** was extracted with warm benzene (150 mL, 37 °C). The pale yellow supernatant liquid was separated from the insoluble material (mainly Mg turnings and some grayish powder) by filtration and was cooled to 4 °C for 1 week to afford big colorless blocks (1−2 mm, 11.50 g), mp 121−124 °C, with gas evolution. Crystals lose mass (THF) when exposed to air.

$MgI(THF)_5I_3$, 6. Leakage of air into the Schlenk flask containing crystals of **4** and the mother liquor resulted in the color of the solution turning pale yellow-brown. After ca. 2 months, some small brown crystals of **6** formed, which were of sufficient quality for X-ray diffraction.

A flask containing **5** (0.92 g, 1.3 mmol), which was partially dissolved in benzene (20 mL), was connected to a flask filled with laboratory air (500 mL), which had been dried over P_4O_{10} for several hours. After 1 h, the initially colorless solution turned yellow, and after an additional 15 h the solution had turned dark yellow-red and small dark red crystals began to preciptitate. The formation of the red crystalline **6** was complete after an additional 1 day (0.36 g), mp 128−132 °C, with gas evolution. MS (electospray, CH_2Cl_2 solution): *m*/*z* 380.7 (I_3^-, 100).

X-ray Crystallography. Crystals were removed from the Schlenk tube under a stream of N_2 gas and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream.[18] The data for **3** were collected at 89(2) K on a Bruker Smart 1000 diffractometer and those for **4**−**6** at 173 (2) K on a Siemens P4 diffractometer using Mo Kα ($\lambda = 0.710\,73$ Å) radiation. The data were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied using SADABS[19] for **3** or φ-scans for **4**−**6**. The structures of **3** and **5** were solved by direct methods, and the structures of **4** and **6** were solved using the heavy atom method. The structures were refined by full-matrix least-squares procedures on F^2 using all reflections. The crystallographic programs employed were those of the SHELXTL program suite, version 5.1 for **3**−**6** and version 5.03 for **4**. In the final refinement cycles of the structures of **3**−**6**, all the non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were included in the refinement with idealized parameters. Further details are provided in Tables 1−4 and the Supporting Information. The structure of **5** was refined in the space group *Pn*-3. However, disorder and high residuals suggest twinning problems. The structure will not be discussed here but is included in the Supporting Information.

Results and Discussion

Diorganomagnesium. Treatment of a THF solution of 2,6-diethyliodobenzene (ca. 0.66 M) with magnesium turnings resulted in the formation of of a thick gray slurry after 20 h at room temperature. Dilution to almost twice the original volume and additional reaction time of 24 h led to the formation of more of the grayish precipitate. An NMR spectrum of a solution sample taken after 24 h indicated that only 25% of the starting material was consumed. After separation of the precipitate by filtration and removal of the solvent from the yellow filtrate, the remaining oil was purified by fractional distillation. The volatile fractions were identified as mainly unreacted 2,6-diethyliodobenzene. The nonvolatile viscous yellow residue solidified after several days at room temperature. Recrystallization attempts from benzene or hexane solutions were unsuccessful, but the oil that was obtained after removal of the hexane solvent solidified into thin needles after several days at room

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Table 1. Crystal Data and Structural Refinement Details for **3**, **4**, and **6**

	3	**4**	**6**
emp formula	$C_{40}H_{52}Mg_2$	$C_{12}H_{24}I_2MgO_3$	$C_{20}H_{40}I_4MgO_5$
formula wt	581.44	494.42	892.43
T, K	89(2)	173(2)	173(2)
wavelength, Å	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic
space group	*P*2(1)/*c*	*C*2/*c*	*C*2/*c*
a, Å	19.481(2)	12.234(4)	16.631(3)
b, Å	12.862(1)	12.600(4)	11.027(2)
c, Å	29.179(2)	12.395(3)	16.174(4)
α, deg	90	90	90
β, deg	108.56(2)	112.67(2)	96.592(15)
γ, deg	90	90	90
V, Å^3	6931.0(10)	1763.0(9)	2946.6(10)
Z	8	4	4
D_{calcd}, Mg/m^3	1.114	1.863	2.012
μ(Mo Kα), mm^{-1}	0.095	3.602	4.276
F(000)	936	952	1696
crystal size, mm^3	0.20 × 0.11 × 0.08	0.62 × 0.54 × 0.38	0.58 × 0.38 × 0.34
crystal color and habit	yellow needle	colorless prism	brown prism
$2\Theta_{max}$, deg	25.00	27.49	26.51
no. of observns	12215	1962	3048
no. of variables	774	83	139
$R_1{}^a$ $[I > 2\sigma(I)]$	0.0768	0.0508	0.0396
$wR_2{}^b$ $[I > 2\sigma(I)]$	0.1601	0.1340	0.0991
goodness-of-fit on F^2	1.004	1.048	1.055
largest diff peak, e Å^{-3}	0.474	2.548	0.981

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (Deg) for **3**

Mg(1)−C(1)	2.121(7)	C(1)−Mg(1)−C(11)	127.1(3)
Mg(1)−C(11)	2.259(7)	C(1)−Mg(1)−C(31)	129.3(3)
Mg(1)−C(31)	2.296(7)	C(11)−Mg(1)−C(31)	103.2(3)
Mg(2)−C(21)	2.114(7)	C(21)−Mg(2)−C(31)	129.8(3)
Mg(2)−C(31)	2.243(7)	C(21)−Mg(2)−C(11)	125.4(3)
Mg(2)−C(11)	2.263(7)	C(31)−Mg(2)−C(11)	104.8(3)
Mg(3)−C(41)	2.100(7)	Mg(1)−C(11)−Mg(2)	76.2(2)
Mg(3)−C(51)	2.228(8)	Mg(1)−C(31)−Mg(2)	75.8(2)
Mg(3)−C(71)	2.298(7)	C(41)−Mg(3)−C(51)	129.5(3)
Mg(4)−C(61)	2.123(8)	C(41)−Mg(3)−C(71)	127.1(3)
Mg(4)−C(71)	2.226(7)	C(51)−Mg(3)−C(71)	103.4(3)
Mg(4)−C(51)	2.306(7)	C(61)−Mg(4)−C(71)	130.8(3)
		C(61)−Mg(4)−C(51)	125.9(3)
		C(71)−Mg(4)−C(51)	103.2(3)
		Mg(3)−C(51)−Mg(4)	76.2(2)
		Mg(3)−C(71)−Mg(4)	76.5(2)

Table 3. Selected Bond Lengths (Å) and Angles (Deg) for **4**

I(1)−Mg(1)	2.7458(14)	I(1)−Mg(1)−I(1A)	121.32(9)
Mg(1)−O(1)	2.092(3)	O(2)−Mg(1)−I(1)	119.34(4)
Mg(1)−O(2)	2.025(5)	O(1A)−Mg(1)−O(1)	167.6(2)
		O(1)−Mg(1)−I(1)	93.94(9)
		O(1)−Mg(1)−I(1A)	92.12(10)
		O(2)−Mg(1)−O(1)	83.81(12)

Table 4. Selected Bond Lengths (Å) and Angles (Deg) for **6**

I(1)−Mg(1)	2.853(2)	I(3)−I(2)−I(3A)	180.000(5)
I(2)−I(3)	2.9136(7)	O(1)−Mg(1)−I(1)	91.48(11)
Mg(1)−O(1)	2.073(3)	O(2)−Mg(1)−I(1)	93.05(10)
Mg(1)−O(2)	2.159(3)	O(3)−Mg(1)−I(1)	180.0
Mg(1)−O(3)	2.110(5)	O(1)−Mg(1)−O(1A)	177.0(2)
		O(1)−Mg(1)−O(2)	91.43(12)
		O(1)−Mg(1)−O(2A)	88.41(13)
		O(1)−Mg(1)−O(3)	88.52(11)
		O(2)−Mg(1)−O(2A)	173.9(2)
		O(3)−Mg(1)−O(2)	86.95(10)

temperature. These needles were of sufficient quality for X-ray diffraction but were covered with oily 2,6-diethyliodobenzene and 1,3-diethylbenzene. Attempts to remove these impurities by vacuum sublimation (100−110 °C, 0.05 Torr) were accompanied by partial decomposition of **3**. The structure was determined by X-ray diffraction as the unique dimeric, donor-free diarylmagnesium compound $[2,6\text{-}Et_2C_6H_3Mg(\mu\text{-}C_6H_3Et_2\text{-}2,6)]_2$, **3** (Figure 1). Apparently, despite the bulk of the 2,6-diethylphenyl substituent, the Schlenk equilibrium (eq 1) is established at a rate comparable to that of the formation of the Grignard compound $2,6\text{-}Et_2C_6H_3MgI(THF)_n$, **1**, so that the solution only contains the THF-solvated diarylmagnesium compound $(Et_2C_6H_3)_2Mg(THF)_n$, **2**, and unreacted starting material. Similar THF-solvated diarylmagnesium compounds, such as $Ph_2Mg(THF)_2$,[6] $Mes_2Mg(THF)_2$ (Mes = 2,4,6-Me_3-C_6H_2),[20] or $Trip_2Mg(THF)_2$ (Trip = 2,4,6-*i*-$Pr_3C_6H_2$),[20] have been synthesized using the dioxane method, and their structures have been determined by X-ray crystallography. It is interesting to note that no precipitate formation has been reported for the synthesis of the Grignard reagent $DippMgI(THF)_n$ (Dipp = 2,6-*i*-$Pr_2C_6H_3$),[21] which is probably due to the larger size of the Dipp substituent. The coordinated THF molecules in **2** were then removed by vacuum distillation at 130 °C to give **3**.

Compound **3** crystallizes in the monoclinic space group *P*2(1)/*c* with two independent molecules per asymmetric unit. Each dimeric molecule contains one terminal and one bridging aryl ligand per magnesium (Figures 1 and 2). The terminal Mg−C distances, which range from 2.100(7) to 2.123(8) Å, compare well with those observed in other low-coordinate magnesium compounds such as 2.077(2) Å in $CH_3Mg\{\eta^2\text{-}(DippNC\text{-}t\text{-}Bu)_2CH\}$[12] or 2.116(3) Å in $Mes^*{}_2Mg$.[22] The aryl bridges are unsymmetrical, affording one short and one long bridging Mg−C bond per magnesium. The short Mg−C distances are in the range 2.226(7)−2.259(7) Å, and the long Mg−C distances are in the range 2.263(7)−2.306(7) Å. These distances are similar to those found for bridging aryl groups in $[4\text{-}CH_3C_6H_4Mg(THF)(\mu\text{-}C_6H_4CH_3\text{-}4)]_2$ (2.245(7) and 2.313(7) Å) or $[Ph_2Mg]_n$ (2.261(2) Å).[6] The aromatic rings are rotated

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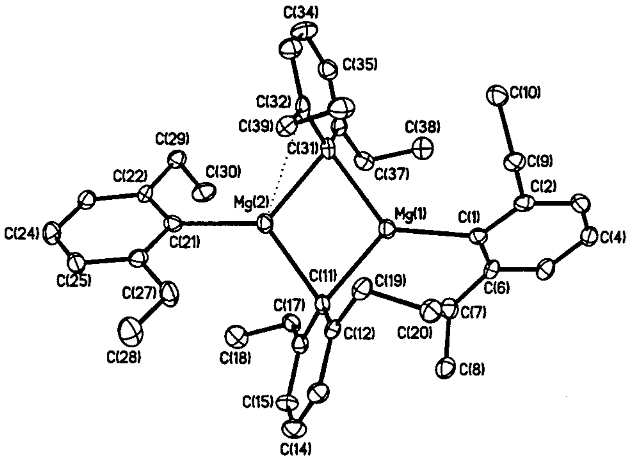

Figure 1. Thermal ellipsoid plot (30% probability ellipsoids) showing the molecular structure of one of the independent molecules of **3**. H-atoms are omitted for clarity.

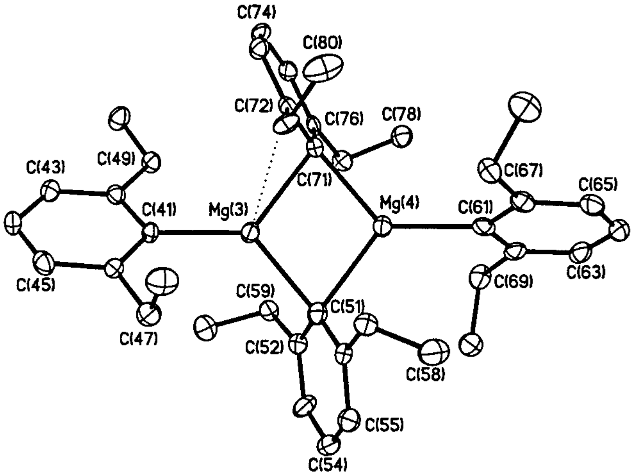

Figure 2. Thermal ellipsoid plot (30% probability ellipsoids) showing the molecular structure of the second independent molecule of **3**. H-atoms are omitted for clarity.

out of the Mg_2C_2 plane in a propeller-like fashion by 42.7−74.6°. The bridging aryl groups are not positioned symmetrically between the magnesium atoms but are leaning toward one of the magnesium atoms as is evidenced by the angles of 12.0° (C(11)), 13.4° (C(31)), 9.8° (C(51)), and 24.2° (C(71)) between the lines connecting the ipso carbons and the C(ipso)−C(para) vector. In molecule 1, both groups are leaning toward Mg(2), whereas in molecule 2 the C(71)−C(76) ring is leaning toward Mg(3) and the C(51)−C(56) ring toward Mg(4). This asymmetry allows for additional Mg···C and Mg···H contacts of 2.795−3.004 and 2.36−2.79 Å involving the ortho carbons and methylene hydrogens, respectively. The Mg−C−Mg angles with an average value of 76.2° are similar to those found in the phenyl- (77.73(9)°) and tolyl-bridged (77.5(2)°) compounds mentioned earlier.[6] The coordination geometry at the magnesium atoms is distorted trigonal planar with the internal angle being the smallest with 103.6° (average).

Three-coordinate magnesium compounds are not very common and have been limited mainly to homoleptic magnesium amides with bulky substituents such as $[Mg[N(SiMe_3)_2]_2]_2$,[23] $[Mg[N(C_6H_{11})_2]_2]_2$,[24] or $[Mg[N(CH_2Ph)_2]_2]_2$.[25] Compound **3** is the first neutral crystallographically characterized diorganomagnesium species with three-coordinate magnesium. Typically, these compounds are polymeric chain molecules with four-coordinate magnesium as in $(Me_2Mg)_n$,[26] $(Et_2Mg)_n$,[27] or $(Ph_2Mg)_n$.[6] Two-coordination has been reported for the very bulky $Mg[C(SiMe_3)_3]_2$[28] and $MgMes^*_2$.[22] The unsymmetrical aryl bridges in **3** suggest that these bridges may open even in noncoordinating solvents such as benzene or toluene. Indeed, ^1H NMR spectra of C_6D_6 or C_7D_8 solutions at room temperature display broad signals indicating a dynamic process. A VT-NMR study in the temperature range of −80 to +115 °C confirms the presence of a dynamic process, and an activation barrier of 15.4(5) kcal mol^{-1} was estimated for this process.[29] The −80 °C ^1H NMR spectrum with two sets of sharp signals is in agreement with the solid-state structure being preserved in solution, whereas the high-temperature spectrum, which displayed only one set of still slightly broadened signals, suggests the presence of monomeric $(2,6\text{-}Et_2C_6H_3)_2Mg$. This is in agreement with the description of the observed dynamic process as being due to the monomer−dimer equilibrium of **3** (eq 3).

$$[2,6\text{-}Et_2C_6H_3Mg(\mu\text{-}C_6H_3Et_2\text{-}2,6)]_2 \rightleftharpoons 2\ (2,6\text{-}Et_2C_6H_3)_2Mg \qquad (3)$$

To the best of our knowledge, there are no studies in the literature describing these kinds of equilibria for unsolvated diorganomagnesium compounds. However, thermodynamic parameters for the monomer−dimer equilibria of some related aluminum compounds such as $[Me_3Al]_2$ are well documented.[1,30]

Magnesium Iodide Compounds. Madeja et al. have analyzed the crystalline, insoluble precepitate obtained from the reaction of alkyl iodides with magnesium in THF solution as $MgI_2(THF)_6$.[7] We have found that the precipitate formed in the reaction of $2,6\text{-}Et_2C_6H_3I$ with magnesium turnings is readily soluble in benzene, and we have obtained well-shaped colorless crystals from these solutions. X-ray diffraction studies of these crystals showed the presence of two different species, $MgI_2(THF)_3$, **4**, and $Mg(THF)_6I_2$, **5**. Crystals of **5** had twinning problems, and the structure will not be discussed here in detail. However, despite these problems it could be determined that the structure of **5** consists of separated $Mg(THF)_6^{2+}$ cations and I^- anions. The fact that compound **5** loses THF slowly upon isolation indicates that the coordinated THF may be removed quite easily. In fact, crystals of **4**, which contain only three THF molecules per magnesium, were isolated after significant reduction of the volume of a diluted benzene solution of crude **5** under reduced pressure, whereas the solution from which crystals of **5** were obtained was not concentrated at all.

Compound **4** crystallizes in the monoclinic space group *C*2/*c*. Its structure (Figure 3) features a slightly distorted, trigonal bipyramidally coordinated magnesium with the large iodide anions occupying two of the equatorial positions. The two halves of the molecule are related by a C_2-axis through Mg(1) and O(2). The angles in the equatorial plane are close to the ideal 120° (I(1)−Mg(1)−I(1A) = 121.32(9)°, O(2)−Mg(1)−I(1) = 119.34(4)°), but the two axial THF ligands are pushed away from the iodide anions toward the equatorial THF, which is

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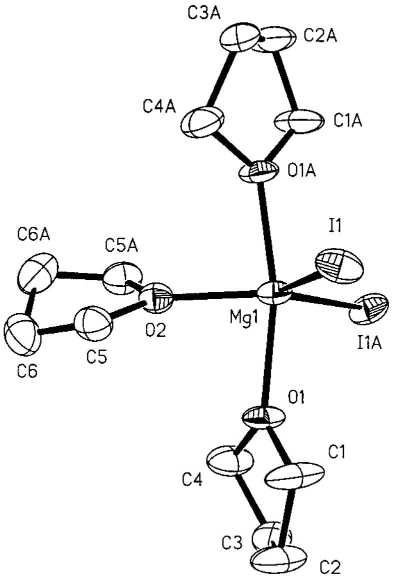

Figure 3. Thermal ellipsoid plot (50% probability ellipsoids) showing the molecular structure of **4**. H-atoms are omitted for clarity.

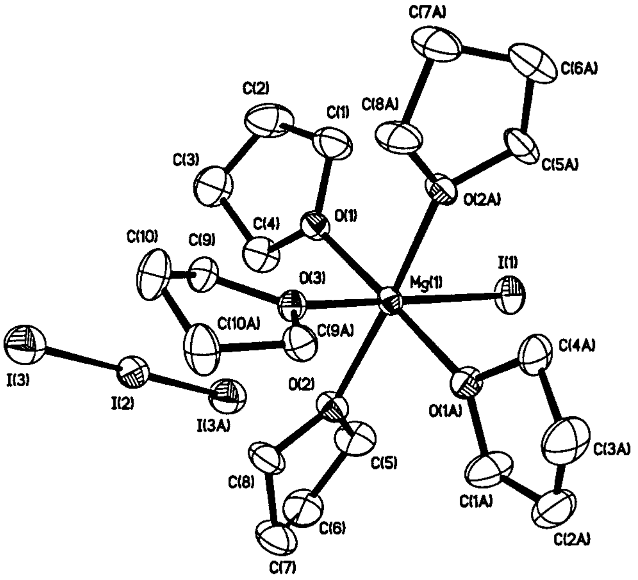

Figure 4. Thermal ellipsoid plot (50% probability ellipsoids) showing the molecular structure of **6**. H-atoms are omitted for clarity.

manifested by the O(1)−Mg(1)−O(1A) angle with a value of 167.6(2)°. The Mg−I bond distances with 2.7458(14) Å are longer than those in the four-coordinate L_2MgI_2 compounds $(Et_2O)_2MgI_2$,[31,32] $[Cp(Me_3SiCH_2)_2WNO]_2MgI_2$,[33] or $[Me_3P{=}N\text{-}(SiMe_3)]_2MgI_2$[34] with values of 2.654(3), 2.76, or 2.764(2), respectively, but shorter than the 2.872(8) Å observed for the cation $(THF)_5MgI^+$, the only other (next to **6**, vide infra) crystallographically characterized magnesium iodide compound with a magnesium coordination number higher than four.[35] The coordination at the oxygen atoms is distorted trigonal planar (Σ(angles) = 359.7°, O(1); 360°, O(2)), and the magnesium oxygen distances (Mg(1)−O(1) = 2.092(3) Å, Mg(1)−O(2) = 2.025(5) Å) are within the range of 1.920−2.180 Å previously reported for five-coordinate magnesium compounds.[36]

Surprisingly, benzene solutions of $MgI_2(THF)_n$ appear to be air-sensitive. Upon accidental exposure to ambient laboratory air, the solution turned pale yellow-brown, and some small red-brown crystals of $MgI(THF)_5I_3$, **6**, formed over a 2-month period at room temperature. This reaction is readily reproducible using benzene solutions of **5** and dried laboratory air. Whereas the mechanism of the formation of **6** is not yet known, it appears that the iodide is oxidized by oxygen to I_2 which is then complexed with I^- in solution to form I_3^-.[37]

The structure of **6** consists of separated $MgI(THF)_5^+$ cations and I_3^- anions (Figure 4). The I−I distances in the linear centrosymmetrical I_3^- anion are 2.9136(7) Å each, a value typical for symmetrical I_3^- anions.[37] The coordination at the magnesium atom in the cation is distorted octahedral. The Mg−O distances average 2.115 Å. The O−Mg−O angles are close to 90° whereas the I−Mg−O angles are slightly larger with values of 91.48(11) (O(1)−Mg(1)−I(1)) and 93.05(10)° (O(2)−Mg(1)−I(1)). Similar values have been observed for the cation in the related structure of $[MgI(THF)_5]^+[MeSi(t\text{-}BuNMgI)_3CH_3{\cdot}THF]^-$.[35]

Summary

The attempted synthesis of the Grignard reagent 2,6-$Et_2C_6H_3$-$MgI(THF)_n$, **1**, led to rapid formation of the diorganomagnesium compound $(2,6\text{-}Et_2C_6H_3)_2Mg(THF)_n$, **2**, and the sparingly soluble salt $Mg(THF)_6I_2$, **5**. Removal of the coordinated THF in **2** under reduced pressure and elevated temperature afforded the unique diorganomagnesium species $[2,6\text{-}Et_2C_6H_3Mg(\mu\text{-}C_6H_3\text{-}Et_2\text{-}2,6)]_2$, **3**, which features three-coordinate magnesium. Compound **3** is fluxional in benzene or toluene solution at room temperature. The THF-insoluble magnesium salt **5** is readily soluble in benzene. Loss of THF gives **4**, and benzene solutions of **4** and **5** are remarkably easily oxidized by laboratory air to $MgI(THF)_5I_3$.

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Supporting Information Available: Four X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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