would seem quite plausible, if not inevitable. While the foregoing steps seem relatively clear, on the basis of previous pentadienyl chemistry, the driving forces for the following steps are not as readily apparent. Intermediate XI still contains a Ti–C single bond, perhaps quite strained, and could again be susceptible to a coordination and coupling of a fourth isocyanide molecule, resulting in an iminoacyl complex[31] which can most easily be represented by XII, although the actual coordination is likely to be more complex (possibly dynamic), as in XIII. Subsequent ortho-metalation, hydride-transfer, and coupling steps would lead to the observed product. While it would be possible to have the ortho metalation precede the coordination of the fourth isocyanide ligand, this alternative is not favored here, though by no means ruled out, as one might expect the ortho-metalation step to require a greater energy of activation than an additional coordination and migratory insertion involving the fourth isocyanide, particularly given the possibility that the bonding of the third isocyanide in XI might still be strained.

The facility with which (pentadienyl)titanium compounds undergo coupling reactions with unsaturated organic molecules such as nitriles, isonitriles, imines, ketones, and acetylenes demonstrates that a rich body of chemistry in this area remains to be explored. It can be expected that some of these reactions will prove useful for the syntheses of organic molecules, particularly if some control can be exerted on the number of incorporated unsaturated molecules.[32] Such a possibility seems likely, and efforts utilizing highly substituted cyclopentadienyl ligands are currently underway.

Registry No. $Ti(C_5H_5)(2,4\text{-}C_7H_{11})[P(C_2H_5)_3]$, 116841-88-4; $Ti(C_5H_5)(2,4\text{-}C_7H_{11})[4\text{-}(C_2H_5)(C_6H_4)NC]_4$, 143063-90-5; $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(C_5H_{10}O)_2$, 143063-91-6; $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(C_6H_5NC)_4$, 143063-92-7; $Ti(C_5H_5)(2,4\text{-}C_7H_{11})[4\text{-}CH_3(C_6H_4)NC]_4$, 143063-93-8; $Ti(C_5H_5)(2,4\text{-}C_7H_{11})[C_6H_5(H)N(CH_3)]$, 143063-94-9; $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(C_3H_6O)_2$, 143063-95-0; phenyl isocyanide, 931-54-4; *p*-tolyl isocyanide, 7175-47-5; 4-ethylphenyl isocyanide, 143063-89-2; benzylidenemethylamine, 622-29-7; acetone, 67-64-1; 3-pentanone, 96-22-0.

Supplementary Material Available: Tables of complete bond distances, bond angles, anisotropic thermal parameters, and positional parameters of hydrogen atoms (10 pages). Ordering information is given on any current masthead page.

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[31] (a) Iminoacyl and related species are not uncommon results of insertion reactions.[31b,c] (b) Simpson, S. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 4063 and references therein. (c) Beshouri, S. M.; Chebi, D. E.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1990**, *9*, 2375 and references therein.

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Synthesis and X-ray Structural Characterization of $Mg(2,4,6\text{-}R_3C_6H_2)_2(THF)_2$ (R = Me, *i*-Pr) and the Three-Coordinate Magnesiate Species $[Li(THF)_{0.6}(Et_2O)_{0.4}][Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3]$

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Addition of 1,4-dioxane to a tetrahydrofuran solution of $(2,4,6\text{-}i\text{-}Pr_3C_6H_2)MgBr$ results in the disproportionation of the Grignard reagent to give $MgBr_2$–dioxane and the bulky diorganomagnesium compound $Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(THF)_2$. Further reaction with $[Li(Et_2O)(2,4,6\text{-}i\text{-}Pr_3C_6H_2)]_2$ yields the magnesiate species $[Li(THF)_{0.6}(Et_2O)_{0.4}][Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3]$. Each compound has been structurally and spectroscopically characterized by X-ray crystallography and ^1H NMR. We also report the X-ray crystal structure of the known species $Mg(Mes)_2(THF)_2$(Mes = $2,4,6\text{-}Me_3C_6H_2$-). $[Li(THF)_{0.6}(Et_2O)_{0.4}][Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3]$ is the first unassociated lithium organomagnesiate compound involving a structure with three-coordinate magnesium. Crystal data at 130 K with Mo Kα (λ = 0.71069 Å) radiation are as follows: $Mg(Mes)_2(THF)_2$, orthorhombic, a = 9.019 (2) Å, b = 28.752 (6) Å, c = 36.782 (6) Å, Z = 16, space group $F2dd$, R = 0.045; $Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(THF)_2$, orthorhombic, a = 33.865 (10) Å, b = 33.912 (11) Å, c = 12.406 (4) Å, Z = 16, space group $Fdd2$, R = 0.040; $[Li(THF)_{0.6}(Et_2O)_{0.4}][Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3]$, monoclinic, a = 12.819 (3) Å, b = 15.103 (3) Å, c = 24.500 (5) Å, β = 91.13 (2)°, Z = 4, space group $P2_1/c$, R = 0.080.

Organic derivatives of magnesium are among the most common organometallic synthetic reagents.[1] Generally, they are categorized as either Grignard reagents or diorganomagnesium compounds which can be represented by the formulas RMgX and MgR_2, respectively (R = alkyl, aryl; X = halide). These descriptions are misleading since two-coordinate magnesium is unknown at room temperature in the donor solvents in which they are synthesized. In addition, their existence in solution is characterized by equilibria 1 and 2. These equilibria are often complicated

$$2RMgX \xrightleftharpoons{\text{solvating medium}} MgR_2 + MgX_2 \qquad (1)$$

$$2R_2Mg \xrightleftharpoons{\text{solvating medium}} MgR^+ + MgR_3^- \qquad (2)$$

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by rapid exchange of R groups.[2] Furthermore, the degree of association of species in solution varies considerably as a function of R and donor solvent.[1] Examples of all these solution species have been crystallized as adducts with various donor molecules, and the structures of organomagnesium species have been the subject of a recent review.[1c] The structures of ethereal adducts, however, have been obtained in the case of RMgX, MgX_2, and the bridged species $[Mg(CH_2C_6H_4CH_2O)(C_4H_8O_2)]_3$,[3] $[(o\text{-anisyl})_2Mg{\cdot}THF]_2$,[4] and $[(p\text{-tolyl})_2Mg{\cdot}THF]_2$[5] and the monomers $MgPh_2(THF)_2$,[5] $Mg(p\text{-tolyl})_2(THF)_2$,[5] and Mg[(9,10-bis(trimethylsilyl)-9,10-anthracenediyl)](THF).[6] Other structures of MgR_2 species appear to be confined to the neutral species $(MgPh_2)_\infty$,[6] $Mg[C(SiMe_3)_3]_2$,[7] and $MgMe_2{\cdot}2B$ (B = NC_7H_{13},[8] TMEDA[9]), the adducts $MgPh_2(TMEDA)$,[10] $Mg(C_7H_{11})_2(TMEDA)$,[11] $MgPh_2$(1,3-xylyl-18-crown-5),[12] $MgEt_2$(18-crown-6),[13] and $Mg(C{\equiv}CPh)_2(TMEDA)_2$,[14] and the sandwich compounds $Mg(\eta^5\text{-}C_5R_5)_2$ (R = H, Me).[15] Our primary interest in organic derivatives of magnesium and the related lithium species (LiR) has been the establishment of their structures on crystallization from ether solvents. Crystallized solvate adducts of this kind are most likely to bear a resemblance to their structures in solution. In this paper we report on the synthesis and structure of the species $Mg(Mes)_2(THF)_2$ (1) and $Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(THF)_2$ (2), which are rare examples of structurally characterized monodentate ether adducts of MgR_2 monomers.

The second objective of the work described here is the isolation of unassociated species of the type $LiMgR_3$. The ionic magnesiate species $[MgR_3]^-$ has been isolated by the addition of crown ethers or cryptands to diorganomagnesium compounds.[16] In addition, enhanced reaction rates and varied chemical behavior have been attributed to the magnesiate species formed.[17] The species MgR_3^- is probably more nucleophilic than the MgR_2 precursor. Closely related complexes of the type $MMgR_3$ (R = alkyl, M = alkali metal) have also been generated in solution by reduction of magnesium alkyls with alkali metals.[18] The complexes were not isolated, however. Magnesiates are most easily prepared by simple mixing of the diorganomagnesium and organolithium compounds:

$$MgR_2 + RLi \rightarrow LiMgR_3 \qquad (3)$$

Their solutions have been shown to exhibit chemical behavior similar to those prepared from MgR_2 and crown ethers or cryptands.[19] As early as 1951, Wittig et al. investigated the diphenylmagnesium/phenyllithium system in solution and proposed the formation of a species with the structural formula $LiMgPh_3$.[20] The addition of TMEDA to solutions of $LiMgPh_3$ has given the dimeric $[Li(TMEDA)]_2[Ph_2MgPh_2MgPh_2]$, which features two Ph groups bridging the magnesium centers; the four other phenyls bridge Li and Mg with the lithiums also coordinated to TMEDA.[21] The structures of additional lithium TMEDA magnesiates involving phenyl, ethynyl, and benzyl ligands have also been reported.[22] In the case of the species $[Li(PhCC)_3Mg(TMEDA)]_2$, the geometry at magnesium is trigonal-bipyramidal in which two of the five sites are occupied by nitrogen donors. In the case of the benzyl species $[Li(TMEDA)_2][(TMEDA)LiBzl_2MgBzl_2]$ (Bzl = CH_2Ph) the magnesium atom is coordinated by benzyl groups, two of which bridge to a TMEDA-coordinated Li. The structure is completed by the countercation $[Li(TMEDA)_2]^+$. Recently it has been suggested that lithium magnesiates with composition $LiMgR_3$ have structures with bridging R groups and sufficient ether molecules bonded to the metal atoms to make each at least tetracoordinate.[19] This view of their structures had already received support from experiments that involved the addition of LiMes to $MgMes_2$, which afforded a complex that was described as $LiMgMes_3(THF)_4$.[23] We now report that addition of an ether solution of $[Li(Et_2O)(2,4,6\text{-}i\text{-}Pr_3C_6H_2)]_2$ to $Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(THF)_2$ in THF gives the species $[Li(THF)_{0.6}(Et_2O)_{0.4}][Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3]$, in which the magnesium is coordinated by three $2,4,6\text{-}i\text{-}Pr_3C_6H_2$ groups, two of which bridge to an ether/THF-complexed lithium.

Experimental Section

General Procedures. All work was performed under anaerobic and anhydrous conditions by using Schlenk techniques or a Vacuum Atmospheres HE-43 Dry Box. MesBr was purchased from a commercial supplier; $2,4,6\text{-}i\text{-}Pr_3C_6H_2Br$ and $2,4,6\text{-}i\text{-}Pr_3C_6H_2Li$ were synthesized as described in the literature.[24] The latter was isolated as its etherate adduct $[Li(Et_2O)(2,4,6\text{-}i\text{-}Pr_3C_6H_2)]_2$.[25] Solvents were freshly distilled under N_2 from Na/K and degassed three times immediately before use. Compounds 2 and 3 gave satisfactory C, H analyses.

Physical Measurements. ^1H NMR spectra were obtained on a General Electric QE-300 spectrometer.

$Mg(Mes)_2(THF)_2$ (1). Compound 1 was synthesized by a literature procedure.[23] Crystals suitable for X-ray structural analyses were grown from Et_2O/THF solution in a −20 °C freezer.

$Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(THF)_2$ (2). A tetrahydrofuran solution of $(2,4,6\text{-}i\text{-}Pr_3C_6H_2)MgBr$ was prepared in a manner similar to that for MesMgBr.[23,26] A solution of 1,4-dioxane (5 g, 56.7 mmol) in THF (20 mL) was added dropwise to the $(2,4,6\text{-}i\text{-}Pr_3C_6H_2)MgBr$ solution (0.386 M, 130 mL). The white slurry was stirred overnight and then allowed to settle for ca. 4 h. The yellow supernatant solution was transferred to another Schlenk flask via a double-

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Table I. Crystallographic Data for the Structural Analyses of 1–3

	1	2	3
formula	$C_{26}H_{38}MgO_2$	$C_{38}H_{62}MgO_2$	$C_{49}H_{77}LiMgO$
fw	406.89	575.22	713.40
temp, K	130	130	130
cryst syst	orthorhombic	orthorhombic	monoclinic
a, Å	9.019 (2)	33.865 (10)	12.819 (3)
b, Å	28.752 (6)	33.912 (11)	15.103 (3)
c, Å	36.782 (6)	12.406 (4)	24.500 (5)
α, deg			
β, deg			91.13 (2)
γ, deg			
V, Å^3	9539 (3)	14 247 (8)	4742 (2)
space group	*F2dd*	*Fdd2*	$P2_1/c$
Z	16	16	4
D_{calc}, g cm^{-3}	1.13	1.07	0.999
μ, cm^{-1}	0.89	0.75	0.68
2θ range, deg	0–55	0–50	0–50
no. of obsd rflns	2146, $I > 3\sigma(I)$	2934, $I > 2\sigma(I)$	4925, $I > 2\sigma(I)$
no. of variables	279	406	457
R, R_w	0.045, 0.052	0.404, 0.042	0.080, 0.085

Table II. Important Atomic Coordinates (×10^4) for 1–3

	x	y	z
	$Mg(Mes)_2(THF)_2$ (1)		
Mg	0	2634 (1)	3518 (1)
O(1)	−1460 (3)	3024 (1)	3210 (1)
O(2)	1190 (4)	3240 (1)	2620 (1)
C(1)	834 (4)	2095 (1)	3154 (1)
C(10)	−653 (4)	2441 (1)	4064 (1)
	$Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(THF)_2$ (2)		
Mg	3346 (1)	846 (1)	2056 (1)
O(1)	3328 (1)	226 (1)	2184 (2)
O(2)	2725 (1)	828 (1)	1925 (2)
C(1)	3404 (1)	1222 (1)	3472 (2)
C(16)	3722 (1)	903 (1)	641 (2)
	$[Li(THF)_{0.6}(Et_2O)_{0.4}][Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3]$ (3)		
Mg	1580 (1)	7105 (1)	4105 (1)
Li	3183 (6)	7305 (6)	4826 (3)
O	4285 (3)	7514 (3)	5313 (1)
C(1)	3138 (3)	7745 (3)	3972 (2)
C(2)	4129 (3)	7350 (3)	3985 (2)
C(16)	353 (3)	7149 (3)	3496 (2)
C(31)	1667 (3)	6584 (3)	4946 (2)
C(32)	1518 (3)	7043 (3)	5446 (2)

Table III. Important Bond Distances (Å) and Angles (deg) for 1–3

	Compound 1		
Mg–C(1)	2.182 (3)	Mg–O(1)	2.067 (3)
Mg–C(10)	2.165 (3)	Mg–O(2)	2.079 (3)
∠C(1)MgC(10)	118.8 (1)	∠C(10)MgO(1)	118.3 (1)
∠C(1)MgO(1)	105.5 (1)	∠C(10)MgO(2)	100.9 (1)
∠C(1)MgO(2)	121.8 (1)	∠O(1)MgO(2)	88.4 (1)
	Compound 2		
Mg–C(1)	2.179 (3)	Mg–O(1)	2.107 (2)
Mg–C(16)	2.177 (3)	Mg–O(2)	2.110 (2)
∠C(1)MgC(16)	123.1 (1)	∠C(16)MgO(1)	99.6 (1)
∠C(1)MgO(1)	121.7 (1)	∠C(16)MgO(2)	121.5 (1)
∠C(1)MgO(2)	99.7 (1)	∠O(1)MgO(2)	87.1 (1)
	Compound 3		
Mg–C(1)	2.249 (4)	Li–C(1)	2.195 (9)
Mg–C(16)	2.147 (4)	Li···C(2)	2.650 (9)
Mg–C(31)	2.206 (4)	Li–C(31)	2.251 (9)
Mg···Li	2.700 (8)	Li···C(32)	2.673 (9)
Li–O	1.858 (8)		
∠C(1)MgC(31)	105.0 (1)	∠OLiC(32)	105.4 (5)
∠LiMgC(16)	171.4 (2)	∠MgLiC(2)	77.5 (5)
∠C(1)MgC(16)	121.8 (2)	∠MgLiC(32)	75.5 (5)
∠C(16)MgC(31)	131.2 (2)	∠C(1)LiC(31)	105.3 (3)
∠OLiMg	176.5 (5)	∠C(1)LiC(32)	125.5 (5)
∠OLiC(1)	124.4 (2)	∠C(2)LiC(31)	122.6 (5)
∠OLiC(2)	101.8 (5)	∠C(2)LiC(32)	152.7 (5)
∠OLiC(31)	130.3 (4)		

tipped needle and was concentrated under reduced pressure. Addition of Et_2O yielded an off-white solid. The solid was redissolved in THF/Et_2O. Cooling overnight in a −20 °C freezer gave the product 2 as colorless crystals: yield 9.09 g, 63%; mp 124–125 °C; ^1H NMR (C_6D_6) δ 1.22 (d, o-$CHMe_2$, $^3J_{HH}$ = 6 Hz), 1.24 (d, p-$CHMe_2$, $^3J_{HH}$ = 6 Hz), 1.44 (broad, THF), 2.70 (sept, o-CH, $^3J_{HH}$ = 6 Hz), 2.96 (sept, p-CH, $^3J_{HH}$ = 6 Hz), 3.54 (broad, THF), 6.95 (s, aryl H).

$[Li(THF)_{0.6}(Et_2O)_{0.4}][Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3]$ (3). An Et_2O solution (40 mL) of $[(2,4,6\text{-}i\text{-}Pr_3C_6H_2)Li(Et_2O)]_2$ (2.08 g, 7.33 mmol) was added dropwise to an Et_2O solution (40 mL) of $Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(THF)_2$ (2; 4.21 g, 7.33 mmol) at 0 °C. The solution was gradually warmed to room temperature, and stirring was continued for 2 days. The solvent was concentrated to ca. 30 mL, and cooling overnight in a −20 °C freezer gave the product 3 as colorless crystals: yield 4.44 g, 85%; ^1H NMR (C_6D_6) δ 1.17 (broad, THF/Et_2O), 1.23 (d, o-$CHMe_2$, $^3J_{HH}$ = 6 Hz), 1.37 (d, p-$CHMe_2$, $^3J_{HH}$ = 6 Hz), 2.50 (broad, THF/Et_2O), 2.79 (sept, p-CH, $^3J_{HH}$ = 6 Hz), 3.05 (sept, o-CH, $^3J_{HH}$ = 6 Hz), 7.05 (s, aryl H).

X-ray Crystallography. Crystals of the compounds were transferred from the Schlenk tube under N_2 to Petri dishes and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber with silicone grease, and immediately placed in the low-temperature nitrogen stream.[27]

The X-ray data for compounds 1–3 were collected by using a Syntex $P2_1$ diffractometer equipped with a locally modified Syntex LT-1 device for low-temperature work and graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Calculations for compounds 1 and 2 were carried out on a Data General Eclipse computer using SHELXTL (Version 5). Calculations for structure 3 were carried out on a Micro VAX 3200 computer using SHELXTL PLUS. Important crystallographic parameters and refinement data are provided in Table I. An ω-scan method was used for all data collections as described in ref 27. No decay in the intensities of two standard reflections was observed during the course of data collections for compounds 1–3. Scattering factors were from common sources.[28] The structure of 1 was solved by a Patterson map for the Mg position. The structures of 2 and 3 were solved by direct methods. All non-hydrogen atoms were refined anisotropically for compounds 1–3. Hydrogen atoms in the structures of 1–3 were included at calculated positions using a riding model with C–H = 0.96 Å and $U_{iso}(H) = 1.2[U_{iso}(C)]$ or $1.2[U^*_{iso}(C)]$, where U^*_{iso} is the equivalent isotropic thermal parameter. Disorder was modeled for two isopropyl groups in compound 3. Disorder was also modeled in the solvent molecule attached to the Li in 3. The presence of either THF or diethyl ether is reasonable. The position and isotropic thermal parameters of relative carbon atoms were optimized for a THF occupancy of 0.6 and a diethyl ether occupancy of 0.4. An absorption correction was applied for all compounds by using the method described in ref 29. The coordinates of important atoms are given in Table II. Important bond distances and angles are listed in Table III.

Description of the Structures of 1–3

$Mg(Mes)_2(THF)_2$ (1). Compound 1 possesses the structure illustrated in Figure 1. There is no crystallographically imposed symmetry. The magnesium has distorted-tetrahedral coordination with angles at the metal

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[27] This method is described in: Hope, H. In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemistry Society: Washington, DC, 1987; Chapter 10.

[28] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

[29] The absorption correction was made using the program XABS by H. Hope and B. Moezzi. The program obtains an absorption tensor from $F_o - F_c$ differences: Moezzi, B. Ph.D. Dissertation, University of California, Davis, CA, 1987.

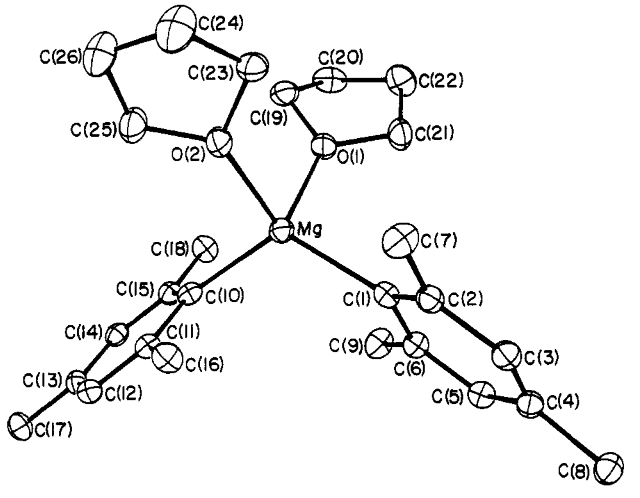

Figure 1. Computer-generated thermal ellipsoid plot of **1**. H atoms are omitted for clarity. Important distances and angles are given in Table III.

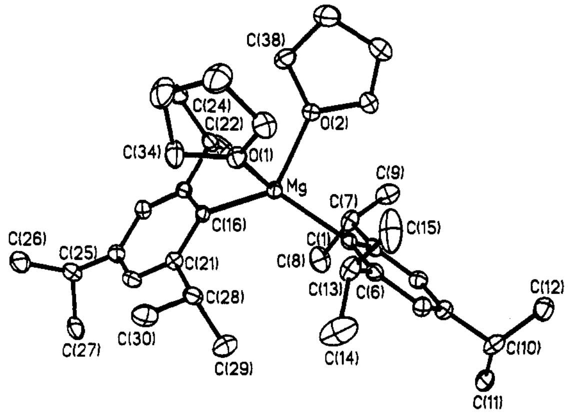

Figure 2. Computer-generated thermal ellipsoid plot of **2**. H atoms are omitted for clarity. Important distances and angles are given in Table III.

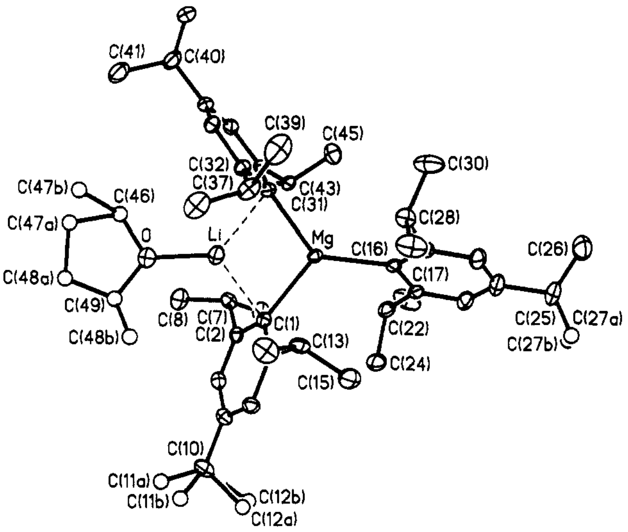

Figure 3. Computer-generated thermal ellipsoid plot of **3**. H atoms are omitted for clarity. Important distances and angles are given in Table III.

that vary from 88.4 (1) to 121.8 (1)°. The angle at magnesium between the two mesityl groups is 118.8 (1)°, whereas an angle of 88.4 (1)° separates the two THF donors. The average Mg–C bond distance is 2.174 (3) Å, and the average Mg–O bond distance is 2.073 (3) Å.

$Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(THF)_2$ (2). The structure of compound **2** (illustrated in Figure 2) is very closely related to that of **1**. There is no crystallographically imposed symmetry, and the angles at magnesium vary from 87.1 (1) to 123.1 (1)°, with the lowest value separating the two THF donors and the largest angle being between the two $2,4,6\text{-}i\text{-}Pr_3C_6H_2$ groups. The average Mg–C and Mg–O bond distances are 2.178 (3) and 2.109 (2) Å, respectively.

$[Li(THF)_{0.6}(Et_2O)_{0.4}][Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3]$ (3). The structure of **3**, which has no symmetry restrictions, is depicted in Figure 3 and involves a contact ion pair between $[Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3]^-$ and $[Li(THF)_{0.6}(Et_2O)_{0.4}]^+$,[30] which results in a short Li···Mg contact of 2.700 (8) Å. The Li, O, Mg, C(1), C(16), and C(31) atoms are coplanar, and the angles at magnesium (105.0 (2), 121.8 (2), and 133.2 (2)°) display considerable distortion from idealized trigonal values. The narrowest angle, ∠C(1)MgC(31), involves the $2,4,6\text{-}i\text{-}Pr_3C_6H_2$ groups bound to the Li^+ ion. The Li–C(ipso) distances are 2.195 (9) Å for C(1) and 2.251 (9) Å for C(31). The Mg–C(1) and Mg–C(31) bond distances of 2.249 (4) and 2.206 (4) Å are significantly longer than the terminal Mg–C(16) bond distance of 2.147 (4) Å. The C(1), C(16), and C(31) aryl rings subtend angles of 63.1, 56.0, and 6.2° with respect to the MgC(1)C(16)C(31) plane. There are angles of 14.4 and 0.6° between the Mg vectors and the respective planes of the C(1) and C(31) rings. The Li–O bond distance is 1.858 (8) Å.

Discussion

Diorganomagnesium Compounds. $Mg(Mes)_2(THF)_2$ (1)[23] and $Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(THF)_2$ (2) can be readily obtained from their respective Grignard solutions in tetrahydrofuran by disproportionation with 1,4-dioxane. Compounds **1** and **2** are useful synthetic reagents for the efficient preparation of several species, including the bulky $RMCl_2$ or R_2MCl compounds (R = Mes, $2,4,6\text{-}i\text{-}Pr_3C_6H_2$; M = Al, Ga).[31] As arylating agents their advantages over the use of the related Grignard reagent involve greater control of reaction stoichiometry and easier purification of reaction products. In addition, diorganomagnesium compounds serve as precursors to magnesiates, which have shown enhanced chemical reactivity in comparison to their neutral precursors.[16,17] As already mentioned in the Introduction, relatively few diorganomagnesium etherate compounds have been structurally characterized. Two crown-ether complexes, Ph_2Mg(1,3-xylyl-18-crown-5) and Et_2Mg(18-crown-6), which exhibit threaded structures with linear MgR_2 moieties, have been reported.[12,13] The octahedrally coordinated species $Mg(C{\equiv}CPh)_2(TMEDA)_2$, which possesses a pseudo-threaded structure with axially bound C≡CPh groups and two TMEDA groups occupying the equatorial sites, has also been reported.[14] In addition, the structures of the sandwich compounds $Mg(\eta^5\text{-}C_5R_5)_2$ (R = H, Me) have appeared.[15] More relevant to the studies described here are the structures of $Ar_2Mg(THF)_2$ (Ar = Ph, *p*-tolyl),[5] which are mononuclear with Mg bound to two terminal Ph or *p*-tolyl groups and THF's. In the Ph species the Mg–C distance is 2.127 (4) Å with a ∠CMgC angle of 122.4 (1)°. The ∠OMgO angle is 94.2 (1)°, and the Mg–O distances average 2.030 (4) Å. The compound also possesses 2-fold symmetry. In the *p*-tolyl derivative the Mg–C distances average 2.128 (8) Å with a ∠CMgC angle

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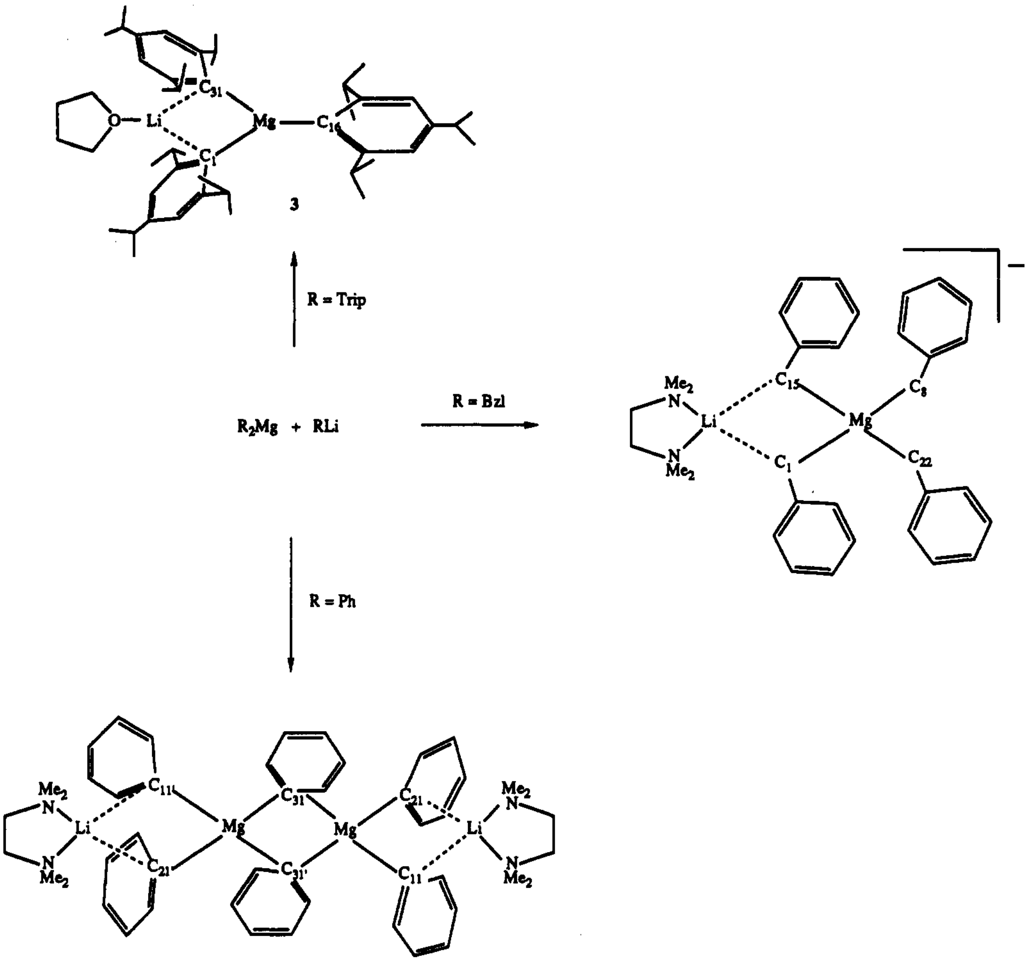
(30) Disorder was modeled in the solvent molecule attached to lithium. The position and isotropic thermal parameters of relative carbon atoms were optimized for a THF occupancy of 0.6 and a diethyl ether occupancy of 0.4.

(31) Waggoner, K. M.; Petrie, M.; Power, P. P.; Dias, H. V. R.; Ruhlandt-Senge, K. Unpublished results.

Scheme I. Effect of the Size of the Organo Group on the Degree of Association of Lithium Magnesiates



of 124.4 (3)°. The ∠OMgO(N) angle is 96.7 (2)°, and the Mg–O bond lengths average 2.041 (6) Å. In addition, an incomplete X-ray analysis of $Mg(C_6H_5)_2(Et_2O)_2$ and solution ^1H NMR data were consistent with a monomeric molecule and tetrahedral coordination at magnesium; however, important bond distances and angles were not described.[32] $Mg(t\text{-}Bu)_2(THF)_2$ was proposed to be dimeric in solution, but the solid-state structure is not known.[33]

It is obvious that the structures of 1 and 2 bear a very close structural resemblance to that of $Ar_2Mg(THF)$ (R = Ph, *p*-tolyl). The Mg–C distances in 1 and 2 are only marginally longer than those observed in the phenyl and *p*-tolyl derivatives. Moreover, the Mg–C distances are consistent with the 2.17-Å value predicted from the sum of the covalent radii.[34] In contrast, the Mg–O distances in the series Ph, Mes, 2,4,6-*i*-$Pr_3C_6H_2$ in 1 and 2 are shorter than those in the Ph or *p*-tolyl derivatives. Another anomaly is that the ∠CMgC angles in 1 and 2 are respectively less than and about equal to those observed in the Ph and *p*-tolyl derivatives. It is notable, however, that the ∠OMgO angles in 1 and 2 are narrower by ca 6°. Increasing the size of the organo substituent from Mes to 2,4,6-*i*-$Pr_3C_6H_2$ results in a small increase in the Mg–O distance, but there is essentially no increase in the ∠CMgC angle between the Ph and 2,4,6-*i*-$Pr_3C_6H_2$ derivatives. The ∠OMgO angles change in a direction that reflects an increase in steric requirements imposed by the Mes and 2,4,6-*i*-$Pr_3C_6H_2$ groups. The Mg–O bonds are also marginally longer in 1 and 2, close to that predicted by the sum of the radii (2.1 Å).[34]

Magnesiates. Magnesiates may be prepared from the corresponding diorganomagnesium compound by a variety of methods. For example, they may be isolated by disproportionation of the diorganomagnesium precursor with crown ethers or cryptands.[16] Magnesiates have also been isolated by reaction of the diorganomagnesium precursor with alkyl- or aryllithium compounds to afford Li–Mg organometallic complexes.[21,22] Although studies of such systems have been known for over 50 years,[20] very few structural studies have appeared.

The species $[Li(THF)_{0.6}(Et_2O)_{0.4}][Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3]$ (3) may be crystallized from solutions formed by the addition of (2,4,6-*i*-$Pr_3C_6H_2$)Li in Et_2O to (2,4,6-*i*-$Pr_3C_6H_2)_2Mg$ in THF. The most outstanding feature of 3 is the 3-fold coordination of the magnesium atom. Only three other structures involving three-coordinate magnesium have been published. One is the recently reported magnesiate of the type formed by the cryptand-induced disproportionation of $MgNp_2$ (Np = neopentyl).[16a] The resulting structure has the formula [NpMg(2,1,1-cryptand)][$MgNp_3$]. The other two involve a rare, naturally occurring zeolite crystal in which magnesium was reported to be bound to three oxygens[35] and the dimeric amido-bridged compound $[s\text{-}BuMg\{\mu\text{-}N(SiMe_3)_2\}]_2$.[36]

The three ∠CMgC bond angles in 3 are 105.0 (1), 121.8 (2), and 133.1 (2)°, which result in distorted-trigonal-planar

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coordination at magnesium. The narrowest ∠CMgC angle is associated with groups that bridge the Li^+ ion. The 2,4,6-*i*-$Pr_3C_6H_2$ groups, which bridge lithium and magnesium, have Mg–C(1) and Mg–C(31) bonds of 2.249 (4) and 2.206 (4) Å. These are somewhat longer than the terminal Mg–C(16) bond length of 2.147 (4) Å. A simplistic explanation for this difference involves the higher effective coordination number of C(1) and C(31) and the consequent lower electron density available for the Mg–C bridge bonds. However, a comparison of the Mg–C distances in **3** with those of [NpMg(2,1,1-cryptand)][$MgNp_3$] (in which the cation–anion separation is greater than 7.18 Å) reveals a similar pattern. The three Mg–C bond lengths in this latter compound are 2.125 (12), 2.240 (12), and 2.296 (16) Å with angles of 116.9 (5), 117.6 (5), and 124.8 (6)°. Whether or not the remarkable similarity of these parameters with those of **3** is coincidental awaits the determination of further examples of three-coordinate Mg species.

A comparison of **3** with the lithium magnesiate species $[Li(TMEDA)]_2[Ph_2MgPh_2MgPh_2]$[21] and $[Li(TMEDA)_2](TMEDA)LiBzl_2MgBzl_2]$ (Bzl = benzyl)[22] illustrates the effect of the size of the organo group on the degree of association observed (see Scheme I). Clearly, the large 2,4,6-*i*-$Pr_3C_6H_2$ substituents impose a coordination number of 3 at magnesium. Oddly, the Mg–C(1) and Mg–C(31) bond distances of 2.249 (4) and 2.206 (4) Å in **3** are longer than the Mg–C(11) and Mg–C(21) distances of 2.186 (3) and 2.182 (3) Å in the phenyl compound, which also involve bridging to lithium. This is in spite of lower coordination of the magnesium in **3**. It is, thus, possible to argue that longer bond lengths are expected because of the increased size of the 2,4,6-*i*-$Pr_3C_6H_2$ groups in **3**. In the benzyl derivative, the bridging Mg–C(1) and Mg–C(15) bond distances are significantly longer and are 2.322 (11) and 2.313 (9) Å, respectively. Part of the reason for this could be the ability of the benzyl ligand to delocalize negative charge, thereby reducing the strength of the Mg–C bond by decreasing the ionic contribution to the bond strength. It is also notable that the magnesium complex bears a negative charge which increases the electron density in the complex and thereby tends to reduce the ionic contribution to the strength of the Mg–C bond. The Li–C(ipso) distances (2.251 (9) and 2.195 (9) Å) in **3** are significantly shorter than the Li–C(ipso) distances in the phenyl compound (2.419 and 2.472 Å). This can be rationalized on the basis of the higher coordination number of the Li^+ ion in the phenyl species. Significantly, the benzyl compound possesses Li–C(Bzl) bond distances (2.229 (21) and 2.272 (16) Å) which are shorter than the Li–C(ipso) distances in either the phenyl compound or compound **3**. One of the reasons for this is that the interaction between the Li^+ ion and the C(ipso) carbons in both **3** and the phenyl species is mainly an interaction with the ring π-electrons.[37] In the case of the benzyl species, some σ-interaction in the Li–C bond is also present. It follows that the Mg–C bonds in the benzyl species must also have π-character (and thereby a lower σ-contribution), which is in agreement with the longer than expected Mg–C bonds, both bridging and terminal. In line with these views, it is notable that there is a small angle of 14.4° between the Mg–C(1) vector and the plane of the C(1) ring. This suggests reduced σ-character in the Mg–C bond and increased σ-character in the Li–C bond. The longer Mg–C(1) and shorter Li–C(1) bonds are in accordance with this view.

These compounds illustrate the structural dependence of intermetallic complexes on the nature of R. For very small R groups, the degree of association increases. For example, dimethylmagnesium and methyllithium in diethyl ether produce complexes of composition Li_2MgR_4 or Li_3MgR_5.[38] As the size of the R group is increased, stable low-coordinate intermetallic magnesiates may be isolated.

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Registry No. **1**, 69997-67-7; **2**, 133421-08-6; **3**, 143104-42-1; (2,4,6-*i*-$Pr_3C_6H_2$)MgBr, 108894-99-1; [(2,4,6-*i*-$Pr_3C_6H_2$)Li(Et_2O)]$_2$, 119131-64-5.

Supplementary Material Available: Full tables of atom coordinates, crystallographic data, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters for **1**–**3** (29 pages). Ordering information is given on any current masthead page.

OM920186D

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