Synthesis, Structure, and Catalytic Studies of Mixed Lithium−Magnesium and Sodium−Magnesium Complexes: Highly Isospecific Initiators for Polymerization of Methyl Methacrylate

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The unusual lithium *n*-butylmagnesium complex $[(\mathrm{EDBP})\mathrm{Mg}(\mu_2\text{-}^n\mathrm{Bu})\mathrm{Li}(\mathrm{Et_2O})]_2$ (**2**) and sodium *n*-butylmagnesium complex $[(\mathrm{EDBP})\mathrm{Na}(\mathrm{Et_2O})\mathrm{Mg}^n\mathrm{Bu}]_2$ (**5**), lithium−magnesium enolate, $\{(\mathrm{EDBP})\mathrm{Mg}[\mu_2\text{-}\mathrm{OC}(\mathrm{Mes})\mathrm{CH_2}]\mathrm{Li}(\mathrm{Et_2O})\}_2$ (**3**), and the sodium aggregate, $[(\mathrm{EDBP})\mathrm{Na_2}]_4$ (**4**), have been synthesized and structurally characterized. Among them, **2**, **3**, and **5** have been used as initiators for the polymerization of methyl methacrylate. The reaction of 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (EDBP-H_2) with ^{n}BuLi in diethyl ether gives $[(\mathrm{EDBP\text{-}H})\mathrm{Li}(\mathrm{Et_2O})_3]$ (**1**). The dimeric lithium *n*-butylmagnesium complex **2** was obtained from the reaction of **1** with a stoichiometric amount of $\mathrm{Mg}^n\mathrm{Bu_2}$. Alternatively, **2** can also be prepared by the reaction of $[(\mathrm{EDBP})\mathrm{Mg}(\mathrm{Et_2O})]_2$ (**A**) with a stoichiometric amount of ^{n}BuLi in Et_2O. Furthermore, the reaction of **2** with 2′,4′,6′-trimethylacetophenone ($\mathrm{MesC(O)CH_3}$, Mes = 2,4,6-$\mathrm{Me_3C_6H_2}$) produces **3**. Reaction of EDBP-H_2 with excess sodium metal in Et_2O furnishes compound **4**. In the presence of a stoichiometric amount of $\mathrm{Mg}^n\mathrm{Bu_2}$ in Et_2O, **4** can be converted to the dimeric sodium−magnesium mixed-metal complex $[(\mathrm{EDBP})\mathrm{Na}(\mathrm{Et_2O})\mathrm{Mg}^n\mathrm{Bu}]_2$ (**5**). Experimental results show that **2**, **3**, and **5** efficiently initiate the anionic polymerization of methyl methacrylate.

Introduction

Alkyllithiums and lithium alkoxides are widely used in modern organic synthesis due to their applications as alkylating and deprotonating reagents as well as catalysts in polymerization.[1] It was recognized that the reactivity of organolithium compounds may be enormously enhanced upon the addition of potassium or sodium alkoxides. These mixed-anion complexes of the type $[\mathrm{RM{\cdot}M'OR}]_n$ (M = Li; M′ = Na, K) are widely known as "superbases".[2] Although several examples have been described in the literature,[1−3] the solid-state structural information available on mixed-anion systems is still limited.[3] It has been known that the bimetallic -ate complexes, such as R_3MgLi and R_4AlLi, have unique chemical properties different from those of the corresponding homometallic complexes. These complexes are extensively used in organic synthesis.[4] The synergistic behavior could lead to different reactivities and selectivities with the formation of activated complexes or intermediates. Recent reports have investigated the reactivities of lithium zincates toward halogen− or tellurium−zinc exchange reactions, Michael addition, carbozincation, epoxide opening,[5] and a catalytic electron transfer (ET) system consisting of a transition metal ate complex ($\mathrm{Me_3M(II)Li}$; M = Co(II), Mn(II), Fe(II)).[6] The first examples of halogen−magnesium exchange via binuclear magnesium−lithium complexes in

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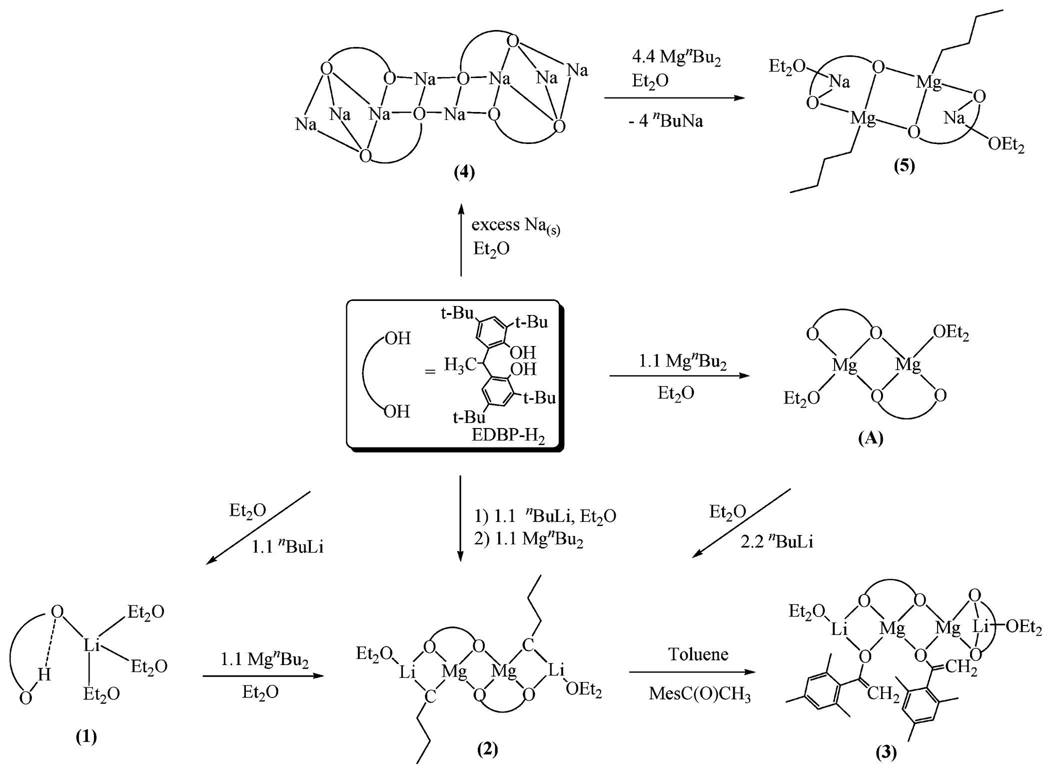
Scheme 1



benzene, pyridine, and thiophene were published by Oshima and co-workers.[7] They found that "$LiMgR_3$" are more effective in halogen−magnesium exchange reactions with aryl- and alkenylmagnesium reagents than their corresponding Grignard counterparts (RMgX).

A highly R-selective addition to ketones was demonstrated by using RMe_2MgLi in place of R_3MgLi.[8] Richey and Farkas have demonstrated that in pyridine alkylation reactions the mixture of dialkylmagnesium and alkyllithium compounds exhibits a behavior different from that of the corresponding organometallic compound.[9] Recently, Mulvey and co-workers reported a series of mixed alkali and alkaline earth metal complexes[10] and inverse crown ethers[11] and their application in highly chemo-/regioselective reactions such as metalation of benzene, toluene, and metallocene[12] and deprotonation of ketones.[13]

In addition, dialkylmagnesium, by itself, is not an active initiator for diene and styrene polymerization. However, in combination with organolithium, it becomes more active and initiates polymerization.[14] Moreover, Deffieux has found that in the presence of akali metal alkoxides, isotactic-rich polystyrene is obtained using bimetallic systems, while syndiotactic-rich polystyrene is obtained using homometallic systems.[15]

Results and Discussion

Synthesis and Characterization. The reaction of 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (EDBP-H_2) with ^nBuLi in diethyl ether gives [(EDBP-H)Li(Et_2O)$_3$] (**1**)[16] in good yield, as shown in Scheme 1. [(EDBP)Mg(μ_2-^{n}Bu)Li(Et_2O)]$_2$ (**2**) was obtained as a white crystalline solid in 81% yield from the reaction of [(EDBP-H)Li(Et_2O)$_3$] (**1**) with Mg^nBu_2 in diethyl ether. Alternatively, **2** can also be prepared directly by the reaction of [(EDBP)Mg(Et_2O)]$_2$ (**A**)[17] with a stoichiometric amount of ^nBuLi in diethyl ether in 91% yield. The addition of

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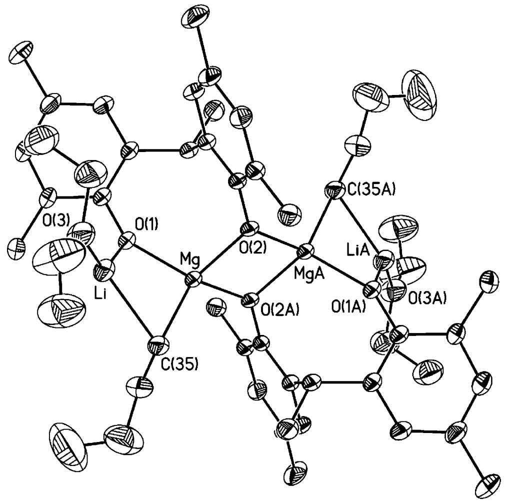

Figure 1. Molecular structure of $\mathbf{2}\cdot 0.5\mathrm{C_6H_{14}}$ as 20% ellipsoids (methyl carbons of the *tert*-butyl groups and all of the hydrogen atoms are omitted for clarity).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $\mathbf{2\cdot 0.5C_6H_{14}}$

Bond Distances			
Mg−O(1)	1.962(2)	Mg−O(2)	2.010(2)
Mg−O(2A)	1.983 (2)	Mg−C(35)	2.175(4)
Li−O(1)	1.873(7)	Li−O(3)	1.928(8)
Li−C(35)	2.263(7)		
Bond Angles			
O(1)−Mg−O(2A)	135.09(10)	O(1)−Mg−O(2)	109.63(9)
O(2A)−Mg−O(2)	82.41(8)	O(1)−Mg−C(35)	94.97(12)
O(2A)−Mg−C(35)	115.04(11)	O(2)−Mg−C(35)	122.65(14)
O(1)−Li−O(3)	131.4(4)	O(1)−Li−C(35)	94.7(3)
O(3)−Li−C(35)	125.0(4)		

2′,4′,6′-trimethylacetophenone to a toluene solution of [(EDBP)Mg(μ_2-^{n}Bu)Li(Et$_2$O)]$_2$ (**2**) afforded {(EDBP)Mg[μ_2-OC(Mes)CH$_2$]Li(Et$_2$O)}$_2$ (**3**) as the major product in 57% yield with the concomitant conversion of the ^{n}Bu group to butane. In addition, the reaction of EDBP-H$_2$ with excess sodium metal in diethyl ether produces [(EDBP)Na$_2$]$_4$ (**4**) in high yield. Compound **4** reacts further with a stoichiometric amount of Mg^{n}Bu$_2$ to yield a dimeric mixed sodium−magnesium complex, [(EDBP)Na(Et$_2$O)Mg^{n}Bu]$_2$ (**5**).

Single crystals suitable for structural characterization of compound **2** were obtained by slow cooling of a warm toluene solution. The molecular structure of **2** is dimeric with the crystallographic center located in the center of the Mg$_2$O$_2$ core, as illustrated in Figure 1. The selected bond lengths and angles are listed in Table 1. This compound consists of two ^{n}Bu groups bridging the lithium and magnesium atoms with a Li−C(35) distance of 2.263(7) Å and a Mg−C(35) distance of 2.175(4) Å. Two oxygen atoms of the EDBP ligand are nonequivalent. One of them is bonded to a lithium atom and a magnesium atom, and the other one is coordinated to two magnesium atoms. Coordination of Li and Li(A) to diethyl ether (Li−O(3) 1.928(8) Å) makes them three-coordinated. Compound **2** is the first example of a mixed-metal model of a ^{n}BuLi-biphenoxide complex including lithium and magnesium metals.

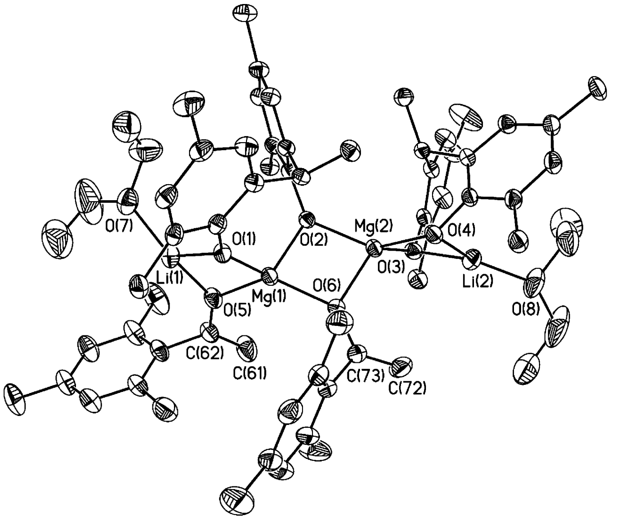

Figure 2. Molecular structure of **3** as 20% ellipsoids (methyl carbons of the *tert*-butyl groups and all of the hydrogen atoms are omitted for clarity).

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

Bond Distances			
Mg(1)−O(1)	1.925(2)	Mg(1)−O(2)	1.982(2)
Mg(1)−O(5)	1.913(2)	Mg(1)−O(6)	1.946(2)
Mg(2)−O(2)	1.973(2)	Mg(2)−O(3)	1.929(2)
Mg(2)−O(4)	1.948(2)	Mg(2)−O(6)	1.977(2)
Li(1)−O(1)	1.960(6)	Li(1)−O(5)	1.864(7)
Li(1)−O(7)	1.925(7)	Li(2)−O(3)	1.915(7)
Li(2)−O(4)	2.049(7)	Li(2)−O(8)	1.901(7)
Bond Angles			
O(5)−Mg(1)−O(1)	87.69(10)	O(1)−Mg(1)−O(6)	133.58(11)
O(5)−Mg(1)−O(2)	115.75(11)	O(1)−Mg(1)−O(2)	111.30(10)
O(5)−Mg(1)−O(6)	127.45(12)	O(6)−Mg(1)−O(2)	82.30(10)
O(3)−Mg(2)−O(4)	91.19(10)	O(3)−Mg(2)−O(2)	119.36(11)
O(4)−Mg(2)−O(2)	134.24(10)	O(3)−Mg(2)−O(6)	123.12(11)
O(4)−Mg(2)−O(6)	110.72(11)	O(2)−Mg(2)−O(6)	81.77(10)
O(5)−Li(1)−O(7)	133.5(4)	O(5)−Li(1)−O(1)	88.0(3)
O(7)−Li(1)−O(1)	126.0(4)	O(8)−Li(2)−O(3)	129.7(4)
O(8)−Li(2)−O(4)	141.7(4)	O(3)−Li(2)−O(4)	88.6(3)

The molecular structure of **3** is asymmetric, as shown in Figure 2, and selected bond lengths and angles are listed in Table 2. Out of two enolate oxygens, one is bridging two magnesium atoms with a Mg(1)−O(6) distance of 1.946(2) Å and a Mg(2)−O(6) distance of 1.977(2) Å and the other enolate oxygen is bonded to a magnesium and a lithium atom with a Mg(1)−O(5) distance of 1.913(2) Å and a Li(1)−O(5) distance of 1.864(7) Å. These distances are within the expected range for magnesium/lithium alkoxides. Both magnesium atoms are four-coordinated, while lithium atoms are three-coordinated. Lithium cations are stabilized by coordination of a diethyl ether molecule (Li(1)−O(7) 1.925(7) Å, Li(2)−O(8) 1.901(7) Å). The closest precedent to **3** is the bimetallic enolate [Na$_2$Mg$_2${OC(=CH$_2$)Mes}$_6$(TMEDA)$_2$].[13c] However, the latter compound, which is a combination of an alkali metal with magnesium, adopts a different molecular structure from that of **3**. To the best of our knowledge, compound **3** is the first example of a mixed-metal enolate compound containing both lithium and magnesium.

Crystals suitable for X-ray structure determination of **4** were obtained from a mixed hexane/Et$_2$O (1:1) solution. The molecular structure of **4** illustrates an aggregation mode in the solid state with eight sodium atoms (Figure 3). Half an Et$_2$O molecule

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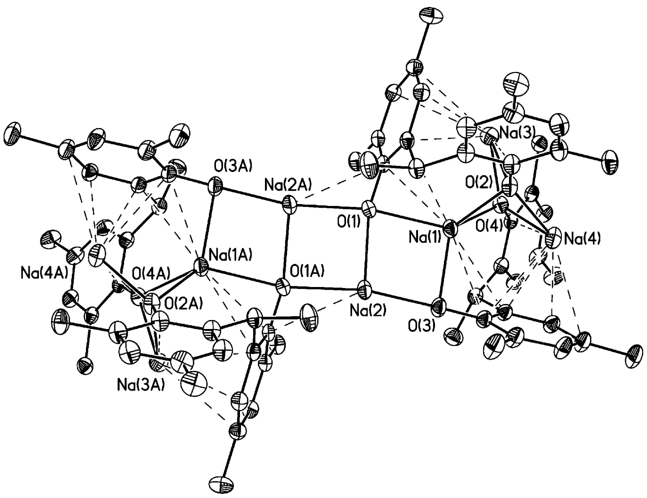

Figure 3. Molecular structure of **4**·Et_2O as 20% ellipsoids (methyl carbons of the *tert*-butyl groups and all of the hydrogen atoms are omitted for clarity).

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 4·Et_2O

	Bond Distances		
Na(1)−O(1)	2.356(2)	Na(1)−O(2)	2.356(2)
Na(1)−O(3)	2.259(2)	Na(1)−O(4)	2.305(2)
Na(1)···C(1)	2.620(2)	Na(1)···C(6)	2.944(2)
Na(1)···C(31)	2.713(3)	Na(1)···C(36)	3.037(2)
Na(2)−O(1)	2.296(2)	Na(2)−O(3)	2.131(2)
Na(2)−O(1A)	2.274(2)	Na(2)···C(1A)	2.922(2)
Na(3)−O(2)	2.305(2)	Na(3)−O(4)	2.291(2)
Na(3)···C(3)	3.100(3)	Na(3)···C(4)	2.885(3)
Na(3)···C(5)	2.710(2)	Na(3)···C(6)	2.830(2)
Na(3)···C(13)	3.104(2)	Na(4)−O(2)	2.306(2)
Na(4)−O(4)	2.350(2)	Na(4)···C(31)	2.998(3)
Na(4)···C(34)	3.032(3)	Na(4)···C(35)	2.728(3)
Na(4)···C(36)	2.693(3)	Na(4)···C(43)	3.055(2)
	Bond Angles		
O(2)−Na(1)−O(1)	120.26(7)	O(3)−Na(1)−O(4)	120.85(7)
O(3)−Na(1)−O(2)	118.73(7)	O(4)−Na(1)−O(2)	78.31(6)
O(3)−Na(1)−O(1)	94.16(7)	O(4)−Na(1)−O(1)	127.25(7)
O(3)−Na(2)−O(1)	99.49(7)	O(3)−Na(2)−O(1A)	168.50(8)
O(1A)−Na(2)−O(1)	91.23(6)	O(4)−Na(3)−O(2)	79.60(6)
O(2)−Na(4)−O(4)	78.38(6)		

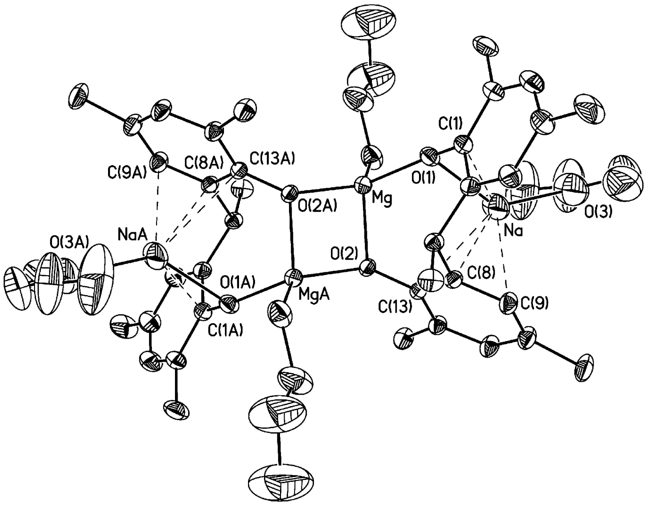

Figure 4. Molecular structure of **5** as 20% ellipsoids (methyl carbons of the *tert*-butyl groups and all of the hydrogen atoms are omitted for clarity).

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for 5

	Bond Distances		
Na−O(1)	2.304(2)	Na−O(3)	2.251(5)
Na−C(1)	2.763(3)	Na−C(8)	2.753(3)
Na−C(9)	3.000(4)	Na−C(13)	2.898(3)
Mg−O(1)	1.931 (2)	Mg−O(2)	2.047(2)
Mg−O(2A)	1.994 (2)	Mg−C(35)	2.140(3)
	Bond Angles		
O(3)−Na−O(1)	137.13(14)	O(1)−Mg−O(2)	102.51(8)
O(1)−Mg−O(2A)	124.78(8)	O(2A)−Mg−O(2)	81.62(7)

in an asymmetric unit cell with the oxygen atom sitting on the C_2 axis is observed. Selected bond lengths and angles are given in Table 3. In the solid state, compound **4** possesses a ring-laddering conformation. This complicated architectural structure of alkali metal chemistry has been discussed extensively in the literature.[18] The molecular structure of the mixed sodium−magnesium complex **5** is given in Figure 4, and its selected structural parameters are listed in Table 4. Compound **5** is also dimeric, with the crystallographic center located in the center of the Mg_2O_2 core. It is worth mentioning that the structure of **5** is somewhat different from that of **2**. In **2**, Li and Mg atoms are bridged by a ^{n}Bu group. In compound **5**, however, the ^{n}Bu group is bonded to a Mg atom only. Na is weakly coordinated to a phenyl ring of the EDBP^{2-} group. The reason for this difference is probably due to the softer nature of the Na cation compared to that of Li, which makes the former more likely to engage in metal−π arene interactions and less likely to be bridged by a ^{n}Bu group. Each magnesium atom binds a ^{n}Bu group with a Mg−C(35) distance of 2.140(3) Å. One of the oxygen atoms of the EDBP ligand is coordinated by a sodium atom and a magnesium atom, and another one is bonded by two magnesium atoms. In addition, Na and Na(A) are compensated by the coordination of diethyl ether with Na−O(3), 2.251(5) Å. Both aryl rings of EDBP ligands of compounds **4** and **5** are involved in cation−π interactions with sodium cations. The noncovalent interaction of alkali metal ions with electron-rich species such as double bonds, triple bonds, and arenes plays an important role in modern chemistry due to its chemical and biological importance.[19]

Anionic Polymerization of Methyl Methacrylate. Increases of the tacticity in poly(methyl methacrylate) increases its high optical clarity. Such a polymer has a wide range of applications due to its lower softening temperature (T_g). For example, a syndiotactic form of PMMA ($rr \approx 67\%$) affords a T_g of ca. 105 °C. However, as the isotacticity is increased, the T_g decreases (to ca. 47 °C for $mm > 90\%$).[20] Although a number of isospecific initiator systems have been described in the literature,[20a,b,21] organolithium compounds are most widely used as initiators due to their high versatility and reactivity. However,

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Table 5. Anionic Polymerization of MMA Initiated by 2, 3, and 5[a] at −30 °C

entry	initiator	PDI	M_n (obsd)[b]	[*mm*][c] (%)	[*mr*][c] (%)	[*rr*][c] (%)	TON[d]	T_g (°C)
1	**2**	1.67	89 600	96.7	2.8	0.5	23	60.3
2	**3**	1.35	58 900	96.1	3.9	0	31	59.6
3	**5**	1.58	86 300	95.4	3.6	1.0	22	58.5

[a] Polymerization conditions: 50 μmol of initiator (I); mole ratio MMA/I = 50; 10 mL of toluene, reaction time = 1 h. [b] Number-average molecular weight (M_n) and polydispersity index (PDI) determined by GPC relative to PS standards. [c] Tacticity (methyl triad distribution) determined by ^{1}H NMR spectroscopy. [d] Turnover number (TON) in units of mol of monomer (mol of I)$^{-1}$ h^{-1}.

organolithium initiators used for alkyl (meth)acrylate monomers generally yield polymers of broad MWD with low conversion and low stereoselectivity.[22] The nonideal behavior of alkyl (meth)acrylates is basically due to the polar ester group, which undergoes many side reactions during both initiation and propagation. Recently, we have developed a synthetic method for the preparation of a single active site of *n*-butyllithium by employing a sterically bulky ligand, 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (EDBP-H_2).

Preliminary studies on the use of **2**, **3**, and **5** as initiators for the anionic polymerization of methyl methacrylate (MMA) have revealed promising results as shown in Table 5. Compound **2** was found to be highly reactive and more isospecific for the MMA polymerization. The polymerization in toluene at −30 °C completes within 1 h, resulting in a molecular weight (M_n) of 89 600, polydispersity index (PDI) of 1.67, and [*mm*] of 96.7%. Compound **5** was also found to be highly reactive and more isospecific for the MMA polymerization, but with a slightly lower PDI than compound **2** under the same conditions (molecular weight (M_n) = 86 300, PDI = 1.58, [*mm*] = 95.4%). Addition of MMA to a toluene solution of compound **3** leads to rapid polymerization with high isotacticity {[*mm*] = 96.1%} and narrow PDI (1.35) with M_n = 58 900 within 1 h. The T_g values are consistent with the reported values for isotactic PMMA.

In conclusion, a lithium *n*-butylmagnesium complex and sodium *n*-butylmagnesium complex (compounds **2** and **5**) as well as a mixed lithium−magnesium enolate (compound **3**) have been synthesized and structurally characterized. Compounds **2**, **3**, and **5** are highly reactive as initiators for highly isoselective polymerization of MMA.

Experimental Section

General Considerations. All manipulations were carried out under a dry nitrogen atmosphere. ^{1}H spectra were recorded on a Varian Mercury-400 (400 MHz) spectrometer with chemical shifts given in ppm from the internal TMS. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. Gel permeation chromatography (GPC) measurements were performed on a Hitachi L-7100 system equipped with a differential Bischoff 8120 RI detector and 5 μm PL gel columns (Phenomenex; 100 Å) in series. The GPC columns were eluted with tetrahydrofuran at 30 °C at 1 mL/min and were calibrated using a polynomial fit to 10 monodisperse polystyrene standards. Glass transition temperatures (T_g) of the samples were determined using a Perkin-Elmer PYRIS Diamond differential scanning calorimeter (DSC) calibrated using indium, and all experiments were carried out under a nitrogen atmosphere. Typically, a sample of about 5 mg was heated from room temperature to 160 °C at a rate of 10 °C/min and held for 5 min to study the thermal history of the sample. The sample was quickly cooled to room temperature and was subsequently reheated from room temperature to 160 °C. Heating was repeated at the same rate. The data obtained from a second scan was used for the T_g determination of the sample.

Materials. Hexane (99%, ACS reagent, TEDIA), toluene (99%, ACS reagent, TEDIA), and diethyl ether (99%, ACS reagent, TEDIA) were distilled from sodium/benzophenone under nitrogen. MMA monomer (99%, Aldrich) was pretreated with CaH_2 powder (95%, Aldrich) overnight to remove dissolved water, followed by vacuum distillation. Final purification involved titration with neat tri(*n*-octyl)aluminum to a yellow end point[23] followed by distillation under reduced pressure. The purified monomers were stored in a −20 °C freezer. 2,2′-Ethylidenebis(4,6-di-*tert*-butylphenol) (EDBP-H_2), ^{n}BuLi (2.5 M in hexane), and Mg^nBu_2 (1.0 M in heptane) were purchased and used as received.

[(EDBP)Mg(Et$_2$O)]$_2$ (A). To an ice cold solution (0 °C) of 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (0.88 g, 2.0 mmol) in diethyl ether (20 mL) was slowly added a 1.0 M solution of Mg^nBu_2 in heptane (2.2 mL, 2.2 mmol). The mixture was stirred for 2 h and concentrated in vacuo. The residue was extracted with hot hexane (30 mL), and the extract was then concentrated to ca. 15 mL. Colorless crystals were obtained on cooling to −20 °C overnight. Yield: 0.91 g (85%).[17]

[(EDBP-H)Li(Et$_2$O)$_3$] (1). ^{n}BuLi (0.88 mL, 2.5 M solution in hexane, 2.2 mmol) was added slowly to an ice cold (0 °C) solution of 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (0.88 g, 2.0 mmol) in diethyl ether (20 mL). The mixture was stirred for 1 h at 0 °C, and the volatile materials were removed under vacuum. The residue was extracted with warm hexane (20 mL), and the extract was concentrated to ca. 10 mL. Colorless crystals were obtained on cooling at −20 °C. Yield: 1.11 g (83%). Anal. Calcd for $C_{42}H_{75}LiO_5$: C, 75.63; H, 11.33. Found: C, 76.18; H, 10.82. ^{1}H NMR (C_6D_6, ppm): δ 7.32, 7.23, 7.19, 7.13 (s, 4H, *Ph*); 5.42 (br, 1H, $-CH(CH_3)$); 3.17 (q, 12H, $-OCH_2CH_3$, J = 6.8 Hz); 1.69 (br, 3H, $-CH(CH_3)$); 1.39, 1.34, 1.17, 0.84 (s, 36H, $-CH(CH_3)_3$); 1.01 (t, 18H, $-OCH_2CH_3$, J = 6.8 Hz).

[(EDBP)Mg(μ_2-^{n}Bu)Li(Et$_2$O)]$_2$ (2). Method A: Mg^nBu_2 (2.2 mL, 1.0 M solution in heptane, 2.2 mmol) was added slowly to an ice cold solution (0 °C) of [(EDBP-H)Li(Et$_2$O)$_3$] (**1**) (1.33 g, 2.0 mmol) in diethyl ether (20 mL). The mixture was stirred for 2 h at 0 °C, and the volatile materials were removed under vacuum. The residue was extracted with warm toluene (20 mL), and the extract was concentrated to ca. 10 mL. Colorless crystals were obtained on cooling at −20 °C. Yield: 0.97 g (81%). Anal. Calcd for $C_{82}H_{140}Li_2Mg_2O_6$: C, 76.68; H, 10.99. Found: C, 76.38; H, 11.06. ^{1}H NMR (C_6D_6, ppm): δ 7.86, 7.46, 7.39, 7.24 (d, 8H, *Ph*); 5.24 (q, 2H, $-CH(CH_3)$, J = 6.8 Hz); 2.76 (q, 8H, $-OCH_2CH_3$, J = 6.8 Hz); 2.10 (d, 6H, $-CH(CH_3)$, J = 6.8 Hz); 1.63, 1.50, 1.28, 1.15 (s, 72H, $-C(CH_3)_3$); 1.47−1.36 (m, 8H, $-CH_2CH_2-$); 0.91 (t, 6H, $-CH_2CH_3$, J = 6.8 Hz); 0.63 (t, 12H, $-OCH_2CH_3$, J = 6.8 Hz); −0.78 (t, 4H, $LiMgCH_2$, J = 6.8 Hz).

Method B: ^{n}BuLi (0.88 mL, 2.5 M solution in hexane, 2.2 mmol) was added slowly to an ice cold (0 °C) solution of [(EDBP)Mg(Et$_2$O)]$_2$ (**A**) (1.07 g, 1.0 mmol) in diether ether (20 mL). The mixture was stirred for 2 h at 25 °C, and the volatile materials were removed under vacuum. The residue was extracted with warm toluene (20 mL), and the extract was concentrated to ca. 10 mL. Colorless crystals were obtained on cooling at −20 °C. Yield: 1.09 g (91%).

{(EDBP)Mg[μ_2-OC(Mes)CH$_2$]Li(Et$_2$O)}$_2$ (3). 2′,4′,6′-Trimethylacetophenone (0.33 mL, 2.0 mmol) was added slowly to an ice cold solution (0 °C) of [(EDBP)Mg(μ_2-^{n}Bu)Li(Et$_2$O)]$_2$ (**2**) (1.20

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Table 6. Crystallographic Data of the Structure Determination of 2−5

	2·0.5C_6H_{14}	**3**	**4**·0.5Et_2O	**5**
empirical formula	$C_{41}H_{63}LiMgO_3$[a]	$C_{90}H_{134}Li_2Mg_2O_8$	$C_{62}H_{93}Na_4O_{4.5}$[a]	$C_{38}H_{63}MgNaO_3$
fw	635.16[a]	1406.47	1002.32[a]	615.18
cryst syst	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2(1)/n$	$C2/c$	$Pccn$
a/Å	10.1149(9)	23.051(2)	41.530(4)	20.7678(12)
b/Å	12.7796(12)	17.2273(16)	14.2515(14)	21.2375(11)
c/Å	18.6450(17)	24.441(2)	27.917(3)	18.4101(11)
α/deg	106.170	90	90	90
β/deg	90.244	109.371(2)	118.808(2)	90
r/deg	100.614	90	90	90
volume/$Å^3$	2271.2(4)	9156.6(15)	14478(2)	8119.9(8)
Z	2	4	8	8
density (calcd)/Mg/m^3	0.929	1.020	0.918	1.006
abs coeff/mm^{-1}	0.068	0.075	0.076	0.084
$F(000)$	696	3072	4360	2704
no. of reflns collected	12 967	51 394	39 947	43 975
no. of indep reflns	8785 [R(int) = 0.0292]	18 028 [R(int) = 0.1033]	14 135 [R(int) = 0.0317]	7997 [R(int) = 0.0835]
no. of data/restraints/params	8787/0/432	18 028/0/946	14 135/0/698	7997/0/398
R1[b]	0.0857	0.0631	0.0688	0.0648
wR2[c]	0.2349	0.1327	0.1818	0.1723
GoF[d]	1.033	0.964	1.046	1.013
min., max. residual density/e $Å^{-3}$	0.452 and −0.289	0.361 and −0.231	0.495 and −0.380	0.323 and −0.222

[a] With disordered solvent contribution (see text). [b] $R1 = |\sum(|F_o| - |F_c|)/\sum|F_o||$. [c] $R2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2} \times w = 0.10$. [d] $GoF = [\sum w(F_o^2 - F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

g, 1.0 mmol) in toluene (20 mL). The mixture was stirred for 2 h at 25 °C, and the volatile materials were removed under vacuum. The residue was extracted with warm toluene (20 mL), and the extract was concentrated to ca. 10 mL. Colorless crystals were obtained on cooling at −20 °C. Yield: 0.80 g (57%). Anal. Calcd for $C_{90}H_{134}Li_2Mg_2O_8$: C, 76.85; H, 9.60. Found: C, 76.08; H, 8.88. ^1H NMR (C_6D_6, ppm): δ 7.57−7.18 (m, 12H, *Ph*); 5.31, 5.00 (s, 4H, CCH_2); 5.42, 4.71 (q, 2H, $-CH(CH_3)$, $J = 6.8$ Hz); 4.06, 3.71 (br, 8H, $-OCH_2CH_3$); 2.75, 2.58, 2.39, 2.22 (s, 18H, $-PhCH_3$); 2.10, 2.08 (d, 6H, $-CHCH_3$, $J = 6.8$ Hz); 1.51, 1.41, 1.38, 1.37, 1.28, 1.27, 1.22 (s, 72H, $-C(CH_3)_3$); 1.12, 1.11 (br, 12H, $-OCH_2CH_3$).

[(EDBP)Na_2]$_4$ (4). An ice cold (0 °C) solution of 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (1.75 g, 4.0 mmol) in diethyl ether (20 mL) was added slowly to excess sodium metal. The mixture was stirred for 12 h at 25 °C until hydrogen gas evolution ceased, and the volatile materials were removed under vacuum. The residue was extracted with a mixture of hexane (15 mL) and Et_2O (15 mL), and the extract was concentrated to ca. 15 mL. Colorless crystals were obtained on cooling at −20 °C. Yield: 1.99 g (95%). Anal. Calcd for $C_{131}H_{192}Na_8O_9$: C, 75.11; H, 9.24. Found: C, 75.37; H, 8.09. ^1H NMR ($CDCl_3$, ppm): δ 7.25−6.75-(m, 16H, *Ph*); 4.20(q, 4H, $CHCH_3$, $J = 6.8$ Hz); 1.48−1.05(m, 156H, $CHCH_3 + C(CH_3)_3$).

[(EDBP)Na(Et_2O)Mg^nBu]$_2$ (5). Mg^nBu_2 (2.2 mL, 1.0 M solution in heptane, 2.2 mmol) was added slowly to an ice cold (0 °C) solution of [(EDBP)Na_2]$_4$ (**4**) (1.05 g, 0.5 mmol) in diether ether (20 mL). The mixture was stirred for 2 h at 25 °C, and the volatile materials were removed under vacuum. The residue was extracted with cold hexane (30 mL), and the extract was concentrated to ca. 10 mL. Colorless crystals were obtained on cooling at −20 °C. Yield: 0.66 g (54%). Anal. Calcd for $C_{76}H_{126}Mg_2Na_2O_6$: C, 74.19; H, 10.32. Found: C, 73.92; H, 10.79. ^1H NMR (C_6D_6, ppm): δ 7.79, 7.44, 7.22, 7.21 (d, 8H, *Ph*); 5.42 (q, 2H, $-CH(CH_3)$, $J = 6.8$ Hz); 2.93 (q, 8H, $-OCH_2CH_3$, $J = 6.8$ Hz); 2.04 (d, 6H, $-CH(CH_3)$, $J = 6.8$ Hz); 1.56, 1.54, 1.49, 1.10 (s, 72H, $-C(CH_3)_3$); 1.47−1.24 (m, 8H, $-CH_2CH_2-$); 0.91 (t, 6H, $-CH_2CH_3$, $J = 6.8$ Hz); 0.78 (t, 12H, $-OCH_2CH_3$, $J = 6.8$ Hz); −0.89 (t, 4H, $MgCH_2$, $J = 6.8$ Hz).

Anionic Polymerization of MMA Initiated by Complex 2. A typical polymerization procedure can be illustrated by the synthesis of PMMA-50 (the number 50 indicates the designed $[MMA]_0/[R^-]_0$) at −30 °C. To a rapidly stirred solution of [(EDBP)Mg(μ_2-^nBu)Li(Et_2O)]$_2$ (**2**) (0.060 g, 0.05 mmol) in toluene (10 mL) was added methyl methacrylate (0.54 mL, 5.0 mmol). The reaction mixture was stirred for 1 h, during which an increase in viscosity was observed. The mixture was then quenched by the addition of methanol (50 mL) to give white crystalline solids. Yield: 0.24 g (45%). The isotactic-rich (96.7%) PMMA-50 was analyzed by ^1H NMR spectroscopic studies.

X-ray Crystallographic Studies. Suitable crystals of **2**−**5** were sealed in thin-walled glass capillaries under nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing ω (width of 0.3° per frame). The absorption correction was based on the symmetry equivalent reflections using the SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package. All non-H atoms were located from successive Fourier maps. All hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Crystallographic data for **2**−**5** are shown in Table 6.

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Supporting Information Available: Full details of the crystal structure determination of **2**−**5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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