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Heteroscorpionate Magnesium Alkyls Bearing Unprecedented Apical σ-C(sp^3)−Mg Bonds: Heteroselective Ring-Opening Polymerization of *rac*-Lactide

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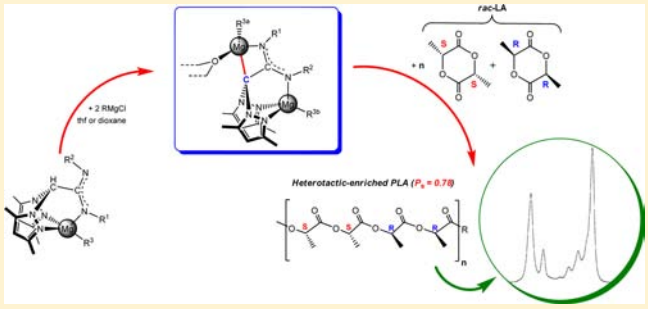
Supporting Information

ABSTRACT: The previously described reaction of the low sterically hindered heteroscorpionate lithium acetamidinates [Li(κ^3-pbpamd)(THF)] and [Li(κ^3-tbpamd)(THF)] with a series of commercially available Grignard reagents RMgCl in an equimolecular ratio yielded the magnesium monoalkyls [Mg(R)(κ^3-NNN)] (NNN = pbpamd, R = CH_2SiMe_3, Et (**1**), Bn (**2**); NNN = tbpamd, R = CH_2SiMe_3, Et (**3**), Bn (**4**)). However, subsequent reaction of these monoalkyls [Mg(R)(κ^3-NNN)] with two additional equivalents of the same RMgCl in tetrahydrofuran gave rise to dinuclear dialkyls of the type [RMg(κ^3-*N,N,N*;κ^2-*C,N*)MgR(thf)] (κ^3-*N,N,N*;κ^2-*C,N* = pbpamd$^-$, R = CH_2SiMe_3 (**5**), Et (**6**); κ^3-*N,N,N*;κ^2-*C,N* = tbpamd$^-$, R = CH_2SiMe_3 (**7**), Et (**8**)). Furthermore, when the reaction was carried out in a mixture of tetrahydrofuran/dioxane with the same stoichiometry, a new family of tetranuclear tetraalkyl magnesium complexes [{RMg(κ^3-*N,N,N*;κ^2-*C,N*)MgR}$_2${μ-*O,O*-(C_4H_8)}] (κ^3-*N,N,N*;κ^2-*C,N* = pbpamd$^-$, R = CH_2SiMe_3 (**9**), Et (**10**), Bn (**11**); κ^3-*N,N,N*;κ^2-*C,N* = tbpamd$^-$, R = CH_2SiMe_3 (**12**), Et (**13**), Bn (**14**)) was obtained. In both families, an apical methine C−H activation process on the heteroscorpionate takes place. The single-crystal X-ray structures of **4**, **8**, **9**, and **12** confirm the nuclearity of each family, with 4-coordinative arrangements for all magnesium atoms. More importantly, the presence in the di- and tetranuclear complexes of unprecedented apical carbanions with a direct σ-C(sp^3)−Mg covalent bond, and as a result, the existence of stereogenic magnesium centers, have been unambiguously confirmed. Interestingly, the dinuclear dialkyls **5** and **7**, as well as the tetranuclear tetraalkyls **9**, **10**, and **12**, can act as highly efficient single-component living initiators for the ring-opening polymerization of ε-caprolactone and lactides. Lactide (LA) polymerizations afforded polylactide (PLA) materials with medium molecular weights in only a few minutes even at 20 °C for L-LA and in a few hours at 50 °C for *rac*-LA propagations. More importantly, microstructural analysis of the poly(*rac*-lactide) materials revealed that the tetranuclear tetraalkyl **12** exerts enhanced levels of heteroselectivity on the PLAs under mild conditions, with P_s values up to 0.78.



INTRODUCTION

Over the past few years, our research group has been interested in the preparation of efficient catalysts[1] for the well-controlled ring-opening polymerization (ROP) of lactide[2] to produce the leading bioderived polymer polylactide (PLA). The biocompatible nature and the lack of toxicity to living tissue of the bioassimilable PLAs[3,4] have attracted attention, and as a result, biocompatible metals such as magnesium[5] or zinc[6] have been incorporated into the catalytic system since the resulting PLAs are widely used in food packaging and biomedical/pharmaceutical applications, e.g., in regenerative medicine,[7] controlled release of drugs,[8] and also wound healing.[9] These emerging materials are also currently employed in ecological applications as bulk commodity materials,[10] including packaging and fiber technology, with the added benefit of biodegradability.[11]

In this context, we have explored the reactivity of a bis(pyrazol-1-yl)methane-derived amidinate-based[12] scorpionate/cyclopentadienyl hybrid[13] and, very recently, chiral[14] and enantiopure[14] alkoxo-based[15] scorpionate ligands for the synthesis of well-defined alkyl magnesium[16−18] and alkyl[17,19−21]-amide[22] zinc complexes of the type [M(R)(κ^3-NNX)] (M = Mg, Zn; R = alkyl, amide; X = N, Cp, O) as efficient single-component living initiators for the ROP of lactides. Moreover, whereas the more sterically hindered heteroscorpionate magnesium alkyls have proven to be extremely active and capable of reaching high levels of heteroselectivity in *rac*-LA polymerization (420 equiv polymerized in 93% yield in 2 min at 20 °C, P_s = 0.79),[18] the less

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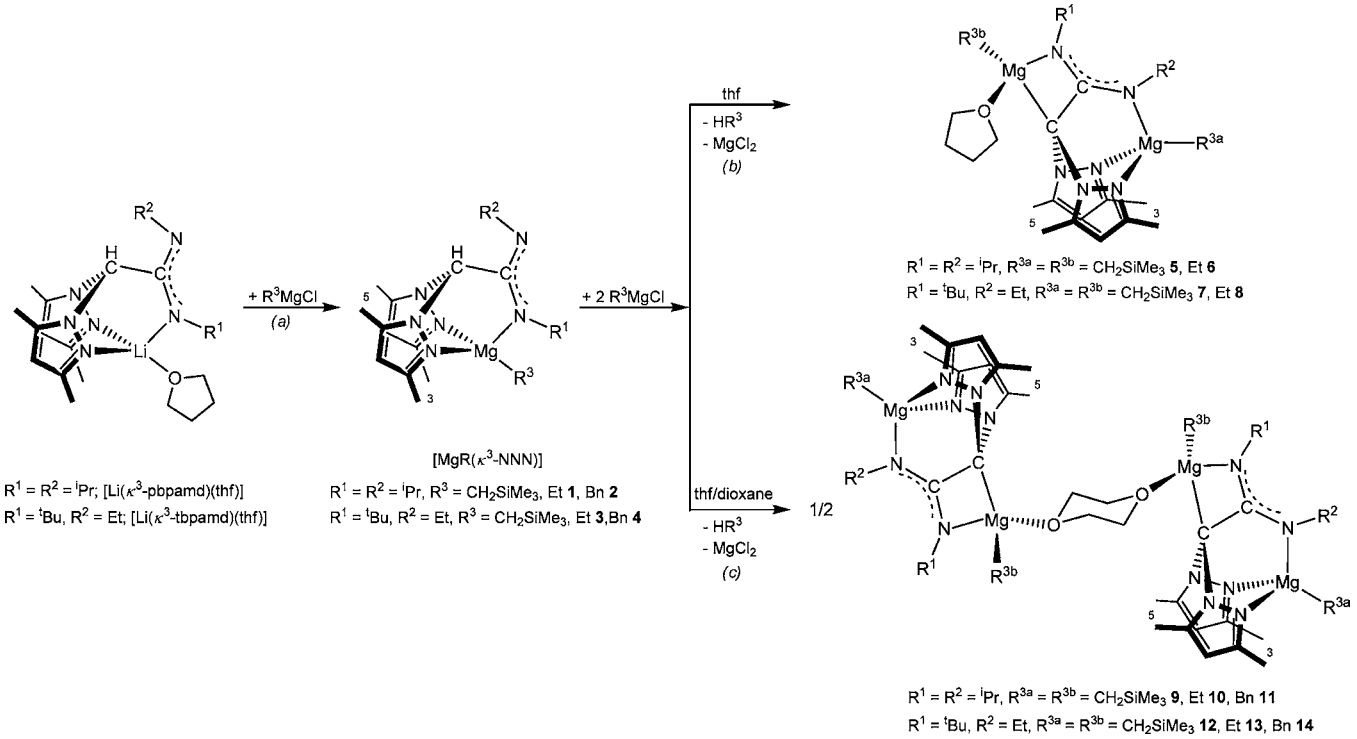
Scheme 1. Sequence of Reactions for the Preparation of the Monoalkyl (1−4), Dinuclear Dialkyl (5−8), and Tetranuclear Tetra-alkyl (9−14) Heteroscorpionate Magnesium Complexes



sterically demanding alkyl analogues[16] produced atactic materials (P_s = 0.52) and showed very limited catalytic activity. This behavior was probably due to the lack of steric influence of the methyl groups, which are insufficient to prevent metal complexes from undergoing the symmetrical (Schlenk)[23] equilibrium to form sandwich species that disfavor catalytic performance. The use of sterically demanding ligands attached to an active metal center[18] or, alternatively, the architecture of complexes with higher order nuclearity arrangements would provide a steric barrier to suppress this undesired side reaction.

We have addressed the problem outlined above by designing a more effective family of initiators based on the low sterically hindered bis(3,5-dimethylpyrazol-1-yl)methane amidinate-derived[12] heteroscorpionate ligand. This approach involved the formation of higher order nuclearity species through C−H activation (deprotonation) of the bridging methine in the previously reported magnesium monoalkyls [Mg(R)(κ^3-NNN)].[16] Only recently have reports appeared concerning this methine C−H activation process, and these include group 3 (Sc, Y),[24] lanthanide (Lu,[24] Nd[25]), and 13 (Al)[26]-based alternative heteroscorpinate complexes. The reactions described give rise to the formation of interesting neutral[25,26] or zwitterionic[24] active species in several polymerization processes. For instance, the neutral dimeric enantiopure heteroscorpionate neodymium amide [Nd{(*S*)-mbpamH}{N(SiHMe$_2$)}]$_2$[25] produced isotactic-enriched poly(*rac*-LA) (P_i = 0.61, conv 10%); the dinuclear acetamidate heteroscorpionate aluminum alkyl [Al$_2$Et$_4$(μ-pbptam)][26] proved to be very active for the synthesis of cyclic carbonates,[27] and the zwitterionic dialkyls [Ln(NNO)(CH$_2$SiMe$_3$)$_2$(thf)][24] presented significant heteroactivity in the ROP of *rac*-LA [P_s = 0.81, Y; 0.87, Lu], albeit with very broad polydispersity values (M_w/M_n = 1.7−1.8). However, to the best of our knowledge, examples of these observations for a magnesium metal center have not been reported to date.

We describe here the preparation of more efficient alkyl initiators based on low sterically hindered heteroscorpionates and the biocompatible magnesium metal. These compounds were obtained through cleavage of the apical methine C−H bond by treatment with excess Grignard reagent, a process that leads to the formation of unprecedented apical carbanions with a direct σ-C(sp^3)−Mg covalent bond in the isolated complexes. An evaluation of the different synthetic routes, the study of the unique structural arrangements observed in the resulting complexes, and their use as efficient single-component living initiators for the heteroselective ROP of *rac*-LA are also discussed in detail.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Monoalkyl, Dinuclear Dialkyl, and Tetranuclear Tetraalkyl Heteroscorpionate Magnesium Complexes. Following our previously described procedure,[16] the treatment in toluene of the low sterically hindered lithium acetamidinates [Li(κ^3-pbpamd)(THF)][12] [pbpamd = *N*,*N*′-diisopropylbis(3,5-dimethylpyrazol-1-yl)acetamidinate] and [Li(κ^3-tbpamd)(THF)][12] [tbpamd = *N*-ethyl-*N*′-*tert*-butylbis(3,5-dimethylpyrazol-1-yl)-acetamidinate] with a series of commercially available Grignard reagents RMgCl (R = CH$_2$SiMe$_3$, Et, and Bn) in an equimolecular ratio yielded, after the appropriate work-up, the magnesium monoalkyls [Mg(R)(κ^3-NNN)] (NNN = pbpamd, R = CH$_2$SiMe$_3$,[16] Et (**1**), Bn (**2**); NNN = tbpamd, R = CH$_2$SiMe$_3$,[16] Et (**3**), Bn (**4**)) as pale yellow crystalline solids in high yields (∼90%; see Scheme 1a). However, subsequent reaction of these monoalkyls [Mg(R)(κ^3-NNN)] with two additional equivalents of the same RMgCl in tetrahydrofuran gave rise to dinuclear dialkyl magnesium

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 4, 8, 9, and 12

4		8		9		12	
			distances (Å)				
Mg(1)−N(1)	2.165(3)	Mg(1)−N(1)	2.153(3)	Mg(1)−N(1)	2.146(2)	Mg(1)−N(1)	2.141(6)
Mg(1)−N(3)	2.152(4)	Mg(1)−N(3)	2.101(3)	Mg(1)−N(3)	2.100(2)	Mg(1)−N(3)	2.092(6)
Mg(1)−N(5)	2.075(4)	Mg(1)−N(5)	2.068(3)	Mg(1)−N(5)	2.067(2)	Mg(1)−N(5)	2.051(5)
Mg(1)−C(19)	2.163(5)	Mg(1)−C(19)	2.117(5)	Mg(1)−C(19)	2.118(3)	Mg(1)−C(19)	2.118(6)
N(5)−C(12)	1.362(5)	Mg(2)−N(6)	2.036(3)	Mg(2)−N(6)	2.036(2)	Mg(2)−N(6)	2.040(5)
N(6)−C(12)	1.300(5)	Mg(2)−O(1)	1.95(1)	Mg(2)−C(11)	2.237(3)	Mg(2)−C(23)	2.131(6)
		Mg(2)−C(21)	2.136(5)	Mg(2)−C(23)	2.131(3)	Mg(2)−O(1)	2.141(5)
		Mg(2)−C(11)	2.269(4)	Mg(2)−O(1)	2.151(2)	Mg(2)−C(11)	2.272(6)
		N(5)−C(12)	1.327(5)	N(5)−C(12)	1.319(3)	N(5)−C(12)	1.320(7)
		N(6)−C(12)	1.340(4)	N(6)−C(12)	1.346(3)	N(6)−C(12)	1.351(7)
			angles (deg)				
N(5)−Mg(1)−N(3)	91.0(1)	N(5)−Mg(1)−N(3)	88.32(12)	N(3)−Mg(1)−N(1)	88.70(9)	N(3)−Mg(1)−N(1)	88.6(2)
N(5)−Mg(1)−C(19)	133.9(2)	N(5)−Mg(1)−C(19)	125.97(17)	N(3)−Mg(1)−C(19)	116.0(1)	N(3)−Mg(1)−C(19)	120.0(3)
N(5)−Mg(1)−N(1)	91.5(1)	N(5)−Mg(1)−N(1)	92.32(13)	N(5)−Mg(1)−N(1)	92.12(9)	N(5)−Mg(1)−N(1)	91.1(2)
N(3)−Mg(1)−N(1)	85.6(1)	N(3)−Mg(1)−N(1)	86.70(12)	N(5)−Mg(1)−N(3)	87.66(9)	N(5)−Mg(1)−N(3)	88.8(2)
C(19)−Mg(1)−N(1)	116.1(2)	C(19)−Mg(1)−N(1)	126.68(19)	N(5)−Mg(1)−C(19)	137.9(1)	N(5)−Mg(1)−C(19)	133.9(3)
C(12)−N(5)−Mg(1)	118.2(3)	O(1)−Mg(2)−N(6)	99.5(3)	C(19)−Mg(1)−N(1)	120.9(1)	C(19)−Mg(1)−N(1)	122.1(3)
C(12)−N(6)−C(13)	122.5(4)	O(1)−Mg(2)−C(21)	97.6(3)	N(6)−Mg(2)−C(23)	144.9(1)	N(6)−Mg(2)−C(23)	134.7(3)
N(6)−C(12)−N(5)	125.5(4)	N(6)−Mg(2)−C(21)	135.2(2)	N(6)−Mg(2)−O(1)	96.32(8)	N(6)−Mg(2)−O(1)	96.1(2)
N(6)−C(12)−C(11)	120.5(4)	O(1)−Mg(2)−C(11)	109.7(3)	C(23)−Mg(2)−O(1)	103.6(1)	C(23)−Mg(2)−O(1)	104.0(2)
N(5)−C(12)−C(11)	114.0(4)	N(6)−Mg(2)−C(11)	65.1(1)	N(6)−Mg(2)−C(11)	66.11(9)	N(6)−Mg(2)−C(11)	65.4(2)
		C(21)−Mg(2)−C(11)	143.1(2)	C(23)−Mg(2)−C(11)	137.6(1)	C(23)−Mg(2)−C(11)	141.4(3)
				O(1)−Mg(2)−C(11)	96.52(9)	O(1)−Mg(2)−C(11)	105.4(2)
				C(12)−N(5)−C(13)	123.6(2)	C(12)−N(5)−C(13)	121.3(5)
				C(12)−N(5)−Mg(1)	115.3(2)	C(12)−N(5)−Mg(1)	111.7(4)
				C(13)−N(5)−Mg(1)	121.1(2)	C(13)−N(5)−Mg(1)	126.2(4)
				C(12)−N(6)−C(16)	124.8(2)	C(12)−N(6)−C(15)	128.0(5)
				C(12)−N(6)−Mg(2)	97.6(2)	C(12)−N(6)−Mg(2)	96.9(4)
				C(16)−N(6)−Mg(2)	137.5(2)	C(15)−N(6)−Mg(2)	134.9(4)

complexes of the type [MgR(κ^3-*N,N,N*;κ^2-*C,N*)MgR(thf)] (κ^3-*N,N,N*;κ^2-*C,N* = pbpamd$^-$, R = CH_2SiMe_3 (**5**), Et (**6**); κ^3-*N,N,N*;κ^2-*C,N* = tbpamd$^-$, R = CH_2SiMe_3 (**7**), Et (**8**); see Scheme 1b) as yellow crystalline solids in good yields (ca. 80%; see Experimental Section). Additionally, when the reaction was carried out in a mixture of tetrahydrofuran/dioxane (9:1) as a solvent with the same stoichiometry, a new family of the tetranuclear tetraalkyl magnesium complexes [{RMg(κ^3-*N,N,N*;κ^2-*C,N*)MgR}$_2${μ-*O,O*-(C_4H_8)}] (κ^3-*N,N,N*;κ^2-*C,N* = pbpamd$^-$, R = CH_2SiMe_3 (**9**), Et (**10**), Bn (**11**); κ^3-*N,N,N*;κ^2-*C,N* = tbpamd$^-$, R = CH_2SiMe_3 (**12**), Et (**13**), Bn (**14**); see Scheme 1c) were obtained as yellow crystalline solids in high yields (ca. 80%). In both families of complexes, i.e. the dinuclear dialkyls (**5**−**8**) and the tetranuclear tetraalkyls (**9**−**14**), an apical C−H methine activation on the scorpionate ligand takes place with the MgR_2 resulting from the Schlenk equilibrium[23] of the two additional equivalents (2RMgX ⇌ MgR_2 + MgX_2). All compounds are extremely air- and moisture-sensitive and decompose in dichloromethane.

The ^{1}H and ^{13}C-{^{1}H} NMR spectra of **1**−**4** in benzene-d_6 at room temperature each show a simple set of resonances for the pyrazole rings, indicating that both pyrazole rings are equivalent. The amidinate moiety, when R_1 = R_2 = ^{i}Pr, gives rise to two sets of resonances for these substituents (the same pattern as for R_1 = ^{t}Bu; R_2 = Et), indicating a monodentate binding of the amidinate fragment to the magnesium atom (see Scheme 1) in a similar way to the binding modes previously observed for analogous complexes.[16,18,19,22] A singlet corresponding to the bridging CH group is also observed at low field.

The ^{1}H NMR spectra of **5**−**14** each show the disappearance of the single signal corresponding to the CH group, which is consistent with C−H bond activation, and the shifting of the C−H signal in the ^{13}C-{^{1}H} NMR at a lower field (∼77 ppm). However, the most significant characteristic in the spectra of the two families, i.e. the dinuclear dialkyls **5**−**8** and the tetranuclear tetraalkyls **9**−**14**, is the appearance of a single set of resonances for the two pyrazole rings, indicating that they are equivalent, although there is no symmetry in the molecule. This situation can be explained in terms of a possible rapid dynamic behavior in which the tetrahydrofuran or the dioxane and the alkyl ligand (R^{3b}) exchange positions through rotation around the σ-C(sp^3)−Mg covalent bond (see Scheme 1), a process that ultimately makes both rings equivalent. VT ^{1}H NMR studies in toluene-d_8 were carried out in an effort to stop this exchange process, which has a very low activation barrier. For instance, derivative **12** exhibits a coalescence temperature of 198.15 K and a free-energy value, $\Delta G^{\ddagger}$, of 40.67 kJ/mol, meaning that the signals of the two pyrazole rings are inequivalent [Figure S1 in the Supporting Information (SI)]. Furthermore, the amidinate moieties in these complexes [R_1 = R_2 = ^{i}Pr (**5**, **6**, **9**−**11**) and R_1 = ^{t}Bu, R_2 = Et (**7**, **8**, **12**−**14**)] show two very closed sets of resonances in the ^{1}H NMR spectrum for each R group (i.e., a difference of less than 0.1 ppm for the two CH groups in the ^{i}Pr substituents in **5**, **6**, **9**−**11**), in contrast to the monoalkyls (i.e., a difference of ∼0.8 ppm for the two CH groups in the ^{i}Pr substituents in **1** and **2**).

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This latter observation is indicative of a bidentate binding of the amidinate moiety to two magnesium centers (see Scheme 1). Additionally, there are two different signals for each Mg-R^3 alkyl group in all complexes, indicating that the two magnesium centers have different arrangements. Finally, one set of signals is observed for a terminal tetrahydrofuran and a bridging dioxane molecule in **5**−**8** and **9**−**14**, respectively, integrating for one molecule in each family of complexes.

^{1}H NOESY-1D experiments were performed in order to corroborate the structure and nuclearity proposed for each family of complexes and to assign unambiguously the signals corresponding to each group (Figure S2 in the SI). For instance, in the case of the tetranuclear tetra-alkyls **9**−**14**, the response from the bridging dioxane protons in complex **12** (Figures S2b and S2c) on irradiating the protons from only one alkyl (Mg−R^{3b}; see Scheme 1) suggests that only one alkyl group is close to the dioxane molecule. The rest of the experiments (Figures S2d and S2e) corroborate the proposed structure. In the case of dinuclear dialkyls **5**−**8**, the same responses on irradiating the tetrahydrofuran molecule are observed. Finally, ^{1}H−^{13}C heteronuclear correlation (g-HSQC) experiments allowed us to assign the resonances corresponding to C^4, Me^3, and Me^5 of the pyrazole rings as well as the carbon signals from R^1, R^2, and $R^{3a,b}$ in all compounds.

Single crystals of complexes [Mg(CH_2SiMe_3)(κ^3-tbpamd)] (the X-ray structure of this complex was established since it had not previously been determined),[16] **4**, **8**, **9**, and **12** suitable for X-ray diffraction were easily grown from toluene or hexane solutions at −26 °C. Selected bond lengths and angles are collected in Table 1 and in Table S1 in the SI for the monoalkyl [Mg(CH_2SiMe_3)(κ^3-tbpamd)].[16] Crystallographic details for all crystal structures are reported in Table S3 in the SI. The molecular structures of **4**, **8**, **9**, and **12** are depicted in Figures 1, 2, 3, and 4, respectively, and the structure of complex [Mg(CH_2SiMe_3)(κ^3-tbpamd)] is shown in Figure S3 in the SI.

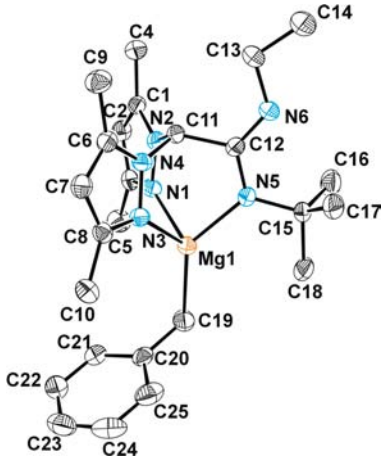

Figure 1. ORTEP view of [Mg(CH_2Ph)(κ^3-tbpamd)] (**4**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Compound **4** consists of a monomeric arrangement in the solid state. The magnesium metal exhibits a distorted tetrahedral geometry in which the pyrazolic nitrogens N(1) and N(3) occupy two positions and the amidinate nitrogen N(5) and the alkyl group occupy the other two positions. The N(1)−Mg(1) and N(3)−Mg(1) bond lengths are well balanced [2.165(3) Å and 2.152(4)Å, respectively] and are

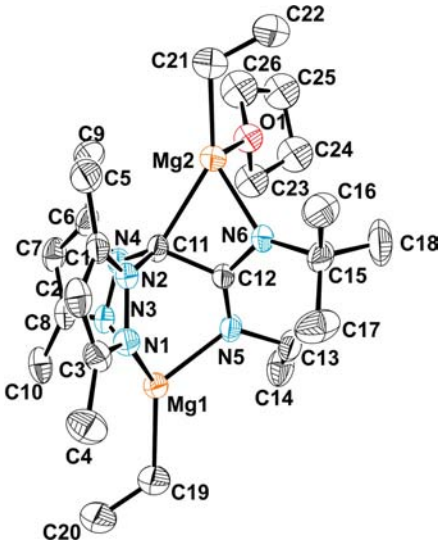

Figure 2. ORTEP view of the *S* enantiomer for [EtMg(tbpamd$^-$)-MgEt(thf)] (**8**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

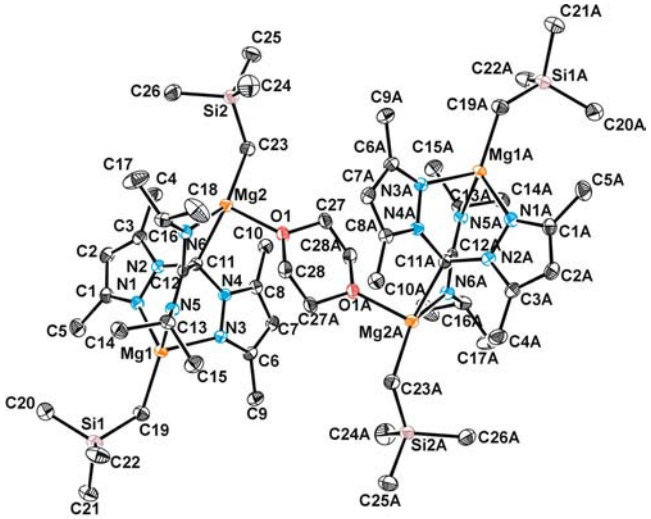

Figure 3. ORTEP view of the *meso* diastereoisomer for [{(CH_2SiMe_3)Mg(pbpamd$^-$)Mg(CH_2SiMe_3)}$_2$ {μ-*O*,*O*-(C_4H_8)}] (**9**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

comparable to those observed in the analogous magnesium heteroscorpionate alkyl complexes [Mg(CH_2SiMe_3)(κ^3-tbpamd)] [2.143(3) Å and 2.139(3) Å in the SI] and [Mg(C_3H_5)(κ^3-tbpamd)][16] [2.126(3) Å and 2.122(3) Å]. The solid-state structure also confirms that the amidinate moiety is coordinated in a monodentate fashion to the Mg atom [N(5)−Mg = 2.075(4)Å], with partial delocalization in the N(5)−C(12)−N(6) core [C(12)−N(5) = 1.362(5) Å, C(12)−N(6) = 1.300(5)Å]—behavior that is common in related families of monomeric organoderivatives.[16,18,19,22]

The X-ray diffraction analysis of **8**, **9**, and **12** confirmed in all cases a centrosymmetric unit cell with the magnesium center Mg(2) being a stereogenic center. These studies also showed that the presence in solution of the corresponding two enantiomers for the dinuclear complex **8** (*R* + *S*) was maintained in the solid state. However, in the tetranuclear

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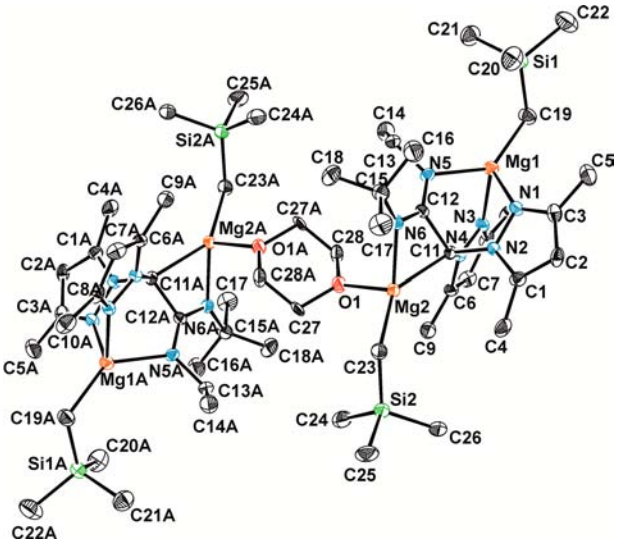

Figure 4. ORTEP view of the *meso* diastereoisomer of [{(CH_2SiMe_3)-Mg(tbpamd$^-$)Mg(CH_2SiMe_3)}$_2${μ-*O*,*O*-(C_4H_8)}] (**12**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

complexes **9** and **12** only the equivalent *meso* diastereomer (*R*,*S*) was present in the unit cell.

Interestingly, complex **8** presents a dinuclear arrangement while, in contrast, complexes **9** and **12** are tetranuclear entities formed by two twin dinuclear units connected through a bridging dioxane molecule. In the three structures, each dinuclear unit contains two different distorted tetrahedral magnesium centers with only one heteroscorpionate ligand: pbpamd$^-$ for **9** and tbpamd$^-$ for **8** and **12**. The first metal center contains the corresponding heteroscorpionate ligand in a κ^3-NNN coordination mode occupying three positions, with the N(1)−Mg(1) and N(3)−Mg(1) bond lengths [2.153(3) Å and 2.101(3) Å for **8**, respectively; 2.146(2) Å and 2.100(2) Å for **9**, respectively; and 2.141(6) Å and 2.092(6) Å for **12**, respectively] unbalanced, and the N(5)−Mg(1) bond lengths [2.068(3) Å (**8**), 2.067(2) Å (**9**), and 2.051(5) Å (**12**)] significantly shorter in comparison with N(1) and N(3)−Mg(1) ones. The fourth position is occupied by an alkyl group [Mg(1)−C(19) = 2.117(5) Å (**8**), 2.118(3) Å (**9**), and 2.118(6) Å (**12**)]. These bond lengths are comparable to those observed in the analogous magnesium heteroscorpionate monoalkyls [Mg(R)(κ^3-tbpamd)] (R = CH_2SiMe_3, CH_2Ph **4**) and [Mg(C_3H_5)(κ^3-tbpamd)],[16] although the N(5)−C(12)−N(6) fragment for **8**, **9**, and **12** presents a symmetrical delocalization with nearly equal bond distances [N(5)−C(12) = 1.327(5) Å and N(6)−C(12) = 1.340(4) Å (**8**); 1.319(3) and 1.346(3) Å (**9**); 1.320(7) Å and 1.351(7) Å (**12**)].

The second magnesium unit presents coordination from the lone pair of electrons on nitrogen N(6) [N(6)−Mg(2) = 2.036(3) Å (**8**), 2.036(2) Å (**9**), 2.040(5) Å **12**)], and given the similarity with the N(5)−Mg(1) bond length, this reaffirms the complete delocalization of the negative charge throughout the N(5)−C(12)−N(6) core. Two additional positions are occupied by the oxygen from the terminal tetrahydrofuran molecule [Mg(2)−O(1) = 1.947(10) Å (**8**)] or the bridging dioxane molecule [Mg(2)−O(1) = 2.1508(19) Å (**9**); 2.141(5) Å (**12**), i.e. significantly longer] and an alkyl group [Mg(2)−C(21) = 2.136(5) Å (**8**); Mg(2)−C(23) = 2.131(3) Å (**9**), 2.131(6) Å (**12**)]. However, the most notable feature in the X-ray molecular structures of complexes **8**, **9**, and **12** is undoubtedly the fourth coordinative vacancy of Mg(2), which corresponds to the covalent bond formed between the sp^3-hybridized apical carbanion C(11) [angles around C(11), such as N(2)−C(11)−N(4) = 107.3(3)°, N(2)−C(11)−C(12) = 105.7(3)°, and N(4)−C(11)−C(12) = 116.3(3)° (**8**); 107.28(19)°, 106.5(2)°, 115.20(19)° (**9**); 107.6(5)°, 106.6(5)°, 114.3(5)° (**12**)] and the magnesium center Mg(2) [C(11)−Mg(2) = 2.269(4) Å (**8**); 2.237(3) Å (**9**); 2.272(6) Å (**12**)]. In this sense, to the best of our knowledge, these are the first unambiguously authenticated examples of heteroscorpionates with apical C−H activation resulting in a methan*ide* carbon that retains the sp^3 hybridization and presents a direct covalent bond to the metal center, since the examples reported to date, including almost all[28] tris-[29] and all bis(pyrazol-1-yl)methane[24−26]-based scorpionates, leave the apical carbanion "*naked*" to produce zwitterionic complexes[24,29] or, alternatively, the carbanion is delocalized throughout adjacent heteroatoms.[25,26] Additionally, the C(11)−Mg(2) bond lengths (2.258 Å on average) in both the di- and the tetra-alkyls are close to the C(19)−Mg(1) (2.115 Å on average) and C(23,21)−Mg(2) (2.133 Å on average) bonds mentioned above, showing the alkyl character of C(11) and the strong covalent σ bond between the C(11) and Mg(2) atoms. Furthermore, the C(11)−C(12) bond lengths [1.534(5) Å (**8**), 1.558(3) Å (**9**), 1.558(8) Å (**12**), i.e. longer than a C−C single bond (∼1.455 Å)] reveal no delocalization of the carbanion sp^3 C(11) throughout this bond with the close amidinate core. Finally, the highly constrained four-membered metallacycle formed by the Mg(2)−N(6)−C(12)−C(11) fragment presents highly tensioned angles such as Mg(2)−N(6)−C(12) and Mg(2)−C(11)−C(12) [96.0(2)° and 81.8(2)° (**8**); 97.59(16)° and 83.82(14)° (**9**); 96.9(4)° and 82.4(4)° (**12**)], which are far from the values expected for an sp^2 and sp^3 hybridization, respectively.

Polymerization Studies. Complexes **5**, **7**, **9**−**11**, and **12** were assessed in the ring-opening polymerization of the polar monomers ε-caprolactone (CL) and L-/*rac*-lactide in tetrahydrofuran under a nitrogen atmosphere in order to compare their activity and stereoselectivity with those of their heteroscorpionate alkyl magnesium starting materials,[16] other alkyls previously reported by our group,[18,19] as well as interesting magnesium initiators published to date (see for example those reported by Chisholm et al.,[30] Lin et al.,[31] Ma and Wang,[32] Cui et al.,[33] and Schaper et al.[34]).

All initiators investigated were found to be very active in the polymerization of CL (see the results in Table S2 in the SI) and proved much more active than the starting materials [Mg(R)-(κ^3-NNN)].[16] Very high conversions were obtained in 1 min at 20 °C to produce medium-low molecular weight materials with low polydispersity values and productivities of more than 13 × 10^5 g PCL (mol Mg)$^{-1}$·h^{-1} (see for example the case of **5**). When toluene was employed as a solvent, all initiators drastically reduce the catalytic activity since the complexation of magnesium ions by the coordinating tetrahydrofuran solvent probably enhances in this case the nucleophilicity of the alkyl initiating group and the alkoxide propagating chain. It was also found that the nature of the substituent R^1 and R^2 (Scheme 1) from the amidinate fragment of the heteroscorpionate ligand affects the catalytic activity as follows: pbpamd$^-$ > tbpamd$^-$.

More interestingly, initiators **5**, **7**, **9**, and **12** were systematically examined for the production of poly(lactides) (PLAs; Table 2). Inspection of the experimental M_n values of

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Table 2. Polymerization of L- and *rac*-Lactide Catalyzed by 5, 7, 9, and 12[a]

entry	initiator	monomer	time (min)	yield (g)	conv (%)[b]	$M_{n(theor)}$ (Da)[c]	M_n (Da)[d]	M_w/M_n[d]	P_s[e]
1	**5**	L-LA	1.5	0.54	21	6 000	5 200	1.03	
2	**5**	L-LA	3	1.09	42	12 100	12 400	1.03	
3	**5**	L-LA	4.5	1.60	62	17 900	16 900	1.05	
4	**5**	L-LA	6	2.04	79	22 800	23 600	1.06	
5	**5**	L-LA	7	2.45	94	27 100	26 000	1.08	
6	**5**[f]	L-LA	14	4.77	92	53 000	51 800	1.09	
7	**7**	L-LA	7	2.32	89	25 600	25 100	1.11	
8	**9**	L-LA	10	2.14	82	23 600	24 300	1.12	
9	**12**	L-LA	10	1.91	74	21 300	21 600	1.09	
10	$[Mg(CH_2SiMe_3)(pbpamd)]$[i]	L-LA	96 h	1.20	93	13 400	12 600	1.19	
11	**5**	*rac*-LA	2 h	1.43	55	15 800	16 200	1.11	0.68
12	**7**	*rac*-LA	2 h	1.32	51	14 700	14 300	1.09	0.71
13	**9**	*rac*-LA	5 h	1.19	46	13 200	12 800	1.13	0.75
14	**12**	*rac*-LA	5 h	0.98	38	10 900	10 200	1.10	0.78
15	**12**[g]	*rac*-LA	10 h	0.28	11	3 100	3 400	1.12	0.77
16	**12**[h]	*rac*-LA	5 h	0.40	15	4 400	4 200	1.13	0.76
17	$[Mg(CH_2SiMe_3)(pbpamd)]$[i]	*rac*-LA	72 h	0.54	42	12 100	11 700	1.09	atactic

[a]Polymerization conditions: 90 μmol of magnesium centers; $[monomer]_0/[Mg]_0 = 200$; 20 mL of tetrahydrofuran at 20 °C for L-lactide and at 50 °C for *rac*-lactide. [b]Percentage conversion of the monomer [(weight of polymer recovered/weight of monomer) × 100]. [c]Theoretical M_n = (monomer/Mg) × (% conversion) × (M_w of lactide). [d]Determined by size exclusion chromatography relative to polystyrene standards in tetrahydrofuran. Experimental M_n was calculated considering Mark–Houwink's corrections[40] for M_n [M_n(obsd) = 0.56 × M_n(GPC)]. [e]The parameter P_s (s = syndiotactic) is the probability of forming a new *s*-dyad. P_s is the probability of syndiotactic (racemic) linkages between monomer units and is determined from the relative intensity in the tetrads obtained in the decoupled ^{1}H NMR experiment by $P_s = 2I_1/(I_1 + I_2)$, with $I_1 = \delta$ 5.20–5.25 ppm (*sis, sii/iis*) and $I_2 = \delta$ 5.13–5.20 ppm (*iis/sii, iii, isi*).[41] [f]Double-feed experiment of 200 equiv of L-LA each. [g]The temperature of the polymerization reaction was 20 °C. [h]Employment of toluene as a solvent. [i]These data have been included for comparison of ROP with the alkyl magnesium precursors.[16] Experimental conditions: $[catalyst]_0 = 90$ μmol of $[Mg(CH_2SiMe_3)(pbpamd)]$; $[monomer]_0/[catalyst]_0 = 100$; 40 mL of toluene at 70 °C for L-lactide and *rac*-lactide.

the PLAs produced revealed, as a common trend, that the molecular weights of the resulting polymer samples closely approximate the expected theoretical calculated values for one polymer chain per magnesium center [M_n(calcd)PLA_{200} = 28 800 g·mol^{-1}] (Table 2). Size exclusion chromatography (SEC) data for the resulting polyesters showed a monomodal weight distribution, with polydispersities ranging from 1.03 to 1.13 (Figure S4 in the SI).

The magnesium alkyl derivatives **5**, **7**, **9**, and **12** acted as very active single-component initiators and polymerized 200 equiv of L-LA in tetrahydrofuran at 20 °C in a few minutes. For instance, the dinuclear trimethylsilylmethyl derivatives **5** and **7** transformed the 94 and 89% of the monomer after 7 min (entries 5 and 7, respectively), while the tetranuclear analogues **9** and **12** gave 82 and 74% conversion, respectively, after 10 min (entries 8 and 9, respectively) under otherwise identical conditions. This difference in activity is probably caused by the presence of the dioxane molecule (in **9** and **12**), which competes for the magnesium centers more effectively than the tetrahydrofuran molecule (in **5** and **7**) for the lactide monomer, thus decreasing the catalytic performance. It is also worth noting the higher activity found for all these initiators in comparison with their monoalkyl precursors (entry 10), where much longer times and more energetic conditions are needed.

The polymerization occurred without epimerization reactions and afforded highly crystalline, isotactic polymers (T_m = 170–177 °C)[35] with medium-low molecular weight and very narrow polydispersity indexes (i.e., M_n = 26 000, M_w/M_n = 1.08, entry 5). The low level of stereochemical imperfections was also revealed in the poly(L-lactide) with M_n > 20 000, for which the optical activity remained almost constant in all cases ($[\alpha]_D^{22} \approx 144°$).[36] The high level of control afforded by these initiators in the polymerization of L-lactide was further exemplified by initiator **5** (entries 1–5), which gave rise to narrow molecular weight distributions in conjunction with linear correlations between M_n and percentage conversion (R^2 = 0.994; Figure S5 in the SI). A double-feed experiment demonstrated the living behavior of catalyst **5** (entries 5 and 6), which resulted in a polymer chain extension[37] with very similar polymer features. These results are characteristic of well-controlled living propagations and the existence of a single type of reaction site.

Moreover, low molecular weight materials produced by these initiators were studied by MALDI–ToF MS[38] (Figure S6 in the SI), and end-group analysis by ^{1}H NMR of a poly(L-lactide) oligomer was also investigated (see Figure S7 in the SI). These two findings provide evidence that the ring-opening of L-LA occurs by the initial addition of the alkyl fragment to the monomer in the materials produced, with cleavage of the acyl-oxygen bond[39] followed by further monomer additions to the (macro)alcohols.

Initiators **5**, **7**, **9**, and **12** were also tested in the polymerization of *rac*-lactide in tetrahydrofuran at 50 °C. In this case, the polymerization reaction was slower. For instance, the dinuclear magnesium dialkyls **5** and **7** afforded 55 and 51% conversion, respectively, after 2 h and gave low molecular weight materials with very low polydispersity indexes (M_n = 14 300, M_w/M_n = 1.09, entry 12). In contrast, the tetranuclear magnesium tetra-alkyls **9** and **12** reached conversions ranging from 46% to 38% after 5 h of reaction (entries 13 and 14), also with low molecular weight PLA materials and narrow polydispersity values (M_n = 10 200, M_w/M_n = 1.10, entry 14), possibly due to the reasons outlined above for the L-LA polymerization.

For the sake of comparison, the dinuclear dialkyls **5** and **7** as well as the tetranuclear tetraalkyls **9** and **12** present higher

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activities than their starting materials [Mg(R)(κ^3-NNN)][16] for both lactide monomers assessed (Table 2, entries 10 and 15). In addition, the activity values of these initiators for the L-LA monomer compare well with that reported for alternative benzyloxide[31] and alkyl[33] magnesium initiators, although they are slower than that published for the *rac*-LA monomer.[30,32,34]

Poly(*rac*-Lactide) Microstructure Analysis. Microstructural analysis of the poly(*rac*-lactide) by ^{1}H NMR spectroscopy revealed that these initiators in tetrahydrofuran exert a moderate heteroactivity on the resulting polymers through a chain end control[42] mechanism, a value which is most probably a result of the average contribution of the two different magnesium centers from each initiator. This situation in contrast to the low sterically hindered magnesium monoalkyl precursors,[16] which offered a low level of stereocontrol and produced amorphous atactic poly(*rac*-lactide) materials (Table 2, entry 17).

For instance, initiators **5** and **7** impart a moderate level of heteroselectivity on the growing polymer microstructure, reaching in the case of **7** a P_s[41] value of 0.71 (Table 2, entry 12). More interestingly, catalysts **9** and **12** show a notable preference for a heterotactic dyad enchainment. Thus, initiator **9** gave a P_s of 0.75 (Table 2, entry 13), while in the case of **12** the value was increased to 0.78 (Figure S8 in the SI, Table 2, entry 14). This higher heterotacticity observed for **9** and **12** could be attributed to the fact that the more sterically demanding environment produced by the dimeric arrangement of these initiators would be maintained during the polymerization process, which in turn would exert a heteroinfluence on the growing polymer chains. A decrease in the reaction temperature (Table 2, entry 15) or the use of toluene as a solvent (Table 2, entry 16) did not lead to an increase in the P_s value, but a significant decrease in activity occurred. It is also noteworthy that although the heteroactivity observed for catalyst **12** is still lower than that of the very selective magnesium initiators reported to date, such as [(nacnac)Mg(O^{t}Bu)(THF)][30a] ($P_s \approx 0.90$), it is significantly higher than that for analogous magnesium silylamido systems supported by a tridentate monoanionic aminophenolato ligand [(L)MgN(SiMe$_3$)$_2$][32] (P_s = 0.65) and other diketiminate-based magnesium alkoxides [(nacnac^{Bn})Mg(O^{t}Bu)(THF)][34] (P_s = 0.52).

CONCLUSIONS

In conclusion, we report here the controlled preparation of heteroscorpionate magnesium alkyls with different order nuclearity through the initial reaction of the low sterically hindered lithium acetamidinates [Li(κ^3-pbpamd)(THF)] and [Li(κ^3-tbpamd)(THF)] with a series of Grignard reagents RMgCl and subsequent reaction of the corresponding magnesium monoalkyls generated, [Mg(R)(κ^3-NNN)], with two additional equivalents of the same RMgCl. The reaction in tetrahydrofuran gave rise to the dinuclear heteroscorpionate dialkyl magnesium complexes [RMg(κ^3-*N*,*N*,*N*;κ^2-*C*,*N*)MgR(thf)]. In contrast, in the presence of dioxane, new tetranuclear tetraalkyls of the type [{RMg(κ^3-*N*,*N*,*N*;κ^2-*C*,*N*)MgR}$_2${μ-*O*,*O*-(C$_4$H$_8$)}] were obtained through an apical methine C−H activation process in both cases. X-ray diffraction analysis of **4**, **8**, **9**, and **12** confirmed the arrangements proposed in all families and, more importantly, that both the dinuclear dialkyl **8** and the tetranuclear tetra-alkyls **9** and **12** present unprecedented apical carbanions with a direct σ-C(sp^3)−Mg covalent bond, an arrangement that has been unambiguously confirmed.

Interestingly, the alkyl nucleophilicity of the di- and tetra-alkyls means that they can act as highly efficient single-site living initiators for the well-controlled polymerization of polar monomers such as ε-caprolactone and lactides under mild conditions. The polymerization of L-LA occurs in minutes and offers very good control at room temperature, as evidenced by the living behavior and the low polydispersity indexes measured for the materials. End group analysis and the MALDI-ToF mass spectra suggest that the polymerization process is initiated by alkyl transfer to the monomer. More importantly, microstructural analysis of the poly(*rac*-lactide) showed that the tetranuclear tetra-alkyl **12** promotes heteroselectivity under mild conditions in the polymerization of *rac*-lactide, producing PLAs with P_s up to 0.78, and evidence that supports that stereoselectivity can be obtained by increasing the nuclearity of the active species.

EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques or a glovebox. Solvents were predried over sodium wire and distilled under nitrogen from sodium (toluene and *n*-hexane) or sodium-benzophenone (THF and diethyl ether). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze−thaw cycles. NMR spectra were recorded on a Varian Inova FT-500 spectrometer and are referenced to the residual deuterated solvent. ^{1}H NMR homodecoupled and NOESY-1D spectra were recorded on the same instrument with the following acquisition parameters: irradiation time, 2 and 256 scans, using standard VARIAN-FT software. 2D NMR spectra were acquired using the same software and processed using an IPC-Sun computer. Microanalyses were performed with a PerkinElmer 2400 CHN analyzer. Gel Permeation Chromatography (GPC) measurements were performed on a Polymer Laboratories PLsize exclusion chromatography-220 instrument equipped with a TSK-GEL G3000H column and an ELSD-LTII light-scattering detector. The GPC column was eluted with THF at 45 °C at 1 mL/min and was calibrated using eight monodisperse polystyrene standards in the range 580−483 000 Da. MALDI-ToF MS data were acquired with a Bruker Autoflex II ToF/ToF spectrometer, using a nitrogen laser source (337 nm, 3 ns) in linear mode with a positive acceleration voltage of 20 kV. Samples were prepared as follows: PLA (20 mg) was dissolved in HPLC quality THF with a matrix and NaI in a 100:5:5 ratio. Before evaporation, 10 μL of the mixture solution was deposited on the sample plate. External calibration was performed by using Peptide Calibration Standard II (covered mass range: 700−3 200 Da) and Protein Calibration Standard I (covered mass range: 5 000−17 500 Da). PLA melting temperatures were measured using a melting point Block (SMP 10). The sample was heated up to 100 °C and then heated at a rate of 1 °C/min up to 165 °C. The microstructures of PLA samples were determined by examination of the methine region in the homodecoupled ^{1}H NMR spectrum of the polymers recorded at room temperature in $CDCl_3$ on a Varian Inova FT-500 spectrometer. The Grignard reagents RMgCl (R = CH_2SiMe_3, Et, Bn) were used as purchased (Aldrich). ε-Caprolactone was dried by stirring over fresh CaH_2 for 48 h, then distilled under reduced pressure and stored over activated 4 Å molecular sieves. L-Lactide and *rac*-lactide were sublimed twice, recrystallized from THF, and finally sublimed again prior to use.

Preparation of Compounds 1−14. *Synthesis of [MgEt(pbpamd)] (1).* In a 250 cm^3 Schlenk tube, [Li(pbpamd)(THF)] (1.00 g, 2.45 mmol) was dissolved in dry toluene (70 mL) and cooled to −70 °C. A 2.8 M toluene solution of EtMgCl (0.87 mL, 2.45 mmol) was added, and the mixture was allowed to warm up to room temperature and stirred for 1 h. The suspension was filtered, and the resulting yellow solution was concentrated to 20 mL. The solution was cooled to −26 °C, and this gave compound **1** as a pale yellow crystalline solid. Yield: 850 mg (2.22 mmol, 91%). Anal. Calcd for $C_{20}H_{34}MgN_6$: C, 62.75; H, 8.95; N, 21.95. Found: C, 62.84; H, 9.05; N, 21.84. ^{1}H NMR (C_6D_6, 297 K): δ 7.35 (s, 1 H, CH), 5.23 (s, 2 H,

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H[4]), 4.62 [m, 1 H, $^3J_{H-H}$ = 6.3 Hz, C*H*−(CH$_3$)$_2$], 3.84 [m, 1 H, $^3J_{H-H}$ = 5.9 Hz, C*H*−(CH$_3$)$_2$], 2.05 (s, 6 H, Me[5]), 2.04 (t, 3 H, $^3J_{H-H}$ = 8.2 Hz, MgCH$_2$C*H*$_3$), 1.78 (s, 6 H, Me[3]), 1.50 [d, 6 H, $^3J_{H-H}$ = 6.3 Hz, CH−(C*H*$_3$)$_2$], 1.34 [d, 6 H, $^3J_{H-H}$ = 5.9 Hz, CH−(C*H*$_3$)$_2$], 0.39 (q, 2 H, $^3J_{H-H}$ = 8.2 Hz, MgC*H*$_2$CH$_3$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 297 K): δ 152.5 (N═C−N), 149.7, 140.5 (C[3or5]), 106.2 (C[4]), 58.2 (CH), 50.0 [*C*H−(CH$_3$)$_2$], 44.6 [*C*H−(CH$_3$)$_2$], 27.8 [CH−(*C*H$_3$)$_2$], 25.1 [CH−(*C*H$_3$)$_2$], 14.1 (MgCH$_2$*C*H$_3$), 12.8 (Me[5]), 10.5 (Me[3]), −2.3 (Mg*C*H$_2$CH$_3$).

*Synthesis of [MgBn(pbpamd)] (**2**).* The synthesis of **2** was carried out in an identical manner to **1**. [Li(pbpamd)(THF)] (1.00 g, 2.45 mmol), BnMgCl (2.0 M in toluene; 1.22 mL, 2.45 mmol). Yield: 985 mg (2.21 mmol, 90%). Anal. Calcd for C$_{25}$H$_{36}$MgN$_6$: C, 67.49; H, 8.16; N, 18.89. Found: C, 67.59; H, 8.31; N, 19.02. ^{1}H NMR (C$_6$D$_6$, 297 K): δ 7.40 (m, 2 H, MgCH$_2$C$_6$*H*$_5$), 7.30 (s, 1 H, CH), 7.25 (m, 2 H, MgCH$_2$C$_6$*H*$_5$), 6.86 (m, 1 H, MgCH$_2$C$_6$*H*$_5$), 5.14 (s, 2 H, H[4]), 4.62 [m, 1 H, $^3J_{H-H}$ = 6.3 Hz, C*H*−(CH$_3$)$_2$], 3.79 [m, 1 H, $^3J_{H-H}$ = 5.9 Hz, C*H*−(CH$_3$)$_2$], 2.27 (s, 2 H, MgC*H*$_2$C$_6$H$_5$), 1.86 (s, 6 H, Me[5]), 1.71 (s, 6 H, Me[3]), 1.45 [d, 6 H, $^3J_{H-H}$ = 6.3 Hz, CH−(C*H*$_3$)$_2$], 1.31 [d, 6 H, $^3J_{H-H}$ = 5.9 Hz, CH−(C*H*$_3$)$_2$]. ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 297 K): δ 152.1 (N═C−N), 150.3, 140.6 (C[3or5]), 155.6, 128.7, 125.0, 118.2 (MgCH$_2$*C*$_6$H$_5$), 106.4 (C[4]), 58.1 (CH), 50.0 [*C*H−(CH$_3$)$_2$], 44.5 [*C*H−(CH$_3$)$_2$], 27.6 [CH−(*C*H$_3$)$_2$], 25.4 [CH−(*C*H$_3$)$_2$], 22.5 (Mg*C*H$_2$C$_6$H$_5$), 12.8 (Me[5]), 10.5 (Me[3]).

*Synthesis of [MgEt(tbpamd)] (**3**).* The synthesis of **3** was carried out in an identical manner to **1**. [Li(tbpamd)(THF)] (1.00 g, 2.45 mmol), EtMgCl (2.8 M in toluene; 0.87 mL, 2.45 mmol). Yield: 860 mg (2.25 mmol, 92%). Anal. Calcd for C$_{20}$H$_{34}$MgN$_6$: C, 62.75; H, 8.95; N, 21.95. Found: C, 62.79; H, 9.02; N, 21.88. ^{1}H NMR (C$_6$D$_6$, 297 K): δ 7.23 (s, 1 H, CH), 5.19 (s, 2 H, H[4]), 3.59 (q, 2 H, $^3J_{H-H}$ = 7.0 Hz, N-C*H*$_2$CH$_3$), 2.08 (s, 6 H, Me[5]), 2.04 (t, 3 H, $^3J_{H-H}$ = 8.2 Hz, MgCH$_2$C*H*$_3$), 1.85 [s, 9 H, N−C(CH$_3$)$_3$], 1.67 (s, 6 H, Me[3]), 1.50 (t, 3 H, $^3J_{H-H}$ = 7.0 Hz, N−CH$_2$C*H*$_3$), 0.37 (q, 2 H, $^3J_{H-H}$ = 8.2 Hz, MgC*H*$_2$CH$_3$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 297 K): δ 153.9 (N═C−N), 149.8, 140.4 (C[3or5]), 106.2 (C[4]), 59.4 (CH), 52.5 [N-*C*(CH$_3$)$_3$], 44.2 (N-*C*H$_2$−CH$_3$), 31.0 [N−C(*C*H$_3$)$_3$], 19.7 (N−CH$_2$−*C*H$_3$), 14.0 (MgCH$_2$*C*H$_3$), 12.9 (Me[5]), 10.4 (Me[3]), −0.9 (Mg*C*H$_2$CH$_3$).

*Synthesis of [MgBn(tbpamd)] (**4**).* The synthesis of **4** was carried out in an identical manner to **1**. [Li(tbpamd)(THF)] (1.00 g, 2.45 mmol), BnMgCl (2.0 M in toluene; 1.22 mL, 2.45 mmol). Yield: 990 mg (2.22 mmol, 91%). The compound was obtained as suitable single crystals for X-ray diffraction analysis. Anal. Calcd for C$_{25}$H$_{36}$MgN$_6$: C, 67.49; H, 8.16; N, 18.89. Found: C, 67.52; H, 8.20; N, 18.92. ^{1}H NMR (C$_6$D$_6$, 297 K): δ 7.37 (m, 2 H, MgCH$_2$C$_6$*H*$_5$), 7.26 (m, 2 H, MgCH$_2$C$_6$*H*$_5$), 7.18 (s, 1 H, CH), 6.88 (m, 1 H, MgCH$_2$C$_6$*H*$_5$), 5.14 (s, 2 H, H[4]), 3.54 (q, 2 H, $^3J_{H-H}$ = 7.0 Hz, N-C*H*$_2$CH$_3$), 2.23 (s, 2 H, MgC*H*$_2$C$_6$H$_5$), 1.92 (s, 6 H, Me[5]), 1.77 [s, 9 H, N−C(CH$_3$)$_3$], 1.63 (s, 6 H, Me[3]), 1.47 (t, 3 H, $^3J_{H-H}$ = 7.0 Hz, N−CH$_2$C*H*$_3$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 297 K): δ 153.7 (N═C−N), 150.2, 140.7 (C[3or5]), 155.6, 128.6, 125.1, 118.1 (MgCH$_2$*C*$_6$H$_5$), 106.5 (C[4]), 59.2 (CH), 52.5 [N-*C*(CH$_3$)$_3$], 44.2 (N-*C*H$_2$−CH$_3$), 31.2 [N−C(*C*H$_3$)$_3$], 24.0 (Mg*C*H$_2$C$_6$H$_5$), 19.6 (N−CH$_2$−*C*H$_3$), 12.9 (Me[5]), 10.4 (Me[3]).

*Synthesis of [(CH$_2$SiMe$_3$)Mg(pbpamd$^-$)Mg(CH$_2$SiMe$_3$)(thf)] (**5**).* In a 250 cm^3 Schlenk tube, [Mg(CH$_2$SiMe$_3$)(pbpamd)] (0.75 g, 1.70 mmol) was dissolved in dry THF (70 mL) and cooled to −70 °C. A 1.3 M THF solution of Me$_3$SiCH$_2$MgCl (2.61 mL, 3.40 mmol) was added, and the mixture was allowed to warm up to room temperature and stirred overnight. The solvent was removed under a vacuum, and the residue was extracted with hexane (2 × 40 mL). The fractions were combined, and the resulting yellow solution was concentrated to 20 mL. The solution was cooled to −26 °C, and this gave compound **5** as a pale yellow crystalline solid. Yield: 870 mg (1.39 mmol, 82%). Anal. Calcd for C$_{30}$H$_{58}$Mg$_2$N$_6$OSi$_2$: C, 57.78; H, 9.37; N, 13.48. Found: C, 57.87; H, 9.48; N, 13.37. ^{1}H NMR (C$_6$D$_6$, 297 K): δ 5.35 (s, 2 H, H[4]), 3.76 [m, 2 H, C*H*−(CH$_3$)$_2$], 3.41 (m, 4 H, C$_4$*H*$_8$O), 2.26 (s, 6 H, Me[5]), 2.14 (s, 6 H, Me[3]), 1.33 [d, 6 H, $^3J_{H-H}$ = 5.9 Hz, CH−(C*H*$_3$)$_2$], 1.16 (m, 4 H, C$_4$*H*$_8$O), 1.03 [d, 6 H, $^3J_{H-H}$ = 6.3 Hz, CH−(C*H*$_3$)$_2$], 0.51 [s, 9 H, Mg[a]CH$_2$Si(C*H*$_3$)$_3$], 0.40 [s, 9 H, Mg[b]CH$_2$Si(C*H*$_3$)$_3$], −0.80 [s, 2 H, Mg[a]C*H*$_2$Si(CH$_3$)$_3$], −1.12 [s, 2 H, Mg[b]C*H*$_2$Si(CH$_3$)$_3$]. ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 297 K): δ 169.6 (N═C−N), 147.7, 143.8 (C[3or5]), 104.9 (C[4]), 77.0 (C[a]), 69.2 (*C*$_4$H$_8$O), 47.4 [*C*H−(CH$_3$)$_2$], 46.3 [*C*H−(CH$_3$)$_2$], 26.7 [CH−(*C*H$_3$)$_2$], 26.1 [CH−(*C*H$_3$)$_2$], 25.0 (*C*$_4$H$_8$O), 13.7 (Me[5]), 13.7 (Me[3]), 5.2 [Mg[a]CH$_2$Si(*C*H$_3$)$_3$], 4.8 [Mg[b]CH$_2$Si(*C*H$_3$)$_3$], −5.2 (Mg[b]*C*H$_2$Si(CH$_3$)$_3$), −7.6 [Mg[a]*C*H$_2$Si-(CH$_3$)$_3$].

*Synthesis of [EtMg(pbpamd$^-$)MgEt(thf)] (**6**).* The synthesis of **6** was carried out in an identical manner to **5**. [Mg(Et)(pbpamd)] (**1**; 0.75 g, 1.95 mmol), EtMgCl (2.8 M in toluene; 1.40 mL, 3.92 mmol). Yield: 830 mg (1.63 mmol, 83%). Anal. Calcd for C$_{26}$H$_{46}$Mg$_2$N$_6$O: C, 61.56; H, 9.14; N, 16.57. Found: C, 61.64; H, 9.23; N, 16.48. ^{1}H NMR (C$_6$D$_6$, 297 K): δ 5.37 (s, 2 H, H[4]), 3.87 [m, 1 H, $^3J_{H-H}$ = 6.3 Hz, C*H*−(CH$_3$)$_2$], 3.78 [m, 1 H, $^3J_{H-H}$ = 5.9 Hz, C*H*−(CH$_3$)$_2$], 3.36 (m, 4 H, C$_4$*H*$_8$O), 2.30 (s, 6 H, Me[5]), 2.12 (s, 6 H, Me[3]), 2.06 (t, 3 H, $^3J_{H-H}$ = 8.2 Hz, Mg[a]CH$_2$C*H*$_3$), 1.83 (t, 3 H, $^3J_{H-H}$ = 8.2 Hz, Mg[b]CH$_2$C*H*$_3$), 1.31 [d, 6 H, $^3J_{H-H}$ = 6.3 Hz, CH−(C*H*$_3$)$_2$], 1.12 (m, 4 H, C$_4$*H*$_8$O), 1.04 [d, 6 H, $^3J_{H-H}$ = 5.9 Hz, CH−(C*H*$_3$)$_2$], 0.38 (q, 2 H, $^3J_{H-H}$ = 8.2 Hz, Mg[a]C*H*$_2$CH$_3$), 0.06 (q, 2 H, $^3J_{H-H}$ = 8.2 Hz, Mg[a]C*H*$_2$CH$_3$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 297 K): δ 168.7 (N═C−N), 147.5, 143.7 (C[3or5]), 104.8 (C[4]), 76.7 (C[a]), 69.0 (*C*$_4$H$_8$O), 46.7 [*C*H−(CH$_3$)$_2$], 46.0 [*C*H−(CH$_3$)$_2$], 26.4 [CH−(*C*H$_3$)$_2$], 26.2 [CH−(*C*H$_3$)$_2$], 25.0 (*C*$_4$H$_8$O), 14.3 (Mg[a]CH$_2$*C*H$_3$), 14.1 (Mg[b]CH$_2$*C*H$_3$), 13.2 (Me[5]), 12.8 (Me[3]), 1.07 (Mg[b]*C*H$_2$CH$_3$), −0.5 (Mg[a]*C*H$_2$CH$_3$).

*Synthesis of [(CH$_2$SiMe$_3$)Mg(tbpamd$^-$)Mg(CH$_2$SiMe$_3$)(thf)] (**7**).* The synthesis of **7** was carried out in an identical manner to **5**. [Mg(CH$_2$SiMe$_3$)(tbpamd)] (0.75 g, 1.70 mmol), Me$_3$SiCH$_2$MgCl (1.3 M in THF; 2.61 mL, 3.40 mmol). Yield: 880 mg (1.41 mmol, 83%). Anal. Calcd for C$_{30}$H$_{58}$Mg$_2$N$_6$OSi$_2$: C, 57.78; H, 9.37; N, 13.48. Found: C, 57.83; H, 9.43; N, 13.39. ^{1}H NMR (C$_6$D$_6$, 297 K): δ 5.34 (s, 2 H, H[4]), 3.50 (m, 4 H, C$_4$*H*$_8$O), 3.45 (q, 2 H, $^3J_{H-H}$ = 7.0 Hz, N-C*H*$_2$CH$_3$), 2.28 (s, 6 H, Me[5]), 2.11 (s, 6 H, Me[3]), 1.29 (m, 4 H, C$_4$*H*$_8$O), 1.23 [s, 9 H, N−C(CH$_3$)$_3$], 1.20 (t, 3 H, $^3J_{H-H}$ = 7.0 Hz, N−CH$_2$C*H*$_3$), 0.53 [s, 9 H, Mg[a]CH$_2$Si(C*H*$_3$)$_3$], 0.38 [s, 9 H, Mg[b]CH$_2$Si(C*H*$_3$)$_3$], −0.77 [s, 2 H, Mg[a]C*H*$_2$Si(CH$_3$)$_3$], −1.13 [s, 2 H, Mg[b]C*H*$_2$Si(CH$_3$)$_3$]. ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 297 K): δ 173.4 (N═C−N), 147.5, 143.6 (C[3or5]), 104.7 (C[4]), 77.7 (C[a]), 69.1 (*C*$_4$H$_8$O), 52.3 [N-*C*(CH$_3$)$_3$], 46.6 (N-*C*H$_2$−CH$_3$), 33.2 [N−C(*C*H$_3$)$_3$], 19.5 (N−CH$_2$−*C*H$_3$), 13.6 (Me[5]), 13.4 (Me[3]), 4.9 [Mg[a]CH$_2$Si(*C*H$_3$)$_3$], 4.6 [Mg[b]CH$_2$Si(*C*H$_3$)$_3$], −5.4 (Mg[b]*C*H$_2$Si(CH$_3$)$_3$), −9.1 [Mg[a]*C*H$_2$Si-(CH$_3$)$_3$].

*Synthesis of [EtMg(tbpamd$^-$)MgEt(thf)] (**8**).* The synthesis of **8** was carried out in an identical manner to **5**. [Mg(Et)(tbpamd)] (**3**; 0.75 g, 1.95 mmol), EtMgCl (2.8 M in toluene; 1.40 mL, 3.92 mmol). Yield: 795 mg (1.57 mmol, 80%). The compound was obtained as suitable single crystals for X-ray diffraction analysis. Anal. Calcd for C$_{26}$H$_{46}$Mg$_2$N$_6$O: C, 61.56; H, 9.14; N, 16.57. Found: C, 61.60; H, 9.19; N, 16.54. ^{1}H NMR (C$_6$D$_6$, 297 K): δ 5.37 (s, 2 H, H[4]), 3.55 (m, 4 H, C$_4$*H*$_8$O), 3.39 (q, 2 H, $^3J_{H-H}$ = 7.0 Hz, N-C*H*$_2$CH$_3$), 2.34 (t, 3 H, $^3J_{H-H}$ = 8.2 Hz, Mg[a]CH$_2$C*H*$_3$), 2.33 (s, 6 H, Me[5]), 2.12 (s, 6 H, Me[3]), 1.90 (t, 3 H, $^3J_{H-H}$ = 8.2 Hz, Mg[b]CH$_2$C*H*$_3$), 1.32 (t, 3 H, $^3J_{H-H}$ = 7.0 Hz, N−CH$_2$C*H*$_3$), 1.22 [s, 9 H, N−C(CH$_3$)$_3$], 1.21 (m, 4 H, C$_4$*H*$_8$O), 0.37 (q, 2 H, $^3J_{H-H}$ = 8.2 Hz, Mg[a]C*H*$_2$CH$_3$), 0.07 (q, 2 H, $^3J_{H-H}$ = 8.2 Hz, Mg[b]C*H*$_2$CH$_3$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 297 K): δ 172.9 (N═C−N), 147.2, 143.8 (C[3or5]), 104.6 (C[4]), 77.8 (C[a]), 69.1 (*C*$_4$H$_8$O), 51.7 [N-*C*(CH$_3$)$_3$], 46.4 (N-*C*H$_2$−CH$_3$), 33.1 [N−C(*C*H$_3$)$_3$], 25.1 (*C*$_4$H$_8$O), 19.1 (N−CH$_2$−*C*H$_3$), 14.2 (Mg[a]CH$_2$*C*H$_3$), 13.6 (Mg[b]CH$_2$*C*H$_3$), 13.1 (Me[5]), 12.7 (Me[3]), 1.08(Mg[b]CH$_2$CH$_3$), −0.5 (Mg[a]*C*H$_2$CH$_3$).

*Synthesis of [{(CH$_2$SiMe$_3$)Mg(pbpamd$^-$)Mg(CH$_2$SiMe$_3$)}$_2${μ-O,O-(C$_4$H$_8$)}] (**9**).* In a 250 cm^3 Schlenk tube, [Mg(CH$_2$SiMe$_3$)(pbpamd)] (0.75 g, 1.70 mmol) was dissolved in 100 mL of a mixture of dry THF and 1,4-dioxane in a ratio of 9:1, and it was cooled to −70 °C. A 1.3 M solution in THF of Me$_3$SiCH$_2$MgCl (2.61 mL, 3.40 mmol) was added to the mixture, which was allowed to warm up to room temperature and stirred overnight. The solvent was removed under a vacuum, and the residue was extracted with hexane (2 × 40 mL). The fractions were combined, and the resulting yellow solution was concentrated to 20 mL. The solution was cooled to −26 °C, and this gave compound **9** as pale yellow single crystals suitable for X-ray diffraction analysis. Yield: 830 mg (0.70 mmol, 82%). Anal. Calcd for C$_{56}$H$_{108}$Mg$_4$N$_{12}$O$_2$Si$_4$: C, 56.47; H, 9.14; N, 14.11. Found: C, 56.54; H, 9.22; N, 14.05. ^{1}H NMR

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(C_6D_6, 297 K): δ 5.32 (s, 4 H, H^4), 3.74 [m, 2 H, $^3J_{H-H}$ = 5.9 Hz, $\underline{CH}-(CH_3)_2$], 3.71 [m, 2 H, $^3J_{H-H}$ = 5.9 Hz, $\underline{CH}-(CH_3)_2$], 3.30 (s, 8 H, $C_4\underline{H_8}O_2$), 2.13 (s, 12 H, Me^5), 2.09 (s, 12 H, Me^3), 1.27 [d, 12 H, $^3J_{H-H}$ = 5.9 Hz, CH$-(\underline{CH_3})_2$], 1.02 [d, 12 H, $^3J_{H-H}$ = 5.9 Hz, CH$-(\underline{CH_3})_2$], 0.52 [s, 18 H, $Mg^aCH_2Si(\underline{CH_3})_3$], 0.36 [s, 18 H, $Mg^bCH_2Si(\underline{CH_3})_3$], −0.81 [s, 4 H, $Mg^a\underline{CH_2}Si(CH_3)_3$], −1.20 [s, 4 H, $Mg^b\underline{CH_2}Si(CH_3)_3$]. $^{13}C-\{^1H\}$ NMR (C_6D_6, 297 K): δ 169.3 (N=C−N), 147.9, 143.6 (C^{3or5}), 105.2 (C^4), 76.8 (C^a), 67.2 ($\underline{C_4}H_8O_2$), 47.4 [$\underline{C}H-(CH_3)_2$], 46.4 [$\underline{C}H-(CH_3)_2$], 26.6 [CH$-(\underline{C}H_3)_2$], 26.2 [CH$-(\underline{C}H_3)_2$], 13.7 (Me^5), 13.7 (Me^3), 5.1 [$Mg^aCH_2Si(\underline{C}H_3)_3$], 4.7 [$Mg^bCH_2Si(\underline{C}H_3)_3$], −5.6 ($Mg^b\underline{C}H_2Si(CH_3)_3$), −7.5 [$Mg^a\underline{C}H_2Si(CH_3)_3$].

*Synthesis of [{EtMg(pbpamd$^-$)MgEt}$_2${μ-O,O-(C_4H_8)}] (**10**).* The synthesis of **10** was carried out in an identical manner to **9**. [Mg(Et)(pbpamd)] (**1**) (0.75 g, 1.95 mmol), EtMgCl (2.8 M in toluene; 1.40 mL, 3.92 mmol). Yield: 792 mg (0.83 mmol, 84%). Anal. Calcd for $C_{48}H_{84}Mg_4N_{12}O_2$: C, 60.15; H, 8.83; N, 17.54. Found: C, 60.26; H, 8.91; N, 17.49. ^1H NMR (C_6D_6, 297 K): δ 5.33 (s, 4 H, H^4), 3.78 [m, 2 H, $^3J_{H-H}$ = 5.9 Hz, $\underline{CH}-(CH_3)_2$], 3.72 [m, 2 H, $^3J_{H-H}$ = 5.9 Hz, $\underline{CH}-(CH_3)_2$], 3.30 (s, 8 H, $C_4\underline{H_8}O_2$), 2.22 (s, 12 H, Me^5), 2.10 (s, 12 H, Me^3), 2.06 (t, 6 H, $^3J_{H-H}$ = 8.2 Hz, $Mg^aCH_2\underline{CH_3}$), 1.75 (t, 6 H, $^3J_{H-H}$ = 8.2 Hz, $Mg^bCH_2\underline{CH_3}$), 1.23 [d, 12 H, $^3J_{H-H}$ = 5.9 Hz, CH$-(\underline{CH_3})_2$], 1.00 [d, 12 H, $^3J_{H-H}$ = 5.9 Hz, CH$-(\underline{CH_3})_2$], 0.37 (q, 4 H, $^3J_{H-H}$ = 8.2 Hz, $Mg^a\underline{CH_2}CH_3$), −0.01 (q, 4 H, $^3J_{H-H}$ = 8.2 Hz, $Mg^a\underline{CH_2}CH_3$). $^{13}C-\{^1H\}$ NMR (C_6D_6, 297 K): δ 168.3 (N=C−N), 147.8, 143.4 (C^{3or5}), 105.0 (C^4), 76.4 (C^a), 67.2 ($\underline{C_4}H_8O_2$), 46.7 [$\underline{C}H-(CH_3)_2$], 46.1 [$\underline{C}H-(CH_3)_2$], 26.3 [CH$-(\underline{C}H_3)_2$], 26.3 [CH$-(\underline{C}H_3)_2$], 14.2 ($Mg^aCH_2\underline{C}H_3$), 13.8 ($Mg^bCH_2\underline{C}H_3$), 13.1 (Me^5), 12.8 (Me^3), −1.0 ($Mg^b\underline{C}H_2CH_3$), −1.8 ($Mg^a\underline{C}H_2CH_3$).

*Synthesis of [{BnMg(pbpamd$^-$)MgBn}$_2${μ-O,O-(C_4H_8)}] (**11**).* The synthesis of **11** was carried out in an identical manner to **9**. [Mg(Bn)(pbpamd)] (**2**) (0.80 g, 1.80 mmol), BnMgCl (2.0 M in THF; 1.80 mL, 3.60 mmol). Yield: 850 mg (0.70 mmol, 78%). Anal. Calcd for $C_{68}H_{92}Mg_4N_{12}O_2$: C, 67.68; H, 7.68; N, 13.93. Found: C, 67.79; H, 7.75; N, 13.85. ^1H NMR (C_6D_6, 297 K): δ 7.41 (m, 4 H, $Mg^aCH_2\underline{C_6H_5}$), 7.30 (m, 4 H, $Mg^aCH_2\underline{C_6H_5}$), 7.17 (m, 4 H, $Mg^bCH_2\underline{C_6H_5}$), 7.09 (m, 4 H, $Mg^bCH_2\underline{C_6H_5}$), 6.90 (m, 2 H, $Mg^aCH_2\underline{C_6H_5}$), 6.80 (m, 2 H, $Mg^bCH_2\underline{C_6H_5}$), 5.25 (s, 4 H, H^4), 3.63 [m, 4 H, $^3J_{H-H}$ = 5.9 Hz, $\underline{CH}-(CH_3)_2$], 3.07 (s, 8 H, $C_4\underline{H_8}O_2$), 2.25 (s, 4 H, $Mg^a\underline{CH_2}C_6H_5$), 2.06 (s, 12 H, Me^5), 1.93 (s, 12 H, Me^3), 1.87 (s, 4 H, $Mg^b\underline{CH_2}C_6H_5$), 1.13 [d, 12 H, $^3J_{H-H}$ = 5.9 Hz, CH$-(\underline{CH_3})_2$], 0.93 [d, 12 H, $^3J_{H-H}$ = 5.9 Hz, CH$-(\underline{CH_3})_2$]. $^{13}C-\{^1H\}$ NMR (C_6D_6, 297 K): δ 168.4 (N=C−N), 148.3, 143.5 (C^{3or5}), 155.5, 128.7, 124.9, 118.2 ($Mg^aCH_2\underline{C_6H_5}$), 154.9, 128.1, 124.6, 118.4 ($Mg^bCH_2\underline{C_6H_5}$), 105.3 ($C^4$), 76.3 ($C^a$), 67.5 ($\underline{C_4}H_8O_2$), 47.2 [$\underline{C}H-(CH_3)_2$], 46.3 [$\underline{C}H-(CH_3)_2$], 26.4 [CH$-(\underline{C}H_3)_2$], 26.4 [CH$-(\underline{C}H_3)_2$], 23.7 ($Mg^b\underline{C}H_2C_6H_5$), 22.8 ($Mg^a\underline{C}H_2C_6H_5$), 13.1 ($Me^5$), 13.0 ($Me^3$).

*Synthesis of [{(CH_2SiMe_3)Mg(tbpamd$^-$)Mg(CH_2SiMe_3)}$_2${μ-O,O-(C_4H_8)}] (**12**).* The synthesis of **12** was carried out in an identical manner to **9**. [Mg(CH_2SiMe_3)(tbpamd)] (0.75 g, 1.70 mmol), Me_3SiCH_2MgCl (1.3 M in THF; 2.61 mL, 3.40 mmol). The compound was obtained as suitable single crystals for X-ray diffraction analysis. Yield: 850 mg (0.71 mmol, 83%). Anal. Calcd for $C_{56}H_{108}Mg_4N_{12}O_2Si_4$: C, 56.47; H, 9.14; N, 14.11. Found: C, 56.52; H, 9.19; N, 14.07. ^1H NMR (C_6D_6, 297 K): δ 5.32 (s, 4 H, H^4), 3.35 (q, 4 H, $^3J_{H-H}$ = 7.0 Hz, N-$\underline{CH_2}CH_3$), 3.26 (s, 8 H, $C_4\underline{H_8}O_2$), 2.24 (s, 12 H, Me^5), 2.09 (s, 12 H, Me^3), 1.20 [s, 18 H, N−C$(\underline{CH_3})_3$], 1.09 (t, 6 H, $^3J_{H-H}$ = 7.0 Hz, N−$CH_2\underline{CH_3}$), 0.50 [s, 18 H, $Mg^aCH_2Si(\underline{CH_3})_3$], 0.32 [s, 18 H, $Mg^bCH_2Si(\underline{CH_3})_3$], −0.80 [s, 4 H, $Mg^a\underline{CH_2}Si(CH_3)_3$], −1.22 [s, 4 H, $Mg^b\underline{CH_2}Si(CH_3)_3$]. $^{13}C-\{^1H\}$ NMR (C_6D_6, 297 K): δ 173.3 (N=C−N), 147.6, 143.5 (C^{3or5}), 104.8 (C^4), 77.8 (C^a), 67.2 ($\underline{C_4}H_8O_2$), 52.5 [N-$\underline{C}(CH_3)_3$], 46.5 (N-$\underline{C}H_2-CH_3$), 33.3 [N−C$(\underline{C}H_3)_3$], 19.5 (N−$CH_2-\underline{C}H_3$), 13.7 (Me^5), 13.4 (Me^3), 4.9 [$Mg^aCH_2Si(\underline{C}H_3)_3$], 4.7 [$Mg^bCH_2Si(\underline{C}H_3)_3$], −5.5 ($Mg^b\underline{C}H_2Si(CH_3)_3$), −9.2 [$Mg^a\underline{C}H_2Si(CH_3)_3$].

*Synthesis of [{EtMg(tbpamd$^-$)MgEt}$_2${μ-O,O-(C_4H_8)}] (**13**).* The synthesis of **13** was carried out in an identical manner to **9**. [Mg(Et)(tbpamd)] (**3**) (0.75 g, 1.95 mmol), EtMgCl (2.8 M in toluene; 1.40 mL, 3.92 mmol). Yield: 772 mg (0.80 mmol, 82%). Anal. Calcd for $C_{48}H_{84}Mg_4N_{12}O_2$: C, 60.15; H, 8.83; N, 17.54. Found: C, 60.22; H, 8.88; N, 17.46. ^1H NMR (C_6D_6, 297 K): δ 5.36 (s, 4 H, H^4), 3.50 (q, 4 H, $^3J_{H-H}$ = 7.0 Hz, N-$\underline{CH_2}CH_3$), 3.36 (s, 8 H, $C_4\underline{H_8}O_2$), 2.30 (s, 12 H, Me^5), 2.11 (t, 6 H, $^3J_{H-H}$ = 8.2 Hz, $Mg^aCH_2\underline{CH_3}$), 2.10 (s, 12 H, Me^3), 1.76 (t, 6 H, $^3J_{H-H}$ = 8.2 Hz, $Mg^bCH_2\underline{CH_3}$), 1.07 (t, 6 H, $^3J_{H-H}$ = 7.0 Hz, N−$CH_2\underline{CH_3}$), 1.20 [s, 18 H, N−C$(CH_3)_3$], 0.07 (q, 4 H, $^3J_{H-H}$ = 8.2 Hz, $Mg^a\underline{CH_2}CH_3$), −0.03 (q, 4 H, $^3J_{H-H}$ = 8.2 Hz, $Mg^b\underline{CH_2}CH_3$). $^{13}C-\{^1H\}$ NMR (C_6D_6, 297 K): δ 172.7 (N=C−N), 147.4, 143.6 (C^{3or5}), 104.7 (C^4), 77.7 (C^a), 67.1 ($\underline{C_4}H_8O_2$), 51.9 [N-$\underline{C}(CH_3)_3$], 46.3 (N-$\underline{C}H_2-CH_3$), 33.2 [N−C$(\underline{C}H_3)_3$], 19.1 (N−$CH_2-\underline{C}H_3$), 14.3 ($Mg^aCH_2\underline{C}H_3$), 13.6 ($Mg^bCH_2\underline{C}H_3$), 13.1 (Me^5), 12.7 (Me^3), −0.6 ($Mg^b\underline{C}H_2CH_3$), −1.6 ($Mg^a\underline{C}H_2CH_3$).

*Synthesis of [{BnMg(tbpamd$^-$)MgBn}$_2${μ-O,O-(C_4H_8)}] (**14**).* The synthesis of **14** was carried out in an identical manner to **9**. [Mg(Bn)(tbpamd)] (**4**; 0.80 g, 1.80 mmol), BnMgCl (1.80 mL, 3.60 mmol). Yield: 870 mg (0.72 mmol, 80%). Anal. Calcd for $C_{68}H_{92}Mg_4N_{12}O_2$: C, 67.68; H, 7.68; N, 13.93. Found: C, 67.72; H, 7.74; N, 13.87. ^1H NMR (C_6D_6, 297 K): δ 7.39 (m, 4 H, $Mg^aCH_2\underline{C_6H_5}$), 7.27 (m, 4 H, $Mg^aCH_2\underline{C_6H_5}$), 7.18 (m, 4 H, $Mg^bCH_2\underline{C_6H_5}$), 7.09 (m, 4 H, $Mg^bCH_2\underline{C_6H_5}$), 6.88 (m, 2 H, $Mg^aCH_2\underline{C_6H_5}$), 6.83 (m, 2 H, $Mg^bCH_2\underline{C_6H_5}$), 5.25 (s, 4 H, H^4), 3.19 (s, 8 H, $C_4\underline{H_8}O_2$), 3.18 (q, 4 H, $^3J_{H-H}$ = 7.0 Hz, N-$\underline{CH_2}CH_3$), 2.23 (s, 4 H, $Mg^a\underline{CH_2}C_6H_5$), 2.09 (s, 12 H, Me^5), 1.92 (s, 12 H, Me^3), 1.85 (s, 4 H, $Mg^b\underline{CH_2}C_6H_5$), 1.13 [s, 18 H, N−C$(CH_3)_3$], 0.98 (t, 6 H, $^3J_{H-H}$ = 7.0 Hz, N−$CH_2\underline{CH_3}$). $^{13}C-\{^1H\}$ NMR (C_6D_6, 297 K): δ 172.6 (N=C−N), 147.9, 143.7 (C^{3or5}), 155.6, 128.6, 124.6, 118.1 ($Mg^aCH_2\underline{C_6H_5}$), 155.5, 128.8, 127.9, 118.3 ($Mg^bCH_2\underline{C_6H_5}$), 104.9 ($C^4$), 77.6 ($C^a$), 67.2 ($\underline{C_4}H_8O_2$), 52.2 [N-$\underline{C}(CH_3)_3$], 46.0 (N-$\underline{C}H_2-CH_3$), 33.2 [N−C$(\underline{C}H_3)_3$], 24.3 ($Mg^a\underline{C}H_2C_6H_5$), 21.5 ($Mg^b\underline{C}H_2C_6H_5$), 19.0 (N−$CH_2-\underline{C}H_3$), 13.0 ($Me^5$), 12.9 ($Me^3$).

Typical Polymerization Procedures. Polymerizations of ε-caprolactone (CL) were carried out on a Schlenk line in a flame-dried round-bottomed flask equipped with a magnetic stirrer. In a typical procedure, the initiator was dissolved in the appropriate amount of solvent, and temperature equilibration was ensured by stirring the solution for 15 min in a temperature-controlled bath. ε-CL was injected, and polymerization times were measured from that point. Polymerizations were terminated by injecting a solution of hydrochloric acid in methanol. Polymers were precipitated in methanol, filtered off, redissolved and reprecipitated in methanol, and dried in vacuo to a constant weight.

Polymerizations of L-lactide and *rac*-lactide (LA) were performed on a Schlenk line in a flame-dried round-bottomed flask equipped with a magnetic stirrer. The Schlenk tubes were charged in the glovebox with the required amount of lactide and initiator, separately, and then attached to the vacuum line. The initiator and monomer were dissolved in the appropriate amount of solvent, and temperature equilibration was ensured in both Schlenk flasks by stirring the solutions for 15 min in a bath. The appropriate amount of initiator was added by syringe, and polymerization times were measured from that point. Polymerizations were stopped by injecting a solution of hydrochloric acid in methanol. Polymers were precipitated in methanol, filtered off, redissolved and reprecipitated in methanol, and dried in vacuo to constant weight.

*X-Ray Crystallographic Structure Determination for Complexes [Mg(CH_2SiMe_3)(κ^3-tbpamd)], **4**, **8**, **9**, and **12**.* Data were collected on a Bruker X8 APEX II CCD-based diffractometer, equipped with a graphite monochromated Mo Kα radiation source (λ = 0.71073 Å). The crystal data, data collection, structural solution, and refinement parameters are summarized in Table S3. Data were integrated using SAINT,[43] and an absorption correction was performed with the program SADABS.[44] The structure was solved by direct methods using the SHELXTL package[45] and refined by full-matrix least-squares methods based on F^2. Compound **8** shows disorder rotational and positional for ethyl and THF groups, respectively. Instructions SAME and SADI of SHELX have been used to restrain these groups. For **12**, different crystals had to be used because of decomposition of the compound during the X-ray exposures. Nevertheless, this information has allowed us to obtain an acceptable resolution. There are two different dimers in the unit cell which only differ in the orientation of

ethyl groups. All non-hydrogen atoms were refined with anisotropic thermal parameters except those of the ethyl and THF disordered groups and the hydrogen atoms, which were geometrically situated.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

VT ^{1}H NMR experiments, NOESY-1D responses, X-ray diffraction studies of complex [Mg(CH_2SiMe_3)(κ^3-tbpamd)], and ring-opening polymerization of ε-caprolactone and L-lactide details as well as X-ray diffraction experimental details of data collection, refinement, and atom coordinates as well as anisotropic displacement parameters for complexes [Mg(CH_2SiMe_3)(κ^3-tbpamd)], **4**, **8**, **9**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Otero, A.; Fernández-Baeza, J.; Lara-Sánchez, A.; Sánchez-Barba, L. F. *Coord. Chem. Rev.* **2013**, *257*, 1806−1868.

(2) (a) Biela, T.; Kowalski, A.; Libiszowski, J.; Duda, A.; Penczek, S. *Macromol. Symp.* **2006**, *240*, 47−55. (b) Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J., Jr.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T. *Science* **2006**, *311*, 484−489.

(3) For reviews in this area, see: (a) Cameron, D. J. A.; Shaver, M. P. *Chem. Soc. Rev.* **2011**, *40*, 1761−1776. (b) Kiesewetter, M. K.; Shin, E. J.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2010**, *43*, 2093−2107. (c) Stanford, M. J.; Dove, A. P. *Chem. Soc. Rev.* **2010**, *39*, 486−494. (d) Carpentier, J.-F. *Macromol. Rapid Commun.* **2010**, *31*, 1696−1705. (e) Thomas, C. M. *Chem. Soc. Rev.* **2010**, *39*, 165−173. (f) Ajellal, N.; Carpentier, J.-F.; Guillaume, C.; Guillaume, S. M.; Helou, M.; Poirier, V.; Sarazin, Y.; Trifonov, A. *Dalton Trans.* **2010**, *39*, 8363−8376. (g) Wheaton, C. A.; Hayes, P. G.; Ireland, B. J. *Dalton Trans.* **2009**, 4832−4846. (h) Place, E. S.; George, J. H.; Williams, C. K.; Stevens, M. M. *Chem. Soc. Rev.* **2009**, *38*, 1139−1151. (i) Platel, R. H.; Hodgson, L. M.; Williams, C. K. *Polym. Rev.* **2008**, *48*, 11−63. (j) Williams, C. K.; Hillmyer, M. A. *Polym. Rev.* **2008**, *48*, 1−10. (k) Dove, A. P. *Chem. Commun.* **2008**, 6446−6470. (l) Amgoune, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J.-F. *Chem. —Eur. J.* **2006**, *12*, 169−179. (m) Wu, J.; Yu, T.-L.; Chen, C.-T.; Lin, C.-C. *Coord. Chem. Rev.* **2006**, *250*, 602−626. (n) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147−6176. (o) Chisholm, M. H.; Zhou, Z. *J. Mater. Chem.* **2004**, *14*, 3081−3092.

(4) For books in this area, see: (a) Auras, R.; Lim, L.-T. *Poly(lactic acid): synthesis structures, properties, processing, and applications*; Wiley: Hoboken, NJ, 2010. (b) Dubois, P.; Coulembier, O.; Raquez, J.-M. *Handbook of ring-opening polymerization*; Wiley-VCH: Weinheim, Germany, 2009. (c) Chisholm, M. H.; Zhou, Z. Stereoselective polymerization of Lactide. In *Stereoselective Polymerization with Single Site Catalysts*; Baugh, L. S., Canich, J. A. M., Eds.; CRC Press, Taylor & Francis: Boca Raton, FL, 2008; pp 645−660.

(5) (a) Cowan, J. A. *The biological chemistry of magnesium*; VCH Publishers: New York, 1995. (b) Campbell, N. A. *Biology*; Benjamin/Cummings Pub. Co.: Redwood City, CA, 1993; pp 718, 811.

(6) (a) Parkin, G. *Chem. Commun.* **2000**, 1971−1985. (b) Mills, C. F. *Zinc in human biology*; Springer-Verlag: London, 1989.

(7) (a) Pêgo, A. P.; Siebum, B.; Van Luyn, M. J.; Gallego y Van Seijen, X. J.; Poot, A. A.; Grijpma, D. W.; Feijen, J. *Tissue Eng., Part A* **2003**, *9*, 981−994. (b) Marler, J. J.; Upton, J.; Langer, R.; Vacanti, J. P. *Adv. Drug Delivery Rev.* **1998**, *33*, 165−182. (c) Frazza, E. J.; Schmitt, E. E. *J. Biomed. Mater. Res. A* **1971**, *5*, 43−58. (d) Dexon and Vicryl are products of Davis & Geek Corp., Wayne, NJ, and Ethicon, Inc., Somerville, NJ, respectively.

(8) (a) Penco, M.; Donetti, R.; Mendichi, R.; Ferruti, P. *Macromol. Chem. Physic.* **1998**, *199*, 1737−1745. (b) Leupron Depot is a product of Takeda Chemical Industries, Ltd., Japan, for drug delivery purposes. (c) Kim, H.; Sung, Y. K.; Jung, J.; Baik, H.; Min, T. J.; Kim, Y. S. *J. Korean Chem. Soc.* **1990**, *34*, 8. (d) Smith, A.; Hunneyball, I. M. *Int. J. Pharm.* **1986**, *30*, 215−220.

(9) (a) Inkinen, S.; Hakkarainen, M.; Albertsson, A.-C.; Södergård, A. *Biomacromolecules* **2011**, *12*, 523−532. (b) Darensbourg, D. J.; Choi, W.; Richers, C. P. *Macromolecules* **2007**, *40*, 3521−3523. (c) Beiser, I. H.; Kanat, I. O. *J. Am. Podiat. Med. Assoc.* **1990**, *80*, 72−75.

(10) (a) Ecochem is a polylactide-based packaging material developed by DuPont−ConAgra. (b) Gruber, P. R.; O'Brien, M. Polyesters III: Applications and Commercial Products. In *Biopolymers*; Doi, Y., Steinbüchel, A., Eds.; Wiley-Blackwell: New York, 2002; Vol. 4, pp 235−249. (c) www.natureworksllc.com/Product-And-Applications.aspx.

(11) (a) Buffet, J.-C.; Okuda, J. *Polym. Chem.* **2011**, *2*, 2758−2763. (b) Shaver, M. P.; Cameron, D. J. A. *Biomacromolecules* **2010**, *11*, 3673−3679. (c) Madhavan Nampoothiri, K.; Nair, N. R.; John, R. P. *Bioresour. Technol.* **2010**, *101*, 8493−8501.

(12) (a) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A.; Sánchez-Barba, L. F.; López-Solera, I.; Rodríguez, A. M. *Inorg. Chem.* **2007**, *46*, 1760−1770. (b) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A.; Sánchez-Barba, L.; Rodríguez, A. M. *Eur. J. Inorg. Chem.* **2004**, 260−266.

(13) (a) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A.; Sánchez-Barba, L.; Rodríguez, A. M.; Maestro, M. A. *J. Am. Chem. Soc.* **2004**, *126*, 1330−1331. (b) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A.; Sánchez-Barba, L. F.; Sánchez-Molina, M.; Rodríguez, A. M.; Bo, C.; Urbano-Cuadrado, M. *Organometallics* **2007**, *26*, 4310−4320. (c) Otero, A.; Fernandez-Baeza, J.; Lara-Sanchez, A.; Antiñolo, A.; Tejeda, J.; Martínez-Caballero, E.; Marquez-Segovia, I.; Lopez-Solera, I.; Sanchez-Barba, L. F.; Alonso-Moreno, C. *Inorg. Chem.* **2008**, *47*, 4996−5005.

(14) Otero, A.; Fernández-Baeza, J.; Lara-Sánchez, A.; Tejeda, J.; Sánchez-Barba, L. F. *Eur. J. Inorg. Chem.* **2008**, 5309−5326.

(15) (a) Otero, A.; Fernández-Baeza, J.; Tejeda, J.; Lara-Sánchez, A.; Sánchez-Molina, M.; Franco, S.; López-Solera, I.; Rodríguez, A. M.; Sánchez-Barba, L. F.; Morante-Zarcero, S.; Garcés, A. *Inorg. Chem.* **2009**, *48*, 5540−5554. (b) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A.; Sánchez-Barba, L. F.; Sánchez-Molina, M.; Franco, S.; López-Solera, M. I.; Rodríguez, A. M. *Inorg. Chem.* **2007**, *46*, 8475−8477. (c) Otero, A.; Fernandez-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sanchez, A.; Sanchez-Barba, L.; Expósito, M. T.; Rodriguez, A. M. *Dalton Trans.* **2003**, 1614−1619.

(16) Sánchez-Barba, L. F.; Garcés, A.; Fajardo, M.; Alonso-Moreno, C.; Fernández-Baeza, J.; Otero, A.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A.; López-Solera, M. I. *Organometallics* **2007**, *26*, 6403−6411.

(17) Garcés, A.; Sánchez-Barba, L. F.; Alonso-Moreno, C.; Fajardo, M.; Fernández-Baeza, J.; Otero, A.; Lara-Sánchez, A.; López-Solera, I.; Rodríguez, A. M. *Inorg. Chem.* **2010**, *49*, 2859−2871.

(18) Sánchez-Barba, L. F.; Garcés, A.; Fernández-Baeza, J.; Otero, A.; Alonso-Moreno, C.; Lara-Sánchez, A.; Rodríguez, A. M. *Organometallics* **2011**, *30*, 2775−2789.

(19) Alonso-Moreno, C.; Garcés, A.; Sánchez-Barba, L. F.; Fajardo, M.; Fernández-Baeza, J.; Otero, A.; Lara-Sánchez, A.; Antiñolo, A.; Broomfield, L.; López-Solera, M. I.; Rodríguez, A. M. *Organometallics* **2008**, *27*, 1310−1321.

(20) Otero, A.; Fernández-Baeza, J.; Sánchez-Barba, L. F.; Tejeda, J.; Honrado, M.; Garcés, A.; Lara-Sánchez, A.; Rodríguez, A. M. *Organometallics* **2012**, *31*, 4191−4202.
(21) Honrado, M.; Otero, A.; Fernández-Baeza, J.; Sánchez-Barba, L. F.; Lara-Sánchez, A.; Tejeda, J.; Carrión, M. P.; Martínez-Ferrer, J.; Garcés, A.; Rodríguez, A. M. *Organometallics* **2013**, *32*, 3437−3440.
(22) Sánchez-Barba, L. F.; Alonso-Moreno, C.; Garcés, A.; Fajardo, M.; Fernández-Baeza, J.; Otero, A.; Lara-Sánchez, A.; Rodriguez, A. M.; López-Solera, I. *Dalton Trans.* **2009**, 8054−8062.
(23) Schlenk-type rearrangement reactions (the so-called "*Schlenk equilibrium*": 2 RMgX ⇌ MgR_2 + MgX_2) depend on a multitude of factors such as the metal−ligand (R) bond (e.g., for the alkaline-earth metals, it generally weakens with increasing metal size: Mg > Ca > Sr > Ba), the steric bulk of the ligand R, the solvent, the temperature, and the concentration of the "*Grignard*'(-type) reagent. (a) Michel, O.; Dietrich, H. M.; Litlabø, R.; Törnroos, K. W.; Maichle-Mössmer, C.; Anwander, R. *Organometallics* **2012**, *31*, 3119−3127. (b) Torvisco, A.; O'Brien, A. Y.; Ruhlandt-Senge, K. *Coord. Chem. Rev.* **2011**, *255*, 1268−1292. (c) Kharasch, M. S. R. O. *Grignard reactions of nonmetallic substances*; Prentice Hall: New York, 1954. (d) Schlenk, W.; Schlenk, W. *Ber. Dtsch. Chem. Ges.* **1929**, *62*, 920−924.
(24) Zhang, Z.; Cui, D. *Chem.—Eur. J.* **2011**, *17*, 11520−11526.
(25) Otero, A.; Fernández-Baeza, J.; Lara-Sánchez, A.; Alonso-Moreno, C.; Márquez-Segovia, I.; Sánchez-Barba, L. F.; Rodríguez, A. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 2176−2179.
(26) Otero, A.; Lara-Sánchez, A.; Fernández-Baeza, J.; Alonso-Moreno, C.; Tejeda, J.; Castro-Osma, J. A.; Márquez-Segovia, I.; Sánchez-Barba, L. F.; Rodríguez, A. M.; Gómez, M. V. *Chem.—Eur. J.* **2010**, *16*, 8615−8619.
(27) Castro-Osma, J. A.; Lara-Sanchez, A.; North, M.; Otero, A.; Villuendas, P. *Catal. Sci. Technol.* **2012**, *2*, 1021−1026.
(28) There is only one example reported of tris(3,5-dimethypyrazol-1-yl)methan*ide* with direct C(sp^3)-M covalent bond (M = Au). See Krummenacher, I.; Ruegger, H.; Breher, F. *Dalton Trans.* **2006**, 1073−1081.
(29) (a) Cushion, M. G.; Meyer, J.; Heath, A.; Schwarz, A. D.; Fernández, I.; Breher, F.; Mountford, P. *Organometallics* **2010**, *29*, 1174−1190. (b) Kuzu, I.; Krummenacher, I.; Hewitt, I. J.; Lan, Y.; Mereacre, V.; Powell, A. K.; Höfer, P.; Harmer, J.; Breher, F. *Chem.—Eur. J.* **2009**, *15*, 4350−4365. (c) Kuzu, I.; Nied, D.; Breher, F. *Eur. J. Inorg. Chem.* **2009**, 872−879. (d) Bigmore, H. R.; Meyer, J.; Krummenacher, I.; Rüegger, H.; Clot, E.; Mountford, P.; Breher, F. *Chem.—Eur. J.* **2008**, *14*, 5918−5934.
(30) (a) Chisholm, M. H.; Gallucci, J.; Phomphrai, K. *Inorg. Chem.* **2002**, *41*, 2785−2794. (b) Chisholm, M. H.; Huffman, J. C.; Phomphrai, K. *J. Chem. Soc., Dalton Trans.* **2001**, 222−224.
(31) Tang, H.-Y.; Chen, H.-Y.; Huang, J.-H.; Lin, C.-C. *Macromolecules* **2007**, *40*, 8855−8860.
(32) Wang, L.; Ma, H. *Macromolecules* **2010**, *43*, 6535−6537.
(33) Wang, Y.; Zhao, W.; Liu, D.; Li, S.; Liu, X.; Cui, D.; Chen, X. *Organometallics* **2012**, *31*, 4182−4190.
(34) Drouin, F.; Whitehorne, T. J. J.; Schaper, F. *Dalton Trans.* **2011**, *40*, 1396−1400.
(35) (a) Becker, J. M.; Pounder, R. J.; Dove, A. P. *Macromol. Rapid Commun.* **2010**, *31*, 1923−1937. (b) Zhong, Z.; Dijkstra, P. J.; Feijen, J. *J. Am. Chem. Soc.* **2003**, *125*, 11291−11298. (c) Radano, C. P.; Baker, G. L.; Smith, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 1552−1553.
(36) Chisholm, M. H.; Eilerts, N. W.; Huffman, J. C.; Iyer, S. S.; Pacold, M.; Phomphrai, K. *J. Am. Chem. Soc.* **2000**, *122*, 11845−11854.
(37) Sarazin, Y.; Liu, B.; Roisnel, T.; Maron, L.; Carpentier, J.-F. *J. Am. Chem. Soc.* **2011**, *133*, 9069−9087.
(38) Poirier, V.; Roisnel, T.; Carpentier, J.-F.; Sarazin, Y. *Dalton Trans.* **2011**, *40*, 523−534.
(39) (a) Sánchez-Barba, L. F.; Hughes, D. L.; Humphrey, S. M.; Bochmann, M. *Organometallics* **2006**, *25*, 1012−1020. (b) Sánchez-Barba, L. F.; Hughes, D. L.; Humphrey, S. M.; Bochmann, M. *Organometallics* **2005**, *24*, 5329−5334.
(40) (a) Baran, J.; Duda, A.; Kowalski, A.; Szymanski, R.; Penczek, S. *Macromol. Rapid Commun.* **1997**, *18*, 325−333. (b) Barakat, I.; Dubois, P.; Jérôme, R.; Teyssié, P. *J. Polym. Sci., Polym. Chem.* **1993**, *31*, 505−514.
(41) (a) Drouin, F.; Oguadinma, P. O.; Whitehorne, T. J. J.; Prud'homme, R. E.; Schaper, F. *Organometallics* **2010**, *29*, 2139−2147. (b) Chisholm, M. H.; Gallucci, J. C.; Phomphrai, K. *Inorg. Chem.* **2005**, *44*, 8004−8010. (c) Cai, C.-X.; Amgoune, A.; Lehmann, C. W.; Carpentier, J.-F. *Chem. Commun.* **2004**, 330−331.
(42) Nomura, N.; Ishii, R.; Yamamoto, Y.; Kondo, T. *Chem.—Eur. J.* **2007**, *13*, 4433−4451.
(43) *SAINT+*, v7.12a; Bruker-Nonius AXS: Madison, WI, 2004.
(44) Sheldrick, G. M. *SADABS*, version 2.03; University of Göttingen: Göttingen, Germany, 2004.
(45) *SHELXTL-NT*, version 6.12; Bruker-Nonius AXS: Madison, WI, 2001.