

A Family of 1,1,3,3-Tetraalkylguanidine (H-TAG) Solvated Zinc Aryloxide Precatalysts for the Ring-Opening Polymerization of *rac*-Lactide

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Reaction of $[\text{Zn}(\mu\text{-TAG})\{\text{N}(\text{SiMe}_3)_2\}_2]$ {TAG = $\text{N}=\text{C}[\text{N}(\text{CH}_2\text{CH}_3)_2\text{N}(\text{CH}_3)_2]$ (DEDMG), $\text{N}=\text{C}[\text{NCH}_2\text{CH}_2\text{CH}_2\text{C}^d\text{H}_2(\text{N}-\text{C}^d)]\text{-N}(\text{CH}_2\text{CH}_3)_2$ (DEPYRG) and $\text{N}=\text{C}[\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}^e\text{H}_2(\text{N}-\text{C}^e)]\text{N}(\text{CH}_2\text{CH}_3)_2$ (DEPIPG)} with 2 equiv. of ethanol (EtOH) and 2 equiv. of HOAr {OAr = $\text{OC}_6\text{H}_3(\text{CMe}_3)_2\text{-}2\text{-(CH}_3)_6$ (BMP) or $\text{OC}_6\text{H}_2[\text{C}(\text{CH}_3)_3]_2\text{-}2,6\text{-(CH}_3)_4$ (4MeDBP)} results in dizinc alkoxides with the general formula $[\text{Zn}(\mu\text{-OEt})(\text{OAr})(\text{H-TAG})]_2$ (**1–3**). Et_2Zn was additionally treated with 2 equiv. of 1,1,3,3-tetramethylguanidine (H-TMG) and H-

BMP or $\text{HOC}_6\text{H}_3(\text{C}_6\text{H}_5)_2\text{-}2,6$ to yield $[\text{Zn}(\text{BMP})_2(\text{H-TMG})_2]$ (**4**) and $[\text{Zn}\{\text{OC}_6\text{H}_3(\text{C}_6\text{H}_5)_2\text{-}2,6\}_2(\text{H-TMG})_2]$ (**5**). Complexes **1**, **2**, **4**, and **5** were characterized by single-crystal X-ray diffraction. Polymerization of *rac*-lactide with **1–5** and $[\text{Zn}(\mu\text{-OMe})(4\text{MeDBP})(\text{H-TMG})]_2$ (**6**) were found to generate polylactide (PLA). The bulk powders for all complexes were found to be in agreement with the crystal structures based on elemental analyses, FTIR spectroscopy, and ^1H and ^{13}C NMR spectroscopic studies.

Introduction

Lactide (LA), the cyclic dimer formed by condensation of lactic acid, is an efficient precursor for the production of the biodegradable and recyclable polymer, polylactide (PLA).^[1,2] The synthesis of PLA poses environmental benefits, and thus its use for various packaging applications has been industrially pursued. Additionally, interest in this commodity has expanded to biomedical applications such as medical implants and drug delivery systems.^[3] The physical properties of PLA are often compared to polystyrene; it has similar modulus and strength.^[4] Notably, the crystallinity of this renewable polymer is linked to the stereochemistry of the monomer units. Isotactic PLA is a crystalline thermoplastic with a relatively high glass transition temperature, T_g , whereas atactic PLA is an amorphous material.^[1]

One method for producing PLA is through a metal alkoxide catalyzed ring-opening polymerization (ROP).^[5] Lithium, aluminum, titanium, zirconium, zinc and yttrium have all been proven effective as catalysts for this process.^[6] The desire to produce PLA with tailorable physical characteristics from *rac*-LA has led to the development of single-site precatalysts for the stereocontrolled ROP.^[7,8] Achieving desired characteristics is leveraged through controlled construction of the ligand architecture around the metal center.

Ideally, to shape the microenvironment, chelating multidentate ligands are used to generate dinuclear and mononuclear compounds with a single reactive site.^[9–11] This is a difficult challenge with respect to designing Zn systems, where the d^{10} shell imparts a constrained coordination geometry.^[6,10–13] To overcome this challenge, the use of bulky aryloxide ligands in conjunction with an auxiliary Lewis base has been proven useful.^[11,14] Recently, we reported a detailed effort to outline the stoichiometric reactivity of hetero-ligated zinc systems involving aryloxide and guanidine ligand sets.^[15] In this previous investigation, the use of the bulky aryloxide ligand 4MeDBP, in conjunction with 1,1,3,3-tetramethylguanidine (H-TMG) was found to assist in producing a well-defined metal aryloxide with a potential single site for reactions. The complexes were subsequently used in the ring-opening polymerization (ROP) of *rac*-LA and exhibited only modest stereoselectivity.^[15]

It was therefore of interest to examine the effect that variation in the OAr/H-TAG ligand set (Figure 1) might have on the resultant stereoselectivity of the Zn-catalyzed ROP. Toward this end, the synthesis of three dinuclear 1,1,3,3-tetraalkylguanidine solvated zinc complexes with the general formula $[\text{Zn}(\mu\text{-OEt})(\text{OAr})(\text{H-TAG})]_2$ (**1–3**) has been performed and is reported herein. Additionally, in an attempt to examine the possibility of isolating alternative H-TMG solvated zinc aryloxides, reactions of Et_2Zn with EtOH, H-TMG and $\text{HOC}_6\text{H}_3(\text{CMe}_3)_2\text{-}2\text{-(CH}_3)_6$ (H-BMP) or $\text{HOC}_6\text{H}_3(\text{C}_6\text{H}_5)_2\text{-}2,6$ were examined. However, instead of isolating dinuclear ethoxide complexes, two monomeric four-coordinate Zn aryloxide complexes were isolated, $[\text{Zn}(\text{BMP})_2(\text{H-TMG})_2]$ (**4**) and $[\text{Zn}\{\text{OC}_6\text{H}_3(\text{C}_6\text{H}_5)_2\text{-}2,6\}_2(\text{H-TMG})_2]$ (**5**).

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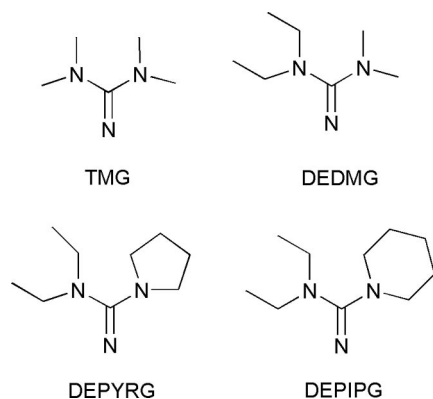


Figure 1. 1,1,3,3-Tetraalkylguanidine (H-TAG) ligands.

Single-crystal X-ray diffraction, elemental analysis, FTIR, ^1H and ^{13}C NMR spectroscopy were performed to characterize the guanidine solvated zinc complexes. To ascertain their utility as precatalysts, complexes **1–5** and the previously reported $[\text{Zn}(\mu\text{-OMe})(4\text{MeDBP})(\text{H-TMG})]_2$ (**6**) were subsequently treated with excess *rac*-LA. ^1H NMR spectroscopy was utilized to examine the resultant tacticity of the PLA.

Results and Discussion

Synthesis

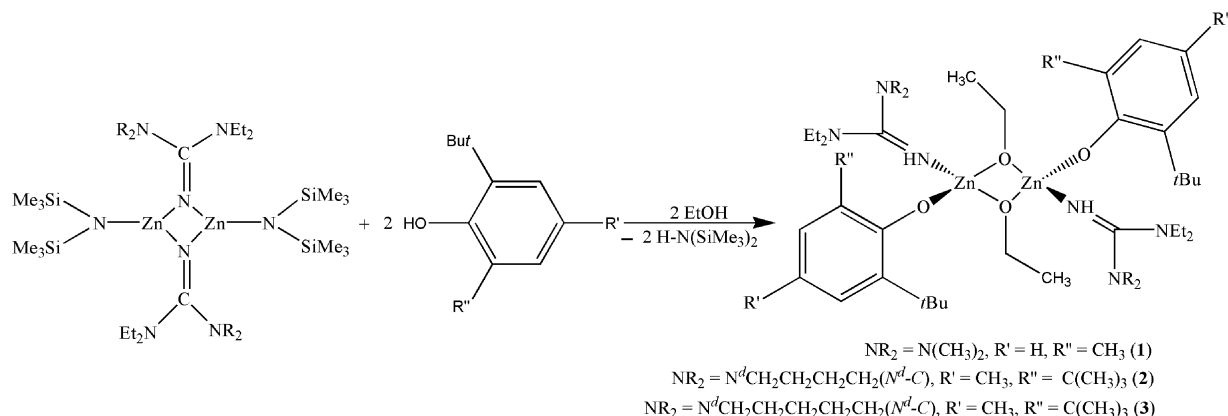
Previous investigations have demonstrated that the OAr/H-TAG ligand set exists as a robust system for isolating main group, d-block, lanthanide, and actinide complexes with low coordination numbers and discrete reactivity.^[15–18] The driving force for the synthesis of these complexes has typically been the elimination of a volatile alkane or amine. In a recent report, the reaction of $[\text{Mn}(\mu\text{-TAG})\{\text{N}(\text{SiMe}_3)_2\}]_2$ with EtOH and $\text{HOC}_6\text{H}_3(\text{CMe}_3)_2\text{-2,6}$ (H-DBP) resulted in retention of the protonated H-TAG and the formation of a dinuclear Mn^{II} alkoxide, $[\text{Mn}(\mu\text{-OEt})(\text{DBP})$

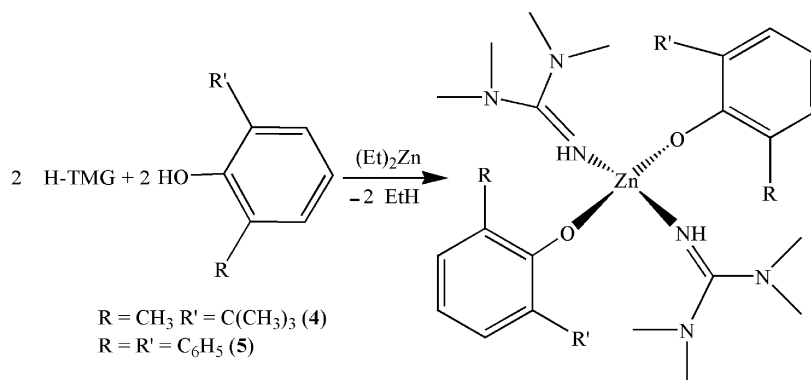
(H-TAG)]₂.^[19] It therefore seemed reasonable to utilize this approach for the synthesis of additional H-TAG solvated Zn aryloxides.

Due to a lack of commercial availability, a structurally diverse series of lithium 1,1,3,3-tetraalkylguanidinato [Li(TAG)] complexes are obtained by the addition of a lithium dialkylamide to a dialkylcyanamide. Derivatives of Li(TAG) may be subsequently used in conjunction with $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ and ZnCl_2 to generate the corresponding hetero-ligated Zn(TAG) complex $[\text{Zn}(\mu\text{-TAG})\{\text{N}(\text{SiMe}_3)_2\}]_2$.^[20]

Upon successful isolation of $[\text{Zn}(\mu\text{-TAG})\{\text{N}(\text{SiMe}_3)_2\}]_2$, the synthesis of **1–3** may be performed as shown in Scheme 1; 1 equiv. of $[\text{Zn}(\mu\text{-TAG})\{\text{N}(\text{SiMe}_3)_2\}]_2$ is added to hexanes solution containing 2 equiv. of EtOH and HOAr (H-BMP or H-4MeDBP); 2 equiv. of $\text{HN}(\text{SiMe}_3)_2$ are presumably eliminated, serving to drive the reaction forward and result in the rapid precipitation of a powder. The powder was re-dissolved by dropwise addition of thf and heating. Crystals of **1** and **2**, suitable for X-ray structural analysis, were obtained by concentrating the solutions and then cooling the respective saturated solutions to -35°C for 24 h. Microcrystalline solid of **3** was obtained according to this approach, and attempts to generate larger single crystals were unsuccessful. The isolated solids of **1–3** were slightly air-sensitive and soluble in hexanes, toluene, diethyl ether, and thf.

In an attempt to examine the possibility of isolating alternative H-TMG solvated Zn aryloxides, reactions similar to those that generated complexes **1–3** were also performed with Et_2Zn , EtOH, H-BMP and $\text{HOC}_6\text{H}_3(\text{C}_6\text{H}_5)_2\text{-2,6}$. However, instead of isolating dinuclear complexes, two monomeric complexes were serendipitously isolated, $[\text{Zn}(\text{BMP})_2(\text{H-TMG})_2]$ (**4**) and $[\text{Zn}\{\text{OC}_6\text{H}_3(\text{C}_6\text{H}_5)_2\text{-2,6}(\text{H-TMG})_2\}]$ (**5**). Upon determination of the structures of **4** and **5**, the complexes were synthesized with the appropriate stoichiometry, and complete characterization was performed (Scheme 2). Crystals suitable for X-ray structural analysis were obtained by slow concentration of solutions in hexanes/thf (1:1). Apparently, there is a steric require-

Scheme 1. Synthesis of **1–3**.

Scheme 2. Synthesis of **4** and **5**.

ment for the use of a “one-pot” approach involving the OAr/H-TMG ligand set. This requirement was also found for similar Mg systems.^[16]

Structural Descriptions

The structures of compounds **1**, **2**, **4**, and **5** are illustrated by the thermal ellipsoid plots depicted in Figures 2, 3, 4, and 5. The data collection parameters are presented in Table 1.

Complexes **1** and **2** crystallized in the triclinic and monoclinic space groups, respectively. Each complex contains a planar Zn_2O_2 core with a distorted tetrahedral Zn atom ($\tau_4 = 0.8$) connected to an adjacent Zn atom by two bridging ethoxide ligands.^[21] The $\text{Zn}\cdots\text{Zn}$ distances are ca. 3 Å for both complexes. The tetrahedral coordination is fulfilled through additional coordination of the Zn atom to one terminal aryloxy ligand and one terminal H-TAG ligand. In both complexes, the Zn–O distances fall within the expected

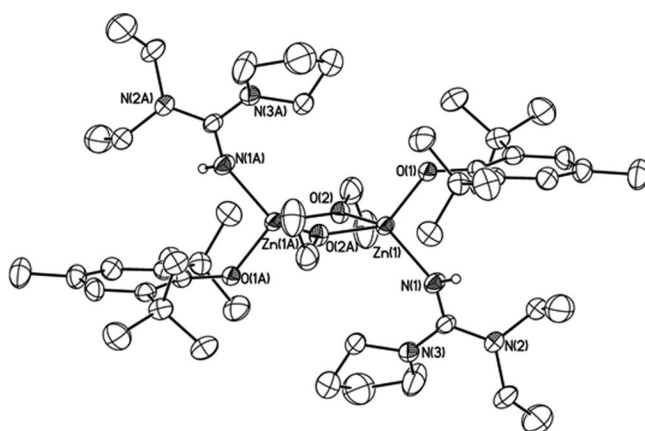


Figure 3. Thermal ellipsoid plot of **2**. Ellipsoids are drawn at the 30% level. H atoms have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Zn(1)–O(1) 1.930(3), Zn(1)–O(2) 1.963(3), Zn(1)–N(1) 2.000(4), O(1)–C(1) 1.339(6), O(2)–C(16) 1.432(8); O(1)–Zn(1)–O(2) 125.61(19), O(1)–Zn(1)–N(1) 102.0(2), C(1)–O(1)–Zn(1) 120.1(3), O(2)–Zn(1)–N(1) 111.38(19), C(12)–O(2)–Zn(1) 127.4(4), C(14)–N(1)–Zn(1) 137.0(5).

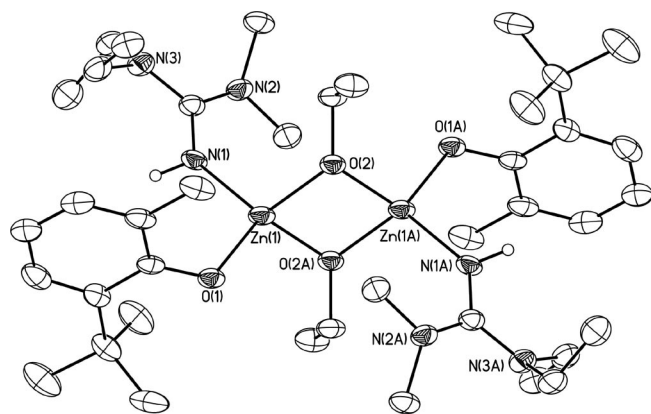


Figure 2. Thermal ellipsoid plot of **1**. Ellipsoids are drawn at the 30% level. H atoms have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Zn(1)–O(1) 1.928(4), Zn(1)–O(2) 1.960(5), Zn(1)–N(1) 1.974(5); O(1)–Zn(1)–O(2) 125.61(19), O(1)–Zn(1)–N(1) 102.0(2), C(1)–O(1)–Zn(1) 120.1(3), C(2)–Zn(1)–N(1) 111.38(19), C(12)–O(2)–Zn(1) 127.4(4), C(14)–N(1)–Zn(1) 137.0(5).

range of 1.928–1.978 Å, whereas the terminal Zn–N distances are ca. 2.0 Å.^[22,23] A distinguishing feature of both compounds is the terminal Zn–O–Ar angles ranging from 120 to 138°. The relatively small Zn–O–Ar angle indicates the absence of π -donation from the aryl ring; a structural feature common in Zn aryloxy compounds.^[19] Compounds **1** and **2** are similar to the previously reported zinc ethoxide, $[\text{Zn}(\mu\text{-OEt})(\text{OAr})(\text{H-TMG})]_2$ (OAr = 4MeDBP).^[15] The C=N bond lengths for the H-TAG in **1** and **2** vary from 1.309 to 1.320 Å, whereas the C–N bonds are longer, ranging from 1.334 to 1.369 Å.

Compounds **4** and **5** contain a distorted tetrahedral zinc core coordinated to two H-TMG ligands and two aryloxy groups ($\tau_4 = 0.83$ for **4** and 0.90 for **5**).^[21] The Zn–O distances are comparable to $[\text{Zn}(\text{DBP})_2(\text{thf})_2]$ [Zn–O_(avg.) = 1.87 Å].^[23] The Zn–O_(avg.) distance is 1.942 Å for **4** and 1.932 Å for **5**. Both complexes are quite similar to the previously reported magnesium complexes, $[\text{Mg}(\text{BMP})_2(\text{H-TMG})_2]$ ($\tau_4 = 0.85$) and $[\text{Mg}\{\text{OC}_6\text{H}_3(\text{C}_6\text{H}_5)_2\cdot 2,6\}_2(\text{H-TMG})_2]$

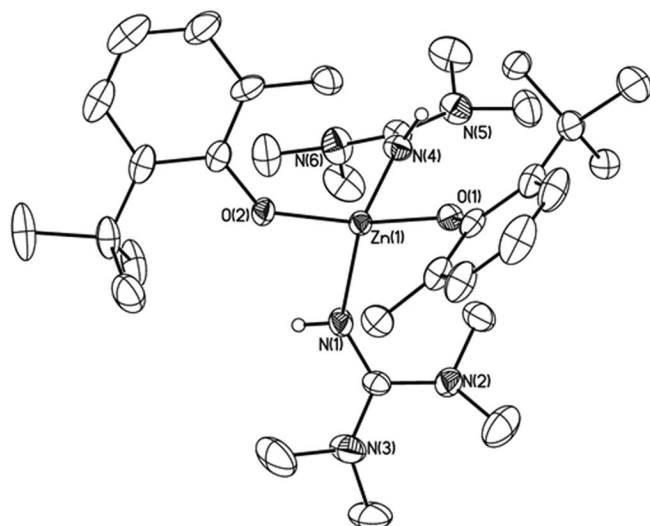


Figure 4. Thermal ellipsoid plot of **4**. Ellipsoids are drawn at the 30% level. H atoms have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Zn(1)–O(1) 1.9465(18), Zn(1)–O(2) 1.9372(18), Zn(1)–N(1) 2.015(2), Zn(1)–N(2) 2.018(2); O(2)–Zn(1)–O(1) 124.90(8), O(2)–Zn(1)–N(1) 94.36(9), O(1)–Zn(1)–N(1) 114.43(8), O(2)–Zn(1)–N(2) 118.51(9), O(1)–Zn(1)–N(2) 91.48(8), N(1)–Zn(1)–N(2) 114.94(9), C(22)–O(1)–Zn(1) 139.35(18), C(11)–O(2)–Zn(1) 135.90(18).

TMG)₂] ($\tau_4 = 0.88$).^[16] Notably, a structurally similar cadmium complex, [Cd{μ-OC₆H₃(C₆H₅)₂-2,6}{OC₆H₃(C₆H₅)₂-2,6}]₂, was reported by Darensbourg and co-workers.^[24] In the Cd structure, the phenyl substituent on the diphenylphenoxide group was shown to interact with the Cd center. The Cd–C bond was reported to be ca. 2.6 Å. In **6**, the closest Zn–C distance is ca. 3.0 Å and thus does not indicate an interaction between the phenyl moiety and the Zn center.

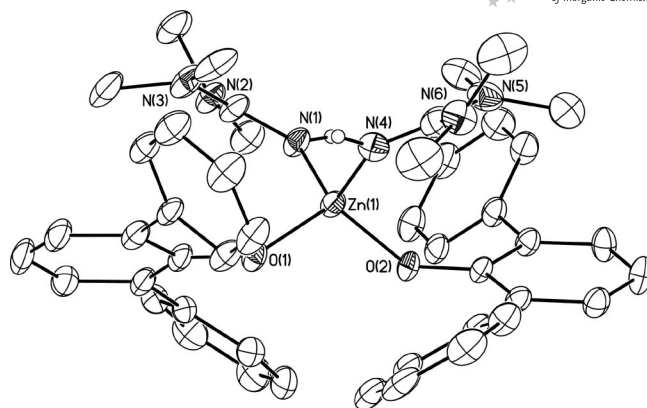


Figure 5. Thermal ellipsoid plot of **5**. Ellipsoids are drawn at the 30% level. H atoms have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Zn(1)–O(2) 1.9287(19), Zn(1)–O(1) 1.934(2), Zn(1)–N(1) 1.998(3), Zn(1)–N(2) 2.021(3); O(2)–Zn(1)–O(1) 116.67(9), O(2)–Zn(1)–N(1) 102.01(9), O(1)–Zn(1)–N(1) 114.43(8), O(2)–Zn(1)–N(2) 112.10(11), O(1)–Zn(1)–N(2) 96.50(11), N(1)–Zn(1)–N(2) 116.30(11), C(11)–O(2)–Zn(1) 133.31(19), C(29)–O(1)–Zn(1) 133.9(2).

Spectroscopy

Crystals of **1–5** were dried in vacuo, and their bulk powders were isolated for spectroscopic analysis. Compounds **1–3** were found to be sparingly soluble in toluene, and compounds **4** and **5** were soluble in chloroform. All compounds exhibited the expected ¹H and ¹³C NMR spectra. In the ¹H NMR spectrum, a broad singlet corresponding to the N–H hydrogen atom was found for each compound and ranged from $\delta = 3.7$ to 5.0 ppm. Several resonances between $\delta = 3.7$ and 1.0 ppm are assigned to the alkyl substituents of the guanidine ligands. The existence of multiple resonances for each alkyl substituent of the H-TAG moiety may be tentatively attributed to the potential zwitterionic resonance

Table 1. Data collection parameters for compounds **1**, **2**, **4**, and **5**.

	1	2	4	5
Empirical formula	C ₄₀ H ₇₄ N ₆ O ₄ Zn ₂	C ₅₂ H ₉₄ N ₆ O ₄ Zn ₂	C ₃₂ H ₅₆ N ₆ O ₂ Zn	C ₅₀ H ₆₀ N ₆ O ₃ Zn
Formula mass	833.79	998.07	622.20	858.41
Temperature [K]	100(2)	100(2)	160(2)	160(2)
Crystal system	triclinic	monoclinic	orthorhombic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	9.027(9)	9.307(2)	16.967(3)	10.4637(12)
<i>b</i> [Å]	9.629(10)	18.965(4)	16.548(3)	12.0936(14)
<i>c</i> [Å]	14.338(15)	16.150(4)	24.687(4)	38.482 (4)
α [°]	72.276(13)			
β [°]	74.194(15)	104.375(3)		93.923 (2)
γ [°]	74.248(14)			
<i>V</i> [Å ³]	1118(2)	2761.3(10)	6931(2)	4858.3(10)
<i>Z</i>	1	2	8	4
<i>D</i> _{calcd.} [Mg/m ³]	1.239	1.200	1.193	1.174
μ (Mo- <i>K</i> α) [mm ^{−1}]	1.116	0.914	0.744	0.551
Number of reflections	3915	4886	6138	8602
obsd.				
<i>R</i> _(int)	0.0899	0.0689	0.0476	0.0871
GOF on <i>F</i> ²	1.099	1.025	1.069	0.930
<i>R</i> ₁ ^[a] (%) (all data)	7.73 (13.20)	5.92 (10.29)	3.76 (6.09)	4.96 (7.78)
<i>wR</i> ₂ ^[b] (%) (all data)	17.29 (21.60)	15.51 (18.82)	11.95 (14.71)	14.43 (15.81)

[a] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| \times 100$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w |F_o|^2]^{1/2} \times 100$.

of the ligand. Rotation about the C–N bond results in the possibility of both isomers present in solution. The central carbon atom “CN₃” of the H-TAG ligand was confirmed through the presence of a weak downfield peak ranging from $\delta = 168$ to 161 ppm in the ¹³C NMR spectrum.^[25]

The FTIR spectra of **1–5** exhibited an absence of stretches associated with –OH ligands, indicative of complete substitution. The expected alkyl and aryl stretches for the aryloxide, alkoxide and guanidine ligands are present for each sample. In **1**, **4** and **5** a characteristic stretch at 750 cm^{–1} may be assigned to the $\gamma(\text{CH})$ vibration of the OAr ring. This has been observed previously in the spectra of lanthanide aryloxide systems.^[17,26] For **1–5**, the presence of $\nu(\text{N–H})$ and $\nu(\text{C=N})$ were confirmed by peaks around 3300 and 1580 cm^{–1}, respectively.^[25] Assignment of the Zn–O bands in aryloxides is often difficult owing to the coupling of the C–O and Zn–O modes.^[23] Comparison of the data for **1–5** with data for HOAr indicates that bands located between 540 and 450 cm^{–1} are most likely associated with the Zn–O bonds.

rac-Lactide Polymerization

An ideal ROP polymerization catalyst would be expected to exhibit high activity, generate a defined molecular weight, provide a polymer with a narrow molecular weight distribution, and demonstrate stereoselectivity in the polymerization of a stereochemically diverse set of cyclic esters.^[6] Although this combination of characteristics has been partially realized through the use of single-site aluminum alkoxides, such conversions are generally attained only at elevated temperatures and over the course of days.^[8,27] Therefore, notwithstanding these reports, understanding the origin of stereocontrol and high activity in LA polymerizations by metal alkoxides is necessary and improvements in catalyst versatility warranted.

Although less versatile from the standpoint of tacticity, Zn complexes have generally shown increased activity. As part of an ongoing effort to address stereocontrol issues, we have synthesized Zn complexes **1–6** with coordinated H-TAG, a unique ligand set with readily tuned steric and electronic properties. The ROP polymerization of *rac*-LA was carried out by dissolving 0.025 mmol of Zn complex in ca. 10 mL of toluene. After adding 100 equiv. of *rac*-LA, the reaction mixture was stirred at 25 °C for 18 h. The solvent was removed under vacuum and PLA was isolated. Monomer conversion was monitored by ¹H NMR spectroscopy by integrating the relative intensities of the methine resonances attributable to the monomer and polymer; ¹H-homonuclear-decoupled spectra were acquired in order to determine the tacticity.

The results for complexes **1–6** are summarized in Table 2. Based upon previous reports, a proposed reaction scheme for the formation of PLA with **1–3** and **6** is shown in Figure S3 (Supporting Information).^[15] An examination of P_r/P_m reveals a slight bias toward isotactic enchainment for complexes **1–4** and **6** (66% for **3**).^[28] The MW_(avg.) values

range from 1180 to 6803. Overall, the tacticity is not significantly influenced by the substituents of the guanidine donor. Interestingly, variation in the substituents on the aryloxide ring also does not significantly result in altering the tacticity. This differs with results reported for salen ligand sets, where dramatic differences in stereocontrol have been found through alternation of the aryloxide architecture.^[13,27]

Table 2. Polymerization data for **1–6**.

Catalyst	Time [h]	Conversion ^[a] [%]	M_n ^[a]	P_r/P_m ^[b]
1	18	99	4394	0.39:0.61
2	18	100	1180	0.40:0.60
3	18	100	4391	0.34:0.66
4	18	99	1412	0.37:0.63
5	18	97	6803	0.47:0.53
6	18	99	1844	0.42:0.58

[a] Conversion and M_n determined by ¹H NMR spectroscopy. [b] P_r and P_m are the probability of hetero- and isotactic enchainment based on ¹H NMR spectroscopy. [LA]/[Zn] = 100, toluene, 25 °C.

In a recent report examining guanidine solvated lanthanide aryloxides, disassociation of H-TMG was found to be possible under catalytic conditions of increased temperature and excess substrate.^[17] As shown in Table 2, **4** and **5** were successful in initiating the ROP of *rac*-LA. Presumably, due to the steric constraints around the Zn center of **4** and **5**, de-solvation of H-TMG is a necessary prerequisite prior to coordination of lactide. This indicates that OAr/H-TAG is perhaps not a robust system for tailoring the microenvironment of a Zn center. In support of this finding, in a few cases, complexes that were transferred from cold solution and placed under vacuum hindered obtaining satisfactory elemental analysis. This is consistent with possible de-solvation of H-TAG.

Conclusions

Five Zn aryloxide complexes have been synthesized and structurally characterized by a facile “one-pot” synthetic approach. The straightforward reaction of a set of amido Zn guanidinate complexes with H-4-MeDBP or H-BMP and EtOH results in the liberation of HN(SiMe₃)₂, retention of the coordinated H-TAG, and the formation of dinuclear Zn ethoxides **1–3**. The two monomeric H-TMG solvated complexes **4** and **5** were also synthesized by using H-BMP or 2,6-diphenylphenol. By utilizing complexes **1–3** and **6**, the ROP of *rac*-lactide was performed, and the resultant PLA was found to exhibit a slight isotactic bias. Notably, alternation of the ligand set did not impart significant variation in stereochemical control. In addition, the coordinatively saturated monomeric Zn complexes **4** and **5** also successfully polymerized *rac*-lactide, indicative of possible H-TAG labiality and a potential drawback in using this combination of ligands.

Experimental Section

General Considerations: All syntheses were handled with rigorous exclusion of water and air by using standard glove-box techniques. All anhydrous solvents were stored under argon and used as received in sure-seal bottles. The following chemicals were acquired from commercial suppliers: LiNEt₂, LiNMe₂, LiN(SiMe₃)₂, *n*BuLi (1.6 M in hexanes), diethylcyanamide, pyrrolidine, ZnCl₂, (Et)₂Zn (1.0 M in hexanes), H-TMG, EtOH, MeOH, H-BMP, H-4MeDBP, and HOC₆H₃(C₆H₅)₂-2,6. [Zn(μ-DEDMG){N(SiMe₃)₂}]₂, [Zn(μ-DEPYRG){N(SiMe₃)₂}]₂, [Zn(μ-DEPIPG){N(SiMe₃)₂}]₂, and [Zn(μ-OMe)(4MeDBP)(H-TMG)]₂ (**6**) were synthesized as previously reported in the literature.^[15,20] FTIR data were obtained with a Bruker Tensor 27 instrument by using KBr pellets under flowing nitrogen. All NMR spectroscopy samples were prepared from synthesized compounds under argon and dissolved in either [D₈]toluene (**1–3**) or CDCl₃ (**4–5**). All solution spectra were obtained with a Bruker DRX400 spectrometer at 400.1 and 100.5 MHz for ¹H and ¹³C NMR spectroscopy experiments, respectively.

Synthesis of 1, 2, and 3: [Zn(μ-TAG){N(SiMe₃)₂}]₂, was dissolved in hexanes, and 2 equiv. of EtOH and H-OAr (H-BMP or H-4MeDBP) were added; thf was added to dissolve the precipitate that formed. After evaporation of the volatile components from the reaction mixture over 24 h, colorless crystals of **1**, **2**, and **3** were isolated.

[Zn(μ-OEt)(BMP)(DEDMG)]₂ (1**):** From [Zn(μ-DEDMG){N(SiMe₃)₂}]₂ (0.25 g, 0.34 mmol), H-BMP (0.11 g, 0.68 mmol), and EtOH (0.03 g, 0.7 mmol). Yield 0.116 g (41%). M.p. 118 °C. ¹H NMR (400 MHz, [D₈]toluene): δ = 7.45 {d, 2 H, OC₆H₃[C(CH₃)₃]-2-(CH₃)-6}, 7.23 {m, 2 H, OC₆H₃[C(CH₃)₃]-2-(CH₃)-6}, 6.77 {d, 2 H, OC₆H₃[C(CH₃)₃]-2-(CH₃)-6}, 4.48 {s, 6 H, OC₆H₃[C(CH₃)₃]-2-(CH₃)-6}, 4.08 {s, 2 H, HN=C[N(CH₃)₂][N(CH₂CH₃)₂]}, 3.60 {d, 4 H, OCH₂CH₃}, 2.83 {q, 8 H, HN=C[N(CH₃)₂][N(CH₂CH₃)₂]}, 2.55 {s, 12 H, HN=C[N(CH₃)₂][N(CH₂CH₃)₂]}, 1.81 {s, 18 H, OC₆H₃[C(CH₃)₃]-2-(CH₃)-6}, 1.50 {t, 6 H, OCH₂CH₃}, 0.78 {t, 12 H, HN=C[N(CH₃)₂][N(CH₂CH₃)₂]}. ¹³C{¹H} NMR (100.5 MHz, [D₈]toluene): δ = 167.7 {HN=C[N(CH₃)₂][N(CH₂CH₃)₂]}, 142.2, 138.7, 138.1, 137.5, 126.0, 120.1 {OC₆H₃[C(CH₃)₃]-2-(CH₃)-6}, 68.0 (OCH₂CH₃), 39.9 {HN=C[N(CH₃)₂][N(CH₂CH₃)₂]}, 35.9 {HN=C[N(CH₃)₂][N(CH₂CH₃)₂]}, 31.2 {OC₆H₃[C(CH₃)₃]-2-(CH₃)-6}, 30.9 {OC₆H₃[C(CH₃)₃]-2-(CH₃)-6}, 26.2 (OCH₂CH₃), 19.4 {HN=C[N(CH₃)₂][N(CH₂CH₃)₂]}, 12.6 {OC₆H₃[C(CH₃)₃]-2-(CH₃)-6} ppm. FTIR (KBr): ν̄ = 3345 (w), 2961 (s), 2130 (w), 1577 (s), 1526 (m), 1459 (m), 1416 (s), 1381 (m), 1269 (m), 1251 (m), 1183 (w), 1126 (m), 1098 (m), 1060 (m), 1005 (w), 933 (m), 885 (m), 849 (m), 798 (w), 748 (m), 668 (w), 656 (w), 535 (w), 505 (w), 441 (w) cm⁻¹. C₄₀H₇₄N₆O₄Zn₂ (833.79): calcd. C 57.62, H 8.95, N 10.08; found C 56.17, H 8.64, N 9.41.

[Zn(μ-OEt)(4MeDBP)(DEPYRG)]₂ (2**):** From [Zn(μ-DEPYRG){N(SiMe₃)₂}]₂ (0.10 g, 0.13 mmol), H-4MeDBP (0.06 g, 0.3 mmol), and EtOH (0.01 g, 0.3 mmol). Yield 0.037 g (29%). M.p. 162 °C. ¹H NMR (400 MHz, [D₈]toluene): δ = 7.02 {s, 4 H, OC₆H₂[C(CH₃)₃]-2,6-(CH₃)-4}, 4.92 [s, 2 H, HN=CN(CH₂CH₃)₂N(C₄H₈)], 4.13 (t, 4 H, OCH₂CH₃), 3.17 [q, 8 H, HN=CN(CH₂CH₃)₂N(C₄H₈)], 2.66 [t, 8 H, HN=CN(CH₂CH₃)₂N(C₄H₈)], 2.41 {s, 6 H, OC₆H₂[C(CH₃)₃]-2,6-(CH₃)-4}, 2.24 (m, 4 H, OCH₂CH₃), 1.76 [m, 8 H, HN=CN(CH₂CH₃)₂N(C₄H₈)], 1.38 {s, 32 H, OC₆H₂[C(CH₃)₃]-2,6-(CH₃)-4}, 1.06 [q, 6 H, OCH₂CH₃], 0.79 [m, 6 H, HN=CN(CH₂CH₃)₂N(C₄H₈)]. ¹³C{¹H} NMR (100.5 MHz, [D₈]toluene): δ = 161.4 {HN=C[N(CH₂CH₃)₂N(C₄H₈)]}, 136.0, 128.9, 128.6, 125.6 [OC₆H₂[C(CH₃)₃]-2,6-(CH₃)-4], 35.5 (OCH₂-

CH₃), 34.8 {HN=C[N(CH₂CH₃)₂N(C₄H₈)]}, 34.2 {H=C[N(CH₂CH₃)₂N(C₄H₈)]}, 32.1 {OC₆H₂[C(CH₃)₃]-2,6-(CH₃)-4}, 31.8 {OC₆H₂[C(CH₃)₃]-2,6-(CH₃)-4}, 30.3 {HN=C[N(CH₂CH₃)₂N(C₄H₈)]}, 22.9 {OC₆H₂[C(CH₃)₃]-2,6-(CH₃)-4}, 21.2 (OCH₂CH₃), 14.1 {HN=C[N(CH₂CH₃)₂N(C₄H₈)]} ppm. FTIR (KBr): ν̄ = 3363 (w), 3304 (w), 2960 (s), 2872 (s), 2720 (w), 2181 (w), 2108 (m), 1742 (w), 1558 (s), 1522 (s), 1443 (s), 1420 (s), 1382 (s), 1358 (m), 1315 (w), 1264 (m), 1230 (m), 1215 (m), 1199 (w), 1160 (w), 1103 (m), 1059 (s), 932 (w), 919 (w), 887 (m), 860 (m), 838 (w), 821 (w), 803 (w), 793 (w), 774 (w), 754 (w), 576 (w), 525 (s) cm⁻¹. C₅₂H₉₄N₆O₄Zn₂ (998.07): calcd. C 55.00, H 8.53, N 11.66; found C 57.02, H 8.67, N 7.42.

[Zn(μ-OEt)(4MeDBP)(DEPIPG)]₂ (3**):** From [Zn(μ-DEPIPG){N(SiMe₃)₂}]₂ (0.11 g, 0.14 mmol), H-4MeDBP (0.06 g, 0.3 mmol), and EtOH (0.01 g, 0.3 mmol). Yield 0.106 g (76.3%). ¹H NMR (400 MHz, [D₈]toluene): δ = 7.00 {s, 4 H, OC₆H₂[C(CH₃)₃]-2,6-(CH₃)-4}, 4.77 [s, 2 H, HN=CN(CH₂CH₃)₂N(C₅H₁₀)], 3.33 {t, 20 H, HN=C[N(CH₂CH₃)₂N(C₅H₁₀)]}, 2.22 {s, 6 H, OC₆H₂[C(CH₃)₃]-2,6-(CH₃)-4}, 1.79 {t, 12 H, HN=C[N(CH₂CH₃)₂N(C₅H₁₀)]}, 1.35 {s, 36 H, OC₆H₂[C(CH₃)₃]-2,6-(CH₃)-4}, 1.07 (t, 6 H, 12 H, OCH₂CH₃), 0.79 {t, 12 H, HN=C[N(CH₂CH₃)₂N(C₅H₁₀)]} ppm. ¹³C{¹H} NMR (100.5 MHz, [D₈]toluene): δ = 166.8 {HN=C[N(CH₂CH₃)₂N(C₅H₁₀)]}, 136.4, 128.8, 127.9, 126.2, {OC₆H₂[C(CH₃)₃]-2,6-(CH₃)-4}, 36.2 (OCH₂CH₃), 34.7 {HN=C[N(CH₂CH₃)₂N(C₅H₁₀)]}, 30.9 {HN=C[N(CH₂CH₃)₂N(C₅H₁₀)]}, 26.5 {OC₆H₂[C(CH₃)₃]-2,6-(CH₃)-4}, 25.2 {OC₆H₂[C(CH₃)₃]-2,6-(CH₃)-4}, 23.5 {HN=C[N(CH₂CH₃)₂N(C₅H₁₀)]}, 21.8 {OC₆H₂[C(CH₃)₃]-2,6-(CH₃)-4}, 14.8 {HN=C[N(CH₂CH₃)₂N(C₅H₁₀)]}, 13.6 (OCH₂CH₃) ppm. FTIR (KBr): ν̄ = 3308 (w), 2956 (s), 2869 (s), 1638 (m), 1560 (s), 1515 (s), 1443 (s), 1382 (m), 1361 (m), 1316 (w), 1246 (m), 1215 (w), 1196 (w), 1159 (m), 1122 (m), 1105 (m), 1060 (w), 1029 (w), 887 (w), 860 (m), 819 (m), 804 (w), 774 (w) cm⁻¹.

Synthesis of 4 and 5: To a solution of 2 equiv. each of H-TMG and H-OAr [H-BMP or HO-C₆H₃(C₆H₅)₂-2,6] in hexanes was added 1 equiv. of (Et)₂Zn. The resulting precipitate was dissolved in thf. After evaporation of the volatile components from the reaction mixture over 24 h, colorless crystals of **4** and **5** were isolated.

[Zn(BMP)₂(H-TMG)₂] (4**):** From (Et)₂Zn (1.24 g, 1.5 mmol), H-TMG (0.35 g, 3.0 mmol), and H-BMP (0.50 g, 3.0 mmol). Yield 0.612 g (57.5%). M.p. 202 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.28 {m, 6 H, OC₆H₃[C(CH₃)₃]-2-CH₃-6}, 5.00 {s, 2 H, HN=C[N(CH₃)₂]}, 2.63 {s, 6 H, OC₆H₃[C(CH₃)₃]-2-CH₃-6}, 2.25 {s, 18 H, OC₆H₃[C(CH₃)₃]-2-CH₃-6}, 1.88 {s, 24 H, HN=C[N(CH₃)₂]}. ¹³C{¹H} NMR (100.5 MHz, CDCl₃): δ = 168.25 {HN=C[N(CH₃)₂]}, 165.32, 154.52, 138.41, 128.93, 120.83, 116.44 {OC₆H₃[C(CH₃)₃]-2-(CH₃)-6}, 41.56 {HN=C[N(CH₃)₂]}, 39.54 {OC₆H₃[C(CH₃)₃]-2-(CH₃)-6}, 38.44 {OC₆H₃[C(CH₃)₃]-2-(CH₃)-6}, 31.49 {OC₆H₃[C(CH₃)₃]-2-(CH₃)-6} ppm. FTIR (KBr): ν̄ = 3371 (s), 2947 (s), 2806 (m), 1577 (s), 1545 (s), 1458 (m), 1417 (s), 1341 (w), 1279 (m), 1225 (s), 1197 (w), 1128 (m), 1096 (m), 1066 (m), 1034 (w), 996 (w), 903 (m), 861 (s), 797 (w), 748 (m), 721 (m), 661 (w), 559 (w), 531 (w) cm⁻¹. C₃₂H₅₆N₆O₂Zn (622.20): calcd. C 61.77, H 9.07, N 13.51; found C 61.57, H 9.38, N 14.50.

[Zn{OC₆H₃(C₆H₅)₂-2,6}₂(H-TMG)₂]·thf (5**):** From (Et)₂Zn (0.73 g, 1.0 mmol), H-TMG (0.23 g, 2.0 mmol), and HOC₆H₃(C₆H₅)₂-2,6 (0.50 g, 2.0 mmol). Yield 0.77 g (98%). M.p. 213 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.09 [m, 10 H, OC₆H₃(C₆H₅)₂-2,6], 7.49, 6.85 [m, 6 H, OC₆H₃(C₆H₅)₂-2,6], 7.41 [m, 10 H, OC₆H₃(C₆H₅)₂-2,6], 3.51 {s, 2 H, HN=C[N(CH₃)₂]}, 2.07 {s, 24 H, HN=C[N(CH₃)₂]}. ¹³C{¹H} NMR (100.5 MHz, CDCl₃): δ = 163.88 {HN=C[N(CH₃)₂]}, 149.90, 133.03, 131.00, 130.34, 129.39,

127.66, 125.43, 114.69 [$\text{OC}_6\text{H}_3(\text{C}_6\text{H}_5)_2$ -2,6], 39.17 [$\text{HN}=\text{C}[\text{N}(\text{CH}_3)_2]_2$] ppm. FTIR (KBr): $\tilde{\nu}$ = 3351 (m), 3050 (m), 3021 (m), 2927 (m), 2806 (m), 1886 (w), 1595 (s), 1569 (s), 1543 (s), 1494 (m), 1455 (m), 1407 (m), 1308 (m), 1290 (m), 1247 (m), 1224 (m), 1177 (m), 1126 (m), 1088 (m), 1069 (m), 1029 (m), 992 (m), 904 (m), 854 (m), 805 (m), 751 (m), 729 (m), 701 (w), 620 (w), 596 (w), 585 (w), 560 (w), 512 (w), 464 (w) cm^{-1} . $\text{C}_{50}\text{H}_{60}\text{N}_6\text{O}_3\text{Zn}$ (858.41): calcd. C 70.26, H 6.67, N 10.69; found C 70.53, H 6.38, N 10.55.

Polymerization Procedure: Under argon, complexes **1–6** were treated with *rac*-lactide (LA). The catalyst (0.025 mmol) and LA (100 equiv.) were dissolved in toluene (10 mL). The reaction mixture was stirred for 18 h, at the completion of which a drop of glacial acetic acid was added to terminate the reaction. The solvent was removed under vacuum, and a colorless solid was isolated. The solid was analyzed by ^1H NMR spectroscopy.

Crystallography: X-ray crystallography was performed, by mounting each crystal onto a thin glass fiber from a pool of FluorolubeTM and immediately placing it under a liquid N_2 stream, with a Bruker AXS diffractometer. Graphite-monochromatized Mo-K_α radiation (λ = 0.7107 Å) was used. The lattice parameters were optimized from a least-squares calculation on carefully centered reflections. Lattice determination, data collection, structure refinement, scaling, and data reduction were carried out by using the APEX2 version 1.0-27 software package.^[29] Each structure was determined by using direct methods. This procedure yielded the Zn atoms along with a number of C, N, and O atoms. Subsequent Fourier synthesis yielded the remaining atom positions. The hydrogen atoms were fixed in positions of ideal geometry and refined within the XSELL software.^[30] These idealized hydrogen atoms had their isotropic temperature factors fixed at 1.2 or 1.5 times the equivalent isotropic U value of the C atoms to which they were bonded. The final refinement of each compound included anisotropic thermal parameters on all non-hydrogen atoms. CCDC-745545, -745546, -745547, -745548 for compounds **1**, **2**, **4** and **5**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ^1H NMR spectra and a reaction scheme are provided in Figures S1–S3.

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