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Structurally Characterized 1,1,3,3-Tetramethylguanidine Solvated Magnesium Aryloxide Complexes: $[Mg(\mu\text{-OEt})(DBP)(H\text{-TMG})]_2$, $[Mg(\mu\text{-OBc})(DBP)(H\text{-TMG})]_2$, $[Mg(\mu\text{-TMBA})(DBP)(H\text{-TMG})]_2$, $[Mg(\mu\text{-DPP})(DBP)(H\text{-TMG})]_2$, $[Mg(BMP)_2(H\text{-TMG})_2]$, $[Mg(O\text{-}2,6\text{-}Ph_2C_6H_3)_2\ (H\text{-TMG})_2]$

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The synthesis and structural characterization of several 1,1,3,3-tetramethylguanidine (H-TMG) solvated magnesium aryloxide complexes are reported. Bu_2Mg was successfully reacted with H-TMG, $HOC_6H_3(CMe_3)_2$-2,6 (H-DBP), and either ethanol, a carboxylic acid, or diphenyl phosphate in a 1:1 ratio to yield the corresponding $[Mg(\mu\text{-L})(DBP)(H\text{-TMG})]_2$ where L = OCH_2CH_3 (OEt, **1**), $O_2CC(CH_3)_3$ (OBc, **2**), $O_2C(C_6H_2\text{-}2,4,6\text{-}(CH_3)_3)$ (TMBA, **3**), or $O_2P(OC_6H_5)_2$ (DPP, **4**). Bu_2Mg was also reacted with two equivalents of H-TMG and $HOC_6H_3(CMe_3)$-2-(CH_3)-6 (BMP) or HO-2,6-$Ph_2C_6H_3$ to yield $[Mg(BMP)_2(H\text{-TMG})_2]$ (**5**) and $[Mg(O\text{-}2,6\text{-}Ph_2C_6H_3)_2(H\text{-TMG})_2]$ (**6**). Compounds **1**−**6** were characterized by single-crystal X-ray diffraction. Polymerization of *l*- and *rac*-lactide with **1** was found to generate polylactide (PLA). A discussion concerning the relevance of compounds **2 - 4** to the structure of Mg-activated phosphatase enzymes is also provided. The bulk powders for all complexes were found to be in agreement with the crystal structures based on elemental analyses, FT-IR spectroscopy, and ^1H, ^{13}C and ^{31}P NMR studies.

Introduction

Structural investigation of both catalytic and biomimetic magnesium systems have typically shown the presence of a dinuclear unit bridged by a carboxylate, phosphate ester, or alkoxide ligand.[1−4] Difficulty in detailing the chemistry of such systems has typically arisen from problems associated with isolating well-defined complexes.[5] One method used to garner controlled formation of such metal species is to add ligands with steric bulk around the metal center. In this vein, a variety of multidentate ligands have been used to support and promote the formation of dinuclear systems. For example, Lippard and co-workers have effectively exploited the dinucleating capability of *o*-phenylenediaminetetraacetate (H_2XDK) to isolate well-defined dimagnesium, dizinc, and dicalcium complexes.[2,3,6,7] In this context, such ligand sets are quite successful in isolating dinuclear systems. However, there is still a need for a more convenient approach to generating a larger library of compounds. Thus, the intent of this report is to describe a facile "one-pot" method for producing dimagnesium complexes that are subsequently utilized either as models for biological systems or as catalysts for the ring-opening polymerization (ROP) of cyclic lactones.

Recently, we reported a detailed effort to outline the stoichiometric reactivity of heteroligated zinc systems in-

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(1) Ejfler, J.; Kobylka, M.; Jerzykiewicz, L. B.; Sobota, P. *Dalton Trans.* **2005**, 2047. Chisholm, M. H.; Phomphrai, K. *Inorg. Chim. Acta* **2003**, *350*, 121. Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229.
(2) Yun, J. W.; Tanase, T.; Lippard, S. J. *Inorg. Chem.* **1996**, *35*, 7590.
(3) Yun, J. W.; Tanase, T.; Pence, L. E.; Lippard, S. J. *J. Am. Chem. Soc.* **1995**, *117*, 4407.
(4) Range, S.; Piesik, D. F. J.; Harder, S. *Eur. J. Inorg. Chem.* **2008**, 3442. Wu, J.; Chen, Y.-Z.; Hung, W.-C.; Lin, C.-C. *Organometallics* **2008**, *27*, 4970. Tang, H.-Y.; Chen, H.-Y.; Huang, J.-H.; Lin, C.-C. *Macromolecules* **2007**, *40*, 8855. Sanchez-Barba, L. F.; Garces, A.; Fajardo, M.; Alonso-Moreno, C.; Fernandez-Baeza, J.; Otero, A.; Antinolo, A.; Tejeda, J.; Lara-Sanchez, A.; Lopez-Solera, M. I. *Organometallics* **2007**, *26*, 6403. Davidson, M. G.; Jones, M. D.; Meng, D.; O'Hara, C. T. *Main Group Chem.* **2006**, *5*, 3. Wu, J.-C.; Huang, B.-H.; Hsueh, M.-L.; Lai, S.-L.; Lin, C.-C. *Polymer* **2005**, *46*, 9784. Yu, T.-L.; Wu, C.-C.; Chen, C.-C.; Huang, B.-H.; Wu, J.; Lin, C.-C. *Polymer* **2005**, *46*, 5909. Dove, A. P.; Gibson, V. C.; Marshall, E. L.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2004**, 570.
(5) Bradley, D. C.; Mehrotra, R. C.; Rothwell, I. P.; Singh, A. *Alkoxo and Aryloxo Derivatives of Metals*; Academic Press: San Diego, 2001.
(6) Tanase, T.; Watton, S. P.; Lippard, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 9401. Tanase, T.; Yun, J. W.; Lippard, S. J. *Inorg. Chem.* **1996**, *35*, 3585.
(7) Tanase, T.; Lippard, S. J. *Inorg. Chem.* **1995**, *34*, 4682. Tanase, T.; Yun, J. W.; Lippard, S. J. *Inorg. Chem.* **1995**, *34*, 4220.

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volving alkoxide, aryloxide (OAr), and 1,1,3,3-tetramethylguanidine (H-TMG) ligands.[8] In this investigation, the use of the bulky aryloxide ligand, $HOC_6H_3(CMe_3)_2$-2,6 (H-DBP), in conjunction with H-TMG was found to assist in producing well-defined dizinc systems. Because of the similarity in ionic radii of Mg(2+) and Zn(2+), it seemed reasonable to explore the utility of the H-TMG/OAr ligand set to assist in facilitating the formation of well-defined dinuclear Mg complexes.

Therefore, in our nascent investigation, Bu_2Mg was reacted with H-TMG, H-DBP, and ethanol (H-OEt) in a 1:1 ratio to form the resultant $[Mg(\mu\text{-OEt})(DBP)(H\text{-TMG})]_2$ (**1**). Dimagnesium alkoxides have previously demonstrated the capability to initiate the ROP of cyclic lactones, such as lactide (LA).[1,9] Accordingly, the results related to the use of **1** as a catalyst for the ROP of *l*-LA and *rac*-LA is reported.

Carboxylate and phosphate ester ligands are commonly found in Mg-activated phosphatase enzymes.[3,10] Thus, Bu_2Mg was additionally reacted with H-TMG, H-DBP, a carboxylic acid, or diphenyl phosphate in a 1:1 ratio to yield $[Mg(\mu\text{-L})(DBP)(H\text{-TMG})]_2$ where L = $O_2CC(CH_3)_3$ (OBc, **2**), $O_2C(C_6H_2$-2,4,6-$(CH_3)_3)$ (TMBA, **3**), or $O_2P(OC_6H_5)_2$ (DPP, **4**). The convenient formation of model bridged complexes provides insight into the structure and the resultant function of Mg in metalloenzyme systems. A discussion concerning the significance of compounds **2**−**4** to the structure of Mg-activated phosphatase enzymes is described herein.

Additionally, in an attempt to examine the possibility of isolating alternative H-TMG solvated Mg aryloxides, reactions with $HOC_6H_3(CMe_3)$-2-(CH_3)-6 (BMP) and HO-2,6-$Ph_2C_6H_3$ was also performed. However, instead of isolating dinuclear complexes, two monomeric four-coordinate Mg complexes were isolated, $[Mg(BMP)_2(H\text{-TMG})_2]$ (**5**) and $[Mg(O\text{-}2,6\text{-}Ph_2C_6H_3)_2(H\text{-TMG})_2]$ (**6**). The synthesis and characterization of these two complexes are reported, and the general advantages and disadvantages of the OAr/H-TMG ligand-set are presented.

Experimental Section

All compounds were handled with rigorous exclusion of air and water using standard glovebox techniques. All anhydrous solvents were stored under argon and used as received in sure-seal bottles. $(Bu)_2Mg$ (1.0 M in hexanes), H-TMG, H-DBP, H-BMP, EtOH, H-OBc, H-TMBA, and H-DPP were used as received from commercial suppliers. FT-IR data were obtained on a Bruker Tensor 27 Instrument using KBr pellets under an atmosphere of flowing nitrogen. Melting points were determined on samples sealed in a glass tube under an atmosphere of argon using an Electrothermal Mel-Temp apparatus and are uncorrected. Elemental analysis was performed on a Perkin-Elmer 2400 Series 2 CHN-S/O Elemental Analyzer. All solution spectra were obtained on a Bruker DRX400 spectrometer at 400.1, 100.5, and 162 MHz for ^{1}H, ^{13}C, and ^{31}P experiments.

Synthesis of 1-6. 1−**6** were synthesized by adding the appropriate amount of $(Bu)_2Mg$ (1.0 M, hexanes) dropwise to a solution of H-TMG, H-DBP or H-BMP, and the appropriate alcohol, acid, or phosphate ester dissolved in hexanes. The precipitate that formed was further dissolved using tetrahydrofuran (THF). The solution was then allowed to evaporate, yielding colorless crystals.

$[Mg(\mu\text{-OEt})(DBP)(H\text{-TMG})]_2$ (1). $(Bu)_2Mg$ (1.5 g, 2.2 mmol), H-TMG (0.25 g, 2.2 mmol), H-DBP (0.45 g, 2.2 mmol), and EtOH (0.1 g, 2.2 mmol) were used. Yield 88% (0.72 g, 0.95 mmol). Mp 183 °C. ^{1}H NMR (benzene-d_6): δ = 7.53 (d, 2H, $OC_6H_3(C(CH_3)_3)_2$-2,6), 7.48 (t, 1H, $OC_6H_3(C(CH_3)_3)_2$-2,6), 4.16 (q, 2H, OCH_2CH_3), 3.59 (s, 1H, $HN{=}C(N(CH_3)_2)_2$), 2.51 (s, 6H, $HN{=}C(N(CH_3)_2)_2$), 1.97 (s, 6H, $HN{=}C(N(CH_3)_2)_2$), 1.76 (s, 18H, $OC_6H_3(C(CH_3)_3)_2$-2,6), 1.32 (t, 3H, OCH_2CH_3). ^{13}C{^{1}H} NMR (benzene-d_6): δ = 168.3 ($HN{=}C(N(CH_3)_2)_2$), 156.1 ($OC_6H_3(C(CH_3)_3)_2$-2,6), 138.2 ($OC_6H_3(C(CH_3)_3)_2$-2,6), 138.0 ($OC_6H_3(C(CH_3)_3)_2$-2,6), 125.3 (OC_6H_3-$(C(CH_3)_3)_2$-2,6), 35.9 (OCH_2CH_3), 32.4 ($HN{=}C(N(CH_3)_2)_2$), 31.7 ($OC_6H_3(C(CH_3)_3)_2$-2,6), 26.9 ($OC_6H_3(C(CH_3)_3)_2$-2,6), 22.3 (OCH_2-CH_3). FT-IR (cm^{-1}): 3344 (m), 3052 (w), 2951 (s), 2802 (m), 1581 (s), 1543 (s), 1462 (m), 1421 (s), 1381 (m), 1302 (m), 1260 (w), 1228 (w), 1198 (w), 1123 (m), 1103 (m), 1067 (m), 1034 (m), 875 (m), 749 (m), 659 (m), 588 (m), 557 (m), 522 (w) 462 (w). Anal. Calcd for $C_{42}H_{78}Mg_2N_6O_4$: C, 64.70; H, 10.08; N, 10.78. Found: C, 63.64; H, 10.02; N, 10.38.

$[Mg(\mu\text{-OBc})(DBP)(H\text{-TMG})]_2$ (2). $(Bu)_2Mg$ (1.5 g, 2.2 mmol), H-TMG (0.25 g, 2.2 mmol), H-DBP (0.45 g, 2.2 mmol), and H-OBc (0.22 g, 2.2 mmol) were used. Yield 64% (0.62 g, 0.70 mmol). Mp 198 °C. ^{1}H NMR (benzene-d_6): δ = 7.47 (m, 2H, OC_6H_3-$(C(CH_3)_3)_2$-2,6), 6.82 (m, 1H, $OC_6H_3(C(CH_3)_3)_2$-2,6), 3.58 (s, 1H, $HN{=}C(N(CH_3)_2)_2$), 2.52 (s, 6H, $HN{=}C(N(CH_3)_2)_2$), 1.97 (s, 6H, $HN{=}C(N(CH_3)_2)_2$), 1.71 (s, 18H, $OC_6H_3(C(CH_3)_3)_2$-2,6), 1.31 (s, 9H, $O_2CC(CH_3)_3$). ^{13}C{^{1}H} NMR (toluene-d_8): δ = 184.6 (O_2CC-$(CH_3)_3$), 164.2 ($HN{=}C(N(CH_3)_2)_2$), 138.3 ($OC_6H_3(C(CH_3)_3)_2$-2,6), 137.5 ($OC_6H_3(C(CH_3)_3)_2$-2,6), 124.6 ($OC_6H_3(C(CH_3)_3)_2$-2,6), 113.4 ($OC_6H_3(C(CH_3)_3)_2$-2,6), 68.1 ($O_2CC(CH_3)_3$), 35.7 ($HN{=}C$-$(N(CH_3)_2)_2$), 31.7 ($OC_6H_3(C(CH_3)_3)_2$-2,6), 26.3 ($OC_6H_3(C(CH_3)_3)_2$-2,6), 23.4 ($O_2CC(CH_3)_3$). FT-IR (cm^{-1}): 3363 (m), 3057 (w), 2955 (s), 2868 (m), 2803 (w), 1672 (m), 1578 (s), 1542 (m), 1468 (m), 1459 (w), 1419 (s), 1380 (m), 1302 (m), 1230 (m), 1260 (w), 1131 (m), 1103 (m), 1065 (w), 1035 (w), 902 (w), 876 (m), 793 (m), 744 (m), 689 (w), 662 (w), 606 (m), 581 (w), 461 (m). Anal. Calcd for $C_{48}H_{86}Mg_2N_6O_6$: C, 64.64; H, 9.72; N, 9.42. Found: C, 64.27; H, 9.54; N, 9.49.

$[Mg(\mu\text{-TMBA})(DBP)(H\text{-TMG})]_2$ (3). $(Bu)_2Mg$ (1.5 g, 2.2 mmol), H-TMG (0.25 g, 2.2 mmol), H-DBP (0.45 g, 2.2 mmol) and H-TMBA (0.36 g, 2.2 mmol) were used. Yield 92% (1.0 g, 0.99 mmol). Mp 188 °C. ^{1}H NMR (toluene-d_8): δ = 7.35 (m, 2H, $OC_6H_3(C(CH_3)_3)_2$-2,6), 6.70 (d, 2H, $O_2C(C_6H_2$-2,4,6-$(CH_3)_3)$) 5.93 (m, 1H, $OC_6H_3(C(CH_3)_3)_2$-2,6), 4.51 (s, 1H, $HN{=}C(N(CH_3)_2)_2$), 2.52 (s, 6H, $HN{=}C(N(CH_3)_2)_2$), 2.46 (s, 6H, $HN{=}C(N(CH_3)_2)_2$), 2.11 (s, 3H, $O_2C(C_6H_2$-2,4,6-$(CH_3)_3)$), 2.06 (s, 6H, $O_2C(C_6H_2$-2,4,6-$(CH_3)_3)$), 1.57, (s, 18H, $OC_6H_3(C(CH_3)_3)_2$-2,6). ^{13}C{^{1}H} NMR (toluene-d_8): δ = 178.1 ($O_2C(C_6H_2$-2,4,6-$(CH_3)_3)$), 168.6 ($HN{=}C$-$(N(CH_3)_2)_2$), 163.9 ($OC_6H_3(C(CH_3)_3)_2$-2,6), 138.3 ($O_2C(C_6H_2$-2,4,6-$(CH_3)_3)$), 138.1 ($O_2C(C_6H_2$-2,4,6-$(CH_3)_3)$), 137.7 ($OC_6H_3(C(CH_3)_3)_2$-2,6), 137.5 ($O_2C(C_6H_2$-2,4,6-$(CH_3)_3)$), 137.3 ($O_2C(C_6H_2$-2,4,6-$(CH_3)_3)$), 124.2 ($OC_6H_3(C(CH_3)_3)_2$-2,6), 113.5 ($OC_6H_3(C(CH_3)_3)_2$-2,6), 38.7 ($HN{=}C(N(CH_3)_2)_2$), 31.7 ($OC_6H_3(C(CH_3)_3)_2$-2,6), 26.1 ($OC_6H_3(C(CH_3)_3)_2$-2,6), 23.5 ($O_2C(C_6H_2$-2,4,6-$(CH_3)_3)$), 14.7 (O_2C-$(C_6H_2$-2,4,6-$(CH_3)_3)$), FT-IR (cm^{-1}): 3344(m), 2946 (s), 2803 (m), 1578 (s), 1542 (s), 1459 (s), 1421 (s), 1305 (s), 1260 (m), 1189

(8) Bunge, S. D.; Lance, J. M.; Bertke, J. A. *Organometallics* **2007**, *26*, 6320.
(9) Tang, H. Y.; Chen, H. Y.; Huang, J. H.; Lin, C. C. *Macromolecules* **2007**, *40*, 8855.
(10) York, J. D.; Ponder, J. W.; Chen, Z.; Mathews, F. S.; Majerus, P. W. *Biochemistry* **1994**, *33*, 13164.

(m), 1123 (s), 1064 (m), 880 (m), 747 (m), 666 (m), 597 (m), 453 (m). Anal. Calcd for $C_{58}H_{90}Mg_2N_6O_6$: C, 68.57; H, 8.93; N, 8.27. Found: C, 68.26; H, 8.49; N, 9.42.

[Mg(μ-DPP)(DBP)(H-TMG)]$_2$ (4). $(Bu)_2Mg$ (1.5 g, 2.2 mmol), H-TMG (0.25 g, 2.2 mmol), H-DBP (0.45 g, 2.2 mmol), and H-DPP (0.55 g, 2.2 mmol) were used. Yield 80% (1.0 g, 0.87 mmol). Mp 187 °C. ^{1}H NMR (THF-d_8): δ = 7.15 (m, 10H, P(OC$_6$*H*$_5$)$_2$), 6.97 (m, 2H, OC$_6$*H*$_3$(C(CH$_3$)$_3$)$_2$-2,6), 6.27 (m, 1H, OC$_6$*H*$_3$(C(CH$_3$)$_3$)$_2$-2,6), 4.60 (s, 1H *H*N=C(N(CH$_3$)$_2$)$_2$), 2.66 (m, 12H, HN=C(N(C*H*$_3$)$_2$)$_2$), 1.38 (s, 18H, OC$_6$H$_3$(C(C*H*$_3$)$_3$)$_2$-2,6). ^{13}C{^{1}H} NMR (THF-d_8): δ = 164.4 (HN=*C*(N(CH$_3$)$_2$)$_2$), 153.3 (P(O*C*$_6$H$_5$)$_2$), 152.8 (O*C*$_6$H$_3$(C(CH$_3$)$_3$)$_2$-2,6), 139.4 (O*C*$_6$H$_3$(C(CH$_3$)$_3$)$_2$-2,6), 130.1 (P(OC$_6$*H*$_5$)$_2$), 124.6 (OC$_6$H$_3$(C(CH$_3$)$_3$)$_2$-2,6), 121.2 (P(OC$_6$*H*$_5$)$_2$), 121.1 (OC$_6$H$_3$(C(CH$_3$)$_3$)$_2$-2,6), 113.5 (P(O*C*$_6$H$_5$)$_2$), 35.8 (HN=C-(N(*C*H$_3$)$_2$)$_2$), 32.4 (OC$_6$H$_3$(C(*C*H$_3$)$_3$)$_2$-2,6), 31.7 (OC$_6$H$_3$(*C*(CH$_3$)$_3$)$_2$-2,6). ^{31}P NMR (THF-d_8): δ = −18.1 (O$_2$*P*(OC$_6$H$_5$)$_2$). FT-IR (cm^{-1}): 3350 (m), 3060 (w), 3008 (w), 2947 (s), 2363 (w), 1868 (w), 1570 (s), 1546 (s), 1491 (s), 1420 (s), 1202 (s), 1137 (m), 937 (m), 875 (m), 778 (m), 691 (m), 537 (s), 519 (w). Anal. Calcd for $C_{62}H_{88}Mg_2N_6O_{10}P_2$: C, 62.68; H, 7.47; N, 7.07. Found: C, 63.10; H, 6.45; N, 6.31.

[Mg(BMP)$_2$(H-TMG)$_2$] (5). $(Bu)_2Mg$ (0.77 g, 1.1 mmol), H-TMG (0.25 g, 2.2 mmol), and H-BMP (0.45 g 2.2 mmol) were used. Yield 69% (0.43 g, 0.74 mmol). Mp 176 °C. ^{1}H NMR (benzene-d_6): δ = 7.38 (m, 1H, OC$_6$*H*$_3$(C(CH$_3$)$_3$)-2-(CH$_3$)-6), 7.23 (m, 1H, OC$_6$*H*$_3$(C(CH$_3$)$_3$)-2-(CH$_3$)-6), 7.15 (m, 1H, OC$_6$*H*$_3$(C(CH$_3$)$_3$)-2-(CH$_3$)-6), 4.07 (s, 1H, *H*N=C(N(CH$_3$)$_2$)$_2$), 2.46 (m, 12H, HN=C(N(C*H*$_3$)$_2$)$_2$), 1.74 (s, 9H, OC$_6$H$_3$(C(C*H*$_3$)$_3$)-2-(CH$_3$)-6), 1.48 (s, 3H, OC$_6$H$_3$(C(CH$_3$)$_3$)-2-(C*H*$_3$)-6). ^{13}C{^{1}H} NMR (toluene-d_8): δ = 173.3 (HN=*C*(N(CH$_3$)$_2$)$_2$), 157.4 (O*C*$_6$H$_3$(C(CH$_3$)$_3$)-2-(CH$_3$)-6), 137.7 (O*C*$_6$H$_3$(C(CH$_3$)$_3$)-2-(CH$_3$)-6), 128.8 (O*C*$_6$H$_3$(C(CH$_3$)$_3$)-2-(CH$_3$)-6), 128.5 (O*C*$_6$H$_3$(C(CH$_3$)$_3$)-2-(CH$_3$)-6), 128.3 (O*C*$_6$H$_3$(C(CH$_3$)$_3$)-2-(CH$_3$)-6), 127.9 (O*C*$_6$H$_3$(C(CH$_3$)$_3$)-2-(CH$_3$)-6), 125.1 (O*C*$_6$H$_3$(C(CH$_3$)$_3$)-2-(CH$_3$)-6), 35.8 (HN=C(N(*C*H$_3$)$_2$)$_2$), 31.4 (OC$_6$H$_3$(C(*C*H$_3$)$_3$)-2-(CH$_3$)-6), 23.5 ((OC$_6$H$_3$(*C*(CH$_3$)$_3$)-2-(CH$_3$)-6), 14.9 (OC$_6$H$_3$(C(CH$_3$)$_3$)-2-(*C*H$_3$)-6). FT-IR (cm^{-1}): 3350 (s), 3047 (w), 2948 (s), 2805 (w), 1740 (m), 1575 (s), 1544 (s), 1460 (s), 1423 (s), 1381 (w), 1295 (s), 1125 (s), 1096 (m), 1066 (m), 900 (m), 868 (s), 749 (s), 671 (m), 560 (m), 511 (m), 454 (w). Anal. Calcd for $C_{32}H_{56}MgN_6O_2$: C, 66.14; H, 9.71; N, 14.46. Found: C, 65.62; H, 9.97; N, 14.41.

[Mg(O-2,6-Ph$_2$C$_6$H$_3$)$_2$(H-TMG)$_2$]*(THF) (6). Bu_2Mg (0.77 g, 1.1 mmol), H-TMG (0.25 g, 2.2 mmol), HOC$_6$H$_3$(C$_6$H$_5$)$_2$-2,6 (0.53 g, 2.2 mmol) were used. Yield 77% (0.62 g, 0.83 mmol). MP 192 °C (Dec). ^{1}H NMR (benzene-d_6): δ = 8.01 (m, 4H, OC$_6$H$_3$(C$_6$*H*$_5$)$_2$-2,6), 7.52 (m, 2H, OC$_6$*H*$_3$(C$_6$H$_5$)$_2$-2,6), 7.39 (m, 4H, OC$_6$H$_3$(C$_6$*H*$_5$)$_2$-2,6), 7.28 (m, 2H, OC$_6$H$_3$(C$_6$*H*$_5$)$_2$-2,6), 6.91 (m, 1H, OC$_6$H$_3$(C$_6$*H*$_5$)$_2$-2,6), 3.55 (s, 1H, *H*N=C(N(CH$_3$)$_2$)$_2$), 2.17 (s, 6H, HN=C(N-(C*H*$_3$)$_2$)$_2$), 1.85 (s, 6H, HN=C(N(C*H*$_3$)$_2$)$_2$). ^{13}C{^{1}H} NMR (benzene-d_6): δ = 167.7 (HN=*C*(N(CH$_3$)$_2$)$_2$), 162.1 (O*C*$_6$H$_3$(C$_6$H$_5$)$_2$-2,6), 144.5 (OC$_6$H$_3$(*C*$_6$H$_5$)$_2$-2,6), 132.6 (OC$_6$H$_3$(*C*$_6$H$_5$)$_2$-2,6), 131.0 (OC$_6$H$_3$-(*C*$_6$H$_5$)$_2$-2,6), 129.0 (OC$_6$H$_3$(*C*$_6$H$_5$)$_2$-2,6), 125.5 (OC$_6$H$_3$(C$_6$H$_5$)$_2$-2,6), 114.5 (O*C*$_6$H$_3$(C$_6$H$_5$)$_2$-2,6), 26.2 (HN=C(N(*C*H$_3$)$_2$)$_2$). FT-IR (cm^{-1}): 3332 (m), 3049 (m), 2948 (m), 2802 (w), 1570 (s) 1402 (s), 1322 (m), 1293 (s), 1250 (s), 1122 (s), 1030 (m), 865 (s), 746 (s), 702 (s), 609 (m), 590 (m), 558 (w), 499 (m). Anal. Calcd for $C_{50}H_{60}MgN_6O_3$: C, 73.47; H, 7.40; N, 10.28. Found: C, 72.29; H, 8.16; N, 9.62.

(6a). In an attempt to synthesize [Mg(μ-OBc)(O-2,6-Ph$_2$C$_6$H$_3$)(H-TMG)]$_2$, Bu_2Mg (1.5 g, 2.2 mmol) was added to a solution of H-TMG (0.25 g, 2.2 mmol) dissolved in hexanes, HOC$_6$H$_3$(C$_6$H$_5$)$_2$-2,6 (0.53 g, 2.2 mmol) dissolved in THF, and H-OBc (0.22 g, 2.2 mmol) dissolved in hexanes. The precipitate that formed was then dissolved in THF, and the solution was allowed to slowly evaporate allowing for the formation of crystals. However, **6** was isolated with a unique unit cell and is reported herein as **6a**.

Table 1. Data Collection Parameters for **1**−**3**

compound	**1**	**2**	**3**
chemical formula	$C_{42}H_{78}Mg_2N_6O_4$	$C_{48}H_{86}Mg_2N_6O_6$	$C_{58}H_{90}Mg_2N_6O_6$
formula weight	779.72	891.85	1015.98
Temp (K)	100(2)	100(2)	100(2)
space group	triclinic, $P\bar{1}$	monoclinic, $P2(1)/n$	monoclinic, $P2(1)/c$
a (Å)	9.817(4)	14.002(3)	12.860(3)
b (Å)	15.642(7)	13.167(3)	10.750(2)
c (Å)	16.383(7)	14.213(3)	22.200(4)
α (deg)	80.553(9)		
β (deg)	87.780(9)	90.798(3)	102.53(3)
γ (deg)	74.550(8)		
V (Å^3)	2391.9(18)	2620.3(10)	2995.9(10)
Z	2	2	2
D_{calcd} (Mg/m^3)	1.083	1.130	1.126
μ(Mo, Kα) (mm^{-1})	0.093	0.095	0.091
R1[a] (%) (all data)	6.23 (20.02)	3.28 (4.19)	3.80 (5.03)
wR2[b](%) (all data)	14.16 (18.20)	10.01 (11.72)	12.33 (13.70)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o| \times 100$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2} \times 100$.

Polymerization Procedure. Under an argon environment complex **1** was reacted with *l*-lactide or *rac*-lactide (LA) ([LA]: **1** = 100) in a Schlenk flask charged with 10 mL of toluene. The mixture was stirred for 8 min at 20 °C. A drop of glacial acetic acid was added to quench the reaction and then volatile materials were removed. The resulting polymer was analyzed by ^{1}H NMR and FT-IR spectroscopy (Supporting Information, Figures S1−S3). The melting point of the PLA (160 °C), generated from *l*-LA, was also obtained.

X-ray Crystal Structure Information. X-ray crystallography was performed by mounting each crystal onto a thin glass fiber from a pool of Fluorolube and immediately placing it under a liquid nitrogen cooled N_2 stream, on a Bruker AXS diffractometer. The radiation used was graphite monochromatized Mo Kα radiation (λ = 0.7107 Å). 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 using APEX2 version 1.0−27 software package.

Each structure was solved using direct methods. This procedure yielded the magnesium atoms, along with a number of the 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 XSHELL software. These idealized hydrogen atoms had their isotropic temperature factors fixed at 1.2 or 1.5 times the equivalent isotropic U of the C atoms to which they were bonded. The final refinement of each compound included anisotropic thermal parameters on all non-hydrogen atoms. Additional information concerning the data collection and final structural solutions of compounds **1**−**6** and **6a** can be found in Tables 1 and 2. Any variations from standard structural solution associated with the representative compounds are discussed below.

Results and Discussion

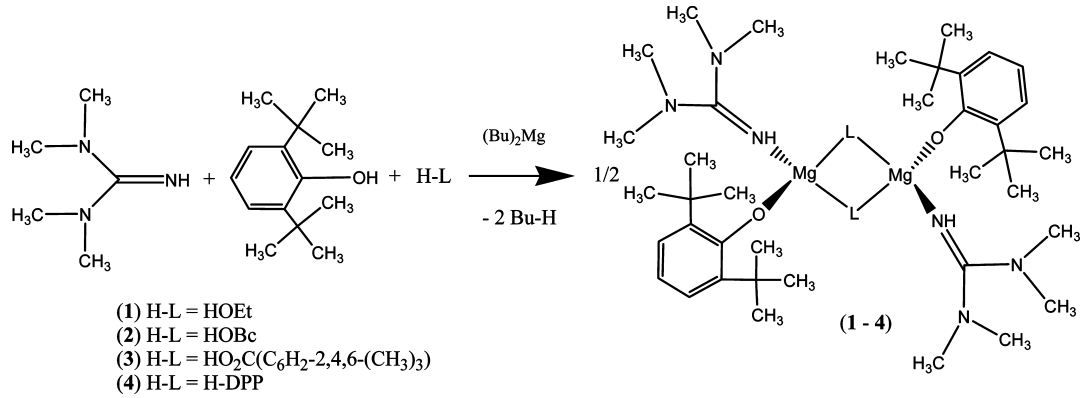
Synthesis. Complexes **1**−**6** were synthesized (Schemes 1 and 2) by the straightforward addition of dibutyl magnesium to a hexanes solution containing various ratios of H-TMG, an alcohol, carboxylic acid, or phosphate ester. Two equiva-

Table 2. Data Collection Parameters for **4**−**6a**

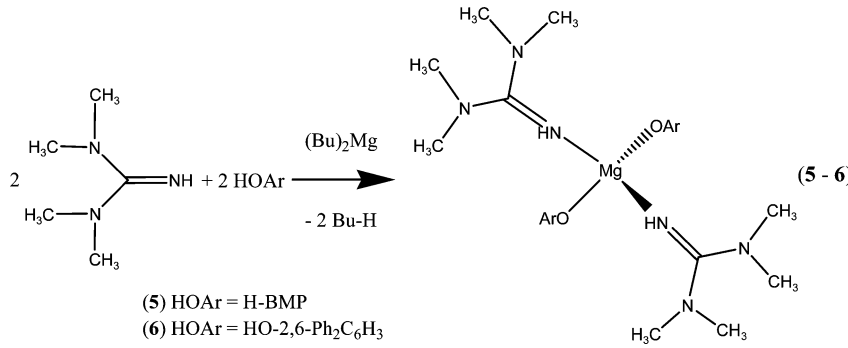
compound	**4**	**5**	**6**	**6a**
chemical formula	$C_{62}H_{88}Mg_2N_6O_{10}P_2$	$C_{32}H_{56}MgN_6O_2$	$C_{46}H_{52}MgN_6O_2$	$C_{46}H_{52}MgN_6O_2$
formula weight	1187.94	581.14	745.25	745.25
temp (K)	160(2)	160(2)	160(2)	160(2)
space group	monoclinic, *P*2(1)/*n*	orthorhombic, *Pbca*	orthorhombic, *Pna*2(1)	monoclinic, *P*2(1)/*n*
a (Å)	15.100(3)	17.203(3)	23.768(4)	16.160(3)
b (Å)	11.260(2)	17.277(3)	17.122(3)	12.509(3)
c (Å)	19.340(4)	23.120(4)	10.0927(18)	20.640(4)
α (deg)				
β (deg)	93.60(3)			91.491(4)
γ (deg)				
V (Å^3)	3281.8(11)	6871(2)	4107.3(13)	4171.0(15)
Z	2	8	4	4
D_{calcd}(Mg/m^3)	1.202	1.124	1.205	1.187
μ(Mo,Kα) (mm^{-1})	0.144	0.087	0.089	0.087
R1[a] (%) (all data)	3.50 (4.35)	5.33 (11.90)	3.22 (3.94)	4.41 (12.11)
wR2[b] (%) (all data)	12.35 (13.41)	13.48 (17.07)	9.60 (10.52)	10.45 (14.47)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o| \times 100$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2} \times 100$.

Scheme 1. Synthesis of Compounds **1**−**4**



Scheme 2. Synthesis of **5** and **6**



lents of butane are presumably eliminated serving to drive the reaction forward and result in the rapid precipitation of a powder. Deprotonation of the alcohol via the butyl group, the formation of Mg−O and C−H bonds were formed, ensuring favorable reaction energies. Notably, adjacent to the aryloxide ligand, the H-TMG remains protonated and coordinated to the metal in each complex. THF is typically added to the reaction mixture while heating the hexanes solution to redissolve the precipitated powder. Upon achieving redissolution, colorless crystals of **1**−**6** were obtained through slow evaporation of the solvent mixture. For elemental analysis, recrystallization was additionally performed by redissolving the solid in a hexanes/THF (1:1) mixture and then placing the sample at −35 °C for 24 h.

Table 3. Spectroscopic Data for Complexes **1**−**6**

	FT-IR data			^{1}H NMR	^{31}P NMR
complex	υ(N−H) cm^{-1}	υ(C=N) cm^{-1}	υ(P−O) cm^{-1}	(N−H)	
1	3344	1581		$\delta = 3.59$	
2	3363	1578		$\delta = 3.58$	
3	3344	1579		$\delta = 4.51$	
4	3350	1570	1203	$\delta = 3.72$	$\delta = -18.1$
5	3350	1575		$\delta = 4.07$	
6	3332	1570		$\delta = 3.55$	

Nonoptimized yields from 69 to 92% were obtained for the resultant magnesium aryloxide complexes.

Spectroscopic Studies. Spectroscopic data is summarized in Table 3. Crystals of **1**−**6** were dried in vacuo to yield the bulk powder and used subsequently in the following analyses. The FTIR spectra of **1**−**6** exhibited no stretches associated

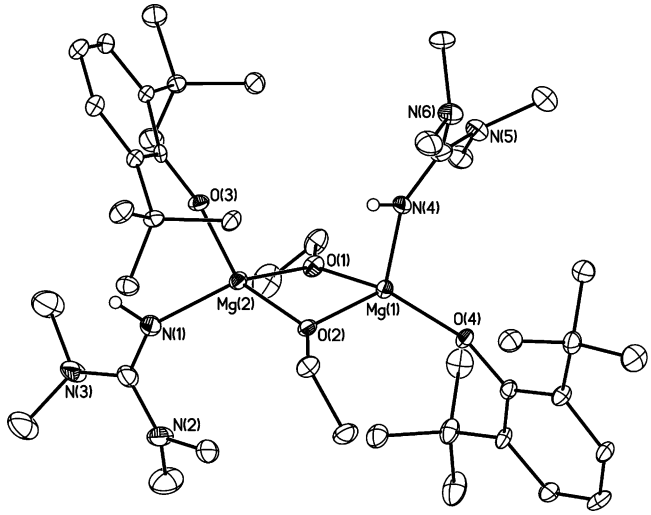


Figure 1. Thermal ellipsoid plot of **1**. Ellipsoids are drawn at the 30% level. H atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Mg(1)−O(1) 1.968(4), Mg(1)−O(2) 1.972(4), Mg(1)−O(4) 1.871(4), Mg(1)−N(4) 2.064(4), Mg(1)−O(1)−Mg(2) 94.02(16), Mg(1)−O(2)−Mg(2) 94.43(16), O(4)−Mg(1)−O(1) 127.50(17), O(4)−Mg(1)−O(2) 121.90(16), O(1)−Mg(1)−O(2), 83.23(15).

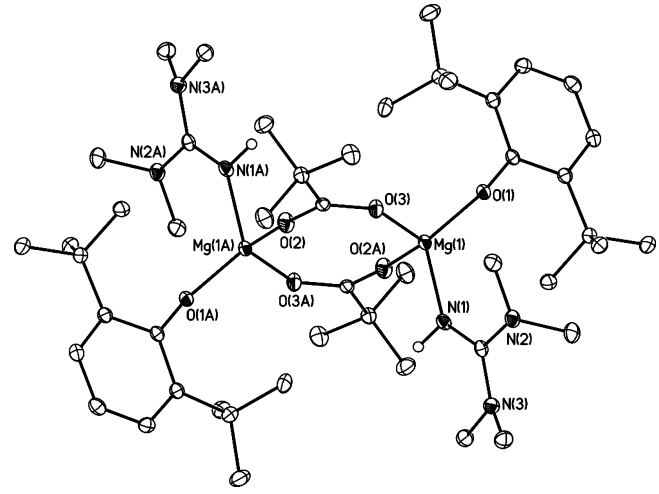


Figure 2. Thermal ellipsoid plot of **2**. Ellipsoids are drawn at the 30% level. H atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Mg(1)−O(1) 1.8685(11), Mg(1)−O(2A) 1.9290(11), Mg(1)−O(3) 1.9600(11), Mg(1)−N(1) 2.0452(13), O(1)−Mg(1)−O(2A) 110.33(5), O(1)−Mg(1)−O(3) 110.94(5), O(3)−Mg(1)−O(2A) 114.37(5).

with −OH ligands indicative of complete substitution. The expected alkyl and aryl stretches for the aryloxide, carboxylate, phosphate, alkoxide, and guanidine ligands are present for each sample. For each complex, the presence of υ(N−H) and υ(C=N) were confirmed by stretching corresponding to peaks around 3300 cm^{-1} and 1580 cm^{-1}, respectively. In addition, for complex **4**, a diagnostic peak at 1203 cm^{-1} can be assigned to the P−O stretch. Because of the complexity of the Mg−O region, it was not possible to definitively assign a Mg−O stretch for each compound. All complexes exhibited expected ^{1}H and ^{13}C resonances in solution NMR spectra. The presence of the N−H bond for the coordinated H-TMG is confirmed with by a singlet ($\delta \sim 4$) in the ^{1}H NMR spectra. The ^{31}P solution NMR for complex **4** was also performed and exhibited a single resonance ($\delta = -18.1$) for the coordinated phosphate ligand.

Structural Descriptions. All six complexes were characterized by X-ray crystallography. Thermal ellipsoid plots and selected interatomic distances and angles of **1**−**6** are presented in Figures 1−6. Structural descriptions for each complex are provided in the following paragraphs.

[Mg(μ-OEt)(DBP)(H-TMG)]$_2$ (1). Compound 1 has a planar Mg_2O_2 core, where each magnesium is tetrahedrally coordinated by two bridging ethoxide groups, one terminal aryloxide, and one terminal H-TMG ligand. The C=N bond distance in the H-TMG ranges from 1.285−1.321 Å while the C−N bond lengths were longer ranging from 1.343 to 1.385 Å. These lengths are similar to those previously reported for the typical lengths of C=N and C−N bonds.[11] This structure is comparable to a dinuclear zinc compound [Zn(μ-OEt)(H-TMG){$OC_6H_3(CMe_3)_2$-2,6}]$_2$ which exhibited a similar planar Zn_2O_2 core, with each zinc tetrahedrally coordinated.[8]

[Mg(μ-OBc)(DBP)(H-TMG)]$_2$ (2) and [Mg(μ-TMBA)-(DBP)(H-TMG)]$_2$ (3). Each magnesium has a distorted tetrahedral coordination with a terminal aryloxide group and a terminal H-TMG ligand. Both complexes have a carboxylate ligands bridging between the two magnesium centers. Compound **2** and **3** are similar in structure to the acetate bridged dinuclear complex [(HC(C(CH_3)N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$)Mg-(ì-O_2CCH_3])$_2$, previously reported by Dove and co-workers.[12] The bond lengths of **2** and **3** between the magnesium and oxygen are similar, and both have asymmetric Mg−O bond lengths at the metal center, 1.960 Å and 1.929 Å for **2**, and 1.948 Å and 1.930 Å for **3**.

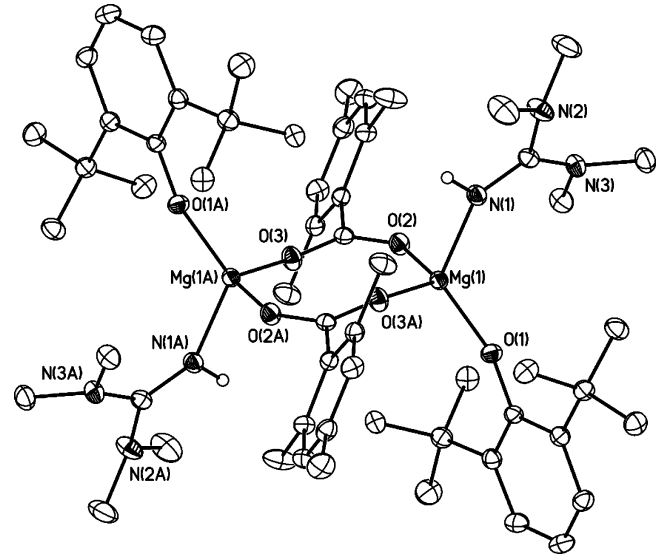


Figure 3. Thermal ellipsoid plot of **3**. Ellipsoids are drawn at the 30% level. H atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Mg(1)−O(1) 1.8497(12), Mg(1)−O(2) 1.9482(12), Mg(1)−O(3A) 1.9296(13) Mg(1)−N(1) 2.0463(14), O(3)−Mg(1A) 1.9296(13), O(1)−Mg(1)−O(3A) 108.81(6), O(1)−Mg(1)−O(2) 114.29(6), O(3A)−Mg(1)−O(2) 115.52(6).

[Mg(μ-DPP)(DBP)(H-TMG)]$_2$ (4). Compound **4** has two phosphate ester bridges connecting the two magnesium centers. The coordination sphere for each magnesium is further coordinated to one terminal aryloxide group and one H-TMG ligand. Yun and co-workers have synthesized two

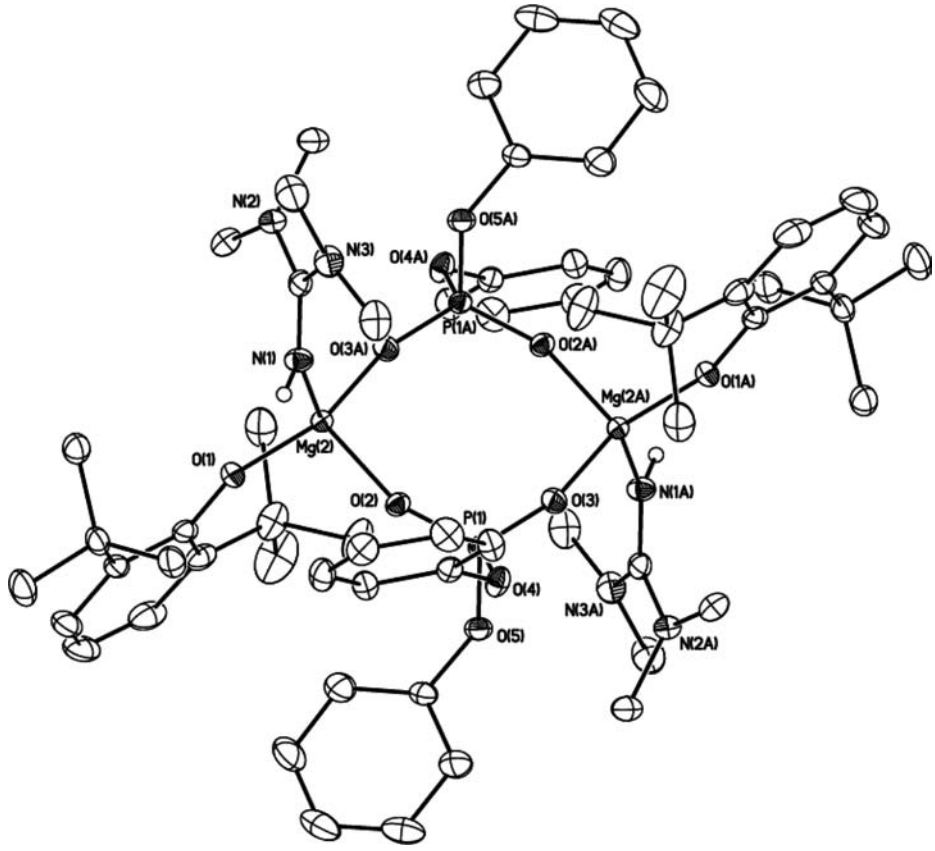


Figure 4. Thermal ellipsoid plot of **4**. Ellipsoids are drawn at the 30% level. H atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Mg(2)−O(1) 1.8807(12), Mg(2)−O(3A) 1.9422(13), Mg(2)−O(2) 1.9622(12), Mg(2)−N(1) 2.0635(15), O(1)−Mg(2)−O(3A) 115.26(6), O(1)−Mg(2)−O(2) 108.91(5), O(3A)−Mg(2)−O(2) 107.72(5).

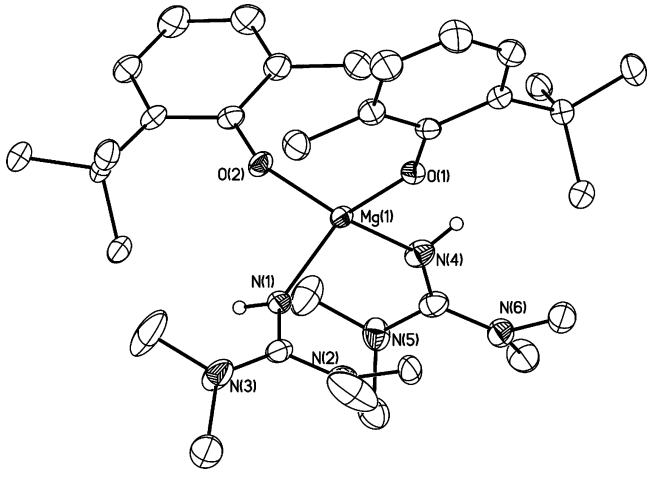


Figure 5. Thermal ellipsoid plot of **5**. Ellipsoids are drawn at the 30% level. H atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Mg(1)−O(2) 1.896(2), Mg(1)−O(1) 1.901(2), Mg(1)−N(4) 2.076(3), Mg(1)−N(1) 2.081(3), O(2)−Mg(1)−O(1) 122.93(10), O(2)−Mg(1)−N(4) 115.74(10), O(1)−Mg(1)−N(4) 93.97(10), O(2)−Mg(1)−N(1) 96.14(9), O(1)−Mg(1)−N(1) 116.70(10).

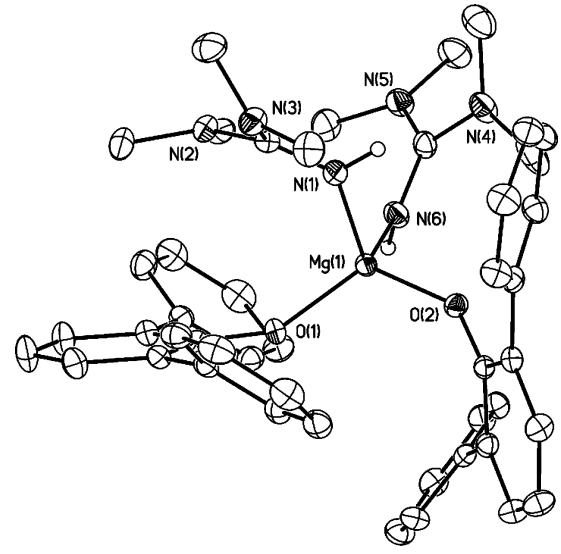


Figure 6. Thermal ellipsoid plot of **6**. Ellipsoids are drawn at the 30% level. H atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Mg(1)−O(2) 1.903(2), Mg(1)−O(1) 1.903(2), Mg(1)−N(4) 2.077(2), Mg(1)−N(1) 2.077(3), O(2)−Mg(1)−O(1) 125.54(9), O(2)−Mg(1)−N(4) 102.37(9), O(1)−Mg(1)−N(4) 110.60(9), O(2)−Mg(1)−N(1) 110.01(10), O(1)−Mg(1)−N(1) 97.46(10).

structures that are comparable to **4**, $[Mg_2(XDK)(\mu\text{-}\eta^2\text{-}(PhO)_2PO_2)(CH_3OH)(H_2O)(NO_3)]$ and $[Mg_2(XDK)\{\mu\text{-}\eta^2\text{-}(PhO)_2PO_2\}\{\eta^1\text{-}(PhO)_2PO_2\}(CH_3OH)_3(H_2O)]$.[2] The Mg···Mg distance on these structures was 4.240 Å while the distance for **4** was 4.856 Å. The phosphorus has a distorted tetrahedral coordination. The O2−P1−O3 angle is 118.65° which is similar to the angle reported by Yun (120° avg.).[2] The P−O bonds to the magnesium (1.484, 1491 Å) are notably shorter than the P−O bonds to the phenyl group (1.602, 1.593 Å). This difference in bond length is typical.[2,6,13,14] The mag-

(11) Coles, M. P. *Dalton Trans.* **2006**, 985.
(12) Dove, A. P.; Gibson, V. C.; Hormnirun, P.; Marshall, E. L.; Segal, J. A.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2003**, 3088.

nesium phosphate plane [Mg1−O2−P1−O3] is approximately perpendicular to both the planes formed by the magnesium and the terminal ligands (80.6° avg.).

[Mg(DBP)$_2$(H-TMG)$_2$] (5) and [Mg(O-2,6-Ph$_2$C$_6$H$_3$)$_2$(H-TMG)$_2$] (6). Compounds **5** and **6** have a distorted tetrahedral magnesium core bonded by two H-TMG ligands and two aryloxide groups. Both of these structures are similar to a tetrahedral monomeric magnesium compound, [Mg(OC$_6$H$_3$-(CMe$_3$)$_2$-2,6)$_2$·2THF] synthesized and characterized by Henderson and co-workers.[15] The Mg−O distances are comparable with the average for [Mg(OC$_6$H$_3$(CMe$_3$)$_2$-2,6)$_2$·2THF] being 1.894 Å. The Mg−O distance is 1.90 Å for **5** and 1.903 for **6.**

A structurally similar cadmium complex was also reported by Darensbourg and co-workers [Cd(OC$_6$H$_3$(CMe$_3$)$_2$-2,6)$_2$·2(pyridine)].[16] In the Cd structure, the phenyl substituent on the diphenyl phenoxide was shown to interact with the Cd metal center. The C−Cd bond was reported to be ∼2.6 Å. In **6**, the closest C−Mg distance is ∼ 3.5 Å and thus does not indicate an interaction between the phenyl group and magnesium.

Relevance to Biological Systems. The magnesium ion has a significant role in biochemical transformations by serving to neutralize anions present in systems.[17] For example, phosphate ester-processing enzymes utilize magnesium in a dimetal unit as a catalyst for the cleavage of phosphate ester bonds. Enzymes that contain such a unit include the Klenow fragment of DNA polymerase I from *Escherichia coli*, ribonuclease H of HIV-1 reverse transcriptase, rat DNA polymerase *â*, fructose-1,6-bisphosphatase, inositol monophosphatase, and inositol polyphosphate 1-phosphatase.[10,18,19] In these diverse systems, the divalent metal atoms are typically found buried in a hydrophobic pocket with both tetrahedral and octahedral coordination geometries. Additionally, the active site contains carboxylate or phosphate esters separating the two metal centers by a distance of ∼ 4 Å.

Although the magnesium ion has been shown to have a significant biological role, there have only been a limited number of structurally investigated model dimagnesium systems.[2,3] It was therefore of interest to synthesize **2**−**4** and examine the capability of the H-TMG/OAr ligand to produce complexes with a structural resemblance to the biological dimetal unit. **2**−**4** exhibit tetrahedrally coordinated Mg metal centers bridged by either carboxylate or phosphate ester ligands (Figures 2−4). Both metals are additionally coordinated to a terminal monoanionic oxygen donor and one neutral guanidine substituent. The Mg···Mg distances of 4.263 Å (**2**), 4.218 Å (**3**), and 4.856 Å (**4**) are similar to the metal···metal distance found in enolase (4.2 Å), rat DNA polymerase (4 Å), and slightly longer than those found in inositol monophosphatase (3.8 Å), inositol polyphosphatase (3.88 Å), fructose 1,6-bisphosphatase (3.7 Å), and *E. coli* DNA polymerase (3.9 Å).[10,18,20] Notably, there is a significant difference in the Mg···Mg distance between the carboxylate bridged **2** and **3** and the Mg···Mg distance of the phosphate ester-bridged complex **4.** This difference indicates that there is significant expansion of the dimetal unit upon addition of the phosphate ester substrate. The observation of a flexible expansion is consistent with previous reports of carboxylate and phosphate bridged dicopper, diiron, dizinc, and dicalcium systems.[2,14,21] In addition to the structural comparisons, notably and perhaps coincidentally, the solution-state ^{31}P NMR of complex **4** ($\delta = -18.1$) is similar to the signal found for the β-P of ATP bound to Mg^{2+} ($\delta = -18.5$).[22] Additional investigations of the nuclearity of **4** in solution are required to further comment on any solution-state structural similarity.

Lactide Polymerization. Polylactide (PLA) has received considerable attention because of its biodegradable properties.[23,24] It has environmental, biomedical, and pharmaceutical applications.[24−27] PLA can be derived from renewable sources such as corn, sugar beets, and cheese whey.[27,28] Ring opening polymerization (ROP) of lactide, the cyclic version of lactic acid, is the most widely used procedure used to synthesize PLA.[28] Both inorganic and organic catalysts have

(13) Armstrong, W. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 3730. Turowski, P. N.; Armstrong, W. H.; Roth, M. E.; Lippard, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 681. Turowski, P. N.; Armstrong, W. H.; Liu, S. C.; Brown, S. N.; Lippard, S. J. *Inorg. Chem.* **1994**, *33*, 636. Krebs, B.; Schepers, K.; Bremer, B.; Henkel, G.; Althaus, E.; Mullerwarmuth, W.; Griesar, K.; Haase, W. *Inorg. Chem.* **1994**, *33*, 1907. Mahroof-Tahir, M.; Karlin, K. D.; Chen, Q.; Zubieta, J. *Inorg. Chim. Acta* **1993**, *207*, 135. Hikichi, S.; Tanaka, M.; Morooka, Y.; Kitajima, N. *J. Chem. Soc., Chem. Commun.* **1992**, 814. Drueke, S.; Wieghardt, K.; Nuber, B.; Weiss, J.; Fleischhauer, H. P.; Gehring, S.; Haase, W. *J. Am. Chem. Soc.* **1989**, *111*, 8622. Norman, R. E.; Yan, S.; Que, L., Jr.; Backes, G.; Ling, J.; Sanders-Loehr, J.; Zhang, J. H.; O'Connor, C. J. *J. Am. Chem. Soc.* **1990**, *112*, 1554.

(14) Jang, H. G.; Hendrich, M. P.; Que, L. *Inorg. Chem.* **1993**, *32*, 911.

(15) Henderson, K. W.; Honeyman, G. W.; Kennedy, A. R.; Mulvey, R. E.; Parkinson, J. A.; Sherrington, D. C. *Dalton Trans.* **2003**, 1365.

(16) Darensbourg, D. J.; Wildeson, J. R.; Lewis, S. J.; Yarbrough, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 7075.

(17) Frausto da Silva, J. J. R.; Williams, R. J. P. *The Biological Chemistry of the Elements*, 2nd ed.; Oxford University Press: New York, 2001.

(18) Beese, L. S.; Steitz, T. A. *EMBO J.* **1991**, *10*, 25. Pelletier, H.; Sawaya, M. R.; Kumar, A.; Wilson, S. H.; Kraut, J. *Science* **1994**, *264*, 1891. Bone, R.; Frank, L.; Springer, J. P.; Atack, J. R. *Biochemistry* **1994**, *33*, 9468.

(19) Davies, J. F., II.; Hostomska, Z.; Hostomsky, Z.; Jordan, S. R.; Matthews, D. A. *Science* **1991**, *252*, 88. Davies, J. F., II.; Almassy, R. J.; Hostomska, Z.; Ferre, R. A.; Hostomsky, Z. *Cell* **1994**, *76*, 1123. Xue, Y. F.; Huang, S. H.; Liang, J. Y.; Zhang, Y. P.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1994**, *91*, 12482. Villeret, V.; Huang, S. H.; Zhang, Y. P.; Lipscomb, W. N. *Biochemistry* **1995**, *34*, 4307.

(20) Larsen, T. M.; Wedekind, J. E.; Rayment, I.; Reed, G. H. *Biochemistry* **1996**, *35*, 4349.

(21) Kato, M.; Tanase, T.; Mikuriya, M. *Inorg. Chem.* **2006**, *45*, 2925. Butcher, R. J.; Gultneh, Y.; Allwar, A. B. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2005**, *61*, M818. Deschamps, J. R.; Hartshorn, C. M.; Chang, E. L. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2002**, *58*, M606. Armstrong, W. H.; Roth, M. E.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 6318. Kuzelka, J.; Spingler, B.; Lippard, S. J. *Inorg. Chim. Acta* **2002**, *337*, 212. Rapta, M.; Kamaras, P.; Brewer, G. A.; Jameson, G. B. *J. Am. Chem. Soc.* **1995**, *117*, 12865.

(22) Gupta, R. K.; Gupta, P.; Yushok, W. D.; Rose, Z. B. *Physiol. Chem. Phys.* **1983**, *15*, 265. Taylor, J. S.; Vigneron, D. B.; Murphy-Boesch, J.; Nelson, S. J.; Kessler, H. B.; Coia, L.; Curran, W.; Brown, T. R. *Proc. Natl. Acad. Sci. U.S.A.* **1991**, *88*, 6810.

(23) Williams, C. K.; Breyfogle, L. E.; Choi, S. K.; Nam, W.; Young, V. G.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2003**, *125*, 11350.

(24) Du, H. Z.; Pang, X.; Yu, H. Y.; Zhuang, X. L.; Chen, X. S.; Cui, D. M.; Wang, X. H.; Jing, X. B. *Macromolecules* **2007**, *40*, 1904.

(25) Chiellini, E.; Solaro, R. *Adv. Mater.* **1996**, *8*, 305. Jeong, B.; Bae, Y. H.; Lee, D. S.; Kim, S. W. *Nature* **1997**, *388*, 860. Uhrich, K. E.; Cannizzaro, S. M.; Langer, R. S.; Shakesheff, K. M. *Chem. Rev.* **1999**, *99*, 3181.

(26) Chabot, F.; Vert, M.; Chapelle, S.; Granger, P. *Polymer* **1983**, *24*, 53.

(27) O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *J. Chem. Soc., Dalton Trans.* **2001**, 2215.

(28) Braun, B.; Dorgan, J. R.; Dec, S. F. *Macromolecules* **2006**, *39*, 9302.

been used for the ROP.[29,30] Typically, the greatest control of lactide polymerization has been achieved by using metal alkoxides.[4,31] However, there are currently problems with side reactions that cause transesterfication which can be prevented with the use of bulky ligands on the metal centers.[9] Previous research in our group has shown zinc complexes which utilize H-TMG and aryloxide ligands can be effective as a initiators for ROP of lactide.[8] Biocompatible metals such as Zn and Mg are of interest because of the propensity for trace amounts of the catalyst to be incorporated within the polymer.[9] Therefore, preliminary research exploring the use of ethoxide-bridged complex **1** as an initiator for the ROP of cyclic lactones has been performed.

Utilizing complex **1**, the ROP of *l*-lactide (*l*-LA) in toluene ([*l*-LA]: **1** = 100) was investigated. The reaction was stirred for 8 min, and the polymerization was terminated with acid addition. ^{1}H NMR, FT-IR, and the melting point determination of the resultant polymer were performed and confirm the presence of PLA. The average molecular weight (M_n = 7.1 kg/mol) could be determined by ^{1}H NMR integration of the methyl resonances (Supporting Information, Figure S1) and is consistent with complete conversion of *l*-LA to PLA. Of note, this weight is indicative of **1** existing as a monomer instead of a dinuclear compound in solution. Pulse-gradient-spin-echo (PGSE) experiments were performed on an isostructural zinc system and confirmed the presence of a monomer in solution. A proposed scheme for the reaction of *l*-LA with **1** is shown in Supporting Information, Figure S2. The melting point of the PLA was obtained and found to be 160 °C, which is consistent with a molecular weight of PLA being ∼7 kg/mol.[24,31]

To further examine if there was any remaining *l*-LA in the isolated PLA, the polymer was characterized by FT-IR spectroscopy. *l*-LA has peaks at 935, 1244, and 1273 cm^{-1} that are assigned to the ring stretching modes.[28] These peaks are characteristically absent in the spectrum for PLA (Supporting Information, Figure S3). In addition, the C−H$_3$ bending mode at 1458 cm^{-1} can be used to determine the amount of *l*-LA present in the isolated PLA. When there is *l*-LA present, the peak at 1458 cm^{-1} has been found to decrease in intensity and a single peak splits into two distinct peaks.[28] The FT-IR of the isolated PLA exhibited a single peak (Supporting Information, Figure S3). This indicates that the catalyst completely converted all monomer to polymer in the 8 min of reaction.

There has also been considerable interest in the polymerization of *rac*-LA and the stereochemistry of the resultant PLA.[8,24,27,31,32] The ROP of *rac*-LA was investigated utilizing complex **1** under similar conditions to those describing the ROP of *l*-LA. Upon isolation of the PLA, ^{1}H NMR was used to examine the tacticity of the resultant polymer. In this spectrum, the characteristic methyl peak was assigned, and selective decoupling of the methine region was performed. The resulting NMR spectrum can be seen in the Supporting Information, Figure S4. The most prominent peak was representative of the tetrad *iii* which indicates a significant number of either RRRR or SSSS stereocenters in the polymer chain.[26] This is indicative of atactic PLA and is comparable to previously reported Mg catalysts that exhibited only modest heterotactic bias.[30,33]

Limitations of the OAr/H-TMG ligand-set. Complexes **1**−**4** utilized the combination of DBP and H-TMG to isolate well-defined systems via a "one-pot" synthetic approach. In an attempt to examine the possibility of isolating alternative H-TMG solvated Mg aryloxides, reactions similar to those that generated complexes **1**−**4** were also performed with H-BMP and HO-2,6-Ph$_2$C$_6$H$_3$. However, instead of isolating dinuclear complexes, two monomeric complexes were serendipitously isolated, [Mg(BMP)$_2$(H-TMG)$_2$] (**5**) and [Mg(O-2,6-Ph$_2$C$_6$H$_3$)$_2$(H-TMG)$_2$] (**6**). Upon determination of the structure of **5** and **6**, the complexes were synthesized with the appropriate stoichiometry and complete characterization was performed (Scheme 2). Apparently, there is a steric requirement for the use of a "one-pot" approach involving the OAr/H-TMG ligand-set. Careful choice of both the aryloxide and the guanidine are necessary to avoid isolation of a mixture of complexes. To further explore the steric requirements, we have recently isolated a larger library of structurally varied 1,1,3,3-tetraalkylguanidine ligands.[34] It is envisioned that these ligands will facilitate the formation of additional dinuclear complexes.

Summary and Conclusion

Overall, six magnesium complexes have been synthesized and structurally characterized. The structures, utility of these complexes, and the advantages and disadvantages of the OAr/H-TMG ligand-set have been discussed. Using H-TMG and H-DBP, four dinuclear magnesium compounds with ethoxide, carboxylate, or phosphate ester bridges have been isolated. Two monomeric H-TMG solvated complexes were also synthesized using H-BMP or diphenylphenol. The carboxylate and phosphate bridged dinuclear compounds were found to be similar to those found in biological systems. The preliminary results of the ROP of lactide were reported. Additional work is underway to further examine the versatility of this ligand-set.

(29) Piao, L.; Deng, M.; Chen, X.; Jiang, L.; Jing, X. *Polymer* **2003**, *44*, 2331. Myers, M.; Connor, E. F.; Glauser, T.; Mock, A.; Nyce, G.; Hedrick, J. L. *J. Polym. Sci., Part A:* **2002**, *40*, 844. Nederberg, F.; Connor, E. F.; Moeller, M.; Glauser, T.; Hedrick, J. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 2712. Kricheldorf, H. R.; Boettcher, C.; Toennes, K. U. *Polymer* **1992**, *33*, 2817. Williams, C. K.; Breyfogle, L. E.; Choi, S. K.; Nam, W.; Young, V. G., Jr.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2003**, *125*, 11350. O'Keefe, B. J.; Breyfogle, L. E.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 4384. Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1316. Jensen, T. R.; Breyfogle, L. E.; Hillmyer, M. A.; Tolman, W. B. *Chem Commun* **2004**, 2504.

(30) Chisholm, M. H.; Gallucci, J.; Phomphrai, K. *Inorg. Chem.* **2002**, *41*, 2785.

(31) Majerska, K.; Duda, A. *J. Am. Chem. Soc.* **2004**, *126*, 1026.

(32) Kricheldorf, H. R.; Boettcher, C.; Tonnes, K. U. *Polymer* **1992**, *33*, 2817. Zell, M. T.; Padden, B. E.; Paterick, A. J.; Thakur, K. A. M.; Kean, R. T.; Hillmyer, M. A.; Munson, E. J. *Macromolecules* **2002**, *35*, 7700.

(33) Chisholm, M. H.; Gallucci, J. C.; Phomphrai, K. *Inorg. Chem.* **2005**, *44*, 8004.

(34) Cleland, T. L.; Bunge, S. D. *Polyhedron* **2007**, *26*, 5506.

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Supporting Information Available: Spectroscopic data for the synthesized PLA is found in Figures S1−S4, and crystallographic data in CIF file format. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 704486 for **1**, CCDC 704487 for **2**, CCDC 704488 for **3**, CCDC 704489 for **4**, CCDC 704490 for **5**, CCDC 704491 for **6**, CCDC 704492 for **6a**. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44-(0)1223−336033; or e-mail, deposit@ccdc.cam.ac.uk).

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