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Monomeric metal alkoxides and trialkyl siloxides: (BDI)Mg(O^{t}Bu)(THF) and (BDI)Zn(OSiPh$_3$)(THF). Comments on single site catalysts for ring-opening polymerization of lactides †

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The monomeric alkoxide (BDI)Mg(O^{t}Bu)(THF) and triphenylsiloxide (BDI)Zn(OSiPh$_3$)(THF) have been prepared and characterized and shown to reversibly dissociate THF in solution on the NMR time scale; both compounds are active precursors for the ring-opening polymerization of lactide and the rate of polymerization is notably faster for the magnesium complex though in the polymerization of *rac*-lactide only the zinc complex shows selectivity for heterotactic tetrads.

We describe here our preparation and characterization of two monomeric compounds of general formula $L_nM(OR)$ which serve as catalyst precursors for the ring-opening polymerization of lactides. In this case L_n represents the combination of the bidentate anionic ligand formed by deprotonation of 2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-diisopropylphenyl)imino]-pent-2-ene, hereafter referred to as BDI, and one tetrahydrofuran, THF, molecule. The metals are magnesium for R = ^{t}Bu and zinc for R = SiPh$_3$. The present report is of particular interest with respect to the recent reports of lactide polymerizations involving $L_nM(OR)$ precursors, where L_n = a sterically demanding tris(3-alkylpyrazolyl)borate or tris(indazolyl)borate and M = Mg or Zn,[1] and the dimeric precursor complex [(BDI)-Zn(μ-O^{i}Pr)]$_2$.[2]

The preparation of the two new compounds is shown in Scheme 1.[4] In both cases the compounds are isolated as white hydrocarbon-soluble, air- and moisture-sensitive crystalline solids. The molecular structure of the magnesium compound, **1**, was determined by a single-crystal X-ray diffraction study[5] and an ORTEP view of the pseudo-tetrahedral coordination about the magnesium atom is given in Fig. 1. The central N_2ZnO_2 core in the zinc complex (BDI)Zn(OSiPh$_3$)(THF), **2**, is believed to have a similar structure to that seen for N_2MgO_2 in Fig. 1. The THF ligands in compounds **1** and **2** are labile to exchange with added THF as judged by variable temperature dynamic ^{1}H NMR studies. The lability of the THF ligand is greater in compound **2** relative to **1** and exchange with free THF is believed to occur by a dissociative interchange mechanism as the VT ^{1}H NMR spectra of **1** in CD_2Cl_2 can most readily be accommodated by the equilibrium shown in eqn. (1).[4] See Fig. 2. For the zinc complex the equilibrium (1) is not frozen out at −70 °C in CD_2Cl_2.

$$\text{(BDI)M(OR)(THF)} \rightleftharpoons \text{(BDI)M(OR)} + \text{THF} \qquad (1)$$

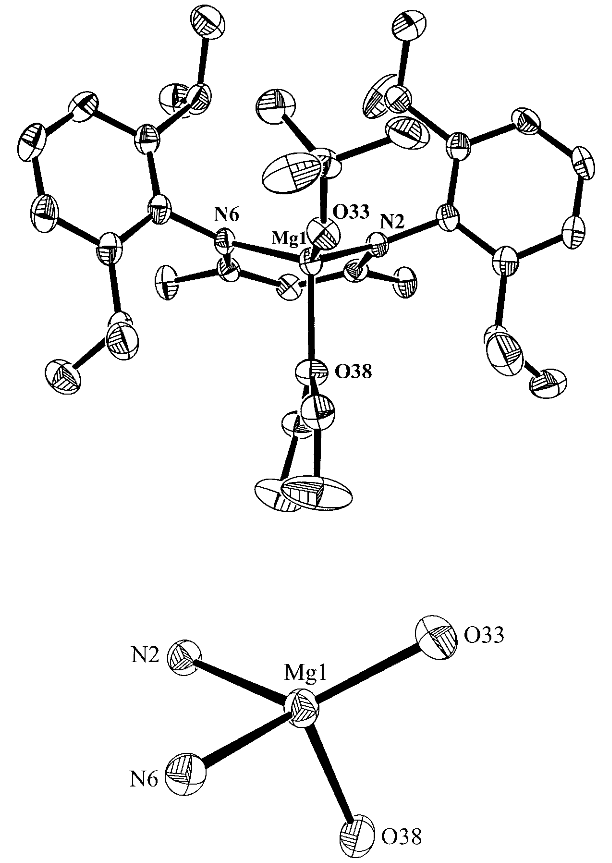

Fig. 1 ORTEP[7] drawing of (BDI)Mg(O^{t}Bu)(THF) shows a pseudo-tetrahedral Mg core. Selected bond distances (Å) and bond angles (°): Mg1–O33 1.844(2), Mg1–O38 2.048(2), Mg1–N2 2.054(2), Mg1–N6 2.059(2), O33–Mg1–O38 98.77(9), O33–Mg1–N2 127.8(1), O33–Mg1–N6 126.1(1), O38–Mg1–N2 103.79(9), O38–Mg1–N6 105.15(9), N2–Mg1–N6 92.20(9).

Both compounds act as precursors for the ring-opening polymerization of lactides (L-lactide and *rac*-lactide). The polymerization brought about by the magnesium complex is much faster than that of the zinc complex. In CD_2Cl_2 as solvent 100 equivalents of *rac*-lactide are polymerized by **1** in less than 10 minutes at room temperature while for **2** the polymerization proceeds to *ca.* 90% completion in 30 hours. These results parallel the previous findings employing related (η^3-trispyrazolylborate)MOR precursors. Upon initiation of polymerization the THF ligand is displaced. The active species in polymerization catalysis is then (BDI)M(OP), where OP is the growing poly(lactide) chain, which can take up lactide in a manner akin to the equilibrium reaction shown in eqn. (1) involving (BDI)-M(OR) and THF.

The slow polymerization brought about by **2** can be traced to the slow initiation step involving insertion of lactide into the Zn–OSiPh$_3$ bond. This result parallels the observations reported by Coates and co-workers in comparing the ROP of

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† Dedicated to Ron Snaith, in memoriam.

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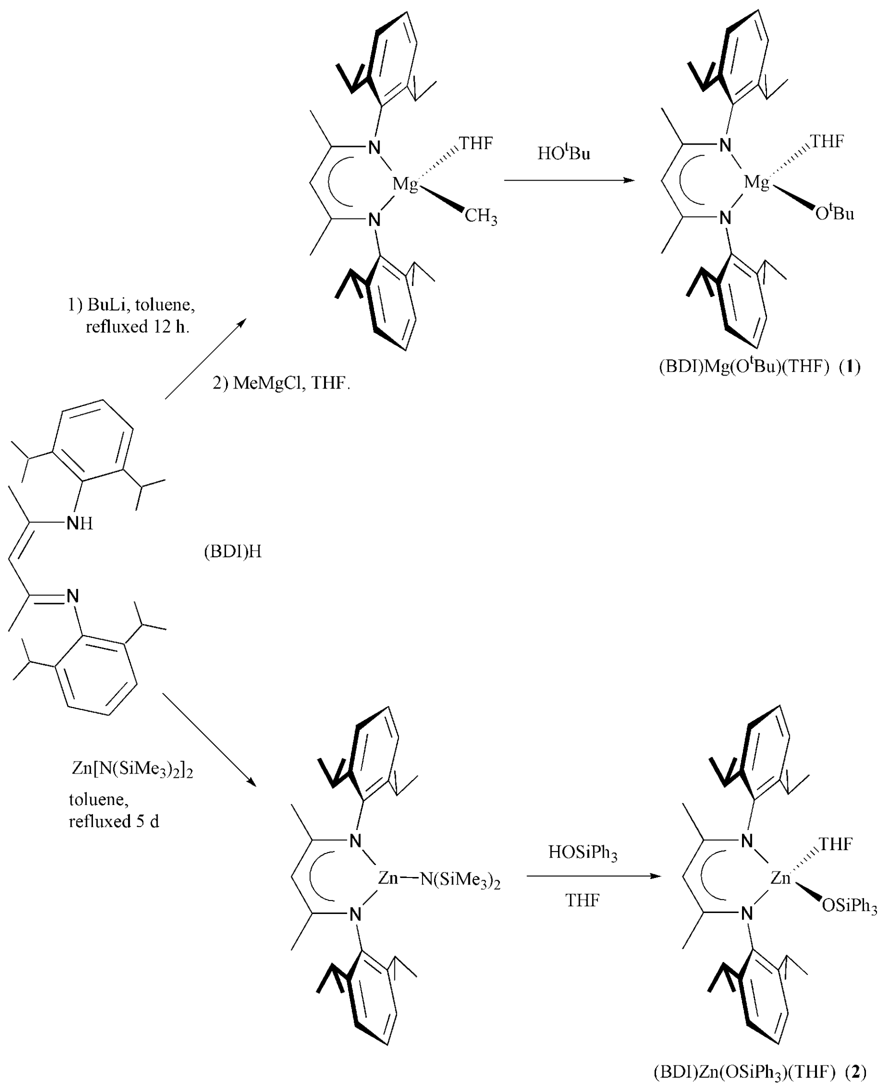

Scheme 1

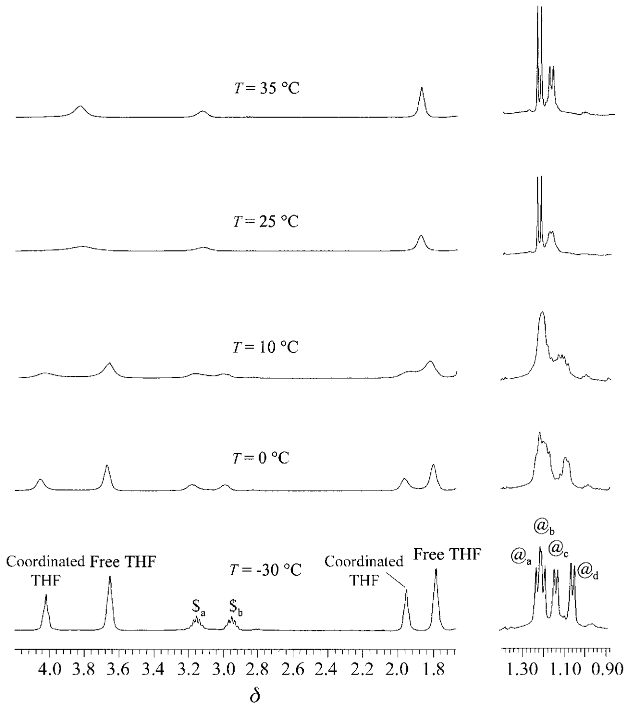

Fig. 2 VT ^{1}H NMR spectra (CD_2Cl_2, 400 MHz) after addition of 1.2 equivalents of THF to **1** where $\$_a$ and $\$_b$ are C*H*MeMe′ and C*H*′Me″-Me‴ protons, and @$_a$, @$_b$, @$_c$ and @$_d$ are nonequivalent CH*Me*Me′, CH′*Me*″Me‴, CH′Me″*Me*‴, and CHMe*Me*′ protons.

lactides by (BDI)ZnN(SiMe$_3$)$_2$ and [(BDI)Zn(μ-O^{i}Pr)]$_2$ where the latter was much faster.[2] We attribute the difference in the rate of initiation of ROP by **1** and **2** to a combination of the basicity of RO$^-$ ligands, ^{t}BuO > Ph$_3$SiO, and the electrophilicity of the metal centers, $Mg^{2+} > Zn^{2+}$. The polymerization reactions employing (BDI)Zn(OSiPh$_3$)(THF) as an initiator [or (BDI)ZnN(SiMe$_3$)$_2$] and *rac*-lactide reveal that the poly(lactide) is greatly enhanced in the heterotactic tetrads **isi** and **sis** as a result of the preference of the consecutive alternate insertion of L- and D-lactide units into the growing chain.[2] Rather interestingly no such preference for heterotactic polymer is seen in the polymerization of *rac*-lactide employing the magnesium complex **1** as a catalyst precursor. See Fig. 3. In the $^{13}C\{^1H\}$ spectrum we find some formation of tetrad sequences usually derived from polymerization of *meso*-lactide (see Fig. 3) which could arise from back-biting in the polymer chain since polymerization of L-lactide shows only **iii** tetrads. Given that Mg^{2+} and Zn^{2+} are of a very similar size and that the stereoselective polymerization leading to heterotactic polylactide with **isi** and **sis** tetrads by the zinc catalyst results from end-group control, we must conclude that the ring-opening event is less selective in the case of magnesium. This would be consistent with our earlier studies in comparing the ROP of lactides by closely related Mg and Zn complexes where k_{ROP} for Mg was much faster than for Zn.[1b] A faster reaction rate is usually less discriminating. However, the steric demands at a metal center such as Mg^{2+} or Zn^{2+} are much greater for a η^3-(3-^{t}Bupz)$_3$BH ligand relative to the η^2-BDI ligand. Thus, the influence of "end-group control" in the ROP of lactides is more influenced by the detailed nature of the geometry of the transition state leading to ring-opening than to the overall steric impedance at the metal center.

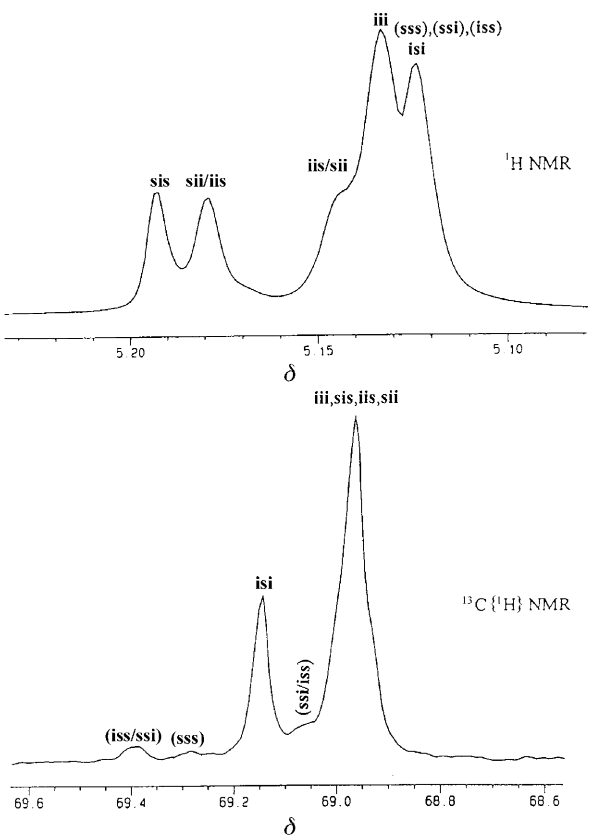

Fig. 3 ^{1}H NMR ($CDCl_3$, 400 MHz) of the homodecoupled C*H* resonance and $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) of the methine carbon signals of poly(*rac*-lactide) initiated by **1**. The tetrad sequence is according to Kricheldorf[6] and the assignment of (**sss**), (**iss**), and (**ssi**) in the ^{1}H homodecoupled and $^{13}C\{^1H\}$ NMR spectra are proposed to arise from back-biting, as these sequences normally are seen only in poly(*meso*-lactide).

Clearly much work needs to be done to gain a full understanding of the factors that are truly important in the molecular design of single-site catalyst precursors for stereoselective ROP of lactides.

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Notes and references

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4 (BDI)Mg(O^{t}Bu)(THF) (**1**): HO^{t}Bu (36 μL, 0.38 mmol) was added dropwise to a solution of (BDI)Mg(CH_3)(THF) (0.20 g, 0.38 mmol, see ref. 3) in 15 mL of CH_2Cl_2 at room temperature. The mixture was stirred for 15 minutes during which time bubbles of CH_4 gas were formed. The solvent was then removed under reduced pressure giving a light yellow powder (0.202 g, 91%). Crystals suitable for the X-ray study were grown from a 1 : 1 mixture of hexane and benzene by slow evaporation of a solution contained in an NMR tube in a drybox. ^{1}H NMR (CD_2Cl_2, 25 °C, δ) 7.12 (m, 6H, ArH), 4.82 (s, 1H, β-CH), 3.82 [br, 4H, O(CH_2)$_2$(CH_2)$_2$], 3.12 (br, 4H, C*H*MeMe′), 1.88 [br, 4H, O(CH_2)$_2$(CH_2)$_2$], 1.64 (s, 6H, α-CH_3), 1.22 (d, $J = 7.2$ Hz, 12H, CH*Me*Me′), 1.17 (br, 12H, CHMe*Me*′), 0.61 (s, 9H, O^{t}Bu); ^{1}H NMR (CD_2Cl_2, −30 °C, δ) 7.15 (m, 6H, ArH), 4.78 (s, 1H, β-CH), 4.02 [br, 4H, O(CH_2)$_2$(CH_2)$_2$], 3.16 (septet, $J = 7.1$ Hz, 2H, C*H*MeMe′), 2.95 (septet, 2H, C*H*′Me″Me‴), 1.96 [br, 4H, O(CH_2)$_2$(CH_2)$_2$], 1.60 (s, 6H, α-CH_3), 1.22 (d, $J = 7.1$ Hz, 6H, CH*Me*Me′), 1.19 (d, $J = 7.2$ Hz, 6H, CH′*Me*″Me‴), 1.13 (d, $J = 6.7$ Hz, 6H, CH′Me″*Me*‴), 1.05 (d, $J = 6.7$ Hz, 6H, CHMe*Me*′), 0.57 (s, 9H, O^{t}Bu).

(BDI)Zn(OSiPh$_3$)(THF) (**2**): A solution of Ph$_3$SiOH (0.215 g, 0.778 mmol) in 10 mL THF was added slowly to a solution of (BDI)ZnN(SiMe$_3$)$_2$ (0.500 g, 0.778 mmol, see ref. 2) in 5 mL THF. The resulting clear solution was stirred over night and the solvent was removed giving a white powder (0.613 g, 95%). ^{1}H NMR (CD_2Cl_2, δ) 7.30 (t, $J = 7.8$ Hz, 2H, *p*-^{i}Pr$_2$ArH), 7.18 (d, $J = 7.8$ Hz, 4H, *m*-^{i}Pr$_2$ArH), 7.13 (m, 3H, *p*-SiArH), 7.01 (t, $J = 6.7$ Hz, 6H, *m*-SiArH), 6.92 (m, 6H, *o*-SiArH), 5.09 (s, 1H, β-CH), 3.68 [m, 4H, O(CH_2)$_2$(CH_2)$_2$], 3.00 (heptet, $J = 7.2$ Hz, 4H, C*H*MeMe′), 1.82 [m, 4H, O(CH_2)$_2$(CH_2)$_2$], 1.79 (s, 6H, α-Me), 1.20 (d, $J = 6.9$ Hz, 12H, CH*Me*Me′), 0.90 (d, $J = 6.9$ Hz, 12H, CHMe*Me*′).

5 Crystal data for **1**: MF = $C_{37}H_{58}MgN_2O_2$, MW = 587.18, monoclinic, $P2_1$, $a = 9.7999(3)$ Å, $b = 16.6069(5)$ Å, $c = 11.5815(3)$ Å, $\beta = 109.345(1)°$, $V = 1778.43$ Å^3, $Z = 2$, $\rho_{calc} = 1.097$ g cm^{-3}, Bruker SMART 6000 sealed-tube system, $\lambda = 0.71073$ Å, $T = 111$ K, Crystal size 0.40 × 0.40 × 0.15 mm, $F(000) = 644$, 27281 reflections measured, 8177 unique reflections, 5047 reflections with $I > 2.33\sigma(I)$, $2\theta_{max} = 55.0°$, $R(F) = 0.0327$, $R_w(F) = 0.0293$. CCDC reference number 186/2304. See http://www.rsc.org/suppdata/dt/b0/b008158m/ for crystallographic files in .cif format.

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