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Synthesis, Characterization, and Structural Determination of Polynuclear Lithium Aggregates and Factors Affecting Their Aggregation

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The reaction of $[(\mu_3,\mu_3\text{-EDBP})Li_2]_2[(\mu_3\text{-}{}^nBu)Li(0.5Et_2O)]_2$ (**1**) [EDBP-H_2 = 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol)] with 1 equiv of ROH in toluene gave $[(\mu_3,\mu_3\text{-EDBP})Li_2]_2[(\mu_3\text{-OR})Li]_2$ [R = Bn (**2**), CH_2CH_2OEt (**3**), and ^{n}Bu (**4**)]. In the presence of 3 equiv of tetrahydrofuran (THF), the hexanuclear compound **1** slowly decomposed to an unusual pentanuclear Li complex, $[(\mu_2,\mu_3\text{-EDBP})_2Li_4(THF)_2][(\mu_3\text{-}{}^nBu)Li]$ (**5**). Further reaction of **5** with ROH gave $[(\mu_2,\mu_3\text{-EDBP})_2Li_4(THF)_3][(\mu_4\text{-OR})Li]$ [R = Bn (**6**), ^{n}Bu (**7**), and CH_2CH_2OEt (**8**)] without a major change in its skeleton. Treatment of **2** with an excess of hexamethylphosphoramide (HMPA) yields $[(\mu_2,\mu_2\text{-EDBP})Li_2(HMPA)_2][(\mu_3\text{-OBn})Li(HMPA)]$ (**9**). Compounds $[(\mu_2,\mu_3\text{-EDBP})_2Li_4(THF)][(\mu_4\text{-OCH}_2CH_2OEt)Li]_2$ (**10**) and $[(\mu_2,\mu_2\text{-EDBP})_2Li_4(\mu_4\text{-OCH}_2CH_2OEt)(HMPA)]^-[Li(HMPA)_4]^+$ (**11**) can be obtained by the reaction of **3** with an "oxygen-donor solvent" such as THF and HMPA, respectively. Among the compounds described above, **8** has shown great reactivity toward ring-opening polymerization of L-lactide, yielding polymers with very low polydispersity indexes in a wide range of monomer-to-initiator ratios.

Introduction

Alkyllithium reagents and lithium alkoxides play an important role in organic synthesis because of their applications as alkylating and deprotonating reagents as well as initiators in anionic polymerization.[1] In general, organolithium species form aggregates associated through C−Li bonds. Their aggregation is usually governed by steric factors depending on the size of the substituents and the presence of heteroatom-containing donor groups, which can be either solvent molecules or inter- or intramolecularly coordinated substituents of the organic moiety. These inter- and intramolecular donor groups are known to affect the synthesis and reactivity of organolithium reagents.[2] For instance, complexes derived from RLi and MOR, namely, as superbases such as ^{n}BuLi·KO^{t}Bu, have been shown to be extremely useful in organic synthesis.[3] It is well-known that [RLi·LiOR] complexes prepared from the reactions of organolithium compounds with alcohols have a tendency to form oligomeric structures in the solid state.[4] The first crystal structure of RLi·LiOR, $[CH_3(CH_2)_3Li\cdot LiOC(CH_3)_3]_4$, was reported by Boche et al. in 1990.[5] Li derivatives containing alkyl ($-CR_3$) or alkoxide ($-$OR) functional groups have been reported to form at least 12 general structure types.[6−8] Factors affecting the molecular structure of Li aggregates include (i) the steric bulk and electron-donation ability of the α atom (C, O, and N) of the ligand, (ii) the bonding ability and number of pendant chains

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($-OR$, $-NR_2$, and $-CR_3$) of the ligand, and (iii) the choice of the reaction solvent (Lewis basicity). Recently, we have been interested in the preparation of single-component networks through the use of lithium alkoxides in which the Lewis basic linker is incorporated as a part of the alkoxide backbone. Under careful control of kinetic and thermodynamic conditions, Li complexes may exhibit remarkable chemo-, regio-, stereo-, and even chronoselectivity, provided by fine tuning of the structural characteristics of the catalytic aggregate. The bulky biphenoxy ligands have been used in the modification of various transition[9,10] and main-group metals,[11] but that of Li[9−12] is rather scant. Herein we report the preparation of a series of mixed-ligand hexanuclear Li aggregates, which further react with Lewis basic solvents such as tetrahydrofuran (THF) and hexamethylphosphoramide (HMPA) to afford novel solvent-solvated lithium alkoxide aggregates. The relationship between the structure of Li derivatives and their catalytic behavior has been explored.

Results and Discussion

Synthesis and Characterization of Mixed-Ligand Li Aggregates. Recently, we have reported that $[(\mu_3,\mu_3\text{-EDBP})Li_2]_2[(\mu_3\text{-}^n\text{Bu})Li(0.5Et_2O)]_2$ [**1**; EDBP-H_2 = 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol)] reacts with 1 equiv of ROH in toluene, yielding $[(\mu_3,\mu_3\text{-EDBP})Li_2]_2[(\mu_3\text{-OR})Li]_2$ [R = Bn (**2**) and CH_2CH_2OEt (**3**)].[11a] In this reaction, a bulky ligand $EDBP^{2-}$ is used to coordinate to the metal center, resulting in a single active site for ring-opening polymerization (ROP). Similarly, a hexanuclear species $[(\mu_3,\mu_3\text{-EDBP})Li_2]_2[(\mu_3\text{-OR})Li]_2$ (**4**; R = ^{n}Bu) can be prepared from the reaction of **1** with *n*-butanol. Because Lewis basic solvents such as THF and HMPA are commonly used in organic reactions. the effect of the presence of THF or HMPA in the structure of the polynuclear Li aggregates seems to be worthy of investigation. An unusual Li aggregate, $[(\mu_2,\mu_3\text{-EDBP})_2Li_4(THF)(\mu_3\text{-}^n\text{Bu})][Li(THF)]$ (**5**), is obtained as a white crystalline solid from the reaction of **1** with 3 mol equiv of THF in toluene, followed by the removal of solvent and crystallization from hexane. The isolation of this Li_5 complex indicates liberation of one Li^{n}Bu group upon incorporation of two THF molecules. The ^{n}Bu group coordinated to a Li ion in **5** can be replaced by any alkoxy group without drastic changes in its skeleton. The treatment of **5** with 1 equiv of BnOH, ^{n}BuOH, or 2-ethoxyethanol in THF gives quantitative yields of **6**, **7**, or **8**, respectively, as shown in Scheme 1. The pentanuclear species $[(\mu_2,\mu_3\text{-EDBP})_2Li_4(THF)_3][(\mu_4\text{-OR})Li]$ [OR = OBn (**6**) and O^{n}Bu (**7**)] can also be prepared by the addition of excess THF to $[(\mu_3,\mu_3\text{-EDBP})Li_2]_2[(\mu_3\text{-OR})Li]_2$ [OR = OBn (**2**) and O^{n}Bu (**4**)], illustrating the liberation of one LiOR group upon coordination of three THF molecules to Li ions at ambient temperature. It is worth mentioning that the alkoxy O bridges four Li atoms. The functional group of the Li aggregate can be easily converted to an alkoxy group without a dramatic change in its skeleton. This was verified by X-ray crystallographic analysis. In addition, **2** reacts with 6 mol equiv of HMPA in toluene, yielding a Li_3 aggregate $[(\mu_2,\mu_2\text{-EDBP})Li_2(HMPA)_2][(\mu_3\text{-OBn})Li(HMPA)]$ (**9**).

In contrast to the monodentate alkoxide (OR = OBn and O^{n}Bu), the reaction product between the bidentate alkoxide **3** (OR = OCH_2CH_2OEt) and a strong Lewis base such as THF or HMPA is much more complicated because of the coordination ability of the ethoxy group. In the presence of excess THF (>50 equiv) at room temperature, **3** produces a mixture of pentanuclear aggregate $[(\mu_2,\mu_3\text{-EDBP})_2Li_4(THF)_3][(\mu_4\text{-OCH}_2CH_2OEt)Li]$ (**8**) and hexanuclear aggregate $[(\mu_2,\mu_3\text{-EDBP})_2Li_4(THF)][(\mu_4\text{-OCH}_2CH_2OEt)Li]_2$ (**10**). Attempts to separate these two complexes via recrystallization were unsuccessful because of their similar solubility. Fortunately, we were able to obtain two individual single crystals for X-ray analysis from the mixture. However, it was also found that compounds **8** and **10** can be independently prepared by mixing 2-ethoxyethanol, EDBP-H_2, THF, and ^{n}BuLi in a 1:2:3:5 or 2:2:1:6 ratio, respectively. On the other hand, a Li_6 aggregate **10** can be obtained from the reaction of **3** with 3 mol equiv of THF, followed by recrystallization from hexane. The unexpected Li aggregate **10** can be considered as an intermediate in the reaction of complex **3** with excess THF, giving complex **8**. The structure of **8** is similar to that of **6** or **7**, except that the O atom of the ethoxy group

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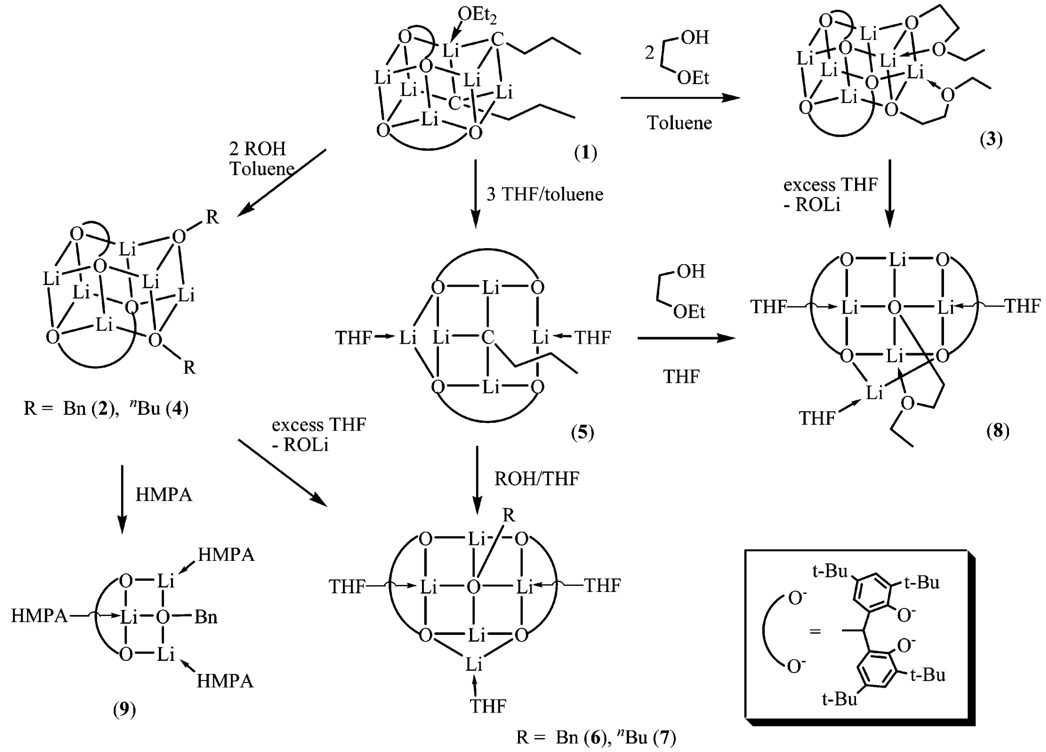
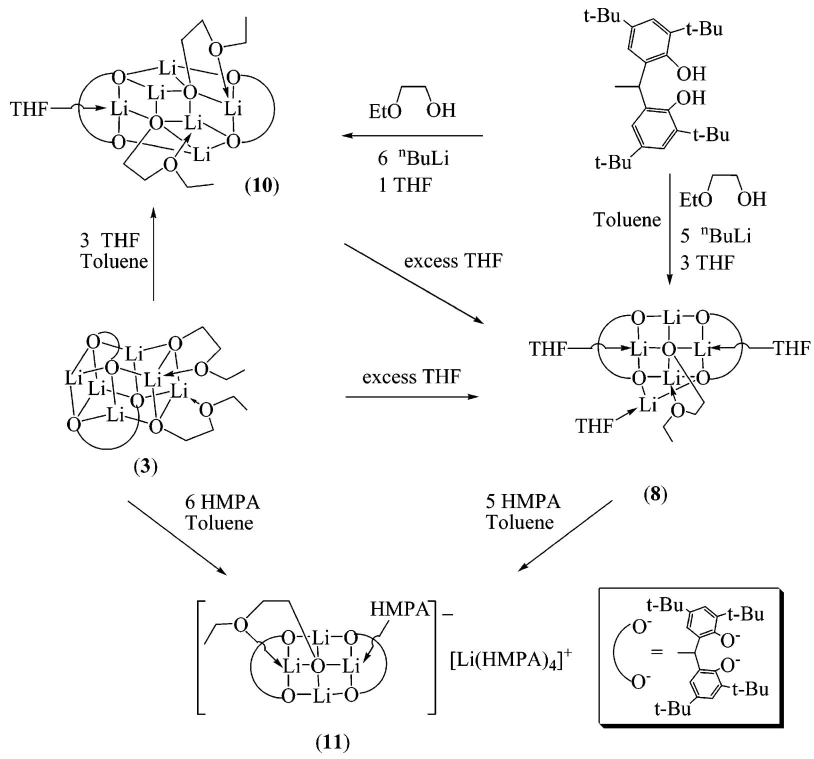
Scheme 1



Scheme 2



coordinates an additional Li atom. Furthermore, **8** reacts with 5 mol equiv of HMPA in toluene to afford an ionic complex [(μ_2,μ_2-EDBP)$_2$Li$_4$(μ_4-OCH$_2$CH$_2$OEt)(HMPA)][Li(HMPA)$_4$] (**11**). Complex **11** can also be synthesized in 62% yield by the reaction of **3** with 6 mol equiv of HMPA, as shown in Scheme 2. It is interesting to note that the Li ion in the [Li(HMPA)$_4$]$^+$ cation is surrounded by four HMPA molecules. Complexes **4**−**11** have been characterized by spectroscopic and X-ray diffraction techniques.

Molecular Structure Studies of 4−11. Although syntheses of lithium alkoxides/phenoxides had been reported previously,[13] most of them lacked structural characterization. The X-ray structure analysis of **4** reveals that it has a C_2 symmetry. Its skeleton is almost the same as that of **2**, except

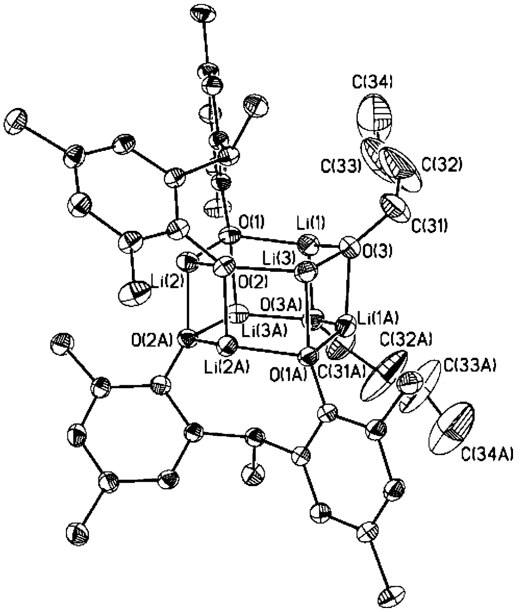


Figure 1. ORTEP drawing of **4** (methyl C atoms of the ^{t}Bu groups and all of the H atoms are omitted for clarity) with thermal ellipsoids drawn at the 10% probability level. Selected bond distances (Å): Li(1)−O(1) 1.937(6), Li(1)−O(3) 1.880(6), Li(1)−O(3A) 1.904(6), Li(2)−O(1) 1.881(5), Li(2)−O(2) 2.110(5), Li(2)−O(2A) 1.891(5), Li(3)−O(2) 1.864(6), Li(3)−O(3) 1.869(6), Li(3)−O(1A) 1.959(5), O(1)−Li(3A) 1.959(5), O(2)−Li(2A) 1.891(5), O(3)−Li(1A) 1.904(6).

that two benzylalkoxy groups are replaced by *n*-butoxide groups, as shown in Figure 1. The hexanuclear complex **4** consists of three different kinds of tricoordinated Li atoms. The average bond distances of Li(1)−O [1.907(6) Å], Li(2)−O [1.961(6) Å], and Li(3)−O [1.897(6) Å] are all compatible with the bond distances observed for complex **2**.[11a]

The molecular structure of **5** is shown in Figure 2. The ^{n}BuLi/EDBPLi$_2$/THF ratio in **5** is 1:2:2. There are four kinds of Li atoms in the Li$_5$ complex **5**. The chemically equivalent tricoordinated Li atoms Li(1) and Li(3) are both bound to two O atoms of the same EDBP ligand and one ^{n}Bu group. While Li(2) and Li(4) are both coordinated by two O atoms of different EDBP ligands and one THF molecule, Li(5) is bound to two different EDBP O atoms and one ^{n}Bu group. Two O atoms of the EDBP ligands are doubly bridging, and the others are triply bridging. It is worth noting that the C atom C(69) of the ^{n}Bu group is bridging three Li cations, Li(1), Li(3), and Li(5), with an average Li−C(69) bond distance of 2.193(7) Å. This is similar to the values of the Li−C(61) [2.192(9) Å] and Li−C(65) [2.197(10) Å] bond distances observed for the triply bridging ^{n}Bu groups in complex **1**.[11a] The Li(2)−O(5) (THF) and Li(4)−O(6) (THF) bond distances are 1.948(7) and 1.931(6) Å, respectively.

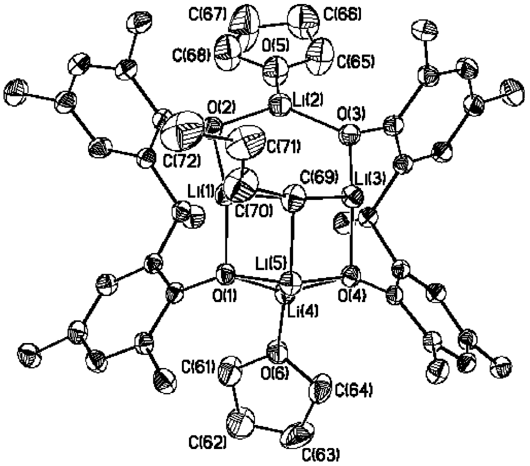


Figure 2. ORTEP drawing of **5** (methyl C atoms of the ^{t}Bu groups and all of the H atoms are omitted for clarity) with thermal ellipsoids drawn at the 20% probability level. Selected bond distances (Å): Li(1)−O(1) 1.956(6), Li(1)−O(2) 1.823(7), Li(1)−C(69) 2.201(7), Li(2)−O(2) 1.866(7), Li(2)−O(3) 1.854(7), Li(2)−O(5) 1.948(7), Li(3)−O(3) 1.804(6), Li(3)−O(4) 1.913(6), Li(3)−C(69) 2.200(7), Li(4)−O(1) 1.888(6), Li(4)−O(4) 1.934(6), Li(4)−O(6) 1.931(6), Li(5)−O(1) 1.904(6), Li(5)−O(4) 1.876(6), Li(5)−C(69) 2.179(7).

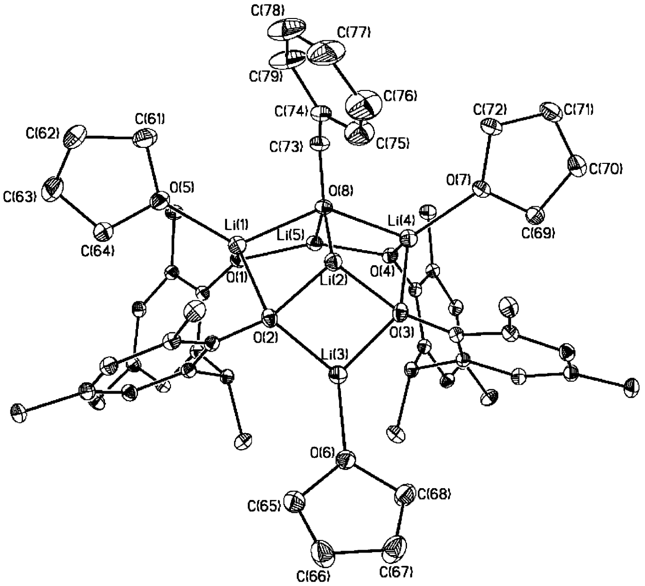


Figure 3. Molecular structure of **6** (methyl C atoms of the ^{t}Bu groups and all of the H atoms are omitted for clarity) with thermal ellipsoids drawn at the 20% probability level. Selected bond distances (Å): Li(1)−O(1) 1.850(6), Li(1)−O(2) 2.243(6), Li(1)−O(5) 2.016(6), Li(1)−O(8) 2.106(6), Li(2)−O(2) 1.824(6), Li(2)−O(3) 1.832(6), Li(2)−O(8) 1.878(6), Li(3)−O(2) 1.908(6), Li(3)−O(3) 1.909(6), Li(3)−O(6) 1.897(6), Li(4)−O(3) 2.308(6), Li(4)−O(4) 1.861(6), Li(4)−O(7) 1.977(6), Li(4)−O(8) 2.075(6), Li(5)−O(1) 1.825(6), Li(5)−O(4) 1.843(6), Li(5)−O(8) 2.015(6).

The molecular structures of **6** and **7** are shown in Figures 3 and 4, respectively. According to the X-ray structure, the LiOBn/EDBPLi$_2$/THF ratio in **6** is 1:2:3. The Li$_5$ complex **6** contains four kinds of Li atoms. Among them, the two tetracoordinated Li atoms are chemically equivalent while the three tricoordinated Li atoms are not. Each of the tetracoordinated Li atoms Li(1) and Li(4) is bonded by two O atoms of the same EDBP ligand, one OBn group, and one THF molecule. Li(2) and Li(5) are both coordinated to two O atoms of different EDBP ligands and one OBn group; Li(3) is bonded to two different EDBP O atoms and one THF molecule. Two O atoms of the EDBP ligands are doubly bridging, and the others are triply bridging. It is worth noting that the O atom of the OBn group, O(8), is bridging four Li cations, Li(1), Li(2), Li(4), and Li(5), with an average Li−

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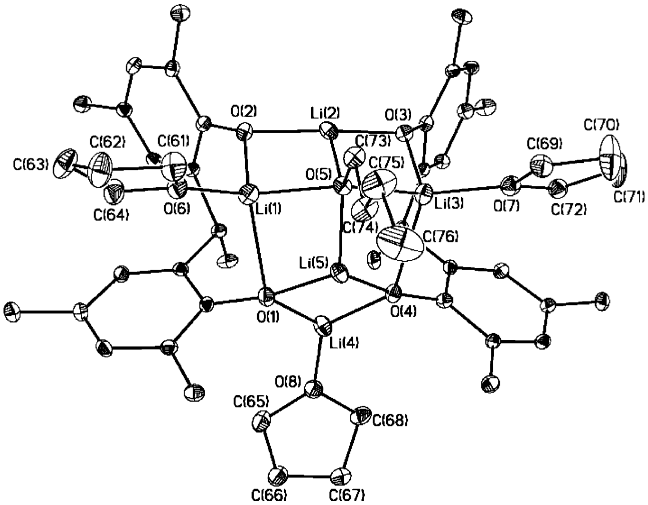

Figure 4. Molecular structure of **7** (methyl C atoms of the ^{t}Bu groups and all of the H atoms are omitted for clarity) with thermal ellipsoids drawn at the 10% probability level. Selected bond distances (Å): Li(1)−O(1) 2.341(14), Li(1)−O(2) 1.873(11), Li(1)−O(5) 2.034(12), Li(1)−O(6) 2.015(11), Li(2)−O(2) 1.816(13), Li(2)−O(3) 1.860(13), Li(2)−O(5) 2.022(5), Li(3)−O(3) 1.871(11), Li(3)−O(4) 2.308(12), Li(3)−O(5) 2.093(10), Li(3)−O(7) 1.971(11), Li(4)−O(1) 1.903(11), Li(4)−O(4) 1.911(12), Li(4)−O(8) 1.891(6), Li(5)−O(1) 1.833(11), Li(5)−O(4) 1.792(12), Li(5)−O(5) 1.880(6).

O(8) bond distance of 2.019(6) Å, which is much longer than the Li−O(3) [1.894(6) Å] and Li−O(4) [1.898(6) Å] bond distances observed for other triply bridging OBn groups in complex **2**. To the best of our knowledge, only a few examples of Li complexes with a quarterly bridged alkoxide O atom have been reported.[14] Coordination of THF molecules to Li atoms results in a Li(1)−O(5) bond distance of 2.016(6) Å, a Li(3)−O(6) bond distance of 1.897(6) Å, and a Li(4)−O(7) bond distance of 1.977(6) Å, respectively. As expected, the O(6)−Li(3) (tricoordinated Li) bond distance is notably shorter than the O(5)−Li(1) and O(7)−Li(4) (tetracoordinated Li) bond distances. Complex **7** differs from complex **6** only in the replacement of the OBn group with a O^{n}Bu group. The average Li−O(5) (μ_4-O^{n}Bu) bond distance is 2.007(8) Å. The bond distances Li(1)−O(6) (THF) at 2.015(11) Å, Li(4)−O(8) (THF) at 1.891(6) Å, and Li(3)−O(7) (THF) at 1.971(11) Å are all similar to the values observed for complex **6**. The molecular structure of **8** (Figure 5) obtained by X-ray diffraction is similar to that of **6**, except that the OBn group is replaced by a OCH_2CH_2OEt group and the O atom of the ethoxy group, O(6), is coordinated to one more Li atom, Li(5). This bonding makes Li(5) tetracoordinated, with a Li(5)−O(6) bond distance of 2.183(7) Å.

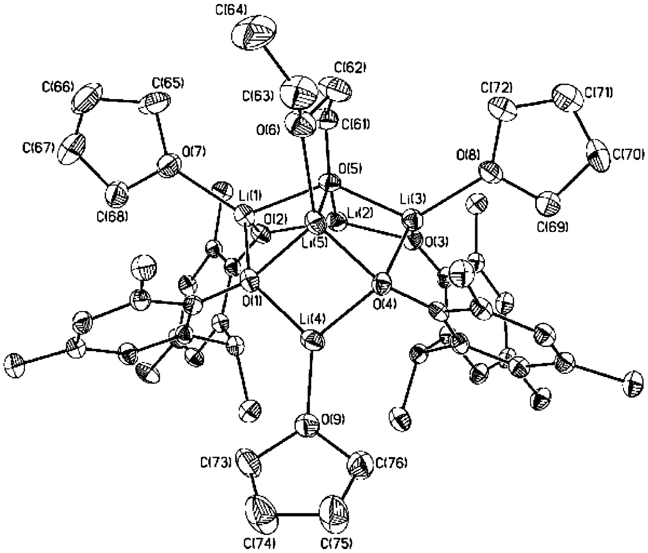

Figure 5. ORTEP drawing of **8** (methyl C atoms of the ^{t}Bu groups and all of the H atoms are omitted for clarity) with thermal ellipsoids drawn at the 20% probability level. Selected bond distances (Å): Li(1)−O(1) 2.141(7), Li(1)−O(2) 1.874(6), Li(1)−O(5) 2.076(7), Li(1)−O(7) 2.015(7), Li(2)−O(2) 1.839(6), Li(2)−O(3) 1.825(6), Li(2)−O(5) 1.965(6), Li(3)−O(3) 1.873(6), Li(3)−O(4) 2.202(7), Li(3)−O(5) 2.016(7), Li(3)−O(8) 2.033(7), Li(4)−O(1) 1.895(7), Li(4)−O(4) 1.891(7), Li(4)−O(9) 1.940(7), Li(5)−O(1) 1.913(7), Li(5)−O(4) 1.918(7), Li(5)−O(5) 1.900(7), Li(5)−O(6) 2.183(7).

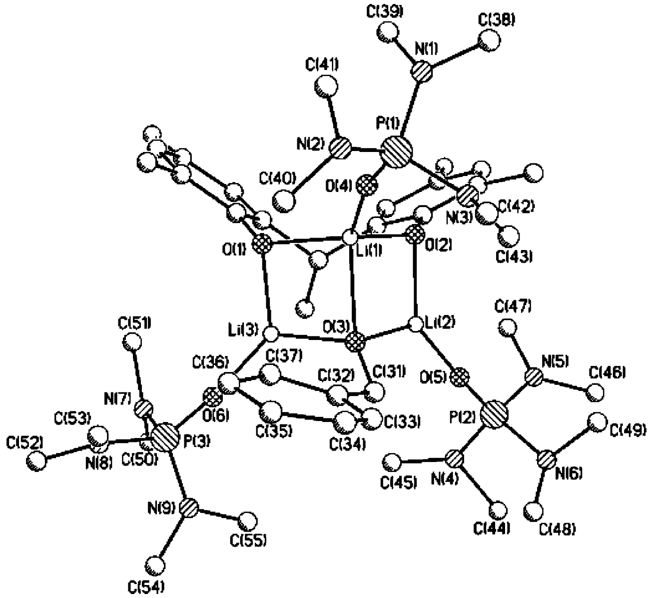

Figure 6. Molecular structure of **9** (methyl C atoms of the ^{t}Bu groups and all of the H atoms are omitted for clarity). Selected bond distances (Å): Li(1)−O(1) 1.932(7), Li(1)−O(2) 1.922(7), Li(1)−O(3) 2.116(7), Li(1)−O(4) 1.900(7), Li(2)−O(2) 1.873(8), Li(2)−O(3) 1.849(7), Li(2)−O(5) 1.818(7), Li(3)−O(1) 1.861(7), Li(3)−O(3) 1.841(8), Li(3)−O(6) 1.838(8).

In the solid state, complex **9**, which contains two different types of Li atoms, consists of one lithium bis(phenoxide), one LiOBn, and three HMPA molecules (Figure 6). Tricoordinated Li cations Li(2) and Li(3) are both bound to a phenyl O atom of the EDBP ligand, a OBn group, and a molecule of HMPA. The tetracoordinated Li(1) is bound to two O atoms of the EDBP ligand, a OBn group, and a molecule of HMPA. The Li(1)−O(4) (HMPA), Li(2)−O(5) (HMPA), and Li(3)−O(6) (HMPA) bond distances are 1.900(7), 1.818(7), and 1.838(8) Å, respectively. Once again, the O(5)−Li(2) and O(6)−Li(3) (tricoordinated Li) bond distances are shorter than O(4)−Li(1) (tetracoordinated Li). The average Li−O(3) (triply bridging OBn) bond distance of 1.935(7) Å is longer than those of 1.894(6) and 1.898(6) Å observed in complex **2**. These results are consistent with our expectation that in complex **9** coordination of strong base HMPA to Li cations would cause their Lewis acidity of Li to decrease.

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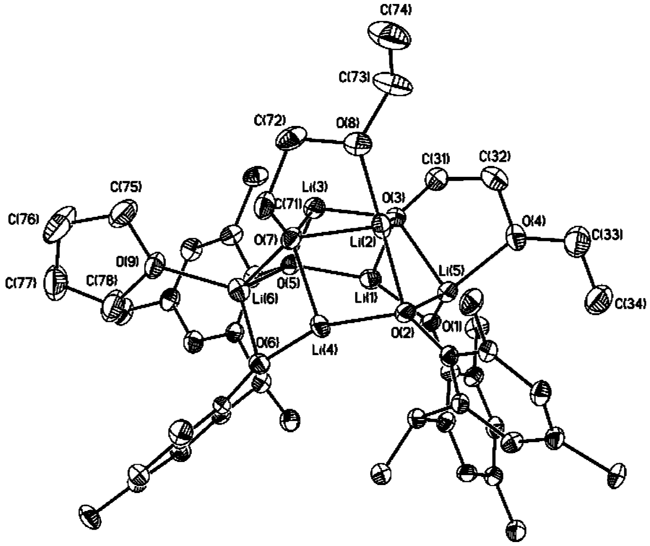

Figure 7. ORTEP drawing of **10** (methyl C atoms of the ^{t}Bu groups and all of the H atoms are omitted for clarity) with thermal ellipsoids drawn at the 20% probability level. Selected bond distances (Å): Li(1)−O(1) 1.777(10), Li(1)−O(3) 2.049(12), Li(1)−O(5) 1.876(10), Li(2)−O(2) 1.954(11), Li(2)−O(3) 1.953(11), Li(2)−O(7) 1.980(10), Li(2)−O(8) 2.047(12), Li(3)−O(3) 1.878(10), Li(3)−O(5) 1.836(12), Li(3)−O(7) 1.875(12), Li(4)−O(2) 1.866(10), Li(4)−O(6) 1.749(10), Li(4)−O(7) 2.011(11), Li(5)−O(1) 1.870(11), Li(5)−O(2) 2.046(10), Li(5)−O(3) 2.067(10), Li(5)−O(4) 1.965(12), Li(6)−O(5) 2.118(11), Li(6)−O(6) 1.863(10), Li(6)−O(7) 2.010(11), Li(6)−O(9) 1.963(11).

The ORTEP drawing of compound **10** is depicted in Figure 7. As determined by X-ray structure analysis, the hexanuclear Li aggregate **10** contains three tricoordinated and three tetracoordinated Li atoms. In contrast to the tricoordinated Li atoms, the tetracoordinated Li atoms Li(2), Li(5), and Li(6) are additionally coordinated by O atoms of the ethoxy group O(8) and O(4) and the THF oxygen O(9), with a Li(2)−O(8) bond distance of 2.047(12) Å, a Li(5)−O(4) bond distance of 1.965(12) Å, and a Li(6)−O(9) bond distance of 1.963(11) Å. It was found that there are two doubly bridging [O(1) and O(6)], two triply bridging [O(2) and O(5)], and two quadruply bridging [O(3) and O(7)] O atoms. The average bond distances Li−O(3) (μ_4-OCH_2CH_2OEt) [1.987(11) Å] and Li−O(7) (μ_4-OCH_2CH_2OEt) [1.967(11) Å] are longer than those of Li−O(3) (μ_3-OCH_2CH_2OEt) [1.901(9) Å] and Li−O(4) (μ_3-OCH_2CH_2OEt) [1.915(9) Å] of triply bridging OCH_2CH_2OEt groups in complex **3**.

The molecular structure of complex **11** shows that it is an ionic compound composed of $LiOCH_2CH_2OEt$, $EDBPLi_2$, and HMPA in a 1:2:5 ratio. As can be seen, the anionic part consists of one $LiOCH_2CH_2OEt$, two $EDBPLi_2$, and one HMPA molecules (Figure 8). Except for the O atom of the OCH_2CH_2OEt group that is quadruply bridging, the EDBP O atoms are doubly bridging. The average Li−O(5) (μ_4-OCH_2CH_2OEt) bond distance of 1.973(11) Å is similar to the values observed in complex **10**. Coordination of HMPA to tetracoordinated Li atom Li(3) results in a Li(3)−O(7) (HMPA) bond distance of 1.942(10) Å, which is slightly longer than the Li(1)−O(4) (HMPA) bond distance of 1.900(7) Å in the neutral complex **9**. In the cationic portion, Li(5) is coordinated by four HMPA molecules, resulting in a distorted tetrahedral arrangement with an average Li(5)−O (HMPA) bond distance of 1.893(12) Å.

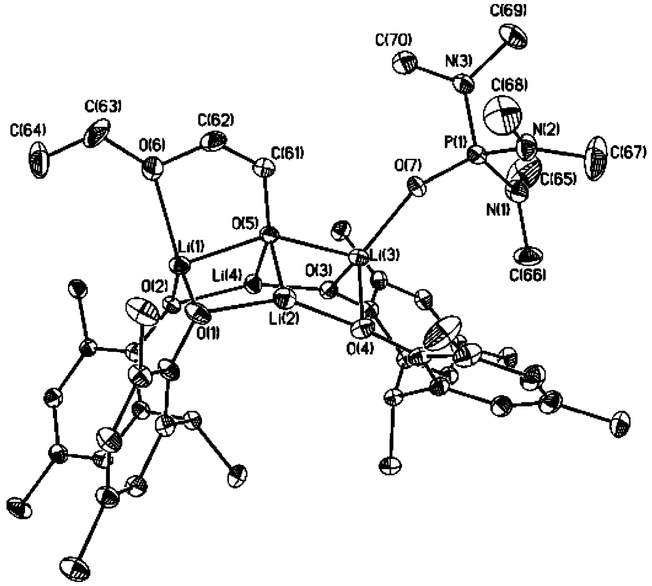

Figure 8. Molecular structure of $[(\mu_2,\mu_2\text{-EDBP})_2Li_4(\mu_4\text{-}OCH_2CH_2OEt)(HMPA)]^-$ (methyl C atoms of the ^{t}Bu groups and all of the H atoms are omitted for clarity) with thermal ellipsoids drawn at the 10% probability level. Selected bond distances (Å) and bond angles (deg): Li(1)−O(1) 1.878(11), Li(1)−O(2) 1.883(11), Li(1)−O(5) 1.998(11), Li(1)−O(6) 2.091(11), Li(2)−O(1) 1.859(13), Li(2)−O(4) 1.793(13), Li(2)−O(5) 1.889(12), Li(3)−O(3) 1.975(11), Li(3)−O(4) 2.012(10), Li(3)−O(5) 2.038(11), Li(3)−O(7) 1.942(10), Li(4)−O(2) 1.851(11), Li(4)−O(3) 1.798(11), Li(4)−O(5) 1.967(10), Li(5)−O(8) 1.892(12), Li(5)−O(9) 1.883(13), Li(5)−O(10) 1.896(12), Li(5)−O(11) 1.900(12); O(8)−Li(5)−O(9) 112.1(6), O(8)−Li(5)−O(10) 111.3(6), O(8)−Li(5)-O(11) 107.3(6), O(9)−Li(5)−O(10) 106.6(6), O(9)−Li(5)−O(11) 111.7(6), O(10)−Li(5)−O(11) 107.8(6).

ROP of L-Lactide Using Complex 8 as an Initiator. As the depletion of petrochemical feedstock draws near, the demand for the production of useful and environmentally friendly polymers is increasing for a sustainable future. Recently, poly(lactides) have attracted a great deal of interest because of their utility in the preparation of biocompatible and biodegradable materials with a wide range of applications. Metal alkoxides have been used as effective initiators for lactide polymerization, giving polymers with high molecular weights in high yields.[15−20] A bulky ligand such as EDBP has been used in our group for the preparation of the catalyst/initiator with a single active site for ROP of lactide

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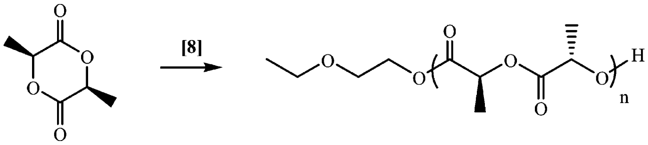
Table 1. ROP of L-Lactide Initiated by Compound **8** (0.05 mmol, 3 h in CH_2Cl_2 (15 mL) at 0 °C)



entry	$[M]_0/[\mathbf{8}]_0$	PDI	M_n(obsd)[a]	M_n (NMR)[b]	CY (%)
1	50	1.06	5200 (3000)	2800	96
2	75	1.07	7600 (4400)	3900	91
3	100	1.07	10800 (6300)	4900	94
4	150	1.06	15600 (9000)	9600	93

[a] Obtained from GPC analysis and calibrated by a polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58.[22] [b] Obtained from ^1H NMR analysis.

and lactones.[21] The ROP of L-lactide by **8** (0.05 mmol) as an initiator was systematically examined in CH_2Cl_2 (15 mL) at 0 °C, as shown in Table 1. It was found that polymerization of L-lactides proceeded smoothly, and complex **8** acted as an efficient initiator for the ROP of L-lactide. Conversion of L-lactide reached more than 91% within 3 h (entries 1−4). However, the polydispersity indexes (PDIs) of poly(L-lactide)s (PLLAs) obtained at 0 °C were quite low, ranging from 1.06 to 1.07, and a linear relationship between the number-average molecular weight (M_n) and the monomer-to-initiator ratio (M_0/I_0) was observed. The ^1H NMR spectrum of PLLA reveals the presence of one CH_2CH_2OEt ester and one hydroxy chain end with the $H_e/H_f/H_g/H_{d+h}$ ratio of 3:2:2:3, suggesting that an initiation occurs through insertion of the OCH_2CH_2OEt group from compound **8** into L-lactide. Furthermore, the homonuclear decoupled ^1H NMR spectrum reveals only one resonance at δ 5.16 ppm in the methine region, indicating that epimerization of the chiral centers in PLLA did not occur.

In conclusion, we have discovered several novel Li aggregates. Their structures have been elucidated by spectroscopic techniques as well as X-ray diffraction. It is interesting to note that, in the presence of Lewis basic solvents such as THF and HMPA, hexanuclear Li complexes (**1**−**4**) engender rearrangement and solvation to yield various kinds of solvated Li aggregates, with their nuclearities being dramatically dependent on the basicity of the solvent. Treatment of **5** with a variety of alcohols in THF gives pentalithium alkoxide complexes (**6**−**8**) by simple displacement of the alkyl group with an alkoxy group without drastic changes in its skeleton. Experimental results also show that compound **8** efficiently initiates the ROP of L-lactide with a narrow PDI. Studies are presently underway to investigate the use of alternative solvent systems as well as anions that carry covalently attached Lewis basic sites.

Experimental Section

General Procedures. All manipulations were performed under a dry N_2 atmosphere using standard Schlenk techniques. All glassware was flame-dried under vacuum before use. Solvents were dried and degassed according to established literature precedents and then stored over 4-Å molecular sieves before use. L-Lactide, *n*-butanol, benzyl alcohol, 2-ethoxyethanol, hexamethylphosphoramide (HMPA), and deuterated solvents were purified before use. 2,2′-Ethylidenebis(4,6-di-*tert*-butylphenol) (EDBP) and ^{n}BuLi (2.5 M in hexane) were used as purchased. $[(\mu_3,\mu_3\text{-EDBP})Li_2]_2[(\mu_3\text{-}^n\text{Bu})Li(0.5Et_2O)]_2$ (**1**) and $[(\mu_3,\mu_3\text{-EDBP})Li_2]_2[(\mu_3\text{-OR})Li]_2$ [R = Bn (**2**) and CH_2CH_2OEt (**3**)] were prepared according to the reported method.[11a] ^1H NMR spectra were recorded on a Varian Mercury-400 (400 MHz) or a Varian Gemini-200 (200 MHz) spectrometer with chemical shifts given in ppm from the internal tetramethylsilane. Microanalyses were performed using a Heraeus CHN−O−RAPID instrument. IR spectra were obtained on a Bruker Equinox 55 spectrometer. The gel permeation chromatography (GPC) measurements were performed on a Hitachi L-7100 system equipped with a differential Bischoff 8120 RI detector using THF (high-performance liquid chromatography grade) as an eluent. Molecular weight and molecular weight distributions were calculated by using polystyrene as the standard. (***Caution!*** *HMPA is a carcinogenic material*.)

$[(\mu_3,\mu_3\text{-EDBP})Li_2]_2[(\mu_3\text{-O}^n\text{Bu})Li]_2$ (4). *n*-Butanol (0.18 mL, 2.0 mmol) was added slowly to an ice cold solution (0 °C) of **1** (1.10 g, 1.0 mmol) in toluene (20 mL). The mixture was stirred for 2 h and then dried in vacuo. The residue was extracted with 25 mL of hexane, and the extract was then concentrated to ca. 5 mL and cooled to −20 °C, giving a white crystalline solid. Yield: 0.82 g (77%). Crystals suitable for X-ray structure determination were obtained from a saturated hexane solution at room temperature. Anal. Calcd for $C_{68}H_{106}O_6Li_6$: C, 76.96; H, 10.07. Found: C, 76.45; H, 10.26. ^1H NMR (−20 °C, $CDCl_3$, ppm): δ 7.51 (d, 2H, Ph, J = 2.4 Hz); 7.23 (d, 2H, Ph, J = 2.4 Hz); 7.22 (d, 2H, Ph, J = 2.4 Hz); 7.02 (d, 2H, Ph, J = 2.4 Hz); 5.64 (q, 2H, $C\mathit{H}(CH_3)$, J = 7.2 Hz); 3.68, 3.60 (m, 4H, $OC\mathit{H}_2CH_2CH_2CH_3$); 1.54 (d, 3H, $CH(C\mathit{H}_3)$, J = 7.2 Hz); 1.48, 1.38, 1.29, 1.20 (s, 72H, ^{t}Bu); 1.42 (br, 4H, $OCH_2C\mathit{H}_2CH_2CH_3$); 1.27 (br, 4H, $OCH_2CH_2C\mathit{H}_2CH_3$); 0.87 (t, 6H, $OCH_2CH_2CH_2C\mathit{H}_3$). IR (KBr, cm^{-1}): 3492.4 (m), 2960.9 (s), 2906.5 (s), 2870.3 (s), 1618.7 (m), 1475.6 (s), 1466.4 (s), 1438.9 (s), 1414.7 (m), 1389.3 (m), 1361.4 (s), 1293.2 (s), 1263.3 (s), 1235.0 (s), 1199.8 (m), 880.4 (m), 829.7 (m), 745.7 (m), 531.1 (s). Mp: 142−144 °C (dec).

$[(\mu_2,\mu_3\text{-EDBP})_2Li_4(THF)_2][(\mu_3\text{-}^n\text{Bu})Li]$ (5). THF (0.48 mL, 6.0 mmol) was added slowly to a solution of **1** (2.20 g, 2 mmol) in 15 mL of toluene. The mixture was stirred for 1 h and evaporated to dryness in vacuo. The residue was extracted with 20 mL of hexane, and the extract was concentrated to a saturated solution followed by cooling to −20 °C to give colorless crystals. Yield: 1.37 g (62%). Anal. Calcd for $C_{72}H_{113}O_6Li_5$: C, 77.95; H, 10.27. Found: C, 78.27; H, 10.32. ^1H NMR (C_6D_6, ppm): δ 7.69 (d, 4H, Ph, J = 2.8 Hz); 7.34 (d, 4H, Ph, J = 2.8 Hz); 5.60 (q, 2H, $C\mathit{H}(CH_3)$, J = 7.2 Hz); 2.88 (m, 8H, $OC\mathit{H}_2CH_2$); 1.80 (d, 6H, $CH(C\mathit{H}_3)$, J = 7.2 Hz); 1.60, 1.52, 1.50, 1.49, 1.45, 1.42 (s, 72H, $C(C\mathit{H}_3)_3$); 1.35 (m, 2H, $CH_2C\mathit{H}_2CH_2CH_3$); 1.23 (m, 2H, CH_2-

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(22) M_n(GPC) is multiplied by a factor of 0.58, giving the actual M_n of poly(lactide). Baran, J.; Duda, A.; Kowalski, A.; Szymanski, R.; Penczek, S. *Macromol. Rapid Commun.* **1997**, *18*, 325.

CH$_2$C*H*$_2$CH$_3$); 1.05 (m, 8H, OCH$_2$C*H*$_2$); 0.86 (t, 3H, CH$_2$CH$_2$CH$_2$C*H*$_3$); −0.24 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$). IR (KBr, cm^{-1}): 3490.8 (m), 2959.3 (s), 2906.0 (s), 2871.4 (s), 1620.4 (m), 1475.9 (s), 1439.3 (s), 1415.6 (m), 1388.9 (m), 1361.3 (s), 1294.3 (s), 1264.4 (s), 1236.1 (s), 1200.3 (m), 1046.2 (m), 879.4 (m), 830.3 (m), 785.3 (m), 538.8 (s). Mp: 131−133 °C (dec).

[(μ_2,μ_3-EDBP)$_2$Li$_4$(THF)$_3$][(μ_4-OBn)Li] (6). THF (10 mL) was added slowly to **2** (1.13 g, 1.0 mmol). The mixture was stirred for 1 h at room temperature and evaporated to dryness under vacuum. The residue was extracted with 50 mL of hot hexane, and the extract was concentrated to ca. 15 mL and cooled to −20 °C to give a white crystalline solid. Yield: 1.02 g (83%). X-ray quality crystals were grown from a hot saturated hexane solution. Anal. Calcd for $C_{79}H_{119}O_8Li_5$: C, 77.05; H, 9.74. Found: C, 76.65; H, 9.38. ^{1}H NMR (CDCl$_3$, ppm): δ 7.34 (d, 4H, Ph, *J* = 2.8 Hz); 6.98 (d, 4H, Ph, *J* = 2.8 Hz); 7.19−7.32 (m, 5H, Ph); 5.26 (q, 2H, C*H*(CH$_3$), *J* = 6.8 Hz); 4.81 (s, 2H, OC*H*$_2$Ph); 3.04 (m, 12H, OC*H*$_2$CH$_2$, *J* = 2.8 Hz); 1.55 (m, 12H, OCH$_2$C*H*$_2$, *J* = 2.8 Hz); 1.48 (d, 6H, CH(C*H*$_3$), *J* = 6.8 Hz); 1.3, 1.23 (s, 72H, C(C*H*$_3$)$_3$). IR (KBr, cm^{-1}): 3489.9 (m), 2959.1 (s), 2904.3 (s), 2874.0 (s), 1626.5 (m), 1464.5 (s), 1437.1 (s), 1415.9 (s), 1386.4 (s), 1360.3 (s), 1333.6 (m), 1299.5 (s), 1265.5 (s), 1234.4 (s), 1199.4 (s), 1141.1 (m), 1047.1 (s), 1028.2 (s), 903.9 (m), 879.6 (s), 834.9 (s), 785.6 (s), 748.5 (m), 681.5 (m), 603.6 (m), 533.7 (s), 467.9 (s). Mp: 146−148 °C (dec).

[(μ_2,μ_3-EDBP)$_2$Li$_4$(THF)$_3$][(μ_4-O^{n}Bu)Li] (7). THF (10 mL) was added slowly to **4** (1.06 g, 1.0 mmol). The mixture was stirred for 1 h at room temperature and evaporated to dryness in vacuo. The residue was extracted with 50 mL of hot hexane, and the extract was concentrated to ca. 10 mL and cooled to −20 °C to furnish a white crystalline solid. Yield: 0.86 g (72%). Crystals suitable for X-ray structure determination were obtained from a hot hexane solution. Anal. Calcd for $C_{76}H_{121}O_8Li_5$: C, 76.23; H, 10.18. Found: C, 75.84; H, 10.11. ^{1}H NMR (CDCl$_3$, ppm): δ 7.33 (d, 4H, Ph, *J* = 2.0 Hz); 6.99 (d, 4H, Ph, *J* = 2.0 Hz); 5.18 (q, 2H, C*H*(CH$_3$), *J* = 7.2 Hz); 3.65 (t, 2H, OC*H*$_2$CH$_2$CH$_2$CH$_3$, *J* = 6.8 Hz); 3.13 (m, 12H, OC*H*$_2$CH$_2$, *J* = 3.2 Hz); 1.59 (m, 12H, OCH$_2$C*H*$_2$); 1.49 (d, 6H, CH(C*H*$_3$), *J* = 7.2 Hz); 1.35 (m, 2H, OCH$_2$C*H*$_2$CH$_2$CH$_3$); 1.21 (m, 2H, OCH$_2$CH$_2$C*H*$_2$CH$_3$)); 1.39, 1.23 (s, 72H, C(C*H*$_3$)$_3$); 0.88 (t, 2H, OCH$_2$CH$_2$CH$_2$C*H*$_3$, *J* = 7.2 Hz). IR (KBr, cm^{-1}): 3488.0 (m), 2955.3 (s), 2905.4 (s), 2871.4 (s),

Table 2. Crystallographic Data of the Structure Determination of **4**−**11**

	4	**5**	**6**	**7**
empirical formula	$C_{68}H_{106}Li_6O_6$	$C_{72}H_{113}Li_5O_6$	$C_{79}H_{119}Li_5O_8$	$C_{76}H_{121}Li_5O_8$
fw	1061.16	1109.32	1231.44	1197.43
cryst syst	monoclinic	triclinic	monoclinic	orthorhombic
space group	*C*2/*c*	$P\bar{1}$	*P*2(1)/*n*	*P*2(1)2(1)2(1)
a/Å	11.1282(13)	13.6331(14)	13.5458(7)	13.6569(9)
b/Å	24.288(3)	14.5892(16)	19.4938(10)	19.4510(13)
c/Å	25.495(3)	19.921(2)	29.5675(15)	29.4656(18)
α/deg	90	69.698(2)	90	90
β/deg	99.113(2)	80.975(2)	91.8430(10)	90
γ/deg	90	79.289(2)	90	90
V/Å^3	6804.0(14)	3633.0(7)	7803.5(7)	7827.3(9)
Z	4	2	4	4
D$_{calcd}$/(Mg/m^3)	1.036	1.014	1.048	1.016
abs coeff/mm^{-1}	0.062	0.061	0.064	0.062
F(000)	2320	1216	2688	2624
reflns collected	19 167	20 712	43 796	44 560
indep reflns	6698 [*R*(int) = 0.0518]	14081 [*R*(int) = 0.0367]	15333 [*R*(int) = 0.0536]	15288 [*R*(int) = 0.0516]
data/restraints/param	6698/0/361	14081/0/754	15333/0/829	8000/0/803
R1^a	0.0873	0.0793	0.0779	0.0593
wR2^b	0.2522	0.2020	0.2221	0.1530
GOF^c	1.161	1.039	1.067	1.043
min, max residual density/(e/Å^3)	0.450, −0.236	0.465, −0.296	0.444, −0.325	0.441, −0.229

	8	**9**	**10**	**11**
empirical formula	$C_{76}H_{121}Li_5O_9$	$C_{55}H_{105}Li_3N_9O_6P_3$	$C_{72}H_{114}Li_6O_9$	$C_{94}H_{187}Li_5N_{15}O_{11}P_5$
fw	1213.43	1102.21	1165.27	1893.14
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	*P*2(1)/*n*	$P\bar{1}$	*Cc*	*P*2(1)/*c*
a/Å	13.4259(7)	11.3654(9)	22.535(2)	21.8309(19)
b/Å	19.2911(10)	13.9750(10)	19.1567(18)	24.2606(19)
c/Å	29.6849(16)	22.8886(18)	18.9544(18)	23.288(2)
α/deg	90	79.727(2)	90	90
β/deg	92.5030(10)	78.357(2)	114.063(2)	96.353(2)
γ/deg	90	84.433(2)	90	90
V/Å^3	7681.1(7)	3496.5(5)	7471.5(12)	12258.4(18)
Z	4	2	4	4
D$_{calcd}$/(Mg/m^3)	1.049	1.047	1.036	1.026
abs coeff/mm^{-1}	0.065	0.132	0.065	0.128
F(000)	2656	1200	2544	4136
reflns collected	43 415	20 007	21 050	64 009
indep reflns	15087 [*R*(int) = 0.0962]	13572 [*R*(int) = 0.0406]	12915 [*R*(int) = 0.0720]	21556 [*R*(int) = 0.2304]
data/restraints/param	15 087/0/812	13 572/0/685	12 915/0/785	21 556/0/1180
R1^b	0.0679	0.0849	0.0583	0.0757
wR2^c	0.1455	0.2116	0.0893	0.1338
GOF^d	1.078	1.079	0.960	1.063
min, max residual density/e Å^{-3}	0.471, −0.313	0.599, −0.386	0.213, −0.239	0.302, −0.210

[a] $R1 = |\Sigma(|F_o| - |F_c|)/\Sigma|F_o||$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = 0.10$. [c] $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(N_{rflns} - N_{papams})]^{1/2}$.

1617.5 (m), 1476.0 (s), 1439.8 (s), 1415.6 (m), 1388.8 (m), 1361.2 (s), 1294.6 (s), 1264.4 (s), 1236.0 (s), 1200.5 (s), 1156.9 (m), 1047.5 (s), 904.9 (s), 829.9 (s), 747.3 (s), 699.1 (s), 597.3 (s), 526.1 (s). Mp: 150−152 °C (dec).

[(μ_2,μ_3-EDBP)$_2$Li$_4$(THF)$_3$][(μ_4-OCH$_2$CH$_2$OEt)Li] (8). A *n*-BuLi solution (8.0 mL, 2.5 M in hexane, 20.0 mmol) was slowly added to a mixture of EDBP (3.52 g, 8.0 mmol), 2-ethoxyethanol (0.38 mL, 4 mmol), and THF (0.96 mL, 12 mmol) in toluene (20 mL) at 0 °C. The mixture was stirred for 1 h at room temperature and evaporated to dryness under vacuum. The residue was washed twice with 10-mL portions of hexane, and the precipitate was dried in vacuo to give a white solid. Yield: 3.13 g (65%). X-ray-quality crystals were grown from a hot saturated hexane solution. Anal. Calcd for $C_{76}H_{121}O_9Li_5$: C, 75.22; H, 10.05. Found: C, 75.44; H, 9.96. ^{1}H NMR (CDCl$_3$, ppm): δ 7.29 (d, 4H, Ph, J = 2.4 Hz); 6.99 (d, 4H, Ph, J = 2.4 Hz); 5.04 (q, 2H, C*H*(CH$_3$), J = 7.2 Hz); 3.97 (t, 2H, OC*H*$_2$CH$_2$OEt, J = 4.4 Hz); 3.48 (t, 2H, OCH$_2$C*H*$_2$-OEt, J = 7.2 Hz); 3.26 (m, 12H, OC*H*$_2$CH$_2$); 3.20 (q, 2H, OC*H*$_2$-CH$_3$, J = 7.2 Hz); 1.64 (m, 12H, OCH$_2$C*H*$_2$); 1.43 (d, 6H, CH(C*H*$_3$), J = 7.2 Hz); 1.40, 1.23 (s, 72H, C(C*H*$_3$)$_3$); 0.29 (t, 3H, OCH$_2$C*H*$_3$, J = 7.2 Hz). IR (KBr, cm^{-1}): 2960.3 (s), 2904.5 (s), 2868.5 (s), 1474.3 (s), 1439.0 (s), 1388.2 (m), 1360.3 (s), 1331.7 (m), 1300.3 (s), 1264.4 (s), 1232.8 (s), 1198.5 (m), 1120.0 (m), 1104.0 (s), 1082.2 (m), 1066.8 (m), 1041.9 (m), 905.3 (m), 877.8 (m), 831.2 (m), 803.9 (m), 784.7 (m), 577.0 (m), 534.9 (m). Mp: 180−182 °C (dec).

[(μ_2,μ_2-EDBP)Li$_2$(HMPA)$_2$][(μ_3-OBn)Li(HMPA)] (9). HMPA (1.05 mL, 6.0 mmol) was added slowly to a solution of **2** (1.13 g, 1.0 mmol) in toluene (20 mL). The final mixture was stirred for 1 h and evaporated to dryness under vacuum. The residue was extracted with 50 mL of hot hexane, and the extract was concentrated to ca. 5 mL and cooled to −20 °C to yield a white solid. Yield: 0.88 g (80%). Crystals suitable for X-ray diffraction were grown in a hot saturated hexane solution. Anal. Calcd for $C_{55}H_{105}N_9O_6P_3Li_3$: N, 11.65; C, 59.82; H, 9.54. Found: N, 11.44; C, 59.93; H, 9.60. ^{1}H NMR (C$_6$D$_6$, ppm): δ 7.32−7.86 (m, 9H, Ph); 5.77 (q, 1H, C*H*(CH$_3$), J = 7.2 Hz); 5.46 (s, 2H, OC*H*$_2$Ph); 2.22 (d, 54H, N(CH$_3$)$_2$, J_{H-P} = 9.2 Hz); 1.94 (d, 3H, CH(C*H*$_3$), J = 7.2 Hz); 1.89, 1.59 (s, 36H, C(C*H*$_3$)$_3$).

[(μ_2,μ_3-EDBP)$_2$Li$_4$(THF)][(μ_4-OCH$_2$CH$_2$OEt)Li]$_2$ (10). THF (0.24 mL, 3.0 mmol) was added slowly to a solution of **4** (1.09 g, 1.0 mmol) in 10 mL of toluene. The mixture was stirred for 1 h and evaporated to dryness in vacuo. The residue was extracted with 40 mL of hexane, and the extract was concentrated to ca. 10 mL and cooled to −20 °C to produce a white solid. Yield: 0.91 g (78%). Crystals suitable for X-ray diffraction were grown from a saturated hexane solution. Anal. Calcd for $C_{72}H_{114}O_9Li_6$: C, 74.21; H, 9.86. Found: C, 73.71; H, 9.28. ^{1}H NMR (CDCl$_3$, ppm): δ 6.98−7.39 (m, 8H, Ph); 5.57 (q, 2H, C*H*(CH$_3$)), 4.77 (br, 2H, C*H*(CH$_3$)); 3.76−3.95 (m, 4H, OC*H*$_2$CH$_2$OEt); 3.45 (m, 4H, OCH$_2$C*H*$_2$OEt); 3.43 (m, 4H, OC*H*$_2$CH$_2$); 3.16−3.32 (m, 4H, OC*H*$_2$CH$_3$); 1.70 (m, 4H, OCH$_2$C*H*$_2$); 1.46 (d, 6H, CH(C*H*$_3$), J = 6.8 Hz); 1.40, 1.30, 1.28, 1.25, 1.24, 1.20, 0.75 (s, 72H, C(CH$_3$)$_3$); 0.85 (t, 6H, OCH$_2$C*H*$_3$, J = 7.2 Hz). IR (KBr, cm^{-1}): 2958.8 (s), 2904.4 (s), 2868.4 (s), 1472.5 (s), 1439.0 (s), 1388.3 (m), 1360.0 (s), 1300.9 (s), 1265.0 (s), 1232.6 (s), 1198.4 (m), 1120.0 (s), 1104.2 (s), 1082.4 (m), 1066.8 (m), 1041.6 (m), 905.5 (m), 877.8 (m), 831.5 (m), 804.1 (m), 784.7 (m), 751.2 (m), 634.9 (m), 577.0 (m), 537.0 (m). Mp: 170−172 °C (dec).

[(μ_2,μ_2-EDBP)$_2$Li$_4$(μ_4-OCH$_2$CH$_2$OEt)(HMPA)][Li-(HMPA)$_4$] (11). HMPA (1.05 mL, 6.0 mmol) was added slowly to a solution of **3** (1.09 g, 1.0 mmol) in toluene (20 mL). The mixture was stirred for 1 h and evaporated to dryness under vacuum. The residue was extracted with 50 mL of hot hexane, and the extract was concentrated to ca. 10 mL and cooled to −20 °C to yield a white solid. Yield: 1.18 g (62%). Crystals suitable for X-ray diffraction were grown from a saturated hexane solution. Anal. Calcd for $C_{94}H_{187}N_{15}O_{11}P_5Li_5$: N, 11.10; C, 59.64; H, 9.96. Found: N, 11.70; C, 59.49; H, 9.38. ^{1}H NMR (C$_6$D$_6$, ppm): δ 6.91−7.13 (m, 8H, Ph); 5.14 (q, 2H, C*H*(CH$_3$), J = 7.2 Hz); 3.86 (br, 2H, OC*H*$_2$-CH$_2$OEt); 3.08 (br, 2H, OC*H*$_2$CH$_3$); 2.58 (d, 90H, N(CH$_3$)$_2$, J_{H-P} = 8.8 Hz); 1.49 (d, 6H, CH(C*H*$_3$), J = 7.2 Hz); 1.40, 1.19 (s, 72H, C(C*H*$_3$)$_3$); 0.21 (br, 3H, OCH$_2$C*H*$_3$).

Polymerization of L-Lactide Initiated by 8. A typical polymerization procedure is exemplified by the synthesis of PLLA-50 (the number 50 indicates the designed [LA]$_0$/[**8**]$_0$) at 0 °C. The conversion yield (96%) of PLLA-50 was analyzed by ^{1}H NMR spectroscopic studies. To a rapidly stirred solution of **8** (0.06 g, 0.05 mmol) in dichloromethane (5 mL) was added a solution of l-lactide (0.36 g, 2.5 mmol) in dichloromethane (10 mL). The reaction mixture was stirred at 0 °C for 3 h, during which time an increase in the viscosity was observed. The mixture was then quenched by the addition of an aqueous acetic acid solution (0.35 N, 10 mL), and the polymer was precipitated as a white solid by pouring the mixture into *n*-hexane (50 mL). Yield: 0.26 g (72%).

X-ray Crystallographic Studies. Suitable crystals of **4**−**11** were sealed in thin-walled glass capillaries under a N$_2$ atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing ω (width of 0.3° per frame). The absorption correction was based on symmetry-equivalent reflections using the *SADABS* program. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct methods using a *SHELXTL* package. All non-H atoms were located from successive Fourier maps, and H atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Crystallographic data are given in Table 2.

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Supporting Information Available: Further details of the crystal structure determination of **4**−**11** (CIF), the polymerization of L-lactide initiated by **8** in CH$_2$Cl$_2$ at 0 °C (Figure S1), and the ^{1}H NMR spectrum of PLLA-100 initiated by **8** (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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