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Synthesis, Characterization, and Catalytic Studies of (Aryloxido)magnesium Complexes

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The reaction of $MgBu_2$ with 1 equiv. of four-coordinating (*R*)- or *rac*-*N*,*N*-bis(3,5-di-*tert*-butylbenzyl-2-hydroxy)tetrahydrofurfurylamine (*R*/*rac*-bpthfa-H_2) gave dinuclear homoleptic [Mg(μ-*R*/*rac*-bpthfa)]$_2$ (*R*/*rac*-**2c**) as white powders in 54–67 % yields. Analogous reactions of $MgBu_2$ with 2 equiv. of two-coordinating *N*-(3,5-di-*tert*-butylbenzyl-2-hydroxy)-*N*-methylcyclohexanamine (tbpca-H; **1e**-H) and (*S*)-*N*-(3,5-di-*tert*-butylbenzyl-2-hydroxy)-*N*,α-dimethylbenzylamine (*S*-tbpmpa-H; *S*-**1f**-H) gave white crystals of homoleptic mononuclear compounds of general formula [Mg(L)$_2$] (**2e** and *S*-**2f**) in 87–89 % yields. The resulting aminophenolates were characterized by spectroscopic methods and, in the case of *R*-**2c** and *S*-**2f**, by X-ray crystallography. The new complexes *R*/*rac*-**2c**, **2e**, and *S*-**2f**, as well as the previously described homo- and heteroleptic tetranuclear [Mg(ddbfo)$_2$]$_4$ (**2a**), [Mg(thffo)$_2$]$_4$ (**2b**), [$Mg_4(\mu_3\text{-}OMe)_2(\mu,\eta^2\text{-}ddbfo)_2(\mu,\eta^1\text{-}ddbfo)_2(\eta^1\text{-}ddbfo)_2(MeOH)_5$]·$CH_3OH$·thf (**3a**·$CH_3OH$·thf) and [$Mg_4(\mu_3,\eta^2\text{-}thffo)_2(\mu,\eta^2\text{-}thffo)_2(Ph_3SiO)_2$] (**4b**), were tested in the polymerization of lactide to reveal good activity only in the case of mononuclear four-coordinate species grafted with an external donor, benzyl alcohol.

Introduction

The potential of magnesium alkoxides and aryloxides has been explored systematically in a variety of chemical processes. Among others, numerous catalytic, noncatalytic, organic, and organometallic reactions, as well as syntheses of advanced materials are noteworthy.[1] Recently, magnesium complexes have also gained considerable attention as initiators in the syntheses of biodegradable polymers.[2] Two important classes of these polymers are polyesters and, in particular, polylactides (PLAs) due to their wide application in biomedical and pharmaceutical fields.[3] Although many strategies have been developed for the preparation of PLAs, the most effective is the ring-opening polymerization (ROP) of lactides initiated by metal alkoxides.[4] Among the known initiators, candidates of primary importance are monomeric complexes with nontoxic and life-essential metals such as magnesium.[2,5]

To date, only a few examples of heteroleptic magnesium compounds that are active as initiators in the ROP of cyclic esters have been described.[2] Recently, interest has also been directed towards homoleptic compounds able to act as initiators for the ROP in the presence of exterior alcohol, which is extremely interesting from the perspective of polymer chain modification.[6] However, only a few magnesium alkoxides and aryloxides have a structure proven by X-ray analysis, which is highly desirable to design well-defined "single-site" initiators.

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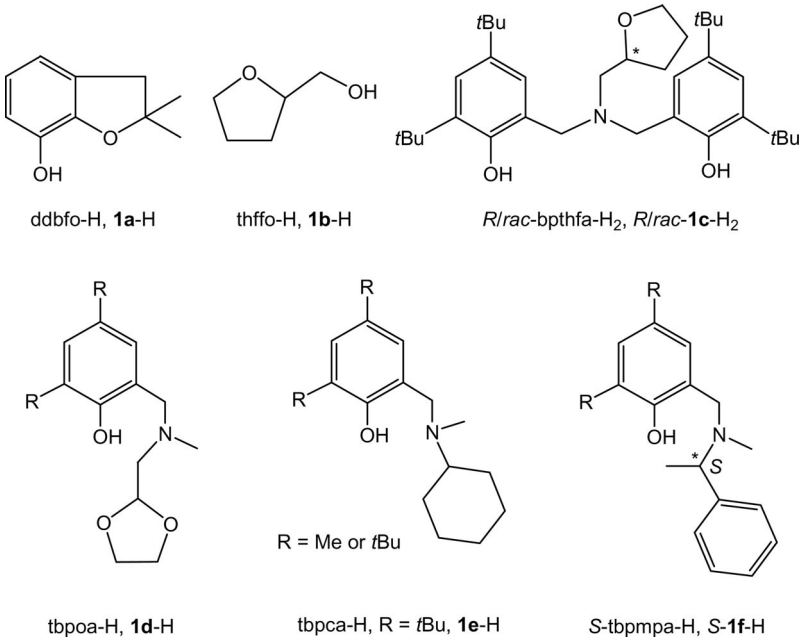
Some of our previous research has already included the synthesis of magnesium alkoxides and aryloxides, where we utilized variety of oxido ligands, including commercially available 2,3-dihydro-2,2-dimethyl-7-benzofuranol (ddbfo-H; **1a**-H) and tetrahydrofurfuryl alcohol (thffo-H; **1b**-H), as well as aminophenolato ligands bpthfa-H_2 (**1c**-H_2),[7] tbpoa-H (**1d**-H),[2b] and tbpca-H (**1e**-H),[2b] which are shown in Scheme 1.

It has been shown that reactions of sterically undemanding bidentate **1a**-H or **1b**-H with $MgBu_2$ or magnesium turnings yield tetranuclear compounds [Mg(ddbfo)$_2$]$_4$ (**2a**)[8a] and [Mg(thffo)$_2$]$_4$ (**2b**),[8b] which have open dicubane geometry. Both molecules possess two five-coordinate magnesium atoms of trigonal-bipyramidal geometry and two six-coordinate octahedral metal centers. The most interesting feature of these compounds is the presence of coordinatively unsaturated metal sites which can react easily with methanol or Ph_3SiOH to form heteroleptic tetrameric magnesium complexes [$Mg_4(\mu_3\text{-}OMe)_2(\mu,\eta^2\text{-}ddbfo)_2(\mu,\eta^1\text{-}ddbfo)_2(\eta^1\text{-}ddbfo)_2(MeOH)_5$]·$CH_3OH$·thf (**3a**·$CH_3OH$·thf)[8a] and [$Mg_4(\mu_3,\eta^2\text{-}thffo)_2(\mu,\eta^2\text{-}thffo)_2(Ph_3SiO)_2$] (**4b**).[8b]

Higher dentate or more bulky bidentate ligands form less aggregated structures that are usually dimeric and perform well as initiators in the ROP of lactides. A few important examples include [(EDBP)Mg(Et_2O)], [(EDBP)Mg(thf)]$_2$ [EDBP = 2,2′-ethylenebis(4,6-di-*tert*-butylphenoxido)],[2a] and a series of dimeric [(L)Mg(μ-OBz)]$_2$ compounds {L = NNO-ketiminate[2d,2i] or 2,4-di-*tert*-butyl-6-[1-(3,5-di-*tert*-butyl-2-phenoxy)ethyl]phenyl benzenesulfonate},[2h] which



Scheme 1. Some of the precursors of alkoxido and aryloxido ligands.

were all designed by Lin and co-workers. Another interesting example, prepared by Cheng et al., is a compound formed in situ from [(BDI)MgN(TMS)$_2$] {BDI = 2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-diisopropylphenyl)imino]-2-pentene} and paclitaxel, a potent chemotherapeutic agent, that is most probably a monomeric species and allows incorporation of the agent into the polylactide chain to form an interesting drug-delivery system.[2g]

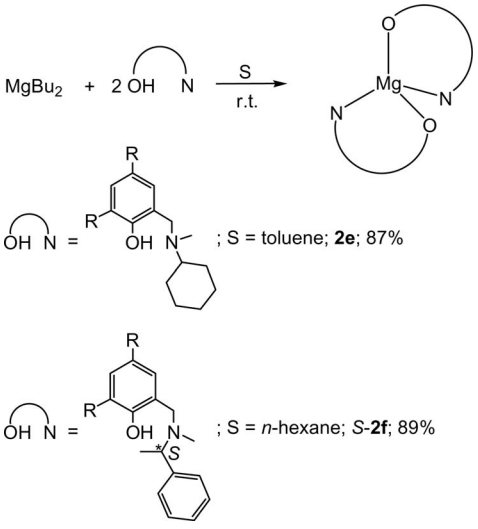
In this paper, we report the preparation of a series of homoleptic magnesium complexes with aryloxido and aminophenolato ligands. The ligands have been varied from two- to four-dentate in order to evaluate the resulting structural motifs. The additional donor arm on the nitrogen atom in the aminophenolato ligands, which could readily involve dynamic behavior in solution, may be an important factor for catalytic applications. Preliminary results of the activity of the compounds in the ROP of lactides are also reported.

Results and Discussion

Synthesis and Characterization of Complexes

The aminophenolato bidentate ligands **1e**-H and *S*-**1f**-H appear to be well suited for the synthesis of monomeric magnesium complexes. The latter was prepared by Mannich condensation from (–)-(*S*)-α,4-dimethylbenzylamine, paraformaldehyde, and 2,4-di-*tert*-butylphenol in refluxing methanol in 54% unoptimized yield as described in the Experimental Section. As already described, the reaction of **1e**-H performed in a mixture of solvents (hexane/thf) gave monomeric octahedral [Mg(tbpca)$_2$(thf)$_2$] (**5**).[2b] It has also been demonstrated that the reaction of $MgBu_2$ with **1d**-H in toluene gave the six-coordinate complex [Mg(tbpoa)$_2$].[2b]

As shown in Scheme 2 ligands **1e**-H or *S*-**1f**-H were treated with 0.5 equiv. of $MgBu_2$ in toluene or hexanes to form monomeric tetrahedral compounds [Mg(tbpca)$_2$] (**2e**) and [Mg(tbpmpa)$_2$] (*S*-**2f**) in 87 and 89% yields, respectively.



Scheme 2. Synthesis of monomeric magnesium complexes **2e** and *S*-**2f**.

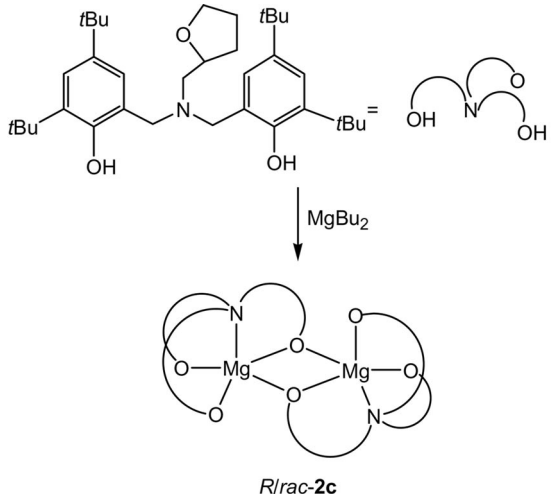
The new complexes **2e** and *S*-**2f** were isolated as colorless solids, which are readily soluble in hydrocarbons, CH_2Cl_2, and thf. Their structures were confirmed by elemental analysis and NMR spectroscopy, as well as X-ray crystallography for *S*-**2f**.

The ^{1}H NMR spectra were routine. The spectrum for **2e** shows one set of resonances for the aryl protons at δ = 7.66 and 7.08 ppm, two singlets from the *tert*-butyl groups at δ = 1.78 and 1.56 ppm, and a signal arising from the *N*-methyl protons at δ = 2.02 ppm. The methylene protons from the

phenyl–CH_2–N linker appear as broad singlets at δ = 4.12 and 3.44 ppm. For *S*-**2f**, the signals of the aminophenolato ligands are broad indicating a fluxional process on the NMR timescale. The aryl protons of the phenolate ring appear as broadened singlets at δ = 7.69 and 6.96 ppm. The methine and methyl protons of the chiral amine substituents also show broad resonances at δ = 3.54 and 1.84 ppm, respectively. The signal of the methylene protons from the phenyl–CH_2–N linker appears at δ = 4.21 ppm.

Attempts to introduce alcohols into the monomeric (aminophenolato)magnesium complexes **2e** and *S*-**2f** were unsuccessful. The reactions between **2e** or *S*-**2f** and EtOH or benzyl alcohol were monitored by NMR spectroscopy, which indicated the synthesis of a mixture of products (presumably due to a reversible reaction), but, after a few days and after a careful workup, the isolated products were identified as the homoleptic starting complexes.

In the next stage of our investigation, the chiral and racemic aminobis(phenolato) ligands *R*-**1c**-H_2 and *rac*-**1c**-H_2 containing additional N,O-donor atoms (going from two- to four-dentate ligands) were used. Their reactions with 1 equiv. of $MgBu_2$ in toluene at room temperature cleanly afforded the dimeric magnesium complexes [Mg(*R*-bpthfa)]$_2$ (*R*-**2c**) and [Mg(*rac*-bpthfa)]$_2$ (*rac*-**2c**) by butane elimination, as presented in Scheme 3. The complexes were isolated in good yields (54–67%) as colorless crystals, soluble in hydrocarbons and chlorinated solvents. Compounds *R*/*rac*-**2c** contain unsaturated five-coordinate metal centers, are unreactive towards alcohols, and remain stable even in hot ethanol. Similarly to **2e** and *S*-**2f**, incorporation of alkoxido ligands and formation of heteroleptic products were not observed.



Scheme 3. Synthesis of dimeric complexes *R*/*rac*-**2c**.

The ^{1}H NMR spectra of the complexes *R*/*rac*-**2c** are identical and show one set of resonances for 1 equiv. of the coordinated bis(phenoxido) ligand, which could be assigned in detail on the basis of 2D ^{1}H-^{1}H COSY, ^{1}H, and ^{13}C NMR experiments. Complementary investigations of these compounds indicated that the NMR features were essentially unchanged in $C_6D_5CD_3$, $CDCl_3$, and CD_3OD up to 60 °C.

X-ray Crystallographic Studies

Colorless, needle-shaped crystals of *R*-**2c**·$2C_6H_5CH_3$·CH_2Cl_2 were obtained by crystallization from a CH_2Cl_2/toluene mixture. The detailed structure was determined as outlined in the Experimental Section. Key metrical parameters are listed in Table 1, and the structure is shown in Figure 1.

Table 1. Selected bond lengths [Å] and angles [°] for *R*-**2c**·$2C_6H_5CH_3$·CH_2Cl_2.

Atoms	Distance	Atoms	Distance
Mg(1)–Mg(2)	3.008(3)	Mg(1)–O(1)	2.027(4)
Mg(1)–O(2)	1.907(4)	Mg(1)–O(3)	2.058(4)
Mg(1)–O(4)	2.014(4)	Mg(1)–N(1)	2.208(5)
Mg(2)–O(1)	1.993(4)	Mg(2)–O(4)	2.018(4)
Mg(2)–O(5)	1.922(4)	Mg(2)–O(6)	2.090(4)
Mg(2)–N(2)	2.205(5)		
Atoms	**Angle**	**Atoms**	**Angle**
O(1)–Mg(1)–O(2)	162.86(19)	O(1)–Mg(1)–O(3)	95.31(15)
O(1)–Mg(1)–O(4)	76.36(15)	O(1)–Mg(1)–N(1)	86.65(16)
O(2)–Mg(1)–O(3)	100.49(18)	O(2)–Mg(1)–O(4)	95.80(16)
O(2)–Mg(1)–N(1)	89.35(17)	O(3)–Mg(1)–O(4)	138.32(17)
O(3)–Mg(1)–N(1)	80.73(16)	O(4)–Mg(1)–N(1)	137.85(18)
O(1)–Mg(2)–O(4)	77.05(14)	O(1)–Mg(2)–O(5)	94.65(16)
O(1)–Mg(2)–O(6)	140.29(18)	O(1)–Mg(2)–N(2)	136.41(19)
O(4)–Mg(2)–O(5)	163.93(19)	O(4)–Mg(2)–O(6)	95.88(15)
O(4)–Mg(2)–N(2)	86.87(16)	O(5)–Mg(2)–O(6)	99.17(17)
O(5)–Mg(2)–N(2)	89.98(17)	O(6)–Mg(2)–N(2)	80.86(16)
Mg(1)–O(1)–Mg(2)	96.88(15)	Mg(1)–O(4)–Mg(2)	96.52(15)

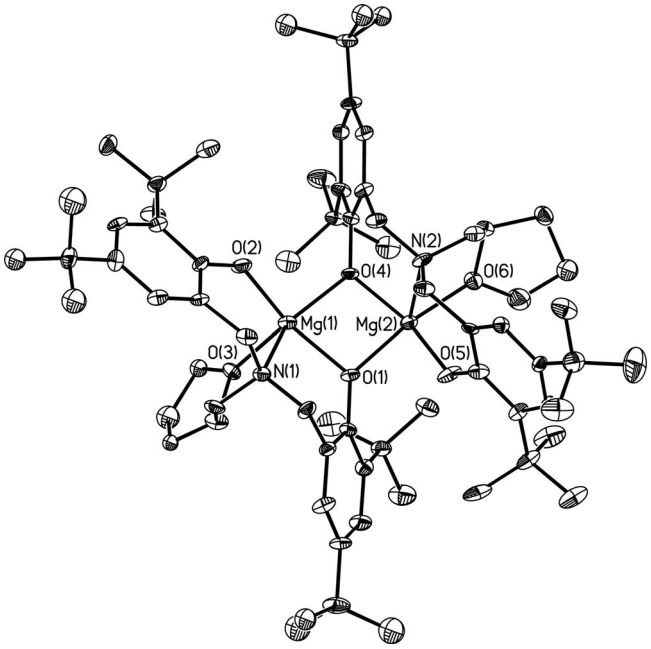


Figure 1. ORTEP view of *R*-**2c**·$2C_6H_5CH_3$·CH_2Cl_2 (H and disordered atoms are omitted for clarity; the displacement ellipsoids are drawn at 40% probability level).

The X-ray analysis shows *R*-**2c**·$2C_6H_5CH_3$·CH_2Cl_2 to be a homoleptic molecular dimer. The two magnesium centers are identically coordinated, each surrounded by two bridging oxygen atoms of two phenoxido ligands coming from

separate aminobis(phenolato) ligands, one terminal phenoxido oxygen atom, one nitrogen atom, and one oxygen atom from the tetrahydrofuran ring.

The pentacoordinate magnesium atoms are in an almost identical arrangement, that is between trigonal-bipyramidal and square-pyramidal geometry with a τ parameter of 0.41 for Mg(1) and 0.39 for Mg(2).[9] In both cases the nitrogen atom resides in the apical position.

Although complexes with pentacoordinate magnesium are quite commonly observed, only two examples of the crystallographically characterized species with a coordination environment similar to *R*-**2c** (MgO_4N comprising two bridging phenoxido groups) were found in the CCDC.[10] The Mg_2O_2 central core in *R*-**2c**·$2C_6H_5CH_3$·CH_2Cl_2 is a distorted rhombohedron with four different Mg–O distances of 2.027(4) [Mg(1)–O(1)], 2.014(4) [Mg(1)–O(4)], 1.993(4) [Mg(2)–O(1)], and 2.018(4) Å [Mg(2)–O(4)]. The distances are similar to those found in the magnesium dimer with bis(α,α-diarylprolinol) [$Mg_2(L)_2$] [Mg–O 1.991(6), 2.031(6), 1.979(6), and 2.016(6) Å].[10a]

The terminal Mg–$O_{aryloxido}$ distances in *R*-**2c**·$2C_6H_5CH_3$·CH_2Cl_2 are 1.907(4) and 1.922(4) Å and are typical. Also typical are the Mg–O–C bond angles for the terminal aryloxido ligands, which are 134.3(3) and 134.9(3)°, and suggest a very small π-character in the Mg–$O_{aryloxido}$ bonds.

Light pink blocks of *S*-**2f** were obtained by slow concentration of a hexane solution. The detailed structure was determined as outlined in Table 1 and described in the Experimental Section. The structure is depicted in Figure 2, and selected bond lengths and angles are listed in the caption.

The X-ray analysis shows *S*-**2f** to be a molecular monomer with the four-coordinate magnesium center surrounded by two pairs of N,O atoms from two aminophenolato ligands forming a distorted tetrahedron. Although such coordination seems typical for magnesium, to our surprise, only one monomeric four-coordinate magnesium aminophenolate was found in the CCDC.[11]

The distances Mg(1)–O(1) and Mg(1)–O(2) in *S*-**2f** are 1.892(3) and 1.900(3) Å, respectively, and are similar to those found in [Mg(2,6-*t*$Bu_2C_6H_4O)_2$(tmeda)] [tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; Mg–O 1.8803(8) and 1.8817(9) Å]. The Mg(1)–N(1) and Mg(1)–N(2) distances in *S*-**2f** of 2.176(4) and 2.166(3) Å are a little shorter than those in [Mg(2,6-*t*$Bu_2C_6H_4O)_2$(tmeda)] [Mg–N 2.2625(11) and 2.2695(11) Å].

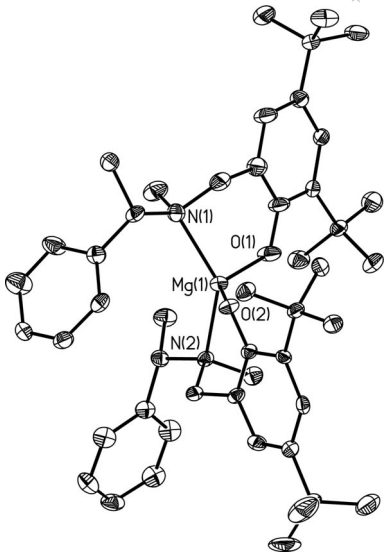


Figure 2. View of *S*-**2f** (H atoms are omitted for clarity; the displacement ellipsoids are drawn at 40% probability level). Selected bond lengths [Å] and angles [°]: Mg(1)–O(1) 1.892(3), Mg(1)–O(2) 1.900(3), Mg(1)–N(1) 2.176(4), Mg(1)–N(2) 2.166(3); O(1)–Mg(1)–O(2) 125.77(15), O(1)–Mg(1)–N(1) 92.68(13), O(1)–Mg(1)–N(2) 105.32(13), O(2)–Mg(1)–N(1) 105.69(14), O(2)–Mg(1)–N(2) 95.71(13), N(1)–Mg(1)–N(2) 136.07(14), Mg(1)–O(1)–C(11) 129.9(3), Mg(1)–O(2)–C(41) 124.5(2).

Lactide Polymerization

Previous research in our group has shown that zinc complexes that incorporate **1e**-H are effective initiators for the ROP of lactide.[12] In addition, the monomeric hexacoordinate magnesium complex **5**[2b] was proved to initiate the polymerization of L-lactic acid (L-LA) in high conversion within 30 min to afford PLA with a moderate M_w of 8600 and a polydispersity index (PDI) of 1.12. In this case, the NMR end-group analysis of the isolated PLA indicated the presence of hydroxy and aminophenolate ester end groups. Biocompatible metals such as Zn and Mg are of great interest in this process because of the propensity for trace amounts of the catalyst to be incorporated within the polymer.[2d] Therefore, preliminary research exploring the use of the above described and characterized aryloxo magnesium complexes as initiators for the ROP of lactide. The tetrameric complexes **2a**–**b**, **3a**, and **4b**, as well as dimeric *R*/*rac*-**2c** were tested and proved to be essentially inactive.

Table 2. Polymerization of L-lactide with initiators (I) **2e**, *S*-**2f**, **2e**/BnOH, and *S*-**2f**/BnOH.[a]

Entry	I	[I]/[L-LA]/[BnOH]	*t* (min)	10^{-3} M_n[b]	10^{-3} M_n	Conv.[c]	PDI[b]
1	**2e**	1:100:0	5 d	–	–	–	–
2	**2e**	1:50:1	1 min	6.88	7.02	96%	1.09
3	**2e**	1:100:1	5 min	15.58	13.37	92%	1.10
4	*S*-**2f**	1:100:0	5 d	–	–	–	–
5	*S*-**2f**	1:50:1	1 min	7.20	6.59	90%	1.02
6	*S*-**2f**	1:100:1	10 min	14.82	13.80	95%	1.08

[a] General polymerization conditions: solvent: toluene (10 mL), T = 25 °C, [I] = 0.025. [b] Conversion determined by ^{1}H NMR spectroscopy. [c] Determined by GPC, PDI calibrated with polystyrene standards.

Monomeric tetrahedral aminophenolate compounds **2e** and *S*-**2f** were tested next. Although they both showed no activity they become extremely active when an external donor was added as described in Table 2.

Polymerization of L-LA initiated by **2e** in the presence of BnOH was very effective, and high conversion was achieved within 5 min for [**2e**]/[L-LA]/BnOH (1:100:1) (Figure 3).

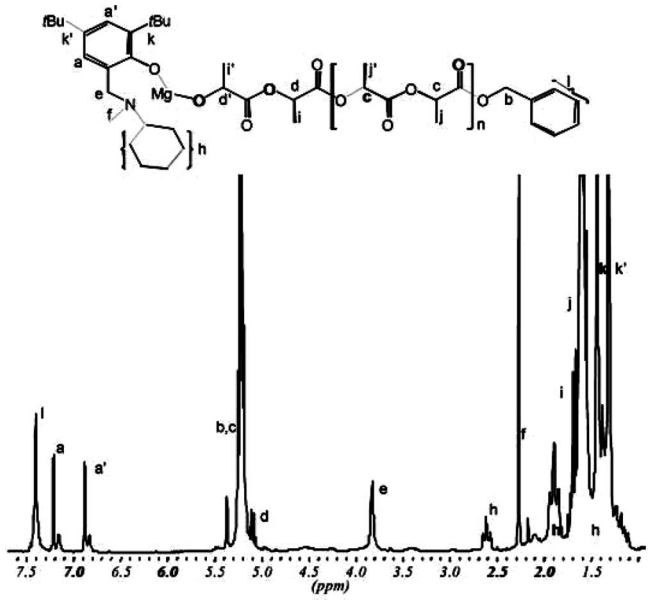


Figure 3. ^{1}H NMR spectrum of a living oligomer in the ROP of L-LA initiated by **2e** in the presence of BnOH.

The predictable molecular weights and narrow PDIs of the obtained PLAs indicate a well-controlled polymerization process. The ^{1}H NMR spectrum of PLA in CD_2Cl_2 prepared by using [**2e**]/[L-LA]/[BnOH] in 1:10:1 ratio showed one benzyl ester and one hydroxy chain end suggesting that the initiation occurred through the insertion of the benzyloxy group into L-lactide (Figure 4).

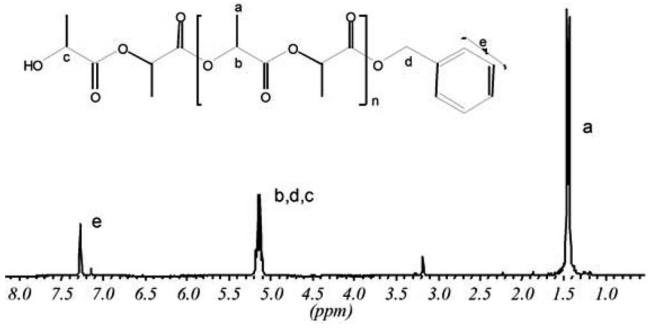


Figure 4. ^{1}H NMR spectrum of PLA synthesized with the **2e**/BnOH initiator.

Similar results were obtained for the polymerization of L-LA initiated with *S*-**2f** in the presence of BnOH performed at room temperature in toluene. A high conversion was achieved within 10 min for [*S*-**2f**]/[L-LA]/[BnOH] (1:100:1). The ^{1}H and ^{13}C NMR spectra of the PLAs obtained in the presence of *S*-**2f** showed that the polymer chains at one end are terminated by benzyl ester with no sign of transesterification products (the OH proton was not observed) (Figure 5).

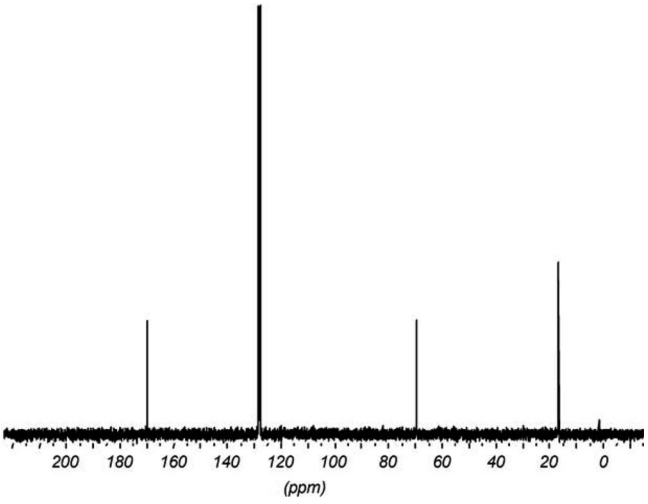


Figure 5. ^{13}C NMR spectrum of PLA synthesized with the *S*-**2f**/BnOH initiator.

All of the initiator systems exhibit molecular weights in close agreement with calculated values, and narrow PDIs are characteristic for well-controlled living propagation.

Conclusions

We have synthesized a new chiral aminophenolato ligand *S*-**1f**-H and four new magnesium aminophenolates *R*/*rac*-**2c**, **2e**, and *S*-**2f**. The compounds were characterized by spectroscopic methods and, in case of *R*-**2c** and *S*-**2f**, by X-ray crystallography, thereby enriching the library of well-defined magnesium aminophenolates. As expected, the compound with the tetracoordinate *R*-bpthfa ligand appeared to be dimeric with five-coordinate magnesium atoms, whereas the compound with the dicoordinate *S*-tbpmpa was monomeric with tetrahedral geometry around the metal atom.

All of the new compounds, as well as few polynuclear magnesium species **2a**–**b**, **3a**, and **4b** synthesized previously, were tested in the polymerization of L-lactide, and all of them proved to be essentially inactive. Nevertheless, in the case of **2e** and *S*-**2f**, grafting with benzyl alcohol led to greatly enhanced polymerization activities resulting in high activity initiators, which gave 92–95% conversion after 5–10 min, and exclusively linear polymers with low PDI values, 1.08–1.10. These results clearly support the advantage of monomeric magnesium species over polynuclear analogs in lactide polymerization.

Experimental Section

General Materials and Experimental Procedures: All the reactions and operations were performed under N_2 by using standard Schlenk techniques. Reagents were purified by standard methods: thf was distilled from CuCl, predried with NaOH, and then dis-

tilled from Na/benzophenone. $C_6H_5CH_3$ was distilled from Na; CH_2Cl_2 and CD_2Cl_2 were distilled from P_2O_5; hexanes were distilled from Na; methanol was distilled from Mg; C_6D_6 and $C_6D_5CD_3$ were distilled from CaH_2. L-LA (98%; Aldrich) was sublimed and recrystallized from toluene prior to use. $MgBu_2$ (Aldrich; 1.0 M solution in hexanes) and (–)-(*S*)-α,4-dimethylbenzylamine (Aldrich, 98%) were used as received. BnOH (Aldrich; >99%) was distilled prior to use. Ligands (tbpca-H), *R*/*rac*-bpthfa-H_2 were prepared according to literature procedures.[2b,7] ^1H and ^{13}C NMR spectra were recorded in the temperature range 298–351 K with Bruker ESP 300E or 500 MHz spectrometers. Chemical shifts are reported in ppm and referenced to the signals of residual protons in deuterated solvents. The weights and number-average molecular weights of the PLAs were determined by gel permeation chromatography (GPC) using an HPLC-HP 1090 II with a DAD-UV/Vis and RI detector HP 1047A, and polystyrene calibration. Microanalyses were conducted with an ARL Model 3410 + ICP spectrometer (Fisons Instruments) and a VarioEL III CHNS (in-house).

Ligand and Complex Synthesis. *S*-1f-H: To a mixture of 2,4-di-*tert*-butylphenol (7.88 g, 38.20 mmol) and (–)-(*S*)-α,4-dimethylbenzylamine (5.60 mL, 38.06 mmol) in methanol (50 mL) was added a 1.5 molar excess of formaldehyde (4.32 mL, 58.01 mmol, 37% solution in water). The solution was then stirred and heated under reflux for 5 d. The solvent was removed to give a yellow oil. Cold methanol was added (10 mL), and the mixture was stirred for 1 h and cooled to –15 °C. After 1 d, colorless crystals of *S*-**1f**-H had formed. Yield 7.21 g (54%). $C_{24}H_{35}NO$ (353.55): calcd. C 81.53, H 9.98, N 3.96; found C 81.62, H 10.12, N 4.11. ^1H NMR (C_6D_6, 298 K): δ = 7.58 (d, J_{HH} = 2.42 Hz, 1 H, Ar*H*), 7.30–7.14 (m, 5 H, Ph), 6.93 (d, J_{HH} = 2.42 Hz, 1 H, Ar*H*), 3.60 (br. s, 2 H, NCH_2Ar), 3.50 (q, J_{HH} = 6.82 Hz, 2 H, C*H*), 1.93 (s, 3 H, NCH_3), 1.82 [s, 9 H, C(CH_3)$_3$], 1.44 [s, 9 H, C(CH_3)$_3$], 1.20 (d, J_{HH} = 6.82 Hz, 3 H, CH_3) ppm. ^{13}C NMR (76 MHz, C_6D_6, 298 K): δ = 19.6 (CH*C*H$_3$), 29.6 [C(*C*H$_3$)$_3$], 31.9 [C(CH$_3$)$_3$], 33.8 [*C*(CH$_3$)$_3$], 35.2 [*C*(CH$_3$)$_3$], 36.3 (N*C*H$_3$), 58.9 (*C*H$_2$), 62.1 (*C*HCH$_3$), 121.1, 121.6, 122.6, 122.8, 123.4, 123.9, 135.7, 140.2, 140.6, 154.1, 155.0 (12 C, 2Ar) ppm.

[Mg(*R*-1c)]$_2$ (*R*-2c): To a solution of *R*-**1c**-H_2 (0.86 g, 1.61 mmol) in toluene (15 mL) was added $MgBu_2$ (1.61 mL, 1.61 mmol) dropwise. The mixture was stirred for 24 h, and the solution was concentrated to dryness. *n*-Hexane was added (25 mL), and the suspension was stirred for 2 h. The resulting white powder was collected by filtration, washed with *n*-hexanes (20 mL) and dried in vacuo to yield ***R*-2c** (0.96 g, 54%, 0.86 mmol). Crystals suitable for X-ray determination were obtained after recrystallization with *n*-hexane/CH_2Cl_2. $C_{70}H_{106}Mg_2N_2O_6$ (1120.23): calcd. C 75.05, H 9.54, N 2.50; found C 74.78, H 9.47, N 2.41. ^1H NMR (C_6D_6, 298 K): δ = 7.47 (d, J_{HH} = 2.5 Hz, 2 H, Ar*H*), 7.41 (d, J_{HH} = 2.5 Hz, 2 H, Ar*H*), 7.10 (d, J_{HH} = 2.6 Hz, 2 H, Ar*H*), 6.92 (d, J_{HH} = 2.6 Hz, 2 H, Ar*H*), 4.65–4.73, 4.74–4.80 (2 m, 4 H, CHOCH_2C$_2$H$_4$), 4.58–4.63 (m, 2 H, C*H*OCH$_2$C$_2$H$_4$), 3.19–3.26, 3.48–3.53 (2 m, 8 H, CH_2Ar), 3.04–3.13 (m, 4 H, NCH_2), 2.55–2.60, 2.63–2.72 (2 m, 8 H, CHOCH$_2$C$_2$*H*$_4$), 1.48, 1.54, 1.56, 1.88 [4 s, 72 H, C(CH_3)$_3$] ppm. ^{13}C NMR (76 MHz, C_6D_6, 298 K): δ = 28.7, 31.7 (4 C, CHOCH$_2$*C*$_2$H$_4$), 29.8, 31.1, 31.9, 32.1 [24 C, C(*C*H$_3$)$_3$], 33.8, 33.9, 35.0, 35.1 [8 C, *C*(CH$_3$)$_3$], 55.5 (2 C, N*C*H$_2$), 65.2, 64.4 (4 C, *C*H$_2$Ar), 68.9 (2 C, CHO*C*H$_2$C$_2$H$_4$), 78.8 (2 C, *C*HOCH$_2$C$_2$H$_4$), 121.5, 123.4 [4 C, *o*-*C*(Ar)-CH$_2$N], 123.9, 125.1 [4 C, *m*-*C*(Ar)], 125.4, 127.1 [4 C, *m*-*C*(Ar)], 137.0, 137.2 [4 C, *o*-*C*(Ar)C(CH$_3$)$_3$], 138.9, 139.7 [4 C, *p*-*C*(Ar)C(CH$_3$)$_3$] ppm.

[Mg(*rac*-1c)]$_2$ (*rac*-2c): *rac*-**1c**-H (2.53 g, 4.72 mmol) and $MgBu_2$ (4.72 mL, 4.72 mmol) were allowed to react according to a procedure analogous to that of *R*-**2c** described above. A similar workup gave *rac*-**2c** in 67% yield (3.52 g, 3.14 mmol). $C_{70}H_{106}Mg_2N_2O_6$ (1120.23): calcd. C 75.05, H 9.54, N 2.50; found 75.14, H 9.37, N 2.34.

[Mg(1e)$_2$] (2e): To a solution of **1e**-H (1.32 g, 4.00 mmol) in toluene (10 mL) was added $MgBu_2$ (2 mL, 2.00 mmol) dropwise. The reaction mixture was stirred for 24 h, and the solvent was removed to give a yellow oil. *n*-Hexane was added (20 mL), and colorless crystals precipitated at room temperature after 1 d. They were collected by filtration, washed with *n*-hexane (10 mL), and dried in vacuo to yield **2e** (2.40 g, 87%, 3.50 mmol). $C_{44}H_{72}MgN_2O_2$ (685.37): calcd. C 77.11, H 10.59, N 4.09; found C 76.68, H 10.31, N 3.98. ^1H NMR (C_6D_6, 298 K): δ = 7.66 (s, 2 H, Ar*H*), 7.08 (s, 2 H, Ar*H*), 4.12 (br. s, 2 H, NCH_2Ar), 3.44 (s, 2 H, NCH_2Ar), 2.27–2.39 (m, 2 H, C_6H_{11}), 2.02 (s, 6 H, NCH_3), 1.78 [s, 18 H, C(CH_3)$_3$], 1.60–1.70 (m, 10 H, C_6H_{11}), 1.56 [m, 18 H, C(CH_3)$_3$], 1.30–1.47 (m, 10 H, C_6H_{11}) ppm. ^{13}C NMR (76 MHz, C_6D_6, 298 K): δ = 25.2 (10 C, C_6H_{11}), 25.5 (10 C, C_6H_{11}), 29.4 [6 C, C(CH$_3$)$_3$], 31.0 (2 C, NCH$_3$), 31.5 [6 C, C(CH$_3$)$_3$], 33.3 [2 C, C(CH$_3$)$_3$], 34.7 [2 C, C(CH$_3$)$_3$], 59.4 (2 C, C_6H_{11}), 60.3 (2 C, NCH$_2$Ar) 62.3, 136.8, 134.6, 125.0, 123.5, 121.0 (24 C, Ar) ppm.

[Mg(*S*-1f)$_2$] (*S*-2f): To a solution of *S*-**1f**-H (1.36 g, 2.00 mmol) in *n*-hexane (10 mL) was added $MgBu_2$ (2.00 mL, 2.00 mmol) dropwise. The reaction mixture was stirred for 24 h, and the solvent was removed to yield a pink oil. *n*-Hexane was added (20 mL) and, after additional stirring at room temperature for 24 h, a pink solid precipitated from the solution. The powder was collected by filtration, washed with *n*-hexane (10 mL), and dried in vacuo to yield *S*-**2f** (1.68 g, 89%, 2.30 mmol). $C_{48}H_{68}MgN_2O_2$ (729.35): calcd. C 79.05, H 9.40, N 3.84; found C 78.95, H 9.53, N 3.94. ^1H NMR (300 MHz, C_6D_6, 298 K): δ = 7.69 (br. s, 2 H, Ar*H*), 7.16–7.21 (m, 5 H, Ar*H*), 6.96 (br. s, 2 H, Ar*H*), 4.21 (br. s, 4 H, NCH_2Ar), 3.54 (br. s, 2 H, C*H*CH$_3$), 1.93 (s, 6 H, NCH_3), 1.84 (br. s, 6 H, CHCH_3), 1.82 [s, 18 H, C(CH_3)$_3$], 1.45 [m, 18 H, C(CH_3)$_3$] ppm. ^{13}C NMR (76 MHz, C_6D_6, 298 K): δ = 29.6 [6 C, C(CH$_3$)$_3$], 29.7 [6 C, C(CH$_3$)$_3$] 31.9 [2 C, C(CH$_3$)$_3$], 34.7 [2 C, C(CH$_3$)$_3$] 35.7 [2 C, C(CH$_3$)$_3$], 36.4 (2 C, NCH$_3$), 59.2 (CH$_2$), 61.3 (CH), 156.3, 155.1, 141.6, 140.3, 131.2, 129.4, 124.0, 123.5, 122.8, 122.9, 122.1, 121.5, 121.3 (24 C, Ar) ppm.

Polymerization Procedure: In a Schlenk flask under argon, a complex I was treated with L-LA, [I]/[L-LA] = 1:100 in toluene (10 mL). The reaction mixture was stirred at the desired temperature for the prescribed time. At certain time intervals, aliquots of about 1 mL were removed for the determination of the conversion by ^1H NMR spectroscopy. After the reaction was complete, it was quenched with methanol; the solution was concentrated in vacuo, and the polymer was precipitated with an excess of cold methanol. A white product was collected by filtration and dried in vacuo.

Details of X-ray Data Collection and Reduction: X-ray diffraction data were collected with a KUMA KM4 CCD (ω-scan technique) diffractometer equipped with an Oxford Cryosystem-Cryostream cooler.[13] The space groups were determined from systematic absences and subsequent least-squares refinement. Lorentz and polarization corrections were applied. The structures were solved by direct methods and refined by full-matrix least squares on F^2 by using the SHELXTL package.[14] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen-atom positions were calculated and added to the structure-factor calculations, but were not refined (Table 3). The *t*Bu groups, C(17)–C(110), C(27)–C(210), and C(47)–C(410), and both tetrahydrofuran rings in **2e** are disordered and were solved with two positions for each moiety. The

Table 3. Summary of crystallographic data for *R*-**2c**·$2C_6H_5CH_3$·CH_2Cl_2 and *S*-**2f**.

	R-**2c**·$2C_6H_5CH_3$·CH_2Cl_2	*S*-**2f**
Empirical formula	$C_{85}H_{124}Cl_2Mg_2N_2O_6$	$C_{48}H_{68}MgN_2O_2$
Formula mass	1389.38	729.35
Crystal system	monoclinic	orthorhombic
Space group	$P2_1$	$P2_12_12_1$
Temperature [K]	120(2)	100(2)
Cell dimensions		
a [Å]	15.3323(10)	10.859(5)
b [Å]	14.3051(10)	19.999(5)
c [Å]	18.5068(14)	20.399(5)
β [°]	93.379(6)	90
V [Å^3]	4052.0(5)	4430(3)
Z	2	4
$D_{calcd.}$ [g/cm^3]	1.139	1.094
μ [mm^{-1}]	0.147	0.078
Crystal dimensions [mm]	$0.45 \times 0.24 \times 0.18$	$0.35 \times 0.20 \times 0.19$
Radiation (λ [Å])	Mo-K_α (0.71073)	Mo-K_α (0.71073)
Reflections measured	31 061	41 850
Range/indices (h, k, l)	–18, 18; –17, 16; –22, 22	–13, 13; –24, 23; –25, 25
θ limit [°]	3.00–25.06	2.74–26.11
Total no. of unique data	12756	8678
No. of observed data [$I > 2\sigma(I)$]	7125	5522
No. of variables	842	486
No. of restraints	17	0
Absolute structure parameter	0.05(13)	–0.1(4)
R_{int}	0.0962	0.1254
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$ (all, observed)	0.1450, 0.0796	0.1417, 0.0762
$wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^4)^{1/2}$ (all, observed)	0.1759, 0.1543	0.1653, 0.1447
GOOF	0.969	0.994
Data completeness	0.997	0.993
Absorption correction (T_{min}, T_{max})	0.947, 0.975	0.929, 0.966
$\Delta\rho$(max, min) [e/Å^3]	0.54, –0.49	0.41, –0.24

FVAR parameter was also refined separately for each group, and these additional parameters are contained within the supplementary crystallographic data for this paper (CCDC-743616 and -743617); these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) S. Kanemasa, M. Nishiuchi, E. Wada, *Tetrahedron Lett.* **1992**, *33*, 1357; b) H. R. Kim, J. H. Song, S. Y. Rhie, E. K. Ryu, *Synth. Commun.* **1995**, *25*, 1801; c) L. Crombie, D. E. Games, A. W. G. James, *J. Chem. Soc. Perkin Trans. 1* **1996**, *22*, 2715; d) F. Luderer, H. Reinke, H. Oehme, *J. Organomet. Chem.* **1996**, *510*, 181; e) E. P. Moore Jr., in *Polypropylene Handbook*, Hanser/Gardner Publications, Cincinnati, **1996**; f) S. G. Hegde, D. C. Myles, *Synth. Commun.* **1997**, *27*, 2111; g) P. Sobota, J. Utko, J. Ejfler, L. B. Jerzykiewicz, *Organometallics* **2000**, *19*, 4929; h) H. O. Davies, A. C. Jones, T. J. Leedham, M. J. Crosbie, P. J. Wright, N. M. Boag, J. R. Thompson, *Chem. Vap. Deposition* **2000**, *6*, 71; i) W. Teng, M. Guino, J. Hitzbleck, U. Englich, K. Ruhlandt-Senge, *Inorg. Chem.* **2005**, *44*, 9531; j) W. L. Leong, S. K. Batabyal, S. Kasapis, J. J. Vittal, *Chem. Eur. J.* **2008**, *14*, 8822.

[2] a) M.-L. Shueh, Y.-S. Wang, B.-H. Huang, C.-Y. Kuo, C.-C. Lin, *Macromolecules* **2004**, *37*, 5155; b) J. Ejfler, M. Kobyłka, L. B. Jerzykiewicz, P. Sobota, *Dalton Trans.* **2005**, 2047; c) M.-L. Hsueh, B.-T. Ko, T. Athar, C.-C. Lin, T.-M. Wu, S.-F. Hsu, *Organometallics* **2006**, *25*, 4144; d) H.-Y. Tang, H.-Y. Chen, J.-H. Huang, C.-C. Lin, *Macromolecules* **2007**, *40*, 8855; e) L. F. Sánchez-Barba, A. Garcés, M. Fajardo, C. Alonso-Moreno, J. Fernández-Baeza, A. Otero, A. Antiñolo, J. Tejeda, A. Lara-Sánchez, M. I. Lopez-Sólera, *Organometallics* **2007**, *26*, 6403; f) B. Lian, C. M. Thomas, O. L. Casagrande Jr., T. Roisnel, J.-F. Carpentier, *Polyhedron* **2007**, *26*, 3817; g) R. Tong, J. Cheng, *Angew. Chem. Int. Ed.* **2008**, *47*, 4830; h) J. Wu, Y.-Z. Chen, W.-C. Hung, C.-C. Lin, *Organometallics* **2008**, *27*, 4970; i) W.-C. Hung, C.-C. Lin, *Inorg. Chem.* **2009**, *48*, 728; j) C. A. Wheaton, P. G. Hayes, B. J. Ireland, *Dalton Trans.* **2009**, 4832; k) R. H. Platel, L. M. Hodgson, C. K. Williams, *Polym. Rev.* **2008**, *48*, 11; l) V. Poirier, T. Roisnel, J.-F. Carpentier, Y. Sarazin, *Dalton Trans.* **2009**, 9820.

[3] a) P. U. Rokkanen, O. Böstman, E. Hirvensalo, E. A. Mäkelä, E. K. Partio, H. Pätiälä, S. Vainionpää, K. Vihtonen, P. Törmälä, *Biomaterials* **2000**, *21*, 2607; b) R. Haag, F. Kratz, *Angew. Chem. Int. Ed.* **2006**, *45*, 1198; c) Z. Zhang, S.-S. Feng, *Biomaterials* **2006**, *27*, 262; d) J. Cheng, B. A. Teply, I. Sherifi, J. Sung, G. Luther, F. X. Gu, E. Levy-Nissenbaum, A. F. Radovic-Moreno, R. Langer, O. C. Farokhzad, *Biomaterials* **2007**, *28*, 869; e) K. Kurokawa, K. Yamashita, Y. Doi, H. Abe, *Biomacromolecules* **2008**, *9*, 1071; f) K. Numata, A. Finne-Wistrand, A.-C. Albertsson, Y. Doi, H. Abe, *Biomacromolecules* **2008**, *9*, 2180; g) A. P. Dove, *Chem. Commun.* **2008**, 6446; h) M. Florczak, A. Duda, *Angew. Chem. Int. Ed.* **2008**, *47*, 9088; i) L. S. Nair, C. T. Laurencin, *Prog. Polym. Sci.* **2007**, *32*, 762.

[4] a) B. J. O'Keefe, M. A. Hillmyer, W. B. Tolman, *J. Chem. Soc., Dalton Trans.* **2001**, 2215; b) O. Dechy-Cobaret, B. Martin-

Vaca, D. Bourissou, *Chem. Rev.* **2004**, *104*, 6147; c) J. Wu, T. L. Yu, C. T. Chen, C.-C. Lin, *Coord. Chem. Rev.* **2006**, *250*, 602.
[5] a) M. Chisholm, J. C. Gallucci, K. Phomphrai, *Inorg. Chem.* **2004**, *43*, 6717; b) L. E. Breyfogle, C. K. Williams, V. G. Young, M. A. Hillmyer, W. B. Tolman, *Dalton Trans.* **2006**, 928; c) D. J. Darensbourg, W. Choi, C. P. Rizhters, *Macromolecules* **2007**, *40*, 3521; d) M. H. Chisholm, J. C. Gallucci, G. Yaman, *Inorg. Chem.* **2007**, *46*, 8676; e) Z. Zheng, G. Zhao, R. Fablet, M. Bouyahyi, C. M. Thomas, T. Roisnel, O. Casagrande Jr., J.-F. Carpentire, *New J. Chem.* **2008**, *32*, 2279; f) D. J. Darensbourg, W. Choi, O. Karroonnirun, N. Bhuvanesh, *Macromolecules* **2008**, *41*, 3493.
[6] a) A. Kowalski, A. Duda, S. Penczek, *Macromolecules* **2000**, *33*, 689; b) S. Sosnowski, S. Słomkowski, A. Lorenc, H. R. Kircheldorf, *Colloid Polym. Sci.* **2002**, *280*, 107; c) T. Zou, S.-X. Cheng, R.-X. Zhuo, *Colloid Polym. Sci.* **2005**, *283*, 1091; d) C. M. Silvernail, L. J. Yao, L. M. R. Hill, M. A. Hillmyer, W. B. Tolman, *Inorg. Chem.* **2007**, *46*, 6565; e) M. G. Davidson, C. T. O'Hara, M. D. Jones, C. G. Keir, M. F. Mahon, G. Kociok-Köhn, *Inorg. Chem.* **2007**, *46*, 7686; f) A. D. Celiz, O. A. Scherman, *Macromolecules* **2008**, *41*, 4115.
[7] S. Groysman, I. Goldberg, M. Kol, E. Genizi, Z. Goldsmidt, *Inorg. Chim. Acta* **2003**, *345*, 137.
[8] a) P. Sobota, J. Utko, K. Sztajnowska, J. Ejfler, J. B. Jerzykiewicz, *Inorg. Chem.* **2000**, *39*, 235; b) P. Sobota, J. Utko, J. Ejfler, J. B. Jerzykiewicz, *Organometallics* **2000**, *19*, 4929.
[9] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* **1984**, 1349.
[10] a) Y. Xiao, Z. Wang, K. Ding, *Macromolecules* **2006**, *39*, 128; b) B. Courcot, D. Firley, B. Fraisse, P. Becker, J.-M. Gillet, P. Pattison, D. Chernyshov, M. Sghaier, F. Zouhiri, D. Desmaele, J. d'Angelo, F. Bonhomme, S. Geiger, N. E. Ghermani, *J. Phys. Chem. B* **2007**, *111*, 6042.
[11] K. W. Henderson, G. W. Honeyman, A. R. Kennedy, R. E. Mulvey, J. A. Parkinson, D. C. Sherrington, *Dalton Trans.* **2003**, 1365.
[12] J. Ejfler, S. Szafert, K. Mierzwicki, L. B. Jerzykiewicz, P. Sobota, *Dalton Trans.* **2008**, 6556.
[13] *CrysAlisRED Software*, Oxford Diffraction, Wrocław, Poland, **1995–2004**.
[14] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

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