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Amido Rare-Earth Complexes Supported by Ansa Bis(amidinate) Ligand with Rigid 1,8-Naphthalene Linker: Synthesis, Structures and Catalytic Activity in rac-Lactide Polymerization and Hydrophosphonylation of Carbonyl Compounds

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A synthetic approach to rare-earth amido complexes coordinated by *ansa* bis(amidinate) ligand with 1,8-naphthalene linker was elaborated and allowed for the synthesis of a series of complexes $[1,8\text{-}C_{10}H_6\{NC(t\text{Bu})N\text{-}2,6\text{-}Me_2C_6H_3\}_2]LnN(SiMe_3)_2(THF)_n$ (Ln = Y, n = 0 (**2**); Ln = Sm, n = 1 (**3**); Ln = Nd, n = 1 (**4**)) in reasonable yields. Complexes **2**-**4** initiate ring opening polymerization (ROP) of *rac*-lactide and enable complete conversion of 100-250 equiv. of monomer within 60-90 min at 25˚C. The obtained polylactides feature atactic structures and moderate molecular-weight distributions (M_w/M_n = 1.30–2.12). The experimental M_n values of the obtained polymers are found to be significantly higher than the calculated ones obviously due to slow initiation stage. Effective immortal ROP of lactide with 3-5 equiv of isopropanol per metal center was performed using complexes **2**-**4** as the catalysts. The systems **2-4**/*i*PrOH exhibit higher activities in ROP and allow for complete conversion of 100-300 equiv. of *rac*-lactide to polymer within 30-60 min at 25˚C and provide "living" polymerization mode and very narrow polydispersities (M_w/M_n = 1.13-1.27). Complexes **2**-**4** as well as related borohydrides $[1,8\text{-}C_{10}H_6\{NC(t\text{Bu})N\text{-}2,6\text{-}Me_2C_6H_3\}_2]Ln(BH_4)(\mu\text{-}BH_4)Li(THF)_2$ (Ln = Sm, Nd) catalyze hydrophosphonylation of aldehydes at room temperature with good reaction rates and hydrophosphonylation of benzylideneacetone at 65˚C.

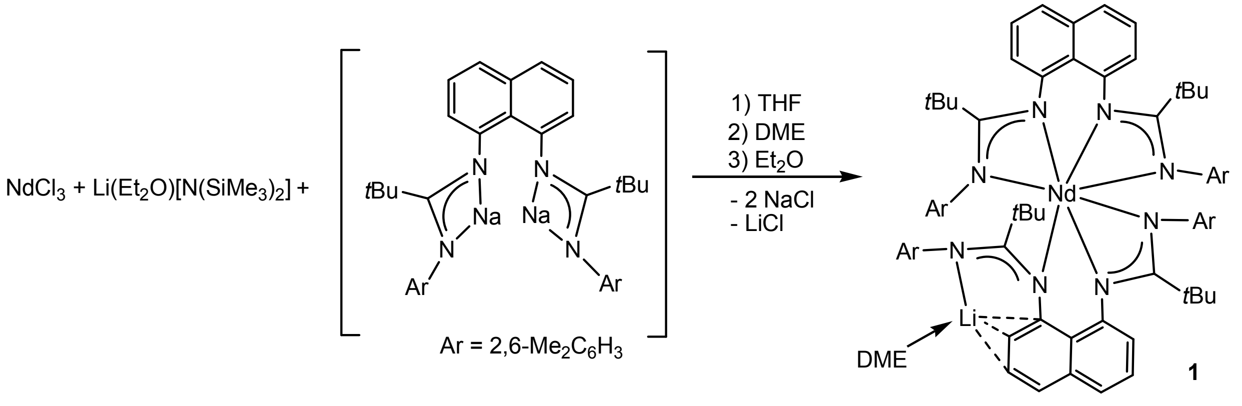
Introduction

The design and development of new ligand systems enabling stabilization of monomeric metal complexes while provoking novel reactivity and providing control of metal mediated reactions remain one of the most intensely explored areas of organorare-earth chemistry.[1-3] This issue acquires particular significance in the case of rare-earth metals possessing large ion sizes[4] and having tendency to ligand redistribution reactions originated from their electropositivity[5] and predominantly ionic nature of metal-ligand bonding. Monoanionic amidinate ligands proved to be a suitable coordination platform[6-8] which allowed for the synthesis and isolation of series of highly reactive species such as mono-, bis(alkyl), cationic alkyl and hydrido complexes.[1-3, 9-16] Alkyl and hydrido rare-earth complexes coordinated by amidinate ligands demonstrated high catalytic activity in olefin polymerization,[9-11] isoprene polymerization,[17-18] acetylene dimerization,[10] olefin hydroboration,[19] hydrosilylation,[20] and hydroamination.[21] The transition from bis(cyclopentadienyl) to linked bis(cyclopentadienyl) ligation system[22] led to the enhancement of catalytic activity of the alkyl and hydrido rare-earth species[23-26] due to opening of the metal coordination sphere and subsequent increase of its accessibility. Recently we developed and successfully applied linked bis(amidinate) ligand systems with rigid *o*-phenylene[27, 28] and 1,8-naphthalene linkers.[29, 30] At about the same time rare-earth complexes coordinated by *ansa* bis(amidinate) ligands with flexible linkers were reported.[31-37] Comparison of the reactivities and catalytic activities of the complexes supported by the linked bis(amidinate) systems with similar bulkiness of the substituents by the amidinate nitrogens and different length, flexibility, nature, structure of the linkers creates a basis for the comparative analysis of structure-reactivity relationship. Moreover estimation of applicability of $[1,8\text{-}C_{10}H_6\{NC(t\text{Bu})N\text{-}2,6\text{-}Me_2C_6H_3\}_2]$ ligand system for the synthesis of various classes of rare-earths presenting potential interest for possible catalytic use was in the focus of our research. Herein we report on the synthesis, structures of rare-earth amido complexes coordinated by $[1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}_2]^{2-}$ ligand and their catalytic activity in ring opening polymerization (ROP) and hydrophosphonylation of carbonyl compounds.

Results and discussion

Synthesis and Characterization of Compounds 1–4

Lanthanide amides proved to be efficient initiators for the ring-opening polymerization of cycle esters,[33, 38-44] components of catalyst systems for isoprene polymerization,[38-44] olefin hydroamination,[43,45-50] hydrophosphination,[47] hydrophosphonylation of carbonyl compounds[51-55,] and aldimines.[51,56] Initially, we intended to prepare bis(amidinate) amido lanthanide complexes by the salt metathesis reactions of $[1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}_2]YCl(DME)$, $[1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2\text{-}C_6H_3\}_2]Nd(DME)(\mu\text{-}Cl)_2Li(DME)$, and $[1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2\text{-}C_6H_3\}_2]Sm(THF)(\mu\text{-}Cl)_2Li(THF)_2$[29] with equimolar amounts of $Li(Et_2O)[N(SiMe_3)_2]$[57] and $Na[N(SiMe_3)_2]$[58] (THF, 60°C, 24 h). However this synthetic approach turned out inefficient, the starting chloro complexes were recovered from the reaction mixtures in nearly quantitative yields (88-91%). Thereby for the synthesis of bis(amidinate) amido lanthanide complexes another synthetic method was elaborated. The equimolar amounts of $NdCl_3$ and $Li(Et_2O)[N(SiMe_3)_2]$ were stirred in THF at 25°C for 24 h. Subsequently a solution of $[1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}_2]Na_2(THF)_n$ *in situ* prepared from $1,8\text{-}C_{10}H_6[NHC(tBu)=N(2,6\text{-}Me_2C_6H_3)][N=C(tBu)NH(2,6\text{-}Me_2C_6H_3)]$ and $NaN(SiMe_3)_2$ (1:2, toluene, 25 °C) was added and the reaction mixture was stirred at 60°C for 24 h. Evaporation of the volatiles in vacuum, extraction of the solid residue with toluene, treatment with DME and recrystallization from Et_2O afforded bimetallic complex $[1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}_2]Nd[\mu\text{-}1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}_2][Li(DME)]$ (**1**) in 43% yield (Scheme 1). *Ate*-complex **1** obviously results from the ligand redistribution reaction. Our attempts to isolate other neodymium containing products failed. All our attempts to isolate the samarium containing product prepared following the same scheme were unsuccessful. Complex **1** was obtained as yellow crystalline moisture- and air-sensitive crystalline solid soluble in THF, Et_2O, toluene and insoluble in hexane. Complex **1** was characterized by the X-ray diffraction analysis. Transparent yellow crystals of **1** suitable for X-ray single crystal structure determination were obtained by slow concentration of the solution in Et_2O at ambient temperature. Complex **1** was isolated as a solvate $\mathbf{1}\cdot(Et_2O)$. The molecular structure of **1** is depicted in Figure 1, the relevant bond lengths and angles are compiled in Table 1, and the structure refinement data are listed in Table 2. The X-ray study revealed that **1** is an *ate*-complex containing both Nd^{3+} and Li^+ ions and two bis(amidinate) ligands. One bis(amidinate) ligand in **1** is terminal and chelates the neodymium center by both amidinate fragments which are located in *cis* position with respect to the naphthalene linker (the dihedral angle between the NNdN planes is 109°). In another ligand just one amidinate fragment is chelating the Nd^{3+} while the second one is μ-bridging: its different nitrogen atoms coordinate different metal ions (Nd^{3+} or Li^+). Unlike the previously published related chloro complexes[29] featuring rather symmetric coordination of the amidinate ligands in **1** the Nd-N bond lengths for the chelating amidinate fragments are different. The two amidinato $1,8\text{-}C_{10}H_6N$ nitrogens are situated noticeably closer to the metal center (2.473(2), 2.497(2), 2.460(2) Å), than the two nitrogen atoms of the $2,6\text{-}Me_2C_6H_3N$ groups (2.556(2), 2.626(2), 2.632(2) Å). The distance from Nd^{3+} and the nitrogen atom of the bridging amidinate ligand falls in the same interval (2.582(2) Å). The average Nd-N bond length (2.55 Å) in **1** is slightly longer than those in the related neodymium complexes coordinated by *ansa* bis(amidinate) ligands.[28-30] The NCN bond angle of the μ-bridging amidinate fragment (120.8(2)°) in **1** is essentially larger than those of the terminal fragments (111.7(2)-112.3(2)°). The bonding situation within the terminal and bridging NCN fragments of complex **1** is similar and indicates negative charge delocalization (1.327(2)-1.356(2) Å). The lithium atom in **1** is bound to one nitrogen atom (Li(1)-N(4) 1.983(6) Å) and also accommodates a DME molecule (Li(1)-O(1) 1.996(4) Å, Li(1)-O(2) 1.997(5) Å). In addition, the Li^+ exhibits short interactions with the π-system of the adjacent aromatic ring of the naphthalene moiety (Li-C 2.510(5)-2.712(5) Å, Li-Ar_{centre} 2.39 Å). The average Li-C distance in **1** (2.59 Å) is much longer compared to that in complex $[Li(TMEDA)]_2[C_{10}H_8]$ (2.370(2) Å) .[59] The similar coordination mode was formerly described for Na^+ in the samarium amidinate *ate*-complex.[60]



Scheme 1 Synthesis of complex $[1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}_2]Nd[\mu\text{-}1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}_2][Li(DME)]$ (**1**).

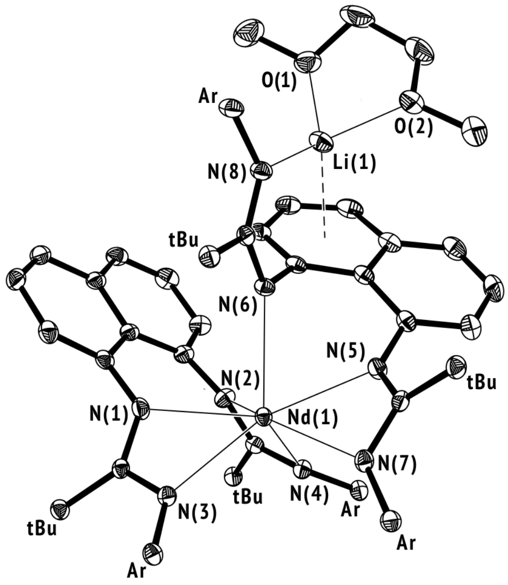


Fig. 1 Molecular structure of **1**, showing the atom numbering scheme. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms, *t*Bu and $(Me)_2C_6H_3$ (Ar) groups of the amidinato ligand and the DME molecule are omitted for clarity.

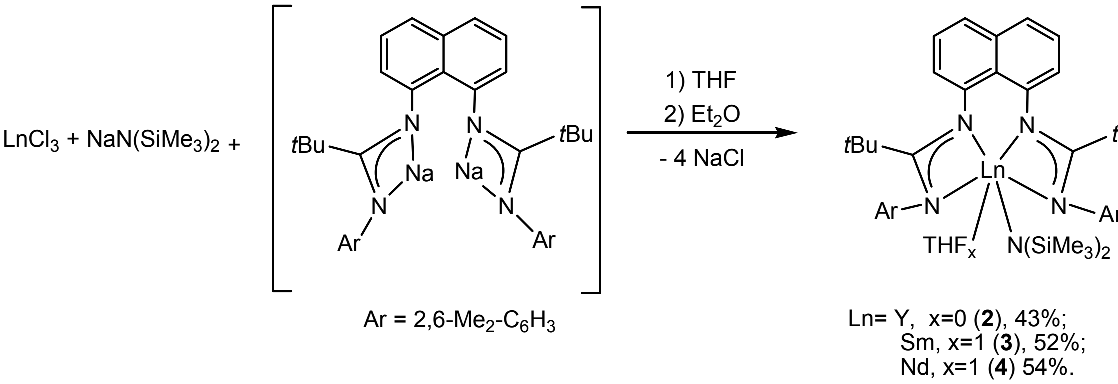
Table 1 Selected bond lengths and angles for compound **1**

Bond lengths, Å		Bond angels, °	
Nd(1)-N(1)	2.473(2)	N(1)-C(11)-N(3)	111.7(2)
Nd(1)-N(2)	2.497(2)	N(2)-C(24)-N(4)	112.3(2)
Nd(1)-N(3)	2.626(2)	N(5)-C(47)-N(7)	112.1(2)
Nd(1)-N(4)	2.556(2)	N(8)-C(60)-N(6)	120.8(2)
Nd(1)-N(5)	2.460(2)		
Nd(1)-N(6)	2.582(2)		
Nd(1)-N(7)	2.632(2)		
Li(1)-N(8)	2.002(4)		
Li(1)-O(1)	1.996(4)		
Li(1)-O(2)	1.997(5)		
Li(1) C(40)	2.510(5)		
Li(1)-C(39)	2.555(4)		
Li(1)-C(41)	2.712(5)		
N(1)-C(11)	1.327(2)		
N(3)-C(11)	1.342(2)		
N(5)-C(47)	1.332(2)		
N(7)-C(47)	1.344(3)		
N(4)-C(24)	1.356(2)		
N(2)-C(24)	1.320(3)		
N(6)-C(60)	1.348(3)		
N(8)-C(60)	1.335(3)		

Sodium is less prone to the formation of *ate*-complexes[61]. In order to suppress the ligand redistribution reaction and the *ate*-complex formation we decided to avoid the presence of Li^+ in the reaction mixture and to use $NaN(SiMe_3)_2$ instead of $Li(Et_2O)[N(SiMe_3)_2]$. The proposed synthetic approach turned out fruitful and allowed us for the synthesis of a series of new bis(amidinate) amido lanthanide complexes. The equimolar amounts of $LnCl_3$ and $NaN(SiMe_3)_2$ were reacted in THF at 25°C for 24 h. Subsequently a solution of $[1,8\text{-}C_{10}H_6\{NC(t\text{Bu})N\text{-}2,6\text{-}Me_2C_6H_3\}_2]Na_2(THF)_n$ *in situ* prepared from $1,8\text{-}C_{10}H_6[NHC(t\text{Bu})=N(2,6\text{-}Me_2C_6H_3)][N=C(t\text{Bu})NH(2,6\text{-}Me_2C_6H_3)]$ and $NaN(SiMe_3)_2$ (1:2, toluene, 25°C) was added and the reaction mixture was stirred at ambient temperature overnight. Evaporation of THF, extraction of the solid residue with toluene, separation of NaCl by filtration followed by recrystallization of the reaction product from Et_2O afforded bis(amidinate) amido lanthanide complexes $[1,8\text{-}C_{10}H_6\{NC(t\text{Bu})N\text{-}2,6\text{-}Me_2C_6H_3\}_2]YN(SiMe_3)_2$ (**2**), $[1,8\text{-}C_{10}H_6\{NC(t\text{Bu})N\text{-}2,6\text{-}Me_2C_6H_3\}_2]SmN(SiMe_3)_2(THF)$ (**3**), $[1,8\text{-}C_{10}H_6\{NC(t\text{Bu})N\text{-}2,6\text{-}Me_2C_6H_3\}_2]NdN(SiMe_3)_2(THF)$ (**4**) in reasonable yields (**2**: 43%, **3**: 52%, **4**: 54%) (Scheme 2). Complexes **2**-**4** were obtained as pale-yellow crystalline moisture- and air-sensitive solids. They are soluble in THF, Et_2O, toluene and slightly soluble in hexane. All complexes were fully characterized by spectroscopic methods and elemental analyses.

The ^1H and $^{13}C\{^1H\}$NMR spectra of the diamagnetic yttrium derivative **2** in C_6D_6 at 20 ºC show the expected set of signals corresponding to the bis(amidinate) and amido ligands. A singlet at -0.07 ppm corresponds to the methyl protons of $N(SiMe_3)_2$ group. The protons of the *t*Bu groups give rise to a singlet at 1.19 ppm and the protons of the Me groups appear as a singlet at 2.49 ppm. The aromatic protons give a set of signals in the interval 6.78-7.43 ppm. Unlike **2** Sm(III) complex **3** having a larger ion size[4] according to the ^1H and $^{13}C\{^1H\}$NMR spectra together with bis(amidinate) ligand and amido group contains one coordinated THF molecule. In the ^1H NMR spectrum of a slightly paramagnetic Sm(III) complex **3** (μ_{eff}= 1.64 μB)[62] the protons of $N(SiMe_3)_2$ group give a broadened singlet at 0.16 ppm. Singlets at 1.16 and 3.11 ppm correspond to the protons of the *t*Bu and Me groups respectively. Two broad singlets at δ = 1.53 and 3.32 ppm correspond to the β-CH_2 and α-CH_2 protons of the THF molecule. The spectrum also exhibits a multiplet at 6.28-7.72 ppm attributed to the aromatic protons. The IR spectra of complexes **2-4** display characteristic bands corresponding to the stretching vibrations of delocalized double C-N bonds of the bis(amidinate) ligand (**2**: 1670, 1638; **3**: 1670, 1637; **4**: 1637 cm^{-1}). Amido group $N(SiMe_3)_2$ shows the absorption bands related to the deformation vibrations of the C-H bonds of the methyl groups (**2** 1246; **3** 1250; **4** 1247 cm^{-1}) as well as the stretching vibrations of Si-N bonds (**2**: 933; **3**: 951; **4**, 962 cm^{-1}).

Clear pale-yellow crystals of **4** suitable for X-ray diffraction studies were obtained by slow concentration of Et_2O solutions at ambient temperature. The X-ray studies revealed that **4** crystallize in the space group *P*2(1)/c. The crystals of **4** contain two crystallographically independent molecules featuring very similar geometrical parameters.



Scheme 2 Synthesis of complexes [1,8-$C_{10}H_6${NC(*t*Bu)N-2,6-$Me_2C_6H_3$}$_2$]$YN(SiMe_3)_2$ (**2**), [1,8-$C_{10}H_6${NC(*t*Bu)N-2,6-$Me_2C_6H_3$}$_2$]$SmN(SiMe_3)_2$(THF) (**3**), [1,8-$C_{10}H_6${NC(*t*Bu)N-2,6-$Me_2C_6H_3$}$_2$]$NdN(SiMe_3)_2$(THF) (**4**).

Thus, only the structure of one molecule will be discussed. The molecular structure of **4** is shown in Figure 2; the relevant bond lengths and angles are reported in Table 3, and the structure refinement data are listed in Table 2. The coordination sphere of the neodymium atom in **4** is set up by four nitrogen atoms of two amidinate fragments, one nitrogen atom of the terminal amido ligand and one oxygen atom of THF molecule. Unlike the related chloro complex[29] the amidinate fragments in **4** adopt a *cis* position with respect to the naphthalene linker (the dihedral angle between the NNdN planes is 69.5°) and the naphthalene linker are slightly distorted (maximum deviation of C atoms from the plane C(1)-C(10) is 0.1 Å). The bonding situation in **4** similar to that previously described for the related lanthanide complexes coordinated by *ansa* bis(amidinate) ligands with *o*-phenylene[28] and $(\text{-CH}_2\text{-})_3$[32] linkers: the two amidinato 1,8-$C_{10}H_6N$ nitrogens are situated noticeably closer to the metal center (2.406(5), 2.413(5) Å), than the two nitrogen atoms of the 2,6-$Me_2C_6H_3N$ groups (2.524(4), 2.568(5) Å) and the average bond N-C lengths (1.34 Å, N-C bonds lenghts lie in the range 1.318(7)-1.358(8) Å) are comparable to those reported for related bis(amidinate) complexes of neodymium[32]. The bonding situation within the amidinate groups of complex **4** indicates delocalization of the negative charge within the NCN fragments. The $Nd\text{-}N(SiMe_3)_2$ bond length (2.239(4) Å) in **4** is considerably shorter compared to the corresponding distances in the amido complexes $L_2NdN(SiMe_3)_2$ (L = 3,5-*t*Bu_2-2-(O)-C_6H_2CH=N-2,6-*i*$Pr_2C_6H_3$, 2.340(4) Å; L = 3,5-*t*Bu_2-2-(O)-C_6H_2CH=N-2,6-$Me_2C_6H_3$, 2.433(5) Å) [63,64].

Catalytic Activity of Bis(amidinate) Amido Complexes in Ring-opening Polymerization (ROP) of Racemic Lactide

Ring-opening polymerization (ROP) of cyclic esters, promoted by single-site metal-based initiators/catalysts that operate *via* coordination/insertion pathways, is definitely the most useful route for preparing polyesters with good control over polymer molecular weight, polydispersity, and microstructure.[65] The development over the past two decades of various types of metal catalysts for the ROP of cyclic esters has demonstrated the crucial influence that both the ancillary ligand and the initiating group exert on the polymerization performance.[66] Among the large variety of investigated metal complexes, group 3 metals and lanthanide

Table 2 Crystallographic data and structure refinement details for **1** and **4**.

Complex	**1**	**4**
Empirical formula	$C_{80}H_{104}LiN_8NdO_3$	$C_{46}H_{68}N_5NdOSi_2$
Formula weight	1376.89	907.47
T, K	150(2)	100(2)
Wavelength, Å	0.71073	
Crystal system	*Triclinic*	*Monoclinic*
Space group	*P-1*	*P2(1)/c*
a [Å]	12.6452(6)	23.950(2)
b [Å]	15.0817(7)	19.426(1)
c [Å]	20.7038(9)	21.871(1)
α [°]	101.662(1)	90
β [°]	97.130(1)	116.878(1)
γ [°]	106.030(1)	90
Volume, $Å^3$	3648.0(3)	9076(1)
Z	2	8
ρ_{calcd}, g/cm^3	1.253	1.328
Absorption coefficient, mm^{-1}	0.764	1.236
F(000)	1454	3800
Crystal size, mm	0.26×0.24×0.13	0.35×0.26×0.23
θ range for data collection, °	1.97 to 27.00	0.95 to 25.00
Index ranges	$-16\leq h\leq 15$ $-13\leq k\leq 19$ $-26\leq l\leq 25$	$-28\leq h\leq 28$ $-23\leq k\leq 23$ $-26\leq l\leq 26$
Reflections collected	23814	69897
Independent reflections	15794	15735
R_{int}	0.0201	0.0415
Completeness to 2*θ*, %	99.1	98.4
Goodness-of-fit on F^2	1.057	1.154
Final *R* indices ($I>2\sigma(I)$)	$R_1 = 0.0405$ $wR_2 = 0.1023$	$R_1 = 0.0770$ $wR_2 = 0.1598$
R indices (all data)	$R_1 = 0.0507$ $wR_2 = 0.1071$	$R_1 = 0.0858$ $wR_2 = 0.1628$
Largest diff. peak and hole, $e/Å^3$	2.097 / -0.597	2.409 / -2.191

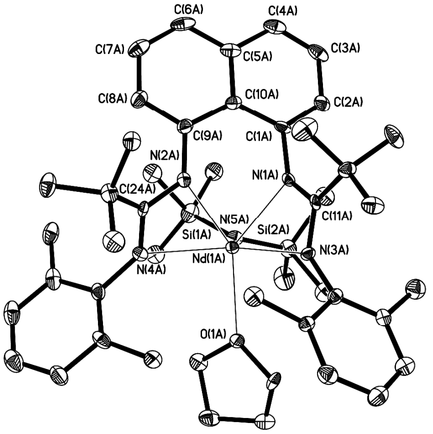


Fig. 2 Molecular structure of **4**. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity

Table 3 Selected bond lengths and angles for compound **4**

Bond lengths, Å		Bond angles, °	
Nd(1A)-N(1A)	2.406(5)	N(3A)-C(11A)-N(1A)	110.2(4)
Nd(1A)-N(2A)	2.413(5)	N(4A)-C(24A)-N(2A)	112.4(4)
Nd(1A)-N(3A)	2.524(4)		
Nd(1A)-N(4A)	2.568(5)		
Nd(1A)-N(5A)	2.329(4)		
Nd(1A)-O(1A)	2.503(4)		
N(1A)-C(11A)	1.343(7)		
N(3A)-C(11A)	1.331(8)		
N(2A)-C(24A)	1.358(8)		
N(4A)-C(24A)	1.318(7)		

derivatives,[66, 67-71] in particular amido, alkoxo and borohydrido complexes supported by *N*-containing ligands have been shown to be efficient. [33, 35, 67-71]

Amido compounds **2-4** were evaluated as initiators for ROP of racemic lactide. The polymerization tests were conducted either in THF or in toluene at room temperature at the concentration of *rac*-lactide of 1 mol·L^{-1}. The results are compiled in Table 4. Complexes **2-4** allowed 89-99% conversion of 100-250 equiv. of *rac*-lactide to polymer within 60-90 min at 25°C in toluene. In THF these complexes showed lower activity than in toluene (Table 4, entries 2, 11, 18 and 1, 10, 17), presumably because of competitive coordination to the catalytic centers between the monomer and THF. A kinetic monitoring of the ROP reaction mediated by **3** in toluene indicated a first-order dependence on lactide concentration, with an apparent first order rate constant $k_{app} = 0.0478$ min^{-1} (Fig. 3). The ^{1}H NMR spectra of the PLAs formed showed atactic microstructures. The P_r (probability of racemic linkage) values are in the range of 0.53-0.56. The PLAs produced with complexes **2-4** showed monomodal GPC traces with moderate molecular-weight distributions in the range M_w/M_n = 1.30–2.12. The experimental M_n values in the most of cases were found to be significantly higher than the calculated ones (Fig 4). It should be noted that this general trend has been often observed for the ROP of lactide initiated by rare-earth amido complexes. It was associated with lower nucleophilicity of the amido group $N(SiMe_3)_2$, acting on the initiation stage as compared to the nucleophilic alkoxide group -OR (R - the growing polymer chain) resulted from opening of the lactide and the insertion of the resulting fragments into M-$N(SiMe_3)_2$) bond. [72-76] It is worthy to note that the previously obtained heterobimetallic lanthanide borohydrides [1,8-$C_{10}H_6${NC(*t*Bu)N-2,6-$Me_2C_6H_3$}$_2$]Ln$(BH_4)_2$Li$(THF)_2$ (Ln = Sm (**5**) Nd (**6**)) supported by the same ligand system which act as single-site diinitiators, featured lower activity both in toluene and in THF, enabling quantitative conversions of 100-120 equiv. of *rac*-LA at room temperature within a few hours. These initiators produced PLAs in a rather controlled fashion in terms of molecular weights and relatively narrow unimodal molecular weight distributions (M_w/M_n = 1.4-1.7), but with only minor bias toward heterotactic sequences[30].

The possibility to achieve immortal polymerization with these systems, that is, to generate several PLA chains per metal center by introducing several equivalents of a chain transfer agent, was explored with complexes **2-4** in the presence of *iso*-propanol which acts as a chain transfer agent.

Table 4 Polymerization of *rac*-lactide initiated by complexes 2-4[a]

Entry	Complex	ROH	$[I]_0/[iPrOH]_0/[Mon]_0$	t [min][b]	Conversion [%][c]	$M_{ncalcd}\times10^{3[e]}$	$M_{nexp}\times10^{3[c]}$	M_w/M_n [d]	P_r
1	2	-	1:100	60	>99	14.25	25.33	1.37	0.55
2	2[f]	-	1:100	60	65	9.36	79.78	1.83	0.55
3	2	*i*PrOH	1:5:100	30	>99	2.85	3.23	1.26	0.52
4	3	-	1:100	60	97	13.97	24.91	2.12	0.53
5	3	-	1:250	15	38	13.68	21.80	1.30	0.54
6	3	-	1:250	30	66	23.76	43.18	1.35	0.55
7	3	-	1:250	45	90	32.40	51.46	1.53	0.54
8	3	-	1:250	60	93	33.48	57.14	1.57	0.54
9	3	-	1:250	75	97	34.92	57.14	1.41	0.54
10	3	-	1:250	90	>99	35.64	59.69	1.53	0.53
11	3[f]	-	1:250	60	71	2.56	67.83	1.97	0.56
12	3	*i*PrOH	1:5:250	30	>99	7.13	5.06	1.23	0.53
13	3	*i*PrOH	1:3:300	10	18	2.59	2.59	1.15	0.53
14	3	*i*PrOH	1:3:300	40	70	10.08	9.52	1.13	0.54
15	3	*i*PrOH	1:3:300	60	87	12.57	12.47	1.26	0.53
16	4	-	1:100	60	93	13.39	13.39	1.30	0.55
17	4	-	1:250	60	89	32.04	16.83	1.41	0.53
18	4[f]	-	1:250	60	64	23.04	42.35	1.49	0.53
19	4	*i*PrOH	1:5:250	30	>99	7.13	3.16	1.27	0.53

[a] General conditions: toluene, [LA] = 1.0 mol·L−1, T = 25 °C. [b] Reaction time was not necessarily optimized. [c] Conversion of monomer, as determined by ^{1}H NMR spectroscopy. [d] Experimental (corrected; see Experimental Section) M_n and M_w/M_n values determined by GPC in THF vs. polystyrene standards. [e] Mn value calculated by assuming one polymer chain per metal center with the relationship: 144×conversion×[Mon]/[Ln]. [f] Catalytic tests carried out in THF.

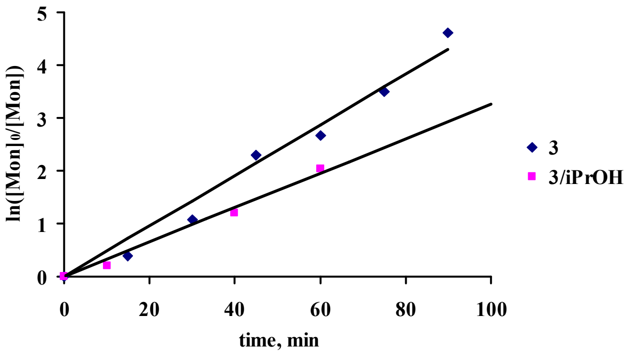


Fig. 3 Plot of ln($[Mon]_0$/[Mon]) as a function of time for the ROP of rac-LA mediated by **3** (linear fit R_2 = 0.9764)and **3**/*i*PrOH (linear fit R_2 = 0.9876) at 25°C in toluene, $[Mon]_0$ = 1.0 mol·L^{-1}, $[I]_0/[Mon]_0$ = 1:250, $[I]_0/[iPrOH]_0/[Mon]_0$ = 1:3:300.

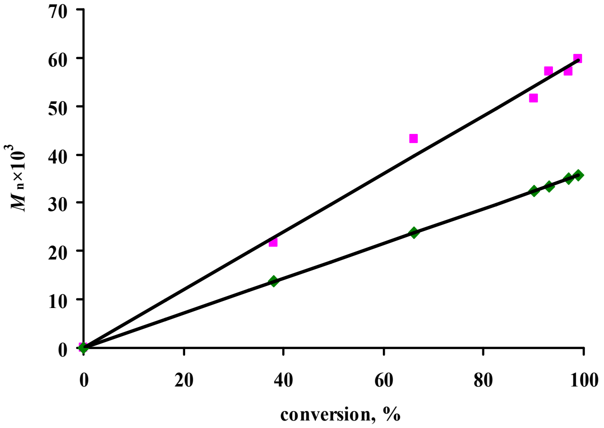


Fig. 4 M_n vs conversion for ROP initiated by **3**. Toluene, 25 °C, $[Mon]_0$ = 1.0 mol·L^{-1}, $[I]_0/[Mon]_0$ = 1:250.

The polymerizations of *rac*-LA with the systems **2-4**/*i*PrOH were conducted in the presence of 3 and 5 equiv (vs Ln) of *i*PrOH. The systems **2-4**/*i*PrOH allowed 87-99% conversion of 100-300 equiv. of *rac*-lactide to polymer within 30-60 min at 25˚C in toluene at a concentration of *rac*-lactide of 1 mol·L^{-1}. A kinetic monitoring of the ROP reaction mediated by **3**/*i*PrOH in toluene indicated a first-order dependence on lactide concentration, with an apparent first order rate constant k_{app} = 0.0326 min^{-1} (Fig 3). The ROP of *rac*-LA with **2-4** proceeded in a much better controlled fashion when iPrOH was added in the reaction (Table 3, entries 3, 12-15, 19). The much narrower polydispersities (M_w/M_n = 1.13-1.27) were observed under these conditions, as compared with those obtained without alcohol added, and the good match between calculated and experimental molecular weights argue for fast and reversible chain transfer. The M_{nexp} increased linearly with the conversion of the monomer recorded and the polydispersities kept in the range of 1.13-1.27 (Fig. 5), indicating the polymerization occurs in a living fashion. The catalytic systems **2-4**/*i*PrOH are not stereoselective since atactic PLAs were recovered (P_r = 0.52-0.54).

Thus the systems **2-4**/*i*PrOH provide much better control over ROP of *rac*-lactide compared to amido **2-4** and borohydrido complexes $[1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}_2]Ln(BH_4)_2Li(THF)_2$ (Ln = Sm, Nd)[13b] and allow to carry out the polymerization process in the "living mode" producing polylactides with defined molecular weight and a very narrow molecular weight distribution.

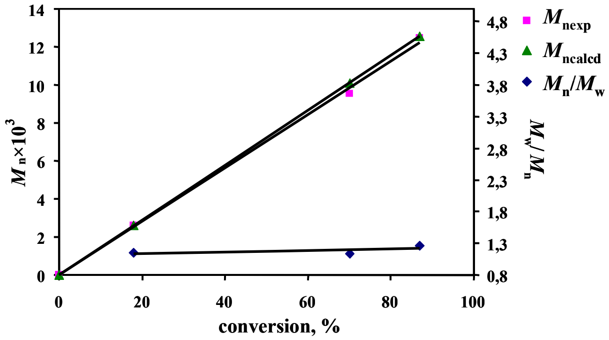


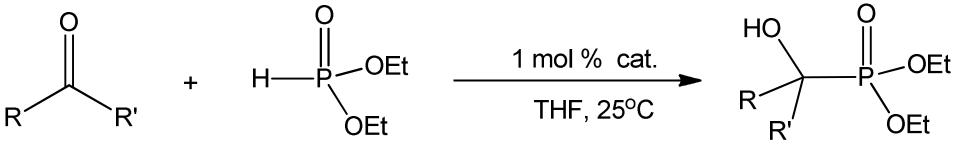
Fig. 5 M_{nexp}, M_{calcd} and M_w/M_n vs conversion for ROP initiated by **3**/*i*PrOH. Toluene, 25 °C, $[M]_0$ = 1.0 mol·L^{-1}, $[I]_0/[iPrOH]_0/[Mon]_0$= 1:3:300.

Hydrophosphonylation of Carbonyl Compounds Catalyzed by Lanthanide Amido and Borohydrido Complexes Containing Bis(amidinate) Ligand with Rigid Naphthalene Linker

The catalytic hydrophosphonylation of aldehydes, ketones and imines is a straightforward and atom-economic method for the formation of P–C bonds, which allows for the synthesis of α-amino and α-hydroxy phosphonic acids possessing important biological activities[77-85].

The amido complexes **2**–**4** were tested as catalysts for hydrophosphonylation of aldehydes and ketones (Scheme 3). The reactions of aldehydes with diethyl phosphite (1:1 molar ratio) were carried out at 25 °C in the presence of 1 mol % of complexes **2**–**4**. The results are summarized in Table 5. We found that the reactions of diethyl phosphite with benzaldehyde and aliphatic aldehydes initiated by **2-4** (1 molar %, THF, 25 °C) afford the corresponding products **7d-7h** in high yields (84-93%) within 24 hours (Table 5, Entry 4-8, 13-17, 22-26). Introduction of any type of substituent (electron donating or electron withdrawing) in the *para*-position of phenyl ring of benzaldehyde results in significant acceleration of the reactions. In these cases quantitative yields of the products **7a-7c** were achieved in a very short time (15 minutes) (Table 5, Entry 1-3, 10-12, 19-21). It should be noted that the Ln^{III} ionic radius has no effect on the rate of the reactions of hydrophosphonylation of aldehydes.[51, 53, 54, 55, 56.]

It is known that hydrophosphorylation reactions of aldimines and ketones require harsher conditions.[51,54] The lanthanide complexes with indolyl[51,55], pyrrole[54], methylene-linked pyrrolyl[56], calix[4]-pyrrolyl[53] ligands were found to be efficient initiators for this transformation. Investigation of the catalytic activity of **2-4** in the reactions of addition of diethyl phosphite to unactivated ketones (BuMeC(O), $Ph_2C(O)$, MePhC(O)) and aldimines (PhN=CHPh, $PhN=CPh_2$, $PhN=CH_2$) was performed at a catalyst concentration of 5 mol % in THF. However, even after 48 hours at 65˚C only starting substrates were isolated from the reaction mixtures. At the same time the reactions of diethylphosphite with benzylideneacetone PhCH=CHC(O)Me (5 mol % of **2-4**, 48 h, 65˚C) resulted in the formation of α-hydroxy phosphonate $PhCH=CHCMe(OH)P(O)(OEt)_2$ **7i** in 35-40% yields (Table 5, Entry 9, 18, 27).



7 a-i

Scheme 3

Table 5 Hydrophosphonylation of aldehydes and ketones catalyzed by the complexes **2-6**[a].

Entry	Complex	R	R'	time	product	Yield, [%][b]
1	**2**	4-Cl-C_6H_4	H	15 min	**7 a**	99
2	**2**	4-Me-C_6H_4	H	15 min	**7 b**	99
3	**2**	4-MeO-C_6H_4	H	15 min	**7 c**	99
4	**2**	Ph	H	24 h	**7 d**	92
5	**2**	Pen	H	24 h	**7 e**	88
6	**2**	Bu	H	24 h	**7 f**	87
7	**2**	*i*Pr	H	24 h	**7g**	85
8	**2**	Pr	H	24 h	**7h**	86
9	**2**[c]	Me	PhCH=CH	48 h	**7i**	35
10	**3**	4-Cl-C_6H_4	H	15 min	**7 a**	99
11	**3**	4-Me-C_6H_4	H	15 min	**7 b**	99
12	**3**	4-MeO-C_6H_4	H	15 min	**7 c**	99
13	**3**	Ph	H	24 h	**7 d**	93
14	**3**	Pen	H	24 h	**7 e**	92
15	**3**	Bu	H	24 h	**7 f**	89
16	**3**	*i*Pr	H	24 h	**7g**	85
17	**3**	Pr	H	24 h	**7h**	84
18	**3**[c]	Me	PhCH=CH	48 h	**7i**	38
19	**4**	4-Cl-C_6H_4	H	15 min	**7 a**	99
20	**4**	4-Me-C_6H_4	H	15 min	**7 b**	99
21	**4**	4-MeO-C_6H_4	H	15 min	**7 c**	99
22	**4**	Ph	H	24 h	**7 d**	92
23	**4**	Pen	H	24 h	**7 e**	89
24	**4**	Bu	H	24 h	**7 f**	87
25	**4**	*i*Pr	H	24 h	**7g**	86
26	**4**	Pr	H	24 h	**7h**	86
27	**4**[c]	Me	PhCH=CH	48 h	**7i**	40
28	**5**	4-Cl-C_6H_4	H	15 min	**7 a**	99
29	**5**	4-Me-C_6H_4	H	15 min	**7 b**	99
30	**5**	4-MeO-C_6H_4	H	15 min	**7 c**	99
31	**5**	Ph	H	24 h	**7 d**	93
32	**5**	Pen	H	24 h	**7 e**	93
33	**5**	Bu	H	24 h	**7 f**	86
34	**5**	*i*Pr	H	24 h	**7g**	88
35	**5**	Pr	H	24 h	**7h**	82
36	**5**[c]	Me	PhCH=CH	48 h	**7i**	40
37	**6**	4-Cl-C_6H_4	H	15 min	**7 a**	99
38	**6**	4-Me-C_6H_4	H	15 min	**7 b**	99
39	**6**	4-MeO-C_6H_4	H	15 min	**7 c**	99
40	**6**	Ph	H	24 h	**7 d**	92
41	**6**	Pen	H	24 h	**7 e**	92
42	**6**	Bu	H	24 h	**7 f**	91
43	**6**	***i*Pr**	H	24 h	**7g**	83
44	**6**	Pr	H	24 h	**7h**	81
45	**6**[c]	Me	PhCH=CH	48 h	**7i**	43

[a] Reaction conditions: diethyl phosphite (1.0 mmol), aldehyde (1.0 mmol), solvent (2 mL), room temperature. [b] Isolated yields; [c] The reactions were carried out at 65 °C in the presence of 5 mol % of complexes.

The catalytic activity of lanthanide borohydrido complexes in hydrophosphonylation of aldehydes and ketones remains less investigated.[28] Previously reported lanthanide borohydrides [1,8-$C_{10}H_6$\{NC(*t*Bu)N-2,6-$Me_2C_6H_3$\}$_2$]Ln(BH_4)(μ-BH_4)Li(THF)$_2$ (Ln = Sm (**5**), Nd (**6**))[30] supported by the same *ansa* bis(amidinate) ligand were tested as catalysts for hydrophosphonylation of carbonyl compounds. The reactions of equimolar amounts of aldehyde and diethyl phosphite (Table 5) were carried out in the presence of 1 molar % of complexes **5**, **6** in THF at 25 °C. The borohydrides **5** and **6** performed catalytic activities similar to those of amido derivatives **2-4**. Thus, the addition of diethyl phosphite to 4-chloro-, 4-methyl- and 4-methoxybenzaldehyde gave the products **7a-7c** in 99% yield in 15 min (Table 5, entry 28-30, 37-39). Under the same reaction conditions, when benzaldehyde and aliphatic aldehydes were used as the substrates the reaction was slower. The products **7d-7h** can be isolated in good to high yields in 24 hours (Table 5, entries 31-35, 40-44). Benzylideneacetone was also applicable to this reaction. The reaction in the presence of the complexes **5**, **6** (5 mol %) in 48 hours (THF, 65˚C) afforded α-hydroxy phosphonate PhCH=CHCMe(OH)P(O)(OEt)$_2$ (**7i**) in 40% and 43% yields respectively (Table 5, Entry 36, 45). It is noteworthy that unlike the lanthanide amido complexes reported by Wang[54] enabling 1,4-addition of diethyl phosphite to benzylideneacetone at 40 °C complexes **2-6** at high temperature afford exclusively the product of 1,2-addition. This is obviously due to the steric hindrance in the lanthanide coordination sphere caused by rigid coordination of the ansa bis(amidinate) ligand system which prevents 1,4-coordination of benzylideneacetone to the catalytic center. The borohydrides **5**, **6** do not initiate the reactions of unactivated ketones (BuMeC(O), Ph_2C(O), MePhC(O)) and aldimines (PhN = CHPh, PhN = CPh_2, PhN = CH_2) with diethylphosphite (catalyst concentration 5 mol %, THF, 65˚C, 48 h).

Experimental Section

All experiments were performed in evacuated tubes, using standard Schlenk-tube techniques, with the rigorous exclusion of traces of moisture and air. After drying over KOH, THF, Et_2O was purified by distillation from sodium/benzophenone ketyl, hexane and toluene by distillation from sodium/triglyme benzophenone ketyl prior to use. Anhydrous YCl_3, $SmCl_3$, $NdCl_3$[86] and Li(Et_2O)[N($SiMe_3$)$_2$][57], NaN($SiMe_3$)$_2$[58] were prepared according to literature procedures. All other commercially available chemicals were used after the appropriate purifications. NMR spectra were recorded on Bruker Avance DRX-400 and DPX-200 spectrometers in C_6D_6 at 20˚C, unless otherwise stated. Chemical shifts for ^{1}H and ^{13}C spectra were referenced internally using the residual solvent resonances and are reported relative to TMS in parts per million (ppm). IR spectra were recorded as Nujol mulls on «IR Prestige-21 Shimadzu» instrument. Lanthanide metal analyses were carried out by complexometric titration[87].

The C, H, N elemental analyses were performed in the microanalytical laboratory of the G. A. Razuvaev Institute of Organometallic Chemistry. GPC was carried out by using a chromatograph "Knauer Smartline" with Phenogel Phenomenex Columns 5u (300×7.8 mm) 10^4, 10^5 and a Security Guard Phenogel Column with RI and UV detectors (254 nm). The mobile phase was THF and the flow rate was 2 mL/min. The columns were calibrated by Phenomenex Medium- and High-Molecular-Weight Polystyrene Standard Kits with peak molecular weights from 2700 to 2570000 Da. The number-average molecular masses (M_n) and polydispersity indexes (M_w/M_n) of the polymers were calculated with reference to a universal calibration vs. polystyrene standards. M_n values of PLAs were corrected with a Mark–Houwink factor of 0.58 to account for the difference in hydrodynamic volumes between polystyrene and polylactide.[88] The microstructures of the PLAs were measured by homo-decoupling ^{1}H NMR spectroscopy at 25°C in $CDCl_3$ with a Bruker Avance DRX-400 spectroscopy.[89]

X-ray diffraction intensity data for compounds **1** and **4** were collected on *Bruker Smart APEX* diffractometer with graphite monochromated *Mo-Kα* radiation (λ = 0.71073 Å) using ω scans. The structures were solved by direct methods and were refined on F^2 using *SHELXTL*[90] package. All non-hydrogen atoms were found from Fourier syntheses of electron density and were refined anisotropically. All hydrogen atoms were placed in calculated positions and were refined in the riding model. *SADABS*[91] were used to perform area-detector scaling and absorption corrections. The details of crystallographic, collection and refinement data are shown in Table 2. CCDC-1022273 (**1**) and 1022274 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via ccdc.cam.ac.uk/community/requestastructure.

Synthesis of [1,8-$C_{10}H_6$\{NC(*t*Bu)N-2,6-$Me_2C_6H_3$\}$_2$]Nd[μ-1,8-$C_{10}H_6$\{NC(*t*Bu)N-2,6-$Me_2C_6H_3$\}$_2$][Li(DME)] (1). A solution of Li(Et_2O)[N($SiMe_3$)$_2$] (0.24 g, 1.03 mmol) in THF (20 mL) was added to a suspension of $NdCl_3$ (0.25 g, 1.03 mmol) in THF (30 mL) at 25 ˚C and the reaction mixture was stirred for 24h. The resulting solution was added to a THF (20mL) solution of [1,8-$C_{10}H_6$-\{NC(*t*Bu)N-2,6-$Me_2C_6H_3$\}$_2$]Na_2(THF)$_n$ *in situ* prepared from 1,8-$C_{10}H_6$\{HNC(*t*Bu)N-2,6-$Me_2C_6H_3$\}\{NC(*t*Bu)HN-2,6-$Me_2C_6H_3$\} (0.55 g, 1.03 mmol) and NaN($SiMe_3$)$_2$ (0.37 g, 2.06 mmol) in toluene (50 mL) at 25°C. The reaction mixture was stirred overnight, the volatiles were removed in vacuum, the solid residue was extracted with toluene (2×20 mL), and the extracts were filtered. Evaporation of toluene and recrystallization of the solid residue from Et_2O afforded pale yellow crystals of **1** (0.61 g, 43%). IR (KBr, Nujol, ν_{max} cm^{-1}): 1653 (w), 1638 (w), 1595 (w), 1564 (w), 1533 (m), 1510 (m), 1292 (m), 1250 (m), 1219 (m), 1178 (m), 1113 (m), 1034 (m), 999 (m), 932 (m), 883 (m), 812 (m), 768 (m), 741 (m), 658 (m), 588 (m). Anal. calcd for [$C_{80}H_{104}LiN_8NdO_3$]: C, 69.78; H, 7.61; Nd, 10.48 %; found: C, 69.39; H, 7.35; Nd, 10.63 %.

Synthesis of [1,8-$C_{10}H_6$\{NC(*t*Bu)N-2,6-$Me_2C_6H_3$\}$_2$]YN($SiMe_3$)$_2$ (2): A solution of NaN($SiMe_3$)$_2$ (0.22 g, 1.18 mmol) in THF (20 mL) was added to a suspension of YCl_3 (0.25 g, 1.18 mmol) in THF (30 mL) at 25 ˚C and reaction mixture was stirred for 24h. The resulting solution was added to a THF (20mL) solution of [1,8-$C_{10}H_6$\{NC(*t*Bu)N-2,6-$Me_2C_6H_3$\}$_2$]Na_2(THF)$_n$ *in situ* prepared from 1,8-$C_{10}H_6$\{HNC(*t*Bu)N-2,6-$Me_2C_6H_3$\}\{NC(*t*Bu)HN-2,6-$Me_2C_6H_3$\} (0.63 g, 1.18 mmol) and NaN($SiMe_3$)$_2$ (0.44 g, 2.37 mmol) in toluene (50 mL). The reaction mixture was stirred overnight, the volatiles were removed in vacuum, the solid residue was extracted with toluene (2×20 mL), and the extracts were filtered. Evaporation of toluene and recrystallization of the solid residue from Et_2O afforded pale yellow crystals of **2** (0.40 g, 43%). NMR (C_6D_6, 20°C, 200 MHz; δ ppm) ^1H: 7.43- 6.78 (m, 12 H, $C_{10}H_6$, $(CH_3)_2C_6H_3$), 2.49 (s, 12 H, CH_3), 1.19 (s, 18 H, $C(CH_3)_3$), -0.07 (s, 18 H, $SiCH_3$). NMR (C_6D_6, 20°C, 100 MHz; δ ppm) $^{13}C\{^1H\}$: 183.0, 153.7, 149.4, 148.0, 147.7, 142.9, 141.7, 137.2, 136.7, 136.3, 130.9, 130.7, 130.6, 129.6, 128.4, 125.0, 124.6, 123.5, 122.8, 120.1, 119.6, 119.1, 118.7 ($C_{10}H_6$, $(CH_3)_2C_6H_3$), 42.7 (s, $C(CH_3)_3$), 30.8 (s, $C(CH_3)_3$), 21.3 (s, CH_3), 3.5 (s, $SiCH_3$), 2.3 (s, $SiCH_3$). IR (KBr, Nujol, ν_{max} cm^{-1}): 1670 (w), 1638 (w), 1566 (w), 1417 (m), 1396 (m), 1361 (m), 1350 (m), 1331 (m), 1246 (m), 1215 (m), 1202 (m), 1175 (m), 1165 (m), 1093 (m), 1045 (m), 1016 (m), 982 (m), 933 (m), 870 (m), 837 (m), 812 (w), 760 (m), 677 (m), 652 (w). Anal. calcd for $[C_{42}H_{60}N_5Si_2Y]$: C, 64.67; H, 7.75; Y, 11.40 %; found: C, 64.25; H, 7.39; Y, 11.68 %.

Synthesis of $[1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}_2]SmN(SiMe_3)_2(THF)$ (3): A solution of $NaN(SiMe_3)_2$ (0.20 g, 1.10 mmol) in THF (20 mL) was added to a suspension of $SmCl_3$ (0.28 g, 1.10 mmol) in THF (30 mL) at 25 ˚C and the reaction mixture was stirred for 24h. The resulting solution was added to a THF (20 mL) solution of $[1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}_2]Na_2(THF)_n$ *in situ* prepared from $1,8\text{-}C_{10}H_6\{HNC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}\{NC(tBu)HN\text{-}2,6\text{-}Me_2C_6H_3\}$ (0.59 g, 1.10 mmol) and $NaN(SiMe_3)_2$ (0.40 g, 2.20 mmol) in toluene (50 mL). The reaction mixture was stirred overnight, the volatiles were removed in vacuum, the solid residue was extracted with toluene (2×20 mL), and the extracts were filtered. Evaporation of toluene and recrystallization of the solid residue from Et_2O afforded pale yellow crystals of **3** (0.52 g, 52%). NMR (C_6D_6, 20°C, 400 MHz; δ ppm) ^1H: 7.72 -6.28 (m, 12 H, $C_{10}H_6$, $(CH_3)_2C_6H_3$), 3.32 (br. s, 12 H, THF, α-CH_2), 3.11 (s, 12 H, CH_3), 1.53 (br. s., 12 H, THF, β-CH_2), 1.16 (s, 18 H, $C(CH_3)_3$), 0.16 (s, 18 H, $SiCH_3$). NMR (C_6D_6, 20°C, 100 MHz; δ ppm) $^{13}C\{^1H\}$: 162.2, 147.5, 147.3, 146.5, 138.2, 135.7, 135.4, 129.7, 124.4, 121.9, 121.4, 120.4, 120.0, 118.2, 116.7, 116.0, 113.6, 98.1, ($C_{10}H_6$, $(CH_3)_2C_6H_3$) 71.89 (s, THF, α-CH_2), 40.4 (s, $C(CH_3)_3$), 39.1 (s, $C(CH_3)_3$), 29.93 (s, THF, β-CH_2), 29.40 (s, $C(CH_3)_3$), 29.72 (s, $C(CH_3)_3$), 16.22 (s, CH_3), 1.05 (s, $SiCH_3$). IR (KBr, Nujol, ν_{max} cm^{-1}): 1670 (w), 1637 (w), 1589 (w), 1556 (m), 1418 (s), 1396 (s), 1361 (s) 1350 (s), 1336 (m), 1294 (m), 1250 (m), 1213 (m), 1172 (m), 1117 (m), 1095 (m), 1065 (m), 1043 (m), 1034 (m), 951 (m), 932 (m), 894 (m.), 841 (m), 826 (m.), 825 (m), 787 (m), 760 (m), 690 (w), 617 (w), 602 (w). Anal. calcd for $[C_{46}H_{68}N_5OSi_2Sm]$: C, 60.47; H, 7.50; Sm, 16.46 %; found: C, 60.08; H, 7.33; Sm, 16.48 %.

Synthesis of $[1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}_2]NdN(SiMe_3)_2(THF)$ (4): A solution of $NaN(SiMe_3)_2$ (0.22 g, 1.18 mmol) in THF (20 mL) was added to a suspension of $NdCl_3$ (0.25 g, 1.18 mmol) in THF (30 mL) at 25 ˚C and the reaction mixture was stirred for 24h. The resulting solution was added to a THF (20mL) solution of $[1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}_2]Na_2(THF)_n$ *in situ* prepared from of $1,8\text{-}C_{10}H_6\{HNC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}\{NC(tBu)HN\text{-}2,6\text{-}Me_2C_6H_3\}$ (0.63 g, 1.18 mmol) with $NaN(SiMe_3)_2$ (0.44 g, 2.37 mmol) in toluene (50 mL). The reaction mixture was stirred overnight, the solvent was evaporated in vacuum, the solid residue was extracted with toluene (20 mL), and extracts were filtered. After recrystallization of the residue from Et_2O, pale yellow crystals of **4** were obtained in a yield of 0.58 g (54%). IR (KBr, Nujol, ν_{max} cm^{-1}): ν□ = 1637 (w), 1589 (m), 1558 (m), 1364 (m), 1335 (m), 1247 (m), 1213 (m), 1194 (m), 1173 (m), 1117 (m), 1098 (m), 1080 (m), 1043 (m), 1032 (m), 962 (m), 889 (m), 824 (m), 688 (w), 617 (w), 602 (w). Anal. calcd for $[C_{46}H_{68}N_5NdOSi_2]$: C, 60.88; H, 7.55; Nd, 15.89 %; found: C, 60.43; H, 7.45; Nd, 15.79 %.

General Experimental Procedure for Polymerization of *rac*-lactide. In a typical experiment (Table 4, entry 3), in a glovebox, a Schlenk flask was charged with a solution of initiator **2** (16 mg, 0.0205 mmol) in toluene (1 mL). To this solution, *rac*-lactide (290 mg, 2.05 mmol, 100 equiv) in toluene (1 mL) was added rapidly (isopropanol was added at this stage for experiments conducted under "immortal" conditions). The mixture was immediately stirred with a magnetic stir bar at 25 °C for 30 min. After an aliquot of the crude material was sampled by pipet for determining monomer conversion by ^1H NMR, the reaction was quenched with acidic methanol (ca. 1 mL of a 1.2 M HCl solution in MeOH), and the polymer was precipitated with excess methanol (ca. 50 mL). The polymer was then filtered and dried under vacuum to constant weight. The P_r values for obtained polylactides were calculated cording to published protocol.[92]

General Experimental Procedure for Hydrophosphonylationof Aldehydes, Ketons and Aldimines.

$HP(O)(OEt)_2$ (1 mmol, 0.138 g, 0.127 mL) was added to a solution of aldehyde (ketone or aldimine) (1 mmol) and catalyst (1 or 5 mol %) in toluene (2 mL). The reaction mixture was stirred at room temperature for 24 h and was subsequently hydrolyzed with water (1.0 mL), extracted with ethyl acetate (3×10.0 mL), dried with anhydrous Na_2SO_4 and filtered. After the solvent was removed under vacuum, the final product was recrystallized from a THF/hexane mixture. The yield of product was determined by weighing.

Conclusions

A series of rare-earth amido complexes $[1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}_2]LnN(SiMe_3)_2(THF)_n$ supported by *ansa* bis(amidinate) ligand was successfully synthesized by the salt metathesis reactions starting from *in situ* generated $[(Me_3Si)_2N]LnCl_2(THF)_2$, while the attempts of substitution of chloro ligand in $[1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}_2]YCl(DME)$ and $[1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}_2]Ln(L)(\mu\text{-}Cl)_2Li(L)_n$ (Ln = Sm, L=DME; Ln=Nd, L=THF) by $[(Me_3Si)_2N]^-$ group failed. The alkaline metal cation plays a crucial role in the outcome of metathesis reaction: in the presence of Li^+ the reaction pathway switches towards formation of amidinate *ate*-complex $[1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}_2]Nd[\mu\text{-}1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}_2][Li(DME)]$.

Amido complexes **2**-**4** initiate ROP of *rac*-lactide under mild conditions and convert 100-250 equiv. of monomer within 60-90 min in polylactides featuring atactic structures and moderate molecular-weight distributions (M_w/M_n = 1.30-2.12). The experimental M_n values of the obtained polymers are found to be significantly higher than the calculated ones presumably due to slow initiation stage. Amido complexes **2-4** turned out to be more efficient ROP catalysts compared to the related borohydrides [1,8-$C_{10}H_6\{NC(t\text{Bu})N\text{-}2,6\text{-}Me_2C_6H_3\}_2]Ln(BH_4)_2Li(THF)_2$. Effectively immortal ROP of lactide with 3-5 equiv of isopropanol per metal center was performed using complexes **2-4** as the catalysts. The systems **2-4**/*i*PrOH exhibit higher activities in ROP and allow for complete conversion of 100-300 equiv. of *rac*-lactide to polymer within 30-60 min at 25˚C and provide "living" polymerization mode and very narrow polydispersities (M_w/M_n = 1.13-1.27). Comparison of the results of the catalytic tests obtained with complexes coordinated by linked bis(amidinate) systems [1,8-$C_{10}H_6\{NC(t\text{Bu})N\text{-}2,6\text{-}Me_2\text{-}C_6H_3\}_2]^{2-}$, [$C_6H_4$-1,2-$\{NC(t\text{Bu})N(2,6\text{-}Me_2C_6H_3)\}_2]^{2-}$,[28] [$C_6H_4$-1,2-$\{NC(Ph)NSiMe_3\}_2]^{2-}$ [28] and [$CH_2\{CH_2NC(Ph)NSiMe_3\}_2]^{2-}$ [32] clearly demonstrate that flexible -$(CH_2)_3$- linker provides better degree of stereocontrol of ROP *rac*-lactide *vs* rigid 1,8-$C_{10}H_6$ and C_6H_4-1,2.

Complexes **2-4** as well as related borohydrides [1,8-$C_{10}H_6\{NC(t\text{Bu})N\text{-}2,6\text{-}Me_2\text{-}C_6H_3\}_2]Ln(BH_4)(\mu\text{-}BH_4)Li(THF)_2$ (Ln = Sm, Nd) catalyze hydrophosphonylation of aldehydes at room temperature with good reaction rates and hydrophosphonylation of benzylideneacetone at 65˚C.

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