NJC

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c4nj01698j

Amido rare-earth complexes supported by an *ansa* bis(amidinate) ligand with a rigid 1,8-naphthalene linker: synthesis, structures and catalytic activity in *rac*-lactide polymerization and hydrophosphonylation of carbonyl compounds†

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Received (in Victoria, Australia)
30th September 2014,
Accepted 11th November 2014

DOI: 10.1039/c4nj01698j

www.rsc.org/njc

A synthetic approach to rare-earth amido complexes coordinated by an *ansa* bis(amidinate) ligand with a 1,8-naphthalene linker was developed and allowed for the synthesis of a series of complexes $[1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}_2]LnN(SiMe_3)_2(THF)_n$ (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 due to a 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**/iPrOH 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 a living polymerization mode and very narrow polydispersities (M_w/M_n = 1.13–1.27). Complexes **2–4** as well as related borohydrides $[1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}_2]Ln(BH_4)(\mu\text{-}BH_4)Li(THF)_2$ (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 a tendency for ligand redistribution reactions originating 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 a 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 a 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 a linked bis(cyclopentadienyl) ligation system[22] led to the enhancement of the 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 a similar bulkiness of the substituents by the amidinate nitrogens and a different length, flexibility, nature and structure of the linkers creates a basis for the comparative analysis of the structure–reactivity relationship. Moreover, estimation of the applicability

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† Electronic supplementary information (ESI) available. CCDC 1022273 and 1022274. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4nj01698j

of a [1,8-$C_{10}H_6${NC(*t*Bu)N-2,6-$Me_2C_6H_3$}$_2$] ligand system for the synthesis of various classes of rare-earths presents the possibility of catalytic use and was therefore the focus of our research. Herein we report on the synthesis and structures of rare-earth amido complexes coordinated by a [1,8-$C_{10}H_6${NC(*t*Bu)N-2,6-$Me_2C_6H_3$}$_2$]$^{2-}$ 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 cyclic 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-$C_{10}H_6${NC(*t*Bu)N-2,6-$Me_2C_6H_3$}$_2$]-YCl(DME), [1,8-$C_{10}H_6${NC(*t*Bu)N-2,6-$Me_2C_6H_3$}$_2$]Nd(DME)(μ-Cl)$_2$-Li(DME), and [1,8-$C_{10}H_6${NC(*t*Bu)N-2,6-$Me_2C_6H_3$}$_2$]Sm(THF)(μ-Cl)$_2$-Li(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 to be inefficient as the starting chloro complexes were recovered from the reaction mixtures in nearly quantitative yields (88–91%). Thereby for the synthesis of the bis(amidinate) amido lanthanide complexes another synthetic method was elaborated. 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-$C_{10}H_6${NC(*t*Bu)N-2,6-$Me_2C_6H_3$}$_2$]-Na_2(THF)$_n$ *in situ* prepared from 1,8-$C_{10}H_6$[NHC(*t*Bu)=N(2,6-$Me_2C_6H_3$)][N=C(*t*Bu)NH(2,6-$Me_2C_6H_3$)] 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 under vacuum, extraction of the solid residue with toluene, treatment with DME and recrystallization from Et_2O afforded the bimetallic complex [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**) 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 a yellow moisture- and air-sensitive crystalline solid soluble in THF, Et_2O, toluene and insoluble in hexane. Complex **1** was characterized by 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 **1**·(Et_2O). The molecular structure of **1** is depicted in Fig. 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 the *cis* position with respect to the naphthalene linker (the dihedral angle between the NNdN planes is 109°). In the

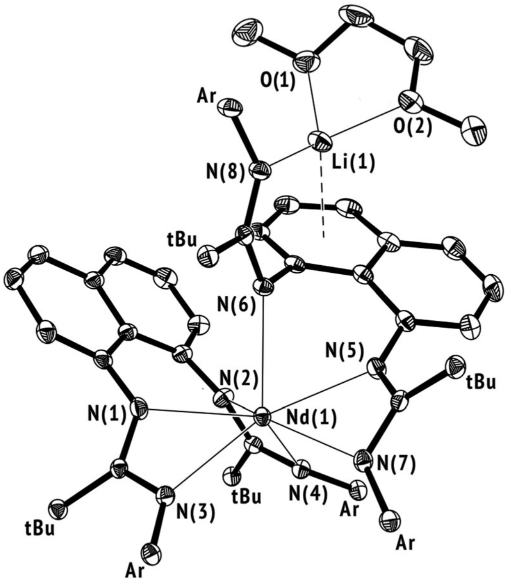
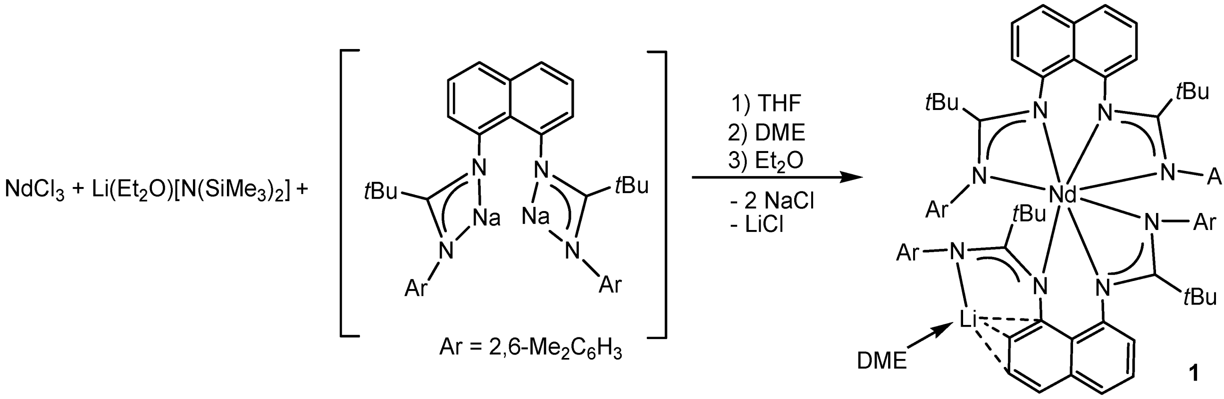


Fig. 1 Molecular structure of **1**, showing the atom numbering scheme. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms, *t*Bu and $(Me)_2C_6H_3$ (Ar) groups of the amidinato ligand and the DME molecule are omitted for clarity.



Scheme 1 Synthesis of complex [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**).

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

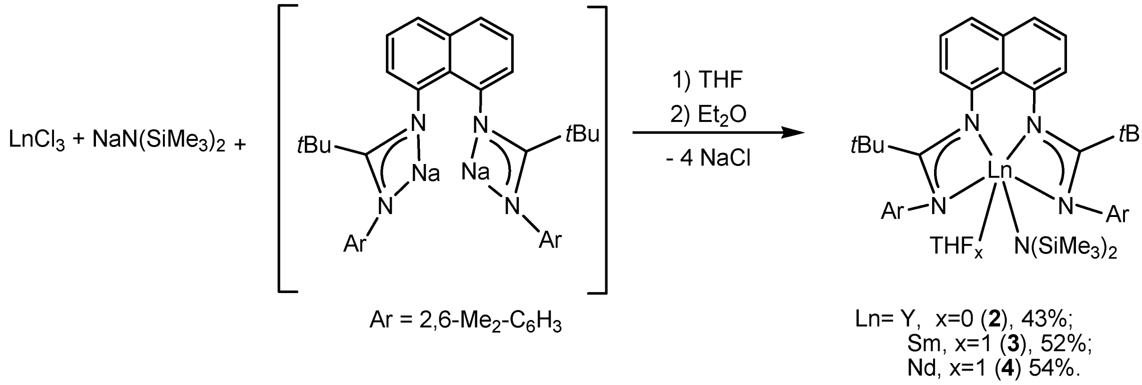
Bond lengths (Å)		Bond angles (°)	
Nd(1)–N(1)	2.473(2)	N(1)–C(11)–N(3)	111.7(2)
Nd(1)–N(2)	2.497(2)	N(2)–C(24)–N(4)	112.3(2)
Nd(1)–N(3)	2.626(2)	N(5)–C(47)–N(7)	112.1(2)
Nd(1)–N(4)	2.556(2)	N(8)–C(60)–N(6)	120.8(2)
Nd(1)–N(5)	2.460(2)		
Nd(1)–N(6)	2.582(2)		
Nd(1)–N(7)	2.632(2)		
Li(1)–N(8)	2.002(4)		
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)		

other 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^+ ion 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, $Li\text{–}Ar_{centre}$ 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]

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 enabled us to synthesize of a series of new bis(amidinate) amido lanthanide complexes. Equimolar amounts of $LnCl_3$ and $NaN(SiMe_3)_2$ were reacted in THF at 25 °C for 24 h. Subsequently a solution of $[1,8\text{-}C_{10}H_6\{NC(tBu)N\text{-}2,6\text{-}Me_2C_6H_3\}_2]\text{-}Na_2(THF)_n$ *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 $NaN(SiMe_3)_2$

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	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/c$
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	$-16 \le h \le 15, -13 \le k \le 19, -26 \le l \le 25$	$-28 \le h \le 28, -23 \le k \le 23, -26 \le l \le 26$
Reflections collected	23814	69897
Independent reflections	15794	15735
R_{int}	0.0201	0.0415
Completeness to 2θ, %	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



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**) and [1,8-$C_{10}H_6${NC(*t*Bu)N-2,6-$Me_2C_6H_3$}$_2$]NdN$(SiMe_3)_2$(THF) (**4**).

(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-$C_{10}H_6${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**) and [1,8-$C_{10}H_6${NC(*t*Bu)N-2,6-$Me_2C_6H_3$}$_2$]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 ^{1}H and $^{13}C\{^{1}H\}$NMR spectra of the diamagnetic yttrium derivative **2** in C_6D_6 at 20 °C 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 the 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** has a larger ion size[4] and according to the ^{1}H and $^{13}C\{^{1}H\}$NMR spectra the bis(amidinate) ligand and amido group contain one coordinated THF molecule. In the ^{1}H NMR spectrum of the slightly paramagnetic Sm(III) complex **3** (μ_{eff} = 1.64 μB)[62] the protons of the 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}). The 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** crystallizes in the space group *P*2(1)/*c*. The crystals of **4** contain two crystallographically independent molecules featuring very similar geometrical parameters. Thus, only the structure of one molecule will be discussed. The molecular structure of **4** is shown in Fig. 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 from two amidinate fragments, one nitrogen atom from the terminal amido ligand

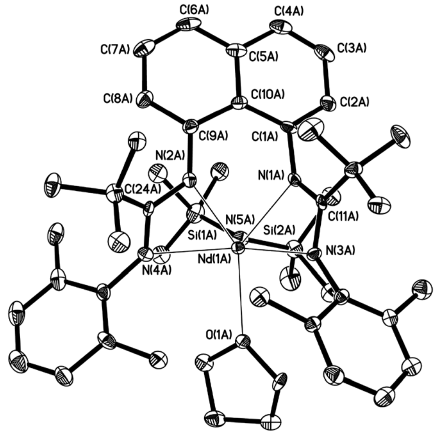


Fig. 2 Molecular structure of **4**. Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

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)		

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

Entry	Complex	ROH	$[I]_0/[iPrOH]_0/[Mon]_0$	t^b (min)	Conversion[c] (%)	$M_{ncalcd} \times 10^{3e}$	$M_{nexp} \times 10^{3c}$	$M_w/M_n{}^d$	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**	iPrOH	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**	iPrOH	1 : 5 : 250	30	>99	7.13	5.06	1.23	0.53
13	**3**	iPrOH	1 : 3 : 300	10	18	2.59	2.59	1.15	0.53
14	**3**	iPrOH	1 : 3 : 300	40	70	10.08	9.52	1.13	0.54
15	**3**	iPrOH	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**	iPrOH	1 : 5 : 250	30	>99	7.13	3.16	1.27	0.53

[a] General conditions: toluene, [lactide] = 1.0 mol L^{-1}, T = 25 °C. [b] Reaction time was not necessarily optimized. [c] Conversion of monomer, as determined by ^1H 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] M_n value calculated by assuming one polymer chain per metal center with the relationship: 144 × conversion × [Mon]/[Ln]. [f] Catalytic tests carried out in THF.

and one oxygen atom from the 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 is 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 $(–CH_2–)_3$ [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 N–C bond lengths (1.34 Å, N–C bond lengths 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–$N(SiMe_3)_2$ 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 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 the ROP of racemic lactide. The polymerization tests were conducted either in THF or in toluene at room temperature at a concentration of 1 mol L^{-1} *rac*-lactide. 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 ^1H NMR spectra of the polylactides formed showed atactic microstructures. The P_r (probability of racemic linkage) values

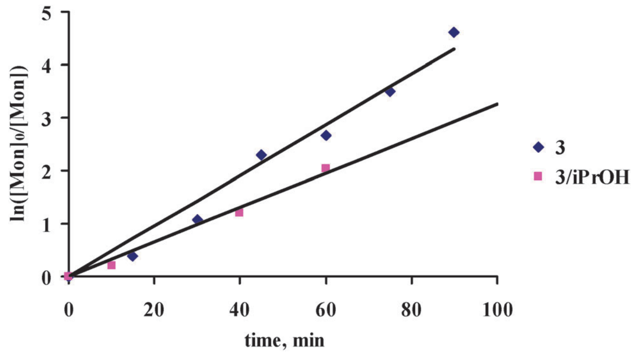


Fig. 3 Plot of ln($[Mon]_0$/[Mon]) as a function of time for the ROP of *rac*-lactide mediated by **3** (linear fit R_2 = 0.9764) and **3**/iPrOH (linear fit R_2 = 0.9876) at 25 °C in toluene, $[Mon]_0$ = 1.0 mol L^{-1}, $[I]_0/[Mon]_0$ = 1 : 250, $[I]_0/[iPrOH]_0/[Mon]_0$ = 1 : 3 : 300.

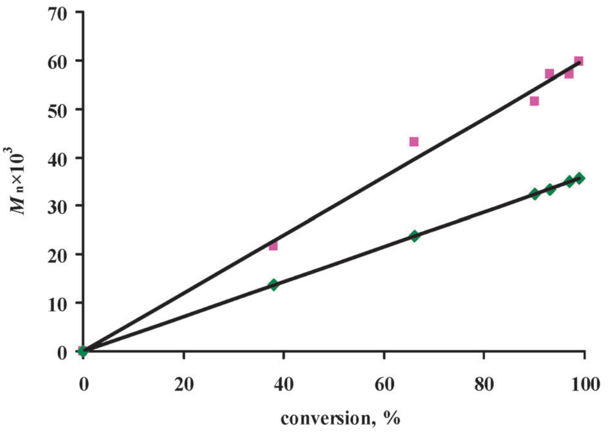


Fig. 4 M_n *vs.* conversion for ROP initiated by **3**. Toluene, 25 °C, $[Mon]_0$ = 1.0 mol L^{-1}, $[I]_0/[Mon]_0$ = 1 : 250.

are in the range of 0.53–0.56. The polylactides 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 most cases were found to be significantly higher than the calculated ones (Fig. 4). It should be noted that this general trend has often been observed for the ROP of lactide initiated by rare-earth amido complexes. It is associated with the 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) resulting from opening of the lactide and the insertion of the resulting fragments into the 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 acts as a single-site diinitiator, featured lower activity both in toluene and in THF, enabling quantitative conversions of 100–120 equiv. of *rac*-lactide at room temperature within a few hours. These initiators produced polylactides 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 isopropanol which acts as a chain transfer agent.

The polymerizations of *rac*-lactide with systems **2–4**/iPrOH were conducted in the presence of 3 and 5 equiv. (*vs.* Ln) of iPrOH. The systems **2–4**/iPrOH 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 1 mol L^{-1} *rac*-lactide. A kinetic monitoring of the ROP reaction mediated by **3**/iPrOH 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*-lactide 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 the addition of alcohol, 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 that it occurs in a living fashion. The catalytic systems **2–4**/iPrOH are not stereoselective since atactic PLAs were recovered (P_r = 0.52–0.54).

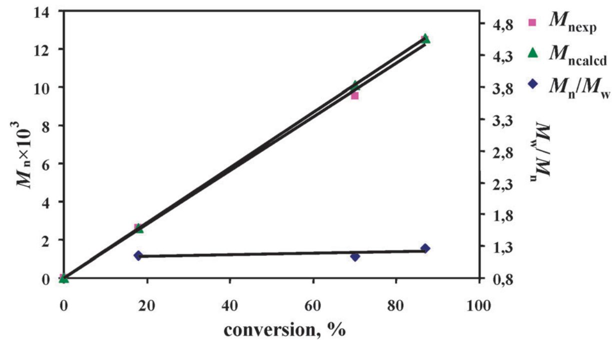


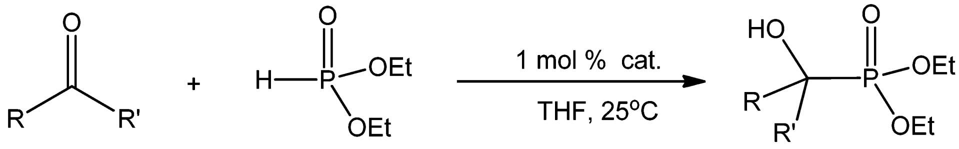
Fig. 5 M_{nexp}, M_{calcd} and M_w/M_n *vs.* conversion for ROP initiated by **3**/iPrOH. Toluene, 25 °C, $[M]_0$ = 1.0 mol L^{-1}, $[I]_0/[iPrOH]_0/[Mon]_0$ = 1 : 3 : 300.

Thus the systems **2–4**/iPrOH provide much better control over the ROP of *rac*-lactide compared to amido **2–4** and borohydrido complexes [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, Nd)[13] and allow the polymerization process to be carried out in the living mode producing polylactides with defined molecular weight and a very narrow molecular weight distribution.

Hydrophosphonylation of carbonyl compounds catalyzed by lanthanide amido and borohydrido complexes containing a bis(amidinate) ligand with a 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, entries 4–8, 13–17, 22–26). Introduction of any type of substituent (electron donating or electron withdrawing) in the *para*-position of the 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, entries 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.[51,53–56]



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	**7a**	99
2	**2**	4-Me–C_6H_4	H	15 min	**7b**	99
3	**2**	4-MeO–C_6H_4	H	15 min	**7c**	99
4	**2**	Ph	H	24 h	**7d**	92
5	**2**	Pen	H	24 h	**7e**	88
6	**2**	Bu	H	24 h	**7f**	87
7	**2**	iPr	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	**7a**	99
11	**3**	4-Me–C_6H_4	H	15 min	**7b**	99
12	**3**	4-MeO–C_6H_4	H	15 min	**7c**	99
13	**3**	Ph	H	24 h	**7d**	93
14	**3**	Pen	H	24 h	**7e**	92
15	**3**	Bu	H	24 h	**7f**	89
16	**3**	iPr	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	**7a**	99
20	**4**	4-Me–C_6H_4	H	15 min	**7b**	99
21	**4**	4-MeO–C_6H_4	H	15 min	**7c**	99
22	**4**	Ph	H	24 h	**7d**	92
23	**4**	Pen	H	24 h	**7e**	89
24	**4**	Bu	H	24 h	**7f**	87
25	**4**	iPr	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	**7a**	99
29	**5**	4-Me–C_6H_4	H	15 min	**7b**	99
30	**5**	4-MeO–C_6H_4	H	15 min	**7c**	99
31	**5**	Ph	H	24 h	**7d**	93
32	**5**	Pen	H	24 h	**7e**	93
33	**5**	Bu	H	24 h	**7f**	86
34	**5**	iPr	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	**7a**	99
38	**6**	4-Me–C_6H_4	H	15 min	**7b**	99
39	**6**	4-MeO–C_6H_4	H	15 min	**7c**	99
40	**6**	Ph	H	24 h	**7d**	92
41	**6**	Pen	H	24 h	**7e**	92
42	**6**	Bu	H	24 h	**7f**	91
43	**6**	iPr	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.

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] and 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, entries 9, 18, 27).

The catalytic activity of lanthanide borohydrido complexes in hydrophosphonylation of aldehydes and ketones remains less investigated.[28] Previously reported lanthanide 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 (**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** and **6** in THF at 25 °C. The borohydrides **5** and **6** had 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, entries 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 reactions in the presence of complexes **5** and **6** (5 mol%) over 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, entries 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 a 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. Borohydrides **5** and **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 and

Et_2O were 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] $Li(Et_2O)[N(SiMe_3)_2]$,[57] and $NaN(SiMe_3)_2$[58] were prepared according to literature procedures. All other commercially available chemicals were used after the appropriate purification. 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 ^1H 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 an "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^{-1}. The columns were calibrated by phenomenex medium- and high-molecular-weight polystyrene standard kits with peak molecular weights from 2700 to 2 570 000 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 the polylactides 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 polylactides were measured by homo-decoupling ^1H NMR spectroscopy at 25 °C in $CDCl_3$ with a Bruker Avance DRX-400 spectroscope.[89]

X-ray diffraction intensity data for compounds **1** and **4** were collected on a Bruker Smart APEX diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using ω scans. The structures were solved by direct methods and were refined on F^2 using a 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**).

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 24 h. The resulting solution was added to a THF (20 mL) solution of [1,8-$C_{10}H_6$-{NC(*t*Bu)N-2,6-$Me_2C_6H_3$}$_2$]$Na_2(THF)_n$ prepared *in situ* 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 a 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 the reaction mixture was stirred for 24 h. The resulting solution was added to a THF (20 mL) solution of [1,8-$C_{10}H_6${NC(*t*Bu)N-2,6-$Me_2C_6H_3$}$_2$]$Na_2(THF)_n$ prepared *in situ* 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 a 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, $C_{10}\mathit{H}_6$, $(CH_3)_2C_6\mathit{H}_3$), 2.49 (s, 12 H, $C\mathit{H}_3$), 1.19 (s, 18 H, $C(C\mathit{H}_3)_3$), −0.07 (s, 18 H, $SiC\mathit{H}_3$). 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 ($\mathit{C}_{10}H_6$, $(CH_3)_2\mathit{C}_6H_3$), 42.7 (s, $\mathit{C}(CH_3)_3$), 30.8 (s, $C(\mathit{C}H_3)_3$), 21.3 (s, $\mathit{C}H_3$), 3.5 (s, $Si\mathit{C}H_3$), 2.3 (s, $Si\mathit{C}H_3$). 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-$C_{10}H_6${NC(*t*Bu)N-2,6-$Me_2C_6H_3$}$_2$]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 24 h. The resulting solution was added to a THF (20 mL) solution of [1,8-$C_{10}H_6${NC(*t*Bu)N-2,6-$Me_2C_6H_3$}$_2$]$Na_2(THF)_n$ prepared *in situ* from 1,8-$C_{10}H_6${HNC(*t*Bu)N-2,6-$Me_2C_6H_3$}{NC(*t*Bu)HN-2,6-$Me_2C_6H_3$} (0.59 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 a 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, $C_{10}\mathit{H}_6$, $(CH_3)_2C_6\mathit{H}_3$), 3.32 (br. s, 12 H, THF, α-$C\mathit{H}_2$), 3.11 (s, 12 H, $C\mathit{H}_3$), 1.53 (br. s, 12 H, THF, β-$C\mathit{H}_2$), 1.16 (s, 18 H, $C(C\mathit{H}_3)_3$), 0.16 (s, 18 H, $SiC\mathit{H}_3$). 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, ($\mathit{C}_{10}H_6$, $(CH_3)_2\mathit{C}_6H_3$) 71.89 (s, THF, α-$\mathit{C}H_2$), 40.4 (s, $\mathit{C}(CH_3)_3$), 39.1

(s, $\mathit{C}(CH_3)_3$), 29.93 (s, THF, β-$\mathit{C}H_2$), 29.40 (s, $C(\mathit{C}H_3)_3$), 29.72 (s, $C(\mathit{C}H_3)_3$), 16.22 (s, $\mathit{C}H_3$), 1.05 (s, Si$\mathit{C}H_3$). 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-$C_{10}H_6$\{NC(*t*Bu)N-2,6-$Me_2C_6H_3$\}$_2$]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 24 h. The resulting solution was added to a THF (20 mL) solution of [1,8-$C_{10}H_6$\{NC(*t*Bu)N-2,6-$Me_2C_6H_3$\}$_2$]Na_2(THF)$_n$ prepared *in situ* from of 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) 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 a 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}): $\tilde{\nu}$ = 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 ^{1}H 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 according to the published protocol.[92]

General experimental procedure for hydrophosphonylation of aldehydes, ketones 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-$C_{10}H_6$\{NC(*t*Bu)N-2,6-$Me_2C_6H_3$\}$_2$]LnN($SiMe_3$)$_2$(THF)$_n$ supported by *ansa* bis(amidinate) ligands was successfully synthesized by the salt metathesis reactions starting from *in situ* generated [(Me_3Si)$_2$N]-$LnCl_2$(THF)$_2$, while the attempts of substitution of a chloro ligand in [1,8-$C_{10}H_6$\{NC(*t*Bu)N-2,6-$Me_2C_6H_3$\}$_2$]YCl(DME) and [1,8-$C_{10}H_6$\{NC(*t*Bu)N-2,6-$Me_2C_6H_3$\}$_2$]Ln(L)(μ-Cl)$_2$Li(L)$_n$ (Ln = Sm, L = DME; Ln = Nd, L = THF) by the [(Me_3Si)$_2$N]$^-$ 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-$C_{10}H_6$-\{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)].

Amido complexes **2–4** initiate ROP of *rac*-lactide under mild conditions and convert 100–250 equiv. of monomer within 60–90 min into 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 the 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*Bu)N-2,6-$Me_2C_6H_3$\}$_2$]Ln(BH_4)$_2$Li(THF)$_2$. 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**/iPrOH 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 a 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*Bu)N-2,6-Me_2-C_6H_3\}$_2$]$^{2-}$, [C_6H_4-1,2-\{NC(*t*Bu)N(2,6-$Me_2C_6H_3$)\}$_2$]$^{2-}$,[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 a flexible –(CH_2)$_3$– linker provides a 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*Bu)N-2,6-Me_2-C_6H_3\}$_2$]Ln(BH_4)(μ-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.

Acknowledgements

This work is supported by the Russian Foundation for Basic Research (Grant No. 14-03-31039 мол_а, 12-03-93109-НЦНИЛ), and the Ministry of Education and Science of the Russian Federation (the agreement of August 27, 2013 No. 02.B.49.21.0003 between The Ministry of Education and Science of the Russian Federation and Lobachevsky State University of Nizhny Novgorod).

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