ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2023, Vol. 49, No. 11, pp. 710–717. © Pleiades Publishing, Ltd., 2023.
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Synthesis and Structure of the (μ^2-OP(O)Ph_2)-Linked Dimeric Amide Lanthanum Complex {[Pzl_2^{Me2}CP(O)Ph_2]La[N($SiMe_3$)$_2$](μ^2-OP(O)Ph_2)}$_2$ Bearing the Tridentate Heteroscorpionate Ligand. Investigation of the Catalytic Activity in *rac*-Lactide and ε-Caprolactone Polymerization

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Received March 28, 2023; revised April 21, 2023; accepted May 3, 2023

Abstract—The dimeric amide lanthanum complex {[Pzl_2^{Me2}CP(O)Ph_2]La[N($SiMe_3$)$_2$](μ^2-OP(O)Ph_2)}$_2$ (Pzl^{Me2} is 3,5-dimethylpyrazole) bearing the *N*,*N*,*O*-tridentate heteroscorpionate ligand is synthesized. As found by X-ray diffraction (XRD) (CIF file CCDC no. 2212274), the complex is binuclear and its lanthanum ions are linked by two bridging monoanionic diphenyl phosphinate ligands. The synthesized lanthanum complex demonstrates a high catalytic activity in the polymerization with ring opening of *rac*-lactide and ε-caprolactone providing the quantitative conversion of 500 equivalents of the monomer to the polymer at room temperature within 360–720 min for *rac*-lactide and 10–30 min for ε-caprolactone. The formed polylactides are characterized by the atactic microstructure (P_r = 0.54–0.56) and polydispersity indices (PDI) of 1.6–2.5, whereas for polycaprolactone PDI = 2.1–2.8.

Keywords: amide complex, heteroscorpionate ligand, polymerization, *rac*-lactide, ε-caprolactone, XRD

DOI: 10.1134/S1070328423600717

INTRODUCTION

Alkyl, amide, and borohydride complexes of rare-earth metals are intensely studied as components of the catalytic systems of diverse monomers, such as dienes [1–6], cyclic esters [7–10], and olefins [1, 3, 11–15], as well as in reactions of C–E bond formation (E = Si, N, P, S) [16–19]. The stability and reactivity of the organic derivatives of these metals are determined, to a high extent, by the coordination and steric saturation of the metallocenter due to their long radii [20, 21], high electrophilicity and Lewis acidity of lanthanide ions [22], and a high degree of ionicity of the metal–ligand bond. In addition, a rational design of the coordination sphere of the metal ion is one of the most important tools providing the control of the selectivity of the metal-promoted reactions [7, 23–27].

Scorpionate ligands become more popular in the chemistry of transition metals and lanthanides owing to their ability to coordinate with metal ions via the κ^3 mode [28–38] and a possibility of modifying their steric and electronic properties in wide ranges. In the modern chemistry of rare-earth metals, scorpionate ligands are mainly presented by tris(pyrazolyl)borate ligands [29, 39–43] and their neutral structural analogs based on tris(pyrazolyl)methane [32, 44]. A number of examples of the compounds with the heteroscorpionate ligands of the bis(pyrazolyl)methane series [31, 33, 39, 40, 45, 46] bearing an additional functional group capable of covalent binding with the metal ion is known. The introduction of bulky substituents into these ligands makes it possible to significantly extend possibilities of molecular design and enhance the stability of the related complexes [12, 13, 24, 33].

The synthesis of the amide lanthanum complex bearing the *N*,*N*,*O*-heteroscorpionate ligand based on bis(pyrazolyl)methane [Pzl_2^{Me2}CP(O)Ph_2] and its structure and catalytic activity in the polymerization with ring opening of *rac*-lactide and ε-caprolactone are described in this work.

EXPERIMENTAL

All procedures on the synthesis and isolation of the products were carried out in a vacuum apparatus using the standard Schlenk technique or in a glove box under a high-purity argon atmosphere. Tetrahydrofuran (THF) was dried over potassium hydroxide and then distilled over sodium benzophenone ketyl. Hexane and toluene were dried by reflux and distillation over metallic sodium, and $La[N(SiMe_3)_2]_3$ [47] was synthesized according to a published procedure. ε-Caprolactone (Acros) was dehydrated over CaH_2 followed by distillation under reduced pressure and stored in vacuo. *rac*-Lactide (Acros) was recrystallized from THF and two times from anhydrous toluene and then dried in vacuo. IR spectra were recorded on a Bruker-Vertex 70 instrument. Samples of the compounds were prepared under an anhydrous argon atmosphere as suspensions in Nujol. Elemental analysis was conducted on an Analyser 2400 Series II CHNS/O instrument (Perkin-Elmer). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were detected on Bruker DPX 200 and Bruker Avance III 400 instruments (25°C, C_6D_6). Chemical shifts are presented in ppm with respect to the known shifts of residual protons of the deuterated solvents. Gel permeation chromatography (GPC) was carried out on a Knauer Smartline chromatograph with the Phenogel Phenomenex 5u columns (300 × 7.8 mm) with an average pore diameter of 10^4 and 10^5 Å and a Security Guard Phenogel Column instrument (UV refractometer as the detector, 254 nm). The mobile phase was THF at a flow rate of 2 mL min^{-1} and T = 40°C. Calibration was conducted using the polystyrene standards with the molecular weights in the range from 2700 to 2570000. The molecular weights (M_n) of the polymer samples were calculated with allowance for a coefficient of 0.56 for polycaprolactone and 0.58 for polylactide [48] taking into account differences in the hydrodynamic behavior of polyesters and polystyrene. The microstructure of polylactide samples was determined by ^1H NMR spectroscopy.

Synthesis of $\{[Pzl_2^{Me2}CP(O)Ph_2]La[N(SiMe_3)_2]$-($\mu^2$-$OP(O)Ph_2)\}_2$ (I). A solution of ligand $Pzl_2^{Me2}CHP(O)Ph_2$ (HL) (0.18 g, 0.44 mmol) in THF (10 mL) was added to a solution of $La[N(SiMe_3)_2]_3$ (0.27 g, 0.44 mmol) in THF (10 mL). The reaction mixture was stirred at 25°C for 24 h. Volatiles were removed in vacuo. The solid residue was recrystallized from a THF–hexane (1 : 7) mixture. Compound **I** was obtained as light yellow transparent crystals in a yield of 0.28 g (34%).

For $C_{82}H_{106}N_{10}O_6Si_4P_4La_2$ (M = 1841.82)

Anal. calcd., %	C, 53.47	H, 5.80	N, 7.60	La, 15.08
Found, %	C, 53.25	H, 5.69	N, 7.39	La, 15.17

^1H NMR (400 MHz; 25°C; C_6D_6; δ, ppm): 0.39 (s, 36H, $Si(C\underline{H}_3)_3$), 1.96 (s, 12H, $Pzl(C\underline{H}_3)_2$), 2.20 (s, 12H, $Pzl(C\underline{H}_3)_2$), 5.51 (s, 4H, $C_3\underline{H}N_2(CH_3)_2$), 6.73–8.41 (m, 40H, Ar–$\underline{H}$). ^{13}C NMR (100 MHz; 25°C; C_6D_6; δ, ppm): 5.2 (s, $Si(\underline{C}H_3)_3$), 12.8, 14.6 ($Pzl(\underline{C}H_3)_2$), 104.8, 125.4, 126.2, 127.6, 127.8, 128.0, 128.5, 129.0, 129.8, 131.3, 131.7, 131.9, 132.1, 132.5, 133.0, 133.4, 135.2 (d, J_{C-P} = 7.2 Hz), 139.4 (d, J_{C-P} = 8.1 Hz), 145.0 (d, J_{C-P} = 7.2 Hz), 146.4 (d, J_{C-P} = 8.1 Hz), 147.9 (Ar–C). ^{31}P NMR (162 MHz; C_6D_6; 298 K; δ, ppm): 30.6, 37.4.

IR (KBr; ν, cm^{-1}): 1959 w, 1946 m, 1899 m, 1749 m, 1589 m, 1550 s, 1305 w, 1276 w, 1232 s, 1192 s, 1176 m, 1158 m, 1124 s, 1085 s, 1030 s, 961 s, 998 s, 930 m, 843 s, 772 s, 754 s, 730 s, 722 s, 704 w, 693 w, 662 s, 607 s, 557 s, 530 s, 478 w.

XRD of a single-crystal of compound **I** (0.28 × 0.24 × 0.10 mm) was carried out on a Bruker D8 Quest diffractometer (MoK_α radiation, ω scan mode, λ = 0.71073 Å, T = 100.0(2) K, 2θ = 54.58°). Experimental sets of intensities were measured and integrated, an absorption correction was applied, and the structures were refined using the APEX3 [49], SADABS [50], and SHELX [51] program packages. Compound **I** ($C_{82}H_{104}La_2N_{10}O_6P_4Si_4$) crystallizes in the space group $P\overline{1}$ (a = 13.2526(5), b = 17.3718(6), c = 20.9349(8) Å, α = 84.7410(10)°, β = 80.9320(10)°, γ = 69.0990(10)°, V = 4443.0(3) $Å^3$, Z = 2, ρ_{calc} = 1.375 g/cm^3, μ = 1.129 mm^{-1}). The number of measured reflections was 126114, and 19911 independent reflections (R_{int} = 0.0559) were used for the solution of the structure and subsequent refinement of 993 parameters by full-matrix least squares for F_{hkl}^2 in the anisotropic approximation for non-hydrogen atoms. Hydrogen atoms in compound **I** were placed in the geometrically calculated positions and refined isotropically with the fixed thermal parameters $U(H)_{iso}$ = $1.2U(C)_{eq}$ ($U(H)_{iso}$ = $1.5U(C)_{eq}$ for methyl groups). After the final refinement, wR_2 = 0.0797 and $S(F^2)$ = 1.042 for all reflections (R_1 = 0.0401 for all 16057 reflections satisfying the condition $F^2 > 2\sigma(F^2)$). The residual electron density maximum and minimum were 1.63/–1.02 e/$Å^3$. Selected bond lengths and bond angles in compound **I** are given in Table 1.

The structure of compound **I** was deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 2212274) and is available at ccdc.cam.ac.uk/structures.

Polymerization of *rac*-lactide (general procedure). Polymerization was carried out in a glove box under an inert nitrogen atmosphere (see Table 2, entry 1). *rac*-Lactide (0.117 g, 0.8 mmol, 100 equiv) was added to a solution of complex **I** (15 mg, 0.008 mmol) in toluene (1.0 mL). The reaction mixture was magnetically stirred at 20°C for 360 min. Then an aliquot of the reaction mixture was taken to determine the conversion by ^1H NMR spectroscopy. The reaction was ceased by the addition of a 10% solution (1 mL) of water in THF to the reaction mixture. The solvents

Table 1. Selected bond lengths (*d*, Å) and bond angles (ω, deg) in compound **I**

Bond	*d*, Å	Angle	ω, deg
La(1)–N(1)	2.655(2)	N(1)La(1)N(4)	76.46(8)
La(1)–N(4)	2.701(2)	N(6)La(2)N(9)	75.82(8)
La(2)–N(6)	2.610(3)		
La(2)–N(9)	2.665(3)		
La(1)–O(5)	2.453(2)	O(5)La(1)N(5)	156.35(8)
La(2)–O(6)	2.457(2)	O(6)La(2)N(10)	156.19(8)
La(1)–N(5)	2.434(2)		
La(2)–N(10)	2.489(3)		
La(1)–O(1)	2.420(2)	O(1)La(1)O(4)	103.68(7)
La(2)–O(2)	2.387(2)	O(2)La(2)O(3)	102.93(7)
La(2)–O(3)	2.403(2)	O(2)P(1)O(1)	116.5(2)
La(1)–O(4)	2.396(2)	O(3)P(2)O(4)	116.5(2)

Table 2. Polymerization of *rac*-lactide and ε-caprolactone in the presence of complex **I***

Entry	M	[M]/[La]	τ, min	*C*, %	$M_n^{\text{calc}} \times 10^{-3}$	$M_n^{\text{exp}} \times 10^{-3}$	M_w/M_n
1	*rac*-LA	100 : 1	360	99	14.3	17.6	1.8
2	*rac*-LA	250 : 1	480	64	23.1	36.8	2.5
3	*rac*-LA	500 : 1	720	97	69.9	70.4	1.6
4	ε-CL	100 : 1	10	99	11.3	12.3	2.1
5	ε-CL	250 : 1	20	99	28.2	30.6	2.1
6	ε-CL	500 : 1	30	99	56.5	57.2	2.8

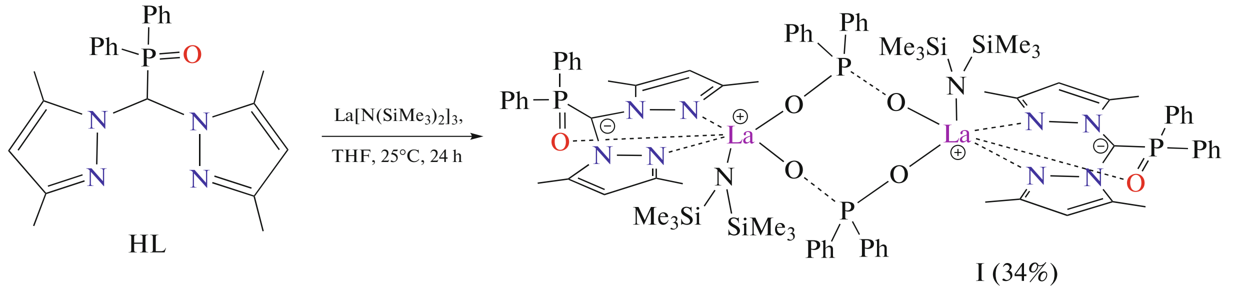
* M is monomer. Polymerization conditions: toluene, [*rac*-LA] = 1.0 mol/L^{-1}, [ε-CL] = 1.0 mol/L^{-1}, T = 20°C, reaction time (τ) was not optimized. *C* is conversion. Molecular weights M_n^{exp} and M_w/M_n were determined by gel permeation chromatography in a THF solution from the polystyrene standards taking into account coefficients of 0.58 for polylactide and 0.56 for polycaprolactone. Molecular weights M_n^{calc} were calculated assuming that one polymer chain develops on one metallocenter by the equation *C* (%) × [*rac*-LA]/[La] × 144.14 (for polylactide) or *C* (%) × [ε-CL]/[La] × 114.14 (for polycaprolactone).

were removed in vacuo, the formed residue was dissolved in THF (2 mL), and the polymer was reprecipitated with hexane (50 mL). The obtained polymer was dried in vacuo to a constant weight, and samples for GPC were taken.

Polymerization of ε-caprolactone (general procedure). Polymerization was carried out in a glove box under an inert nitrogen atmosphere (see Table 2, entry 4). ε-Caprolactone (0.06 mL, 0.062 g, 0.5 mmol, 100 equiv) was poured to a solution of complex **I** (10.0 mg, 0.005 mmol) in toluene (1.0 mL). The reaction mixture was magnetically stirred at 20°C for 10 min. The reaction was ceased by the addition of a 10% solution (1 mL) of water in THF to the reaction mixture. The solvents were removed in vacuo, the formed residue was dissolved in THF (2 mL), and the polymer was reprecipitated with hexane (50 mL). The obtained polymer was dried in vacuo to a constant weight, and samples for GPC were taken. The conversion of the monomer was determined by gravimetry.

RESULTS AND DISCUSSION

The amide derivatives of rare-earth metals are known to be active catalysts of polymerization with ring opening of cyclic esters [8]. The reaction of $\text{Pzl}_2^{\text{Me2}}\text{CHP(O)Ph}_2$ (HL) (Pzl^{Me2} is 3,5-dimethylpyrazole) synthesized by a known procedure [52] with $\text{La[N(SiMe}_3)_2]_3$ was carried out in THF at room temperature (24 h) and afforded the unexpected product: lanthanum complex $\{[\text{Pzl}_2^{\text{Me2}}\text{CP(O)Ph}_2]\text{La[N(SiMe}_3)_2](\mu^2\text{-OP(O)Ph}_2)\}_2$ (**I**) (Scheme 1). After the solvent and volatile reaction products were removed in vacuo and solid residues were recrystallized from a THF–hexane (1 : 7) mixture, amide complex **I** was isolated as light yellow crystals in a yield of 34%.



Scheme 1.

The ^1H and ^{31}P NMR spectra of the initial ligand HL confirm that HL contains no HOP(O)Ph_2. It is most likely that this complex is formed due to the unintentional oxidation of the diphenylphosphine oxide group with air oxygen. Thus, compound **I** is the result of the C–P bond cleavage in the initial ligand. The formation of similar fragments was described [53–55]. Compound **I** is highly soluble in ethereal and aromatic solvents and is restrictedly soluble in aliphatic solvents (hexane, pentane). The complex is very sensitive to air oxygen and moisture but can be stored for a long time in an inert atmosphere or vacuum without decomposition. In the IR spectrum of complex **I**, the $N(SiMe_3)_2$ amide group appears as an absorption band at 1232 cm^{-1} corresponding to bending vibrations of the C–H bonds of the methyl groups and an absorption band at 961 cm^{-1} corresponding to stretching vibrations of the Si–N bonds. The IR spectrum exhibits the following strong absorption bands: the band at 1550 cm^{-1} corresponds to stretching vibrations of the C=N bonds, and that at 1192 cm^{-1} corresponds to stretching vibrations of the P=O bonds in the pyrazole ligand $Pzl_2^{Me2}CP(O)Ph_2$. The strong absorption band at 1030 cm^{-1} corresponds to stretching vibrations of the P–O bonds in the bridging monoanionic diphenyl phosphinate groups. In the ^1H NMR spectrum (400 MHz, C_6D_6, 298 K) of complex **I**, the protons of the methyl substituents of the $N(SiMe_3)_2$ amide groups appear as a singlet at 0.39 ppm and hydrogens of the methyl groups of the pyrazolyl fragments give singlets at 1.98 and 2.20 ppm. A set of multiplets in a range of 6.73–8.41 ppm corresponds to the aromatic protons. The $^{31}P\{^1H\}$ NMR spectrum of lanthanum complex **I** exhibits two singlets with chemical shifts of 30.6 and 37.4 ppm thus confirming that the molecule contains phosphorus atoms of two types and different nature. The complete signal assignment in the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra for complex **I** is given in Experimental. The structure of complex **I** is shown in Fig. 1.

The XRD study shows that compound **I** crystallizes in the space group $P\bar{1}$ being the dimeric bis(trimethylsilyl)amide lanthanum complex with the tridentate heteroscorpionate ligand L^-. The independent part of the crystalline cell contains one molecule of the complex. Each La^{3+} cation is bound to one oxygen atom and two nitrogen atoms of one heteroscorpionate ligand, one nitrogen atom of one amide group, and two oxygen atoms of two μ^2-bridging OP(O)Ph_2 ligands. Thus, the coordination number of the lanthanum atom in complex **I** is six, and its coordination environment is a distorted octahedron.

The pyrazole fragments of the *N*,*N*,*O*-heteroscorpionate ligand in compound **I** are nearly symmetrically coordinated on the La^{3+} ions. The La–N_{pzl} distances in complex **I** are in the 2.610(2)–2.701(2) Å range, comparable with the La–N coordination bond lengths in the hexacoordinate amide lanthanum complexes [ONNO]La[$N(SiMe_3)_2$]THF (2.669(4)–2.721(3) Å) [56], and appreciably longer than the La–N_{Tp} distances in the [$(Tp^{^tBu,\ Me})$La[(μ-CH_2){(μ-CH_3)Al(CH_3)$_2$}$_2$]] complex (2.567(2)–2.608(2) Å) [57]. The La(1)–O(5) and La(2)–O(6) bond lengths are 2.453(2) and 2.457(2) Å, respectively, and comparable with similar La–O(P=O) bond lengths in the amide lanthanum complex [(3,5-$^tBu_2C_6H_2OCH_2$)$_2$-$NCH_2C_6H_5$]LaN($SiHMe_2$)$_2$-($OPPh_3$)$_2$ (2.456(2) Å) [58] but significantly shorter than the La–O(THF) coordination bond in the hexacoordinate complexes {[2,6-{[2,6-(*i*-Pr)$_2C_6H_5$]NC(CH_2)}$_2$-(C_5H_3N)]La(THF)}-(μ-Cl)$_2$[Li(THF)$_2$] (2.623(2) Å) [59] and [ONNO]La-[$N(SiMe_3)_2$](THF) (2.619(7) Å) [56].

The distances between the La^{3+} ion and oxygen atoms of the bridging monoanionic diphenyl phosphinate ligands range from 2.387(2) to 2.420(2) Å. This is noticeably shorter than the distances between the La^{3+} ion and oxygen atoms of the neutral triphenylphosphine oxide ligands in the [(3,5-$^tBu_2C_6H_2OCH_2$)$_2$-$NCH_2C_6H_5$]LaN($SiHMe_2$)$_2$($OPPh_3$)$_2$ complex (2.456(2) Å) [58]. At the same time, these distances considerably exceed the La–O covalent bond lengths in the same complex [(3,5-$^tBu_2C_6H_2OCH_2$)$_2$-$NCH_2C_6H_5$]LaN($SiHMe_2$)$_2$($OPPh_3$)$_2$ (2.258(2), 2.263(2) Å) [58]. Interestingly, the plane of the formed metallocycle LaOPOLaOPO in complex **I** is somewhat distorted: the average deviation of the atoms from the plane is 0.12 Å. The $N(SiMe_3)_2$ amide groups are

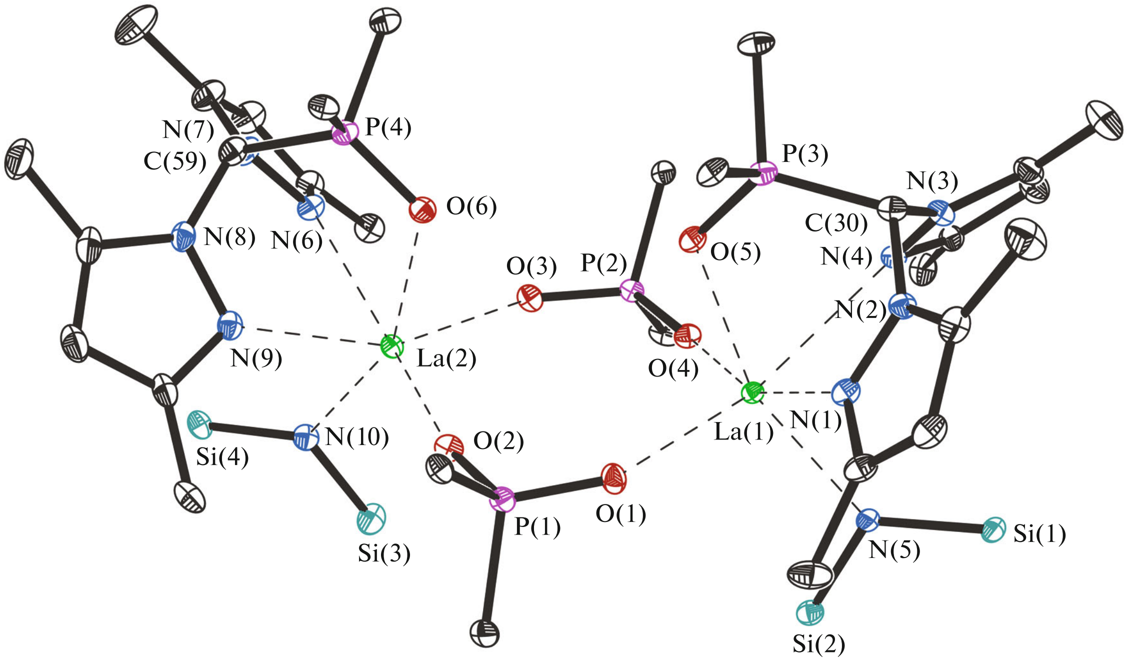


Fig. 1. Molecular structure of the lanthanum compound $\{[\mathrm{Pzl}_2^{\mathrm{Me2}}\mathrm{CP(O)Ph_2}]\mathrm{La[N(SiMe_3)_2](\mu^2\text{-}OP(O)Ph_2)}\}_2$ (**I**). Thermal ellipsoids are given with 30% probability. Methyl substituents $N(SiMe_3)_2$ and CH fragments of aryl substituents are omitted.

arranged at one side from the metallocycle plane. The $\mathrm{La{-}N_{amide}}$ bond lengths are 2.434(2) and 2.489(3) Å and comparable with the corresponding values in the hexacoordinate complex $[\mathrm{ONNO}]\mathrm{La[N(SiMe_3)_2]}$(THF) (2.422(7) Å) [56].

Complex **I** was studied as a catalyst of the polymerization with ring opening of *rac*-lactide and ε-caprolactone. The reactions were carried out in toluene at 20°C, and the polymerization time was not optimized. The results of the catalytic tests are given in Table 2. Complex **I** demonstrated a medium catalytic activity in the polymerization of *rac*-lactide (*rac*-LA) and makes it possible to achieve the quantitative conversion of 100–500 equiv of the monomer within 360–720 min under mild conditions (Table 2, entries 1, 2, 3). In the case of ε-caprolactone (ε-CL), the catalytic activity usually turned out to be much higher: only 10–30 min were required to achieve the complete conversion of the monomer (100–500 equiv) (Table 2, entries 4, 5, 6) (toluene, 20°C, [*rac*-LA] = 1.0 mol L^{-1}, [ε-CL] = 1.0 mol L^{-1}).

According to the ^{1}H NMR spectroscopy data, the polylactide samples obtained using compound **I** have the atactic microstructure (P_r = 0.54–0.56) in all cases. At low loads of lactide ($[M_0]/[I_0]$ = 100, $[M_0]$ is the monomer amount, $[I_0]$ is the initiator amount), the experimental molecular weights (M_n^{exp}) of the polymers only insignificantly exceed the theoretically calculated values (M_n^{calc}) by ~1.2 times, which indicates a good control of the molecular weights of the formed polymers. At the ratio $[M_0]/[I_0]$ = 250, the values of M_n^{exp} of the polymers somewhat exceed the theoretically calculated M_n^{calc}. It is most likely that this is caused by a relatively slow initiation of the polymerization. The polymerization of *rac*-LA initiated by amide complex **I** occurs with the formation of the polymers with average polydispersity indices (M_w/M_n = 1.8–2.5) (Table 2, entries 1 and 2). The highest control of the polymerization process is achieved at the ratio $[M_0]/[I_0]$ = 500 (Table 2, entry 3): the number average molecular weight is close to the theoretically calculated value, and the polymer is characterized by a fairly low polydispersity index (M_w/M_n = 1.6).

The polymerization with ring opening of ε-CL initiated by complex **I** was studied under the conditions analogous to the polymerization of *rac*-LA. The polymerization of ε-CL catalyzed by complex **I** is faster and makes it possible to achieve the quantitative conversion of 100–500 equiv of the monomer within 10–30 min. The formed polymers are characterized by the monomodal somewhat broadened molecular weight distribution (M_w/M_n = 2.1–2.8). The experimental molecular weights exceed the calculated values by 1.0–1.1 times providing a sufficiently high degree of control of the polymerization with ring opening of ε-CL (Table 2, entries 4–6).

Catalytic tests of the polymerization in the presence of isopropanol were carried out to decrease the polydispersity of the formed polylactides. The addition of two equivalents of *i*-PrOH to complex **I** was assumed to result in the protonolysis of La–N bonds and formation of the corresponding isopropoxides due to which the difference in the initiation and chain propagation rate constants would decrease thus leading to a decrease in the polydispersity. However, it turned out that in the presence of 2 equiv of isopropanol complex **I** does not initiate *rac*-LA and ε-CL polymerization: only polymer traces are formed within 12 h.

Complex **I** makes it possible to conduct *rac*-LA polymerization under milder conditions (T = 20°C) compared to the known dimeric amide complexes bearing the diketiminate ligand, (2-hydroxy-5-*tert*-butylphenyl)imino-2-pentanone [60]. In the case of these conditions, *rac*-LA polymerization requires a significantly higher temperature (T = 70°C). At the same time, the activity of complex **I** in the initiation of the polymerization with ring opening of *rac*-LA is somewhat lower than that of the previously published dimeric amide lanthanum complexes {(*o*-$OCH_3C_6H_4$)NCH_2(3,5-${}^tBu_2$-C_6H_2O)La[N$(SiMe_3)_2$]$\}_2$ and {(NC_5H_4)NCH_2(3,5-${}^tBu_2C_6H_2O$)La[N-$(SiMe_3)_2$](THF)$\}_2$ that make it possible to perform *rac*-LA polymerization within a shorter time (for 12–20 min, T = 25°C) reaching the 73–82% conversion of 3000–4000 equiv of the monomer [61].

Thus, the reaction of La[N$(SiMe_3)_2]_3$ with Pzl_2^{Me2}CHP(O)Ph_2 in a molar ratio of 1 : 1 unexpectedly results in the formation of the monoamide lanthanum complex {[Pzl_2^{Me2}CP(O)Ph_2]La[N$(SiMe_3)_2$]-(μ^2-OP(O)Ph_2)$\}_2$ with the dimeric structure due to two bridging monoanionic diphenyl phosphinate groups. The coordination of the heteroscorpionate ligand with the lanthanum ion proceeds via the κ^3-*N*,*N*,*O* mode. Complex **I** initiates the polymerization with ring opening of *rac*-lactide and ε-caprolactone. The quantitative conversion of 500 equiv of *rac*-lactide is achieved within 720 min, whereas only 30 min are needed for the polymerization of the same amount of ε-caprolactone. Complex **I** provides the formation of atactic polylactides (P_r = 0.54–0.56). The formed polymers are characterized by a relatively narrow molecular weight distribution (M_w/M_n = 1.6–2.5 and 2.1–2.8 for polylactide and polycaprolactone, respectively). Amide complex **I** was found to catalyze *rac*-lactide polymerization at the ratio $[M_0]/[I_0]$ = 500, which makes it possible to achieve a high control of the polymerization process. The polymerization of ε-caprolactone catalyzed by complex **I** leads to the formation of the polymers characterized by a good correspondence between the experimental and calculated values of M_n.

ACKNOWLEDGMENTS

The workers of the Nesmeyanov Institute of Organoelement Compounds (Russian Academy of Sciences) are grateful to the Ministry of Science and Higher Education of the Russian Federation for financial support.

FUNDING

The XRD and NMR studies of the compounds were carried out using the equipment of the Center for Collective Use “Analytical Center of Institute of Organometallic Chemistry of Russian Academy of Sciences” and supported by the project “Provision of Development of Material Technical Infrastructure of Centers for Collective Use of Scientific Equipment” (unique identifier RF–2296.61321X0017, agreement no. 075-15-2021-670).

CONFLICT OF INTEREST

The author of this work declares that they has no conflicts of interest.

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Translated by E. Yablonskaya