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Yttrium and Lithium Keto-β-Diketiminate Complexes $[\{2,6\text{-}Me_2C_6H_3N{=}C(Me)\}_2CC(tert\text{-}Bu){=}O]_2Y(\mu^2\text{-}Cl)_2Li(THF)_2$ and $\{[\{2,6\text{-}Me_2C_6H_3N{=}C(Me)\}_2CC(tert\text{-}Bu){=}O]Li(THF)\}_n$. Synthesis, Molecular Structures, and Catalytic Activity in ε-Caprolactone Polymerization

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Abstract—The reaction of lithium β-diketiminate $[\{2,6\text{-}Me_2C_6H_3N{=}CMe\}_2CH]Li$ with benzophenone in toluene at 25°C affords the coordination complex $[\{2,6\text{-}Me_2C_6H_3N{=}CMe\}_2CH]Li(Ph_2C{=}O)$ (**I**). New keto-β-diketimine $\{2,6\text{-}Me_2C_6H_3N{=}C(Me)\}_2CHC(tert\text{-}Bu){=}O$ (**II**) is synthesized by the reaction of *tert*-Bu(C=O)Cl with $[\{2,6\text{-}Me_2C_6H_3N{=}CMe\}_2CH]Li$. The metallation of keto-β-diketimine **II** with *n*-butyllithium in THF at 0°C gives lithium keto-β-diketiminate $\{[\{2,6\text{-}Me_2C_6H_3N{=}C(Me)\}_2CC(tert\text{-}Bu){=}O]Li(THF)\}_n$ (**III**). The exchange reaction of YCl_3 with compound **III** (molar ratio 1 : 2, THF) affords the yttrium bis(keto-diketiminate) complex $[\{2,6\text{-}Me_2C_6H_3N{=}C(Me)\}_2CC(tert\text{-}Bu){=}O]_2Y(\mu^2\text{-}Cl)_2L\text{-}(THF)_2$ (**IV**). The molecular structures of complexes **I**, **III**, and **IV** are determined by X-ray diffraction analysis (CIF files CCDC nos. 2001131 (**I**), 2001132 (**III**), and 2001133 (**IV**)). Complex **IV** in the crystalline state exists as an *ate* complex with one LiCl molecule. Complexes **I**, **III**, and **IV** are catalysts of ring-opening polymerization of ε-caprolactone in toluene at 25°C.

Keywords: rare-earth metals, alkaline metals, keto-diketiminate ligand, synthesis, structure, catalysis, ε-caprolactone, polymerization

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INTRODUCTION

The N,N- and N,O-containing ligands differed in the number of donor groups and in the length and nature of the bridge between the coordination sites are presently among the most used classes of non-cyclopentadienyl ligands in the chemistry of rare-earth elements. The amide, amidinate, and ketiminate ligands with the variable denticity and steric properties were used in the chemistry of rare-earth element derivatives as the stabilizing coordination environment [1–8]. Interest in ligands of the non-cyclopentadienyl type is primary evoked by the fact that a series of reactive compounds of transition *d* metals and rare-earth metals (REM) were synthesized owing to the application of these ligands. The synthesized compounds were catalytically active in the polymerization of dienes and methyl methacrylate, ring-opening polymerization of *rac*-lactide and ε-caprolactone, hydrogenation and hydrosilylation of olefins, and copolymerization of epoxides with CO_2 [6–14]. In addition, the role of the ligand environment is very high in the case of electropositive REM with large ion radii that form predominantly ionic metal–ligand bonds and are prone to ligand exchange reactions (Schlenk equilibrium). The chelate ligand is responsible for the suppression of the ligand redistribution and provides the kinetic stability of the complex. Therefore, the synthesis of polydentate N,N- and N,O-ligands capable of forming labile coordination bonds with the metal ion along with the strong covalent bond is among of important tasks. The necessary saturation of the coordination sphere of the metal ion in the complex is achieved due to these coordination bonds.

In this work, we report the synthesis of the new tridentate keto-β-diketiminate ligand $\{2,6\text{-}Me_2C_6H_3N{=}C(Me)\}_2CHC(tert\text{-}Bu){=}O$ (**II**) and the study of possible coordination modes of the $[\{2,6\text{-}Me_2C_6H_3N{=}C(Me)\}_2CC(tert\text{-}Bu){=}O]^-$ anion with lithium and yttrium cations and the catalytic activity of the diketiminate and ketodiketiminate complexes [{2,6-

$Me_2C_6H_3N{=}CMe\}_2CH]Li(Ph_2C{=}O)$ (**I**), $\{[\{2,6\text{-}Me_2C_6H_3N{=}C(Me)\}_2CC(tert\text{-}Bu){=}O]Li(THF)\}_n$ (**III**), and $[\{2,6\text{-}Me_2C_6H_3N{=}C(Me)\}_2CC(tert\text{-}Bu){=}O]_2YCl_2Li(THF)_2$ (**IV**) in the ring-opening polymerization of ε-caprolactone.

EXPERIMENTAL

All procedures on the synthesis and isolation of the products were carried out in a vacuum apparatus using the standard Schlenk techniques. Tetrahydrofuran (THF) was dried with potassium hydroxide and distilled over sodium benzophenone ketyl. Hexane and toluene were dehydrated by reflux and distillation over metallic sodium. Deuterated pyridine (C_5D_5N) was dried with calcium hydride, degassed, and condensed in vacuo. Deuterated benzene (C_6D_6) was dried over metallic sodium, degassed, and condensed in vacuo. Compounds $\{2,6\text{-}Me_2C_6H_3N{=}CMe\}_2CH_2$ [11] and YCl_3 [15] were synthesized according to published procedures. Benzophenone, ε-caprolactone, C_5D_5N, C_6D_6, $CDCl_3$, and 2,6-dimethylaniline were commercial reagents (Acros). IR spectra were recorded on a Bruker-Vertex 70 instrument. Samples of the compounds were prepared in a dry argon atmosphere as suspensions in Nujol. ^1H, ^{13}C, ^7Li, and HSQC $^1H{-}^{13}C$ NMR spectra were detected on Bruker Avance III and Bruker DRX-200 instruments (25°C, C_5D_5N, C_6D_6, $CDCl_3$). Chemical shifts are presented in ppm with respect to the known shifts of residual protons of the deuterated solvents. Elemental analyses were carried out on a Perkin-Elmer Series II CHNS/O Analyser 2400 instrument. The yttrium content was determined by complexonometric titration (Trilon B) using xylenol orange as the indicator [16].

Synthesis of lithium (2,6-dimethylphenyl)-4-(((2,6-dimethylphenyl)imino)pent-2-en-2-yl)anilide diphenylketonate (I). *n*-Butyllithium (2.40 mL, 2.78 mmol, 1.16 M solution in hexane) was added to a solution of $\{2,6\text{-}Me_2C_6H_3N{=}CMe\}_2CH_2$ (0.800 g, 2.61 mmol) in toluene (20 mL) at 0°C. The reaction mixture was stirred at 0°C for 1 h, benzophenone (0.476 g, 2.61 mmol) was added, and the mixture was stirred at 25°C for 12 h. Toluene was removed in vacuo, and the solid residue was dissolved in warm hexane (30 mL). Red crystals of compound **I** obtained by the slow concentrating of the hexane solution were dried in vacuo for 30 min. The yield was 0.970 g (75%).

For $C_{34}H_{35}N_2OLi$ (*FW* = 494.58)

Anal. calcd., %	C, 82.57	H, 7.13	N, 5.66
Found, %	C, 82.23	H, 7.35	N, 5.40

^1H NMR (400 MHz, 25°C, C_6D_6), δ, ppm: 1.88 (s, 6 H, $CH_3C{=}N$); 2.25 (s, 12 H, $C_6H_3(CH_3)_2$); 5.05 (s, 1 H, C*H*); 6.90–7.14 (m, 16 H, $C_6H_3(CH_3)_2$, $(C_6H_5)_2C{=}O$). ^{13}C NMR (100 MHz, 25°C, C_6D_6), δ, ppm: 19.1 ($C_6H_3(CH_3)_2$); 22.9 ($CH_3C{=}N$); 93.2 (*C*H); 121.9, 128.2, 128.5, 130.9, 131.1, 133.3, 136.7, 153.2, 163.3 ($C_6H_3(CH_3)_2$, $CH_3C{=}N$, $(C_6H_5)_2C{=}O$); 200.7 $(C_6H_5)_2C{=}O$). ^7Li NMR (155.5 MHz, 25°C, C_6D_6), δ, ppm: 3.0. IR (ν, cm^{-1}): 1667 s, 1648 s, 1626 s, 1597 s, 1557 s, 1325 s, 1277 s, 1176 s, 1088 s, 1076 s, 1025 s, 976 s, 941 s, 924 s, 823 s, 812 s, 761 s, 701 s, 639 s, 628 s, 611 s, 540 s, 487 s.

Synthesis of 5-((2,6-dimethylphenyl)imino)-4-(1-((2,6-dimethylphenyl)imino)ethyl)-2,2-dimethylhexan-3-one (II). *n*-Butyllithium (6.20 mL, 7.20 mmol, 1.16 M solution in hexane) was added to a solution of $\{2,6\text{-}Me_2C_6H_3N{=}CMe\}_2CH_2$ (2.000 g, 6.50 mmol) in toluene (35 mL) at 0°C. The reaction mixture was stirred at 0°C for 1 h, and a solution of *tert*-Bu(C=O)Cl (0.868 g, 7.20 mmol) in toluene (10 mL) was added. The reaction mixture was stirred for 48 h, the solution was decanted from a precipitate of LiCl, and the solvents were removed in vacuo. The solid residue was washed with hexane (10 mL) and dried in vacuo for 1 h. Ketodiketimine **II** with T_m = 103°C was isolated as a white powder in a yield of 2.030 g (80%).

For $C_{26}H_{34}N_2O$ (*FW* = 390.57)

Anal. calcd., %	C, 79.96	H, 8.77	N, 7.17
Found, %	C, 79.67	H, 8.95	N, 6.87

MS (EI, 70 eV), *m/z* (I_{rel} (%)): 390.57 $[M]^+$ (20). ^1H NMR (major isomer (69%), 400 MHz, 25°C, $CDCl_3$), δ, ppm: 1.30 (s, 9 H, $C(CH_3)_3$); 1.65 (s, 6 H, $CH_3C{=}N$); 2.17 (s, 12 H, $C_6H_3(CH_3)_2$); 6.87–7.08 (m, 6 H, $C_6H_3(CH_3)_2$); 13.12 (s, 1 H, N*H*). ^1H NMR (minor isomer (31%), 400 MHz, 25 °C, $CDCl_3$), δ, ppm: 1.36 (s, 9 H, $C(CH_3)_3$); 1.78, 2.02, 2.11 (s, all 18 H, $CH_3C{=}N$, $C_6H_3(CH_3)_2$); 5.42 (s, 1 H, C*H*); 6.87–7.08 (m, 6 H, $C_6H_3(CH_3)_2$). ^{13}C NMR (both isomers, 100 MHz, 25°C, $CDCl_3$), δ, ppm: 18.5, 18.7, 19.5, 19.7 ($CH_3C{=}N$, $C_6H_3(CH_3)_2$); 26.6, 28.7 ($C(CH_3)_3$); 46.3, 47.1 ($C(CH_3)_3$); 68.7 (*C*H, ketodiimine), 108.1 ($CH_3C{=}C$); 123.2, 124.8, 128.1, 128.2, 131.9, 142.8, 158.5, 211.1, 217.4 ($C_6H_3(CH_3)_2$, $CH_3C{=}N$, *tert*-Bu*C*=O). IR (ν, cm^{-1}): 3304 m, 1697 s, 1656 s, 1593 s, 1302 s, 1254 s, 1233 s, 1196 s, 1181 s, 1092 s, 1061 s, 1033 s, 986 s, 918 s, 854 m, 829 s, 805 s, 793 s, 762 s, 683 s, 649 m, 598 m, 579 m, 526 m, 511 m, 461 m.

Synthesis of lithium (2,6-dimethylphenyl)(3-(1-((2,6-dimethylphenyl)imino)ethyl)-5,5-dimethyl-4-oxohex-2-en-2-yl)anilide tetrahydrofuranate (III). *n*-Butyllithium (2.00 mL, 2.32 mmol, 1.16 M solution in hexane) was added to a solution of compound **II** (0.810 g, 2.07 mmol) in hexane (40 mL) at 0°C, and the reaction mixture was stirred at 25°C for 12 h. Hexane was removed in vacuo, and the solid residue was dried for 20 min and then dissolved in THF (5 mL). Light yellow crystals of compound **III** were obtained by the slow condensation of hexane in a concentrated solution of the complex in THF at 25°C. The crystals

were washed with cold hexane and dried in vacuo at 25°C for 30 min. The yield of light yellow crystals of complex **III** was 0.720 g (74%).

For $C_{60}H_{82}N_4O_4Li_2$ (*FW* = 937.17)

Anal. calcd., %	C, 76.89	H, 8.82	N, 5.98
Found, %	C, 76.55	H, 8.89	N, 5.70

^{1}H NMR (400 MHz, 25°C, C_5D_5N), δ, ppm: 1.57 (br.s, 9 H, C(CH_3)$_3$); 1.64 (m, 4 H, β-CH_2, THF); 1.98 (br.s, 6 H, CH_3C=N); 2.06 (br.s, 12 H, C_6H_3(CH_3)$_2$); 3.67 (m, 4 H, α-CH_2, THF); 7.00 (t, 2 H, C_6H_3(CH_3)$_2$, $^3J_{H,H}$ = 7.3 Hz); 7.12 (d, 4 H, C_6H_3(CH_3)$_2$, $^3J_{H,H}$ = 7.3 Hz). ^{13}C NMR (100 MHz, 25°C, C_5D_5N), δ, ppm: 19.3 (C_6H_3(CH_3)$_2$); 23.0 (CH_3C=N); 26.3 (β-CH_2, THF); 29.3 (C(CH_3)$_3$); 47.4 (C(CH_3)$_3$); 68.3 (α-CH_2, THF); 109.0 (CH_3C=C), 122.3, 125.8, 128.8, 131.0, 153.0, 160.5, 211.2, 216.6 (C_6H_3(CH_3)$_2$, CH_3C=N, *tert*-BuC=O). ^{7}Li NMR (155.5 MHz, 25°C, C_5D_5N), δ, ppm: 2.7. IR (ν, cm^{-1}): 1648 s, 1541 s, 1292 s, 1251 s, 1197 s, 1154 s, 1094 s, 1053 s, 1008 s, 993 s, 921 s, 896 s, 829 s, 809 s, 790 s, 760 s, 676 s, 646 s, 600 m, 568 s, 529 s, 503 s.

Synthesis of lithium bis[(2,6-dimethylphenyl)(3-(1-((2,6-dimethylphenyl)imino)ethyl)-5,5-dimethyl-4-oxohex-2-en-2-yl)anilide]dichloroyttrate(III) ditetrahydrofuranate (IV). A solution of complex **III** (0.402 g, 0.43 mmol) in THF (15 mL) was poured to a suspension of YCl_3 (0.084 g, 0.43 mmol) in THF (10 mL) at 25°C. The reaction mixture was stirred for 12 h, and THF was removed in vacuo. The reaction product was extracted with toluene (25 mL) and decanted from an insoluble precipitate. The solvent was removed, and the substance was dried in vacuo for 20 min and dissolved in THF (2 mL). White crystals of complex **IV** were obtained by the slow condensation of hexane in a concentrated solution of the complex in THF at 25°C. The crystals were washed with cold hexane and dried in vacuo at 25°C for 20 min. The yield of the white crystals of complex **IV** was 0.323 g (67%).

For $C_{63.5}H_{89.5}N_4O_{4.5}Cl_2LiY$ (*FW* = 1147.64)

Anal. calcd., %	C, 66.46	H, 7.86	N, 4.88	Y, 7.75
Found, %	C, 66.37	H, 7.95	N, 4.70	Y, 8.03

^{1}H NMR (400 MHz, 25°C, C_6D_6), δ, ppm: 1.38 (m, 10 H, β-CH_2, THF); 1.43 (br.s, 18 H, C(CH_3)$_3$); 2.20, 2.28 (br.s, 36 H, CH_3C=N, C_6H_3(CH_3)$_2$); 3.58 (m, 10 H, α-CH_2, THF); 6.92–7.05 (m, 12 H, C_6H_3(CH_3)$_2$). ^{13}C NMR (100 MHz, 25°C, C_6D_6), δ, ppm: 19.6, 20.3 (CH_3C=N, C_6H_3(CH_3)$_2$); 25.7 (β-CH_2, THF); 30.3 (C(CH_3)$_3$); 42.1 (C(CH_3)$_3$); 68.6 (α-CH_2, THF); 116.7 (CH_3C=C), 123.5, 125.1, 129.3, 131.8, 147.9, 158.7, 170.1, 185.2 (C_6H_3(CH_3)$_2$, CH_3C=N, *tert*-BuC=O). ^{7}Li NMR (155.5 MHz, 25°C, C_5D_5N), δ, ppm: 5.1. IR (ν, cm^{-1}): 1681 s, 1627 s, 1608 s, 1530 s, 1334 s, 1271 s, 1251 s, 1218 s, 1188 s, 1096 s, 1073 s, 1047 s, 985 s, 959 s, 918 s, 896 s, 839 s, 817 s, 798 s, 764 s, 748 s, 690 s, 675 s, 646 s, 600 s, 575 m, 543 s, 516 s, 489 s).

Polymerization of ε-caprolactone (general procedure). Complex **I** (5.0 mg, 0.01 mmol) was dissolved in toluene (2.5 mL) in an inert atmosphere of a glove box, and ε-caprolactone (0.285 g, 2.50 mmol) was added. The reaction mixture was stirred at 25°C for 5 min, and an aliquot was taken to determine the conversion of the monomer by the NMR method. Then a 1.2 M solution of HCl in ethanol (1 mL) was added to the reaction mixture, and the polymer was precipitated with ethanol excess (20 mL). The solid residue was separated and dried in vacuo to a constant weight. The yield was determined by gravimetry.

X-ray diffraction analyses (XRD) for compounds **I**, **III**, and **IV** were carried out on Bruker D8 Quest (**I**) and Rigaku OD Xcalibur (**III**, **IV**) diffractometers (MoK_α radiation, ω scan mode, λ = 0.71073 Å, T = 100(2) K). Experimental sets of intensities were measured and integrated using the APEX2 [17] and CrysAlis^{Pro} [18] program packages. An absorption correction was applied and the structures were solved and refined using the ABSPack (CrysAlis^{Pro}), SADABS [19], and SHELX [20] program packages. The structures were solved by a direct method and refined by full-matrix least squares for F^2_{hkl} in the anisotropic approximation for non-hydrogen atoms. All hydrogen atoms were placed in the geometrically calculated positions and refined isotropically with the fixed thermal parameters $U(H)_{iso}$ = 1.2$U(C)_{equiv}$ ($U(H)_{iso}$ = 1.5$U(C)_{equiv}$ for methyl groups). The crystallographic data and parameters of XRD experiments and structure refinement for compounds **I**, **III**, and **IV** are presented in Table 1. Selected bond lengths and bond angles are given in Table 2.

The structures were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC no. 2001131 (**I**), 2001132 (**III**), and 2001133 (**IV**), ccdc.cam.ac.uk/structures).

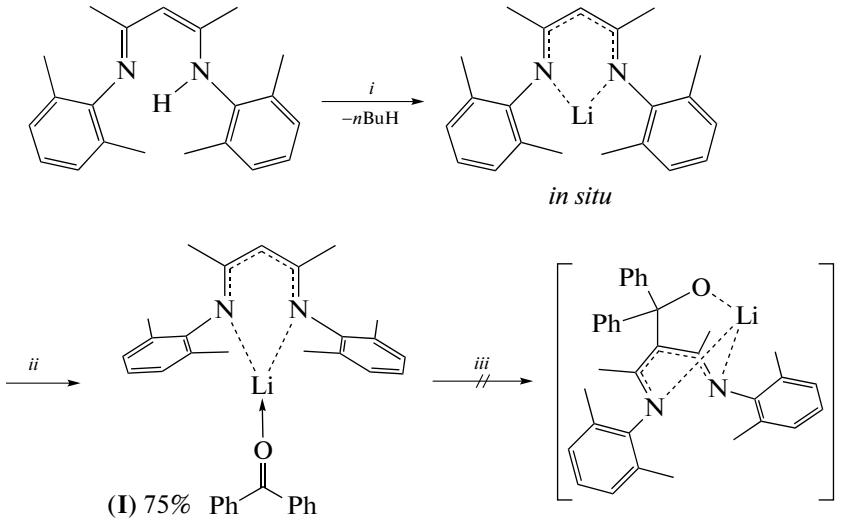
RESULTS AND DISCUSSION

In order to obtain the new diketiminate alkoxide κ^3-*N*,*N*,*O*-ligand of the scorpionate type [{2,6-$Me_2C_6H_3N$=C(Me)}$_2$CHCPh_2O]$^-$, we carried out the reaction of benzophenone with [{2,6-$Me_2C_6H_3N$=CMe}$_2$CH]Li synthesized *in situ* by the metallation of {2,6-$Me_2C_6H_3N$=CMe}$_2CH_2$ [11] with *n*-butyllithium in toluene at 0°C (Scheme 1). It was found that no addition of lithium diketiminate at the C=O bond of benzophenone occurred and the reaction afforded the adduct with benzophenone [(2,6-$Me_2C_6H_3N$=CMe)$_2$CH]Li(Ph_2C=O) (**I**) in which the latter acted as the neutral ligand coordinated to the lithium ion. The removal of the solvent in vacuo followed by the

Table 1. Crystallographic data and the parameters of XRD experiments and structure refinement for compounds **I**, **III**, and **IV**

Parameter	**I**	**III**	**IV**
FW	494.58	937.17	1147.64
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a, Å	9.6948(10)	13.9888(4)	16.7492(7)
b, Å	9.7829(10)	19.2892(5)	17.6465(8)
c, Å	15.2592(15)	21.0326(6)	22.5936(10)
α, deg	93.050(2)	90	90
β, deg	91.478(2)	107.696(3)	107.192(5)
γ, deg	100.707(2)	90	90
V, Å^3	1419.1(2)	5406.7(3)	6379.5(5)
Z	2	4	4
Crystal sizes, mm	0.29 × 0.20 × 0.12	0.50 × 0.30 × 0.20	0.25 × 0.15 × 0.05
ρ_{calc}, g/cm^3	1.157	1.151	1.195
μ, mm^{-1}	0.069	0.071	1.045
Scan range over θ, deg	2.44–29.98	2.96–30.03	2.92–30.03
Number of measured reflections	17394	108752	38094
Number of independent reflections with $I > 2\sigma(I)$	5919	12093	9384
R_{int}	0.0497	0.0667	0.0923
Number of refined parameters	349	649	740
$S(F^2)$	1.016	1.041	1.004
R_1 ($I > 2\sigma(I)$)	0.0644	0.0581	0.0717
wR_2 (for all data)	0.1856	0.1342	0.1818
Residual electron density (min/max), e/Å^3	0.54/–0.30	0.71/–0.30	0.93/–1.03

recrystallization of the reaction product from hexane gave the adduct with benzophenone (**I**) as red crystals in a yield of 75%. Complex **I** is sensitive to air oxygen and moisture and highly soluble in ethereal and aromatic solvents and moderately insoluble in aliphatic hydrocarbons. The composition and structure of the complex were determined by elemental analyses, IR and NMR spectroscopy, and XRD.



Reagents: *i*. Toluene, *n*BuLi; *ii*. Toluene, $Ph_2C{=}O$, 25°C; *iii*. Toluene, 110°C; THF, 70°C

Scheme 1.

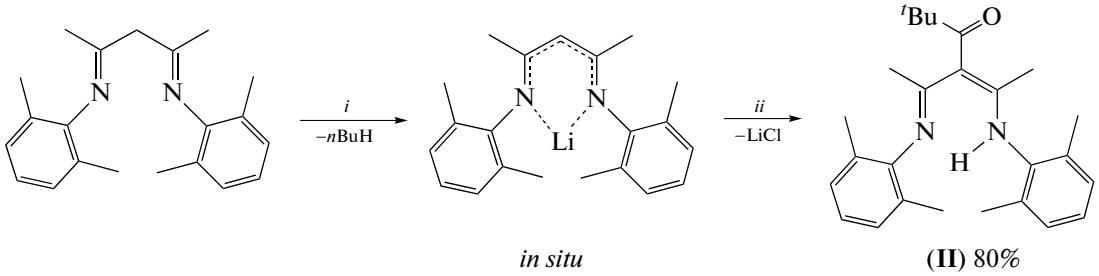
Table 2. Selected bond lengths (*d*) and bond angles (ω) in compounds **I**, **III**, and **IV**

Bond	*d*, Å	Angle	ω, deg
		I	
Li(1)–O(1)	1.825(3)	O(1)Li(1)N(1)	129.3(2)
Li(1)–N(1)	1.897(3)	O(1)Li(1)N(2)	129.8(2)
Li(1)–N(2)	1.898(3)	N(1)Li(1)N(2)	100.2(2)
O(1)–C(22)	1.228(2)	C(22)O(1)Li(1)	169.0(2)
N(1)–C(1)	1.314(2)	C(1)N(1)C(6)	122.0(2)
N(2)–(C3)	1.318(2)		
C(1)–C(2)	1.412(2)		
C(2)–C(3)	1.407(2)		
		III	
Li(1)–O(2)	1.946(3)	O(2)Li(1)N(2)	115.8(2)
Li(1)–N(2)	1.988(3)	O(2)Li(1)N(1)	119.3(2)
Li(1)–N(1)	1.994(3)	N(2)Li(1)N(1)	92.3(2)
Li(1)–O(3)	2.024(2)	O(2)Li(1)O(3)	104.6(2)
Li(2)–O(1)	1.970(3)	N(2)Li(1)O(3)	111.23(2)
Li(2)–N(3)	1.986(3)	N(1)Li(1)O(3)	113.6(2)
Li(2)–N(4)	1.988(3)	O(1)Li(2)N(3)	115.1(2)
Li(2)–O(4)	2.050(3)	O(1)Li(2)N(4)	113.9(2)
O(1)–C(6)	1.228(2)	N(3)Li(2)N(4)	92.2(2)
O(2)–C(32)	1.228(2)	O(1)Li(2)O(4)	109.6(2)
N(1)–C(1)	1.322(2)		
N(2)–C(3)	1.314(2)		
C(1)–C(2)	1.429(2)		
C(2)–C(3)	1.439(2)		
		IV	
Y(1)–O(2)	2.157(2)	O(2)Y(1)O(1)	106.20(9)
Y(1)–O(1)	2.171(2)	O(2)Y(1)N(3)	71.1(2)
Y(1)–N(3)	2.443(3)	O(1)Y(1)N(3)	95.1(2)
Y(1)–N(1)	2.436(3)	O(2)Y(1)N(1)	92.2(2)
Y(1)–Cl(1)	2.659(2)	O(1)Y(1)N(1)	72.6(2)
Y(1)–Cl(2)	2.676(2)	N(3)Y(1)N(1)	156.0(2)
Cl(1)–Li(1)	2.318(7)	O(2)Y(1)Cl(1)	161.00(7)
Cl(2)–Li(1)	2.344(7)	O(1)Y(1)Cl(1)	87.95(7)
O(1)–C(1)	1.309(4)	N(3)Y(1)Cl(1)	95.48(7)
O(2)–C(27)	1.307(4)	N(1)Y(1)Cl(1)	104.36(7)
N(1)–C(3)	1.306(4)	O(2)Y(1)Cl(2)	87.89(7)
N(1)–C(19)	1.449(4)	O(1)Y(1)Cl(2)	161.04(7)
N(2)–C(8)	1.283(4)	N(3)Y(1)Cl(2)	101.57(7)
N(2)–C(10)	1.430(4)	N(1)Y(1)Cl(2)	94.72(7)
N(3)–C(29)	1.312(4)	Cl(1)Y(1)Cl(2)	81.56(3)
N(3)–C(45)	1.445(5)		
N(4)–C(34)	1.285(5)		
N(4)–C(36)	1.437(5)		
C(1)–C(2)	1.395(5)		
C(2)–C(3)	1.473(5)		
C(27)–C(28)	1.399(5)		
C(28)–C(29)	1.467(5)		

The reaction of benzophenone with lithium diketiminate [{2,6-$Me_2C_6H_3N$=CMe}$_2$CH]Li under more drastic conditions in a solution of toluene (10 h, 110°C) or THF (7 h, 70°C) gave no desirable result, and the same adduct **I** was isolated from the reaction mixture after the recrystallization of the product from hexane (Scheme 1).

Transparent red crystals of complex **I** were obtained by slow concentrating from a hexane solution at room temperature. According to the XRD data, compound **I** is a Li(I) complex in which the metal cation is bound to two nitrogen atoms of the diketiminate ligand and one oxygen atom of the benzophenone molecule. Thus, the κ^2-*N*,*N*-coordination mode usual for ligands of this type is observed in complex **I**. The molecular structure of complex **I** is presented in Fig. 1a. The Li–N bond lengths in complex **I** (1.897(3), 1.898(3) Å) are close to each other and noticeably shorter than similar values in the lithium ketoiminate (1.983(8)–2.022(2) Å) [21–23], diketiminate (1.955(2)–2.009(4) Å) [24, 25], and triketiminate (1.958(2), 1.973(2) Å) [8, 26] complexes. The N–C (1.314(2)–1.318(2) Å) and C–C (1.407(2)–1.412(2) Å) distances in the LiNCCCN metallocycle lie in narrow ranges and indicate the electron density delocalization inside the diketiminate fragment. The metallocycle is nearly planar: the angle between the NLiN and NCCCN planes is 170.4(2)°. The Li–O distance in complex **I** (1.824(3) Å) is much shorter than the coordination bond Li–O (1.972(6) Å) in the lithium diketiminate complex [{Me_3SiNCPh}$_2$CH]Li(Ph_2CO)$_2$ [27] and is comparable with the Li–O distance (1.860(3) Å) in the lithium triketiminate complex [(2,6-$Me_2C_6H_3N$=CMe)$_3$C]Li(THF) [26]. The O(1)–C(22) bond length is 1.228(2) Å.

The ketodiketiminate κ^3-*N*,*N*,*O*-ligand of the scorpionate type (2,6-$Me_2C_6H_3N$=CMe)$_2$CH-(Bu^{t}C=O) (**II**) was synthesized by the reaction of *tert*-Bu(C=O)Cl with lithium diketiminate [{2,6-$Me_2C_6H_3N$=CMe}$_2$CH]Li in toluene and isolated as a white powder in a yield of 80% (Scheme 2). Keto-β-diketimine **II** was characterized by elemental analysis, NMR and IR spectroscopy, and mass spectrometry.



in situ (**II**) 80%

Reagents: *i*. Toluene, *n*BuLi; *ii*. *tret*-Bu(C=O)Cl

Scheme 2.

The study of the ^{1}H and ^{13}C NMR spectra of compound **II** showed that the ligand existed in a solution as two prototropic tautomers: ketoenaminimine (69%) and ketodiimine (31%). It was found by the NMR method (2D HSQC ^{1}H–^{13}C NMR spectrum, $CDCl_3$) that the singlet at 5.42 ppm corresponded to the methine proton α-C*H* of the central fragment CHCCC of ketodiimine (minor isomer) and the protons of the N*H* groups of ketoenaminimine appeared as a singlet at 13.12 ppm. It should be mentioned that the ^{13}C NMR spectrum also exhibits two sets of signals corresponding to the ketoenaminimine and ketodiimine tautomeric forms of compound **II**. The IR spectrum of compound **II** contains an intense absorption band at 1656 cm^{-1} corresponding to asymmetric vibrations of the C=N multiple bonds of the keto-β-diketiminate ligand and an intense absorption band at 1697 cm^{-1} assigned to stretching vibrations of the C=O bond of the keto group. It should be mentioned that the IR spectrum of compound **II** in CH_2Cl_2 contains an absorption band in the range characteristic of vibrations of the N–H bond (3304 cm^{-1}). Thus, the study of compound **II** by NMR (^{1}H, ^{13}C) and IR spectroscopy suggests that the compound exists in a solution in the ketoenaminimine and ketodiimine forms.

Lithium ketodiketiminate {[{2,6-$Me_2C_6H_3N$=C(Me)}$_2$CC(*tert*-Bu)=O]Li(THF)}$_n$ (**III**) was synthesized by the metallation of keto-β-diketimine **II** with *n*-butyllithium in THF at 0°C (Scheme 3).

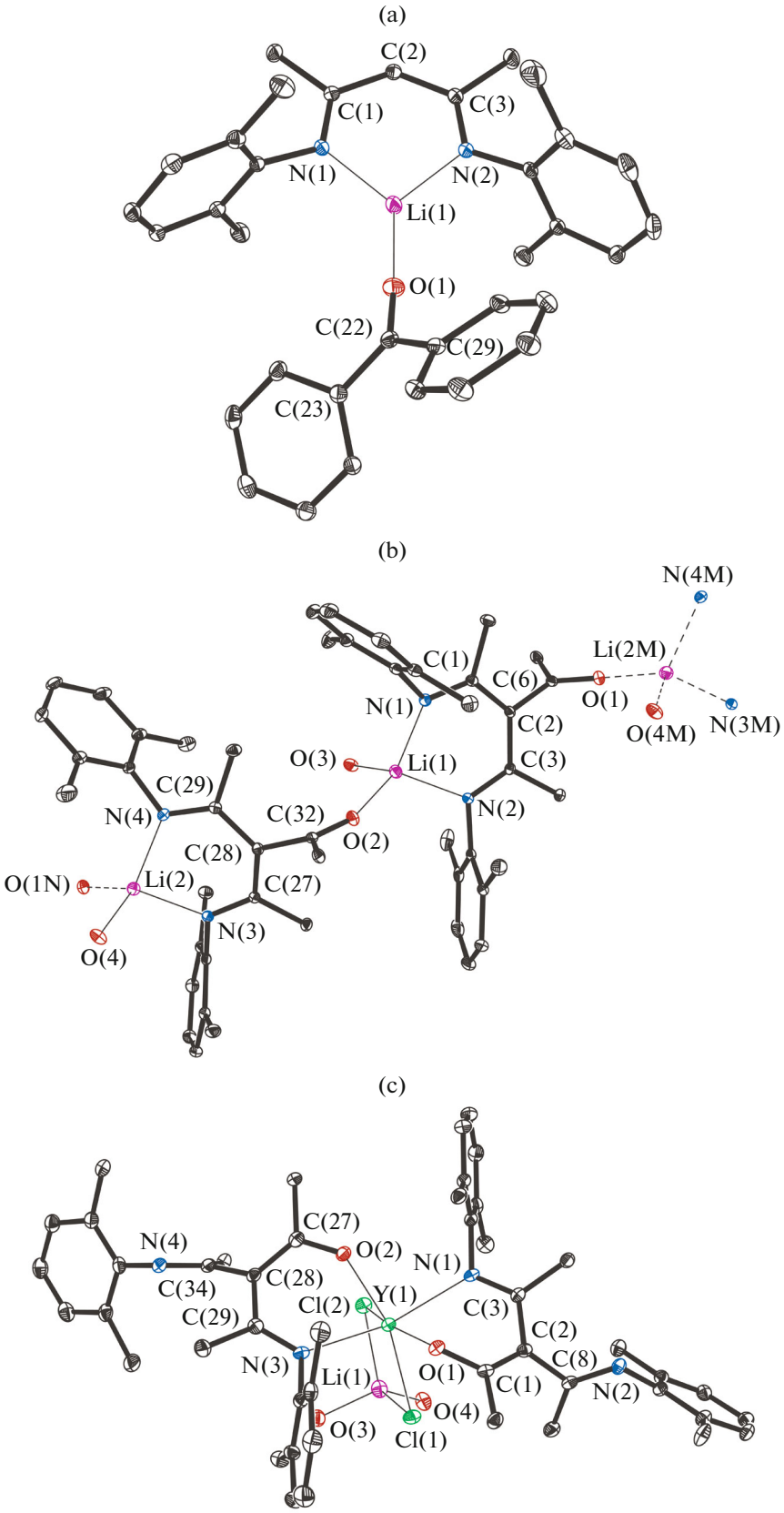
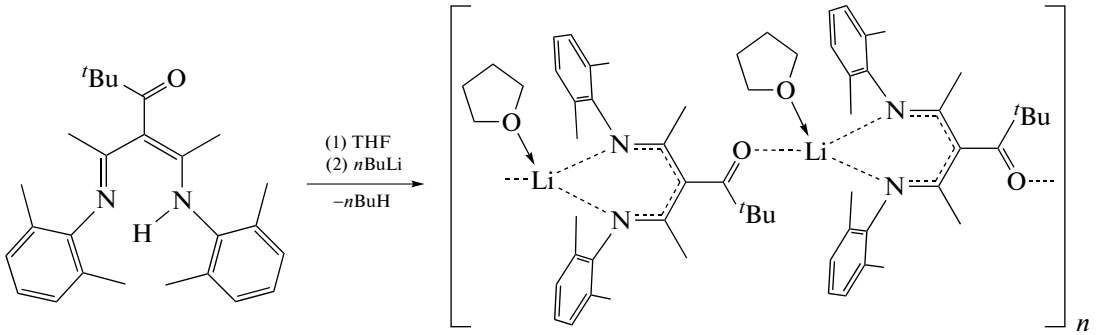


Fig. 1. Molecular structures of compounds (a) **I**, (b, fragment) **III**, and (c) **IV**. Thermal ellipsoids are given with 30% probability. Hydrogen atoms and methyl substituents of the *tert*-butyl groups and CH_2 group of the THF molecules (b, c) are omitted for clarity.



(II) **(III)** 74%

Scheme 3.

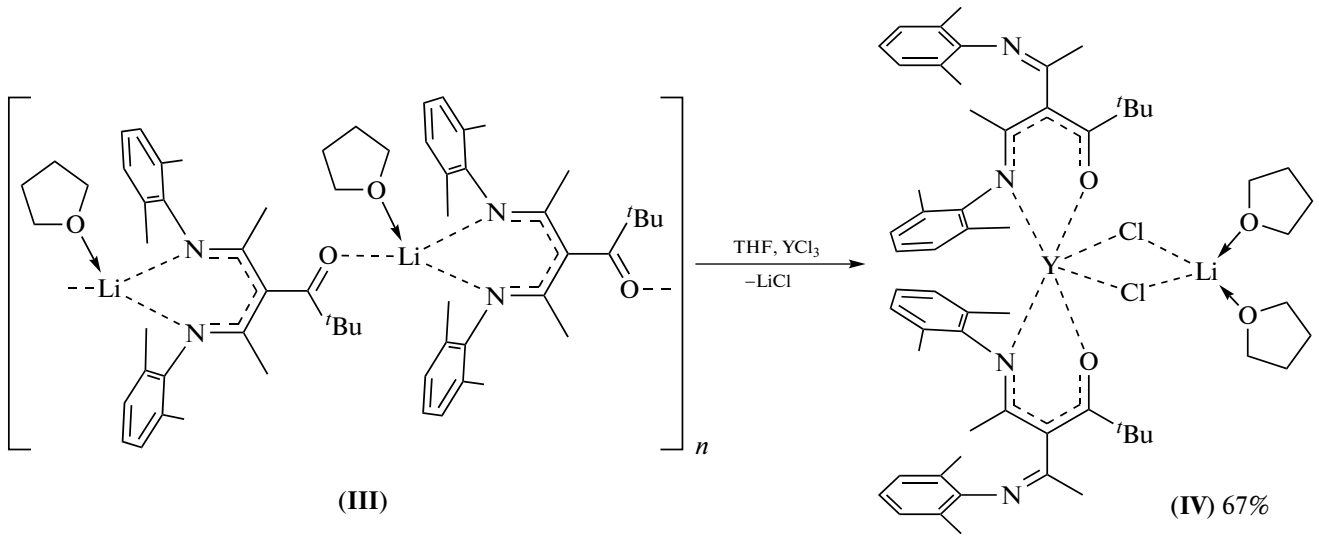
Complex **III** was isolated as light yellow crystals in a yield of 74%. Keto-β-diketiminate **III** is sensitive to air moisture and oxygen and highly soluble in aromatic hydrocarbons and ethereal solvents.

In the ^{1}H NMR spectrum of diamagnetic complex **III**, the protons of the *tert*-Bu substituents appear as a singlet at 1.57 ppm. Two broadened singlets at 1.98 and 2.06 ppm correspond to the protons of the methyl groups of the (2,6-$Me_2C_6H_3N$=CMe) fragments. Aromatic protons appear in a weak field as triplet (7.00 ppm, $^3J_{H,H}$ = 7.3 Hz) and doublet (7.12 ppm, $^3J_{H,H}$ = 7.3 Hz). The coordinated THF molecules in the ^{1}H NMR spectrum of complex **III** give two multiplets at 1.64 and 3.67 ppm attributed to the β- and α-methylenic protons. The ^{7}Li NMR spectrum of complex **III** exhibits the single signal at 2.7 ppm (155.5 MHz, 25°C, C_5D_5N).

Transparent light yellow crystals of complex **III** were obtained by the slow condensation of hexane in a concentrated solution of the compound in THF. The κ^2-*N*,*N*-coordination mode of the ketodiketiminate ligand by the lithium cation occurs in complex **III** like in complex **I**. However, it is shown by XRD that each Li^+ in compound **III** is additionally bound to the oxygen atom of the C=O group of the keto-β-diketiminate ligand of the adjacent molecule. Thus, complex **III** represents the 1D coordination polymer $\{[\{2,6\text{-}Me_2C_6H_3N{=}C(Me)\}_2CC(tert\text{-}Bu){=}O]Li(THF)\}_n$ in which each metal cation is linked to two nitrogen atoms of one ketodiketiminate ligand, the oxygen atom of the keto group of the second ketodiketiminate ligand, and the oxygen atom of the THF molecule. The fragment of the crystal structure of complex **III** is presented in Fig. 1b.

The Li–N bond lengths in complex **III** lie in a narrow range of 1.986(3)–1.994(3) Å. They are appreciably longer than analogous values in complex **I** (1.897(3), 1.898(3) Å) and comparable with the Li–N distances in the related lithium ketoiminate [21–23], diketiminate, and triketiminate complexes (1.958(2)–2.022(2) Å) [8, 24–26]. The N–C (1.313(2)–1.322(2) Å) and C–C (1.427(2)–1.439(2) Å) bond lengths indicate the electron density delocalization over the NCCCN fragment. Interestingly, the LiNCCCN metallocycles in complex **III** are distorted much more strongly than those in complex **I**. For example, the angles between the NLiN and NCCCN planes in complex **III** are 154.88(9)° and 158.5(2)°. The Li(1)–O(2) (1.946(3) Å) and Li(2)–O(1) (1.970(3) Å) bond lengths in compound **III** are somewhat shorter than the Li(1)–O(3) and Li(2)–O(4) distances (2.024(2), 2.050(3) Å) and significantly longer than Li(1)–O(1) in complex **I** (1.825(3) Å). The C=O bond length in the keto-diketiminate ligand is 1.228(2) Å.

The REM complexes in the *N*,*N*-diketiminate and *N*,*N*,*N*-triketiminate ligand environment demonstrated a fairly high catalytic activity in the ring-opening polymerization of *rac*-lactide and ε-caprolactone [8, 28]. To study the influence of the coordination environment on the catalytic activity of the metal complexes and possible coordination modes of the new chelate *N*,*N*,*O*-ligand by REM ions, we carried out the reaction of complex **III** with anhydrous YCl_3 in anhydrous THF at a reactant ratio of 2 : 1 for 12 h (Scheme 4). After the reaction product was extracted with toluene and recrystallized from a THF–hexane mixture, the $[\{2,6\text{-}Me_2C_6H_3N{=}C(Me)\}_2CC(tert\text{-}Bu){=}O]_2Y(\mu^2\text{-}Cl)_2Li(THF)_2$ complex (**IV**) was isolated as colorless crystals in a yield of 67%. Complex **IV** was characterized by elemental analysis and NMR and IR spectroscopy and represents a compound sensitive to air moisture and oxygen and highly soluble in aromatic hydrocarbons and ethereal solvents.



Scheme 4.

The crystals of complex **IV** were obtained by the slow cooling of a concentrated solution of the compound in a THF–hexane (1 : 4) mixture to –20°C. It is shown by XRD that compound **IV** represents a monomeric *ate* complex and crystallizes as the solvate $[\{2,6\text{-}Me_2C_6H_3N{=}C(Me)\}_2CC(tert\text{-}Bu){=}O]_2YCl_2Li(THF)_2 \cdot 1/2THF \cdot 1/4Hex$ (the molecular structure of complex **IV** is shown in Fig. 1c).

Unlike complex **III**, complex **IV** exhibits the κ^2-*N*,*O*-coordination mode of the keto-diketiminate ligand by the metal atom. The Y^{3+} cation in complex **IV** is linked with two oxygen atoms and two nitrogen atoms of two ketodiketiminate ligands and two μ^2-bridging chlorine ligands. Thus, the CN of the yttrium atom in complex **IV** is formally equal to six. Both potentially tridentate ketodiketiminate ligands in compound **IV** are coordinated by the metallocenter via the bidentate mode, whereas the third coordination site of each ligand is not involved in the interaction with the metal. In turn, the Li^+ cation is linked with two chlorine atoms and two oxygen atoms of two THF molecules.

The keto-β-diketiminate ligand in compound **IV** is nonsymmetrically coordinated by the yttrium cation. The Y–O bond lengths are 2.171(2) and 2.157(2) Å, whereas the Y–N distances in complex **IV** are considerably longer (2.436(3), 2.443(3) Å) and somewhat exceed the corresponding values in the yttrium β-diketiminate complexes $[\{HC(2\text{-}RC_6H_4N{=}CMe)_2\}YCl_3Li(Et_2O)_2]_2$ (2.315(6), 2.317(6), 2.3427(19), 2.377(2) Å; R = *iso*-Pr, *tert*-Bu) [29] and $[HC(PhN{=}CMe)_2]_3Y$ (2.406(4), 2.404(3) Å) [9]. The Y–Cl distances are 2.659(2) and 2.676(2) Å and comparable with analogous distances in the β-diketiminate derivatives $[\{HC(2\text{-}RC_6H_4N{=}CMe)_2\}YCl_3Li(Et_2O)_2]_2$ (2.611(2), 2.660(2), 2.6294(6), 2.6169(6) Å; R = *iso*-Pr, *tert*-Bu) [29]. The Li–Cl bond lengths are 2.218(7) and 2.344(7) Å. The electron density delocalization in the metallocycles is less pronounced for compound **IV** than that in complexes **I** and **III**. The C(1)–O(1) and C(27)–O(2) distances are 1.309(4) and 1.307(4) Å, respectively, and the N(1)–C(3) and N(3)–C(29) distances (1.306(4), 1.312(4) Å) are insignificantly longer than the lengths of the N(2)–C(8) and N(4)–C(34) double bonds (1.283(5), 1.285(5) Å) [30]. In spite of the fact that the C–C bond lengths lie in a wide range of 1.395(5)–1.507(5) Å, they characterize the delocalization of the negative charge in the ketoiminate fragment rather than the alternation of the C–C distances. The YNCCCO metallocycles are strongly distorted: the angles between the NYO and NCCCO planes are 135.3(2)° and 140.60(9)°.

Complexes **I**, **III**, and **IV** catalyze the ring-opening polymerization of ε-caprolactone under mild conditions (25°C, toluene). For catalysis by lithium complexes **I** and **III**, the complete conversion of the monomers (1000 equiv.) is achieved within 30 min. The polydispersion indices of the samples of the synthesized polymers are characterized by mean values (M_w/M_n = 1.4–2.3), and the molecular weights of the polymers range from 10500 to 43200 (Table 3, entries *1*–*8*). It is found as a result of the performed series of experiments involving catalysts **I** and **III** that the values of M_n^{exp} are strongly underestimated (Fig. 2) at high loadings of the monomer (500/1, 1000/1), which is due, most likely, to the competitive transesterification reaction (Table 3, entries *3*, *4*, *7*, *8*). When the polymerization of ε-caprolactone is carried out in the presence of complex **III** in both toluene and polar THF, the quantitative conversion of the monomer is attained within 2–30 min in both cases, but the samples of polylactones characterized by higher values of M_n^{exp} were obtained in the polar solvent at the high

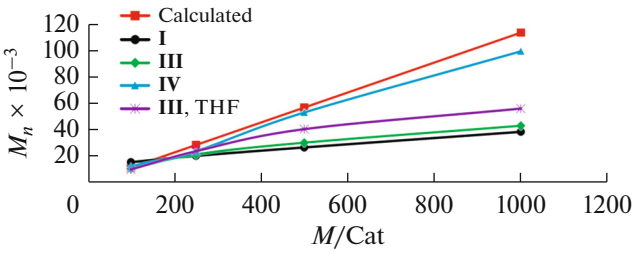


Fig. 2. M_n vs $[M]_0/[\mathrm{Cat}]_0$. Polymerization of ε-caprolactone. Conditions: catalysts **I**, **III**, and **IV**; toluene (**III**, THF), 25°C, $[M]_0 = 1.0$ mol L^{-1}.

loading of the monomer (500/1, 1000/1) (Table 3, entries *7*, *8*, *11*, *12*). It should be mentioned that yttrium bis(keto-diketiminate) chloride complex **IV** demonstrated a substantially lower catalytic activity in the ring-opening polymerization of ε-caprolactone compared to lithium complexes **I** and **III**. For catalysis by yttrium complex **IV**, the complete conversion of the monomer (1000 equiv.) is achieved within 24 h. Along with a good agreement of the experimental and calculated values of M_n (Fig. 2), the polylactone samples characterized by a fairly narrow molecular weight distribution M_w/M_n = 1.6–1.8 and the high molecular weight M_n = 53300–99900 (Table 3, entries *15*, *16*) were obtained in the case of compound **IV**.

Thus, the reaction of [{2,6-$Me_2C_6H_3N$=CMe}$_2$CH]Li with benzophenone produces the coordination complex [{2,6-$Me_2C_6H_3N$=CMe}$_2$-CH]Li-(Ph_2C=O) (**I**), and no addition of lithium diketiminate at the C=O bond of benzophenone and no formation of lithium diketiminate alkoxide are observed. Keto-β-diketimine {2,6-$Me_2C_6H_3N$= C(Me)}$_2$CHC-(*tert*-Bu)=O (**II**) was synthesized by the reaction of pivaloyl chloride *tert*-Bu(C=O)Cl with lithium diketiminate [{2,6-$Me_2C_6H_3N$=CMe}$_2$-CH]Li. The reaction of ketodiketimine **II** with *n*-butyllithium afforded the lithium complex {[{2,6-$Me_2C_6H_3N$= C(Me)}$_2$CC(*tert*-Bu)=O]Li(THF)}$_n$ (**III**). Complex **III** in the crystalline state is a coordination polymer. The first example of the REM complex with the anionic keto-β-diketiminate ligand [{2,6-$Me_2C_6H_3N$= C(Me)}$_2$CC(*tert*-Bu)=O]$^-$ was synthesized and structurally characterized. Yttrium bis(ketodiketiminate) [{2,6-$Me_2C_6H_3N$=C(Me)}$_2$CC(*tert*-Bu)=O]$_2$$YCl_2$Li-$(THF)_2$ (**IV**), being an *ate* complex with one LiCl molecule, was synthesized by the exchange reaction of YCl_3 with lithium derivative **III**. It is found by the XRD method that the monoanionic ketodiketiminate ligand in yttrium complex **IV** acts as the bidentate one and coordinates to the metal ion only via the nitrogen and oxygen atoms, whereas the third coordination site is not involved in the interaction with the metal, which is due, most likely, to the electronic state of the ligand

Table 3. Polymerization of ε-caprolactone initiated by complexes **I**, **III**, and **IV***

Entry	Complex	Solvent	$[M]_0/[\mathrm{Cat}]_0$	t, min	$M_n^{\mathrm{calc}} \times 10^{-3}$	$M_n^{\mathrm{exp}} \times 10^{-3}$	M_w/M_n
1	**I**	Toluene	100	2	11.4	15.5	2.2
2	**I**	Toluene	250	5	28.5	20.3	1.8
3	**I**	Toluene	500	15	57.1	26.7	1.4
4	**I**	Toluene	1000	30	114.1	38.6	1.7
5	**III**	Toluene	100	2	11.4	10.5	2.3
6	**III**	Toluene	250	5	28.5	21.4	2.2
7	**III**	Toluene	500	15	57.1	30.3	2.1
8	**III**	Toluene	1000	30	114.1	43.2	2.0
9	**III**	THF	100	2	11.4	9.9	2.0
10	**III**	THF	250	5	28.5	23.8	2.5
11	**III**	THF	500	15	57.1	40.6	1.9
12	**III**	THF	1000	30	114.1	56.3	2.4
13	**IV**	Toluene	100	120	11.4	12.2	2.1
14	**IV**	Toluene	250	320	28.5	24.0	1.5
15	**IV**	Toluene	500	690	57.1	53.3	1.6
16	**IV**	Toluene	1000	1440	114.1	99.9	1.8

* Conditions: toluene, $[M] = 1.0$ mol L^{-1}; THF, $[M] = 1.0$ mol L^{-1}; $T = 25$°C. The conversion of the monomer M was determined by ^{1}H NMR and is equal to 100% in all experiments. The molecular weights of the polymers M_n^{exp} were determined by gel permeation chromatography using polystyrene standards, and M_n^{calc} were calculated by the following equation: $114.14Y \times [M]/[\mathrm{Ln}]$ (Y is the yield).

rather than the ion radius of the metal. Complexes **I**, **III**, and **IV** initiate the ring-opening polymerization of ε-caprolactone in toluene at 25°C.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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