Yttrium and Lithium Keto-β-Diketiminate Complexes

\[
\{2,6-\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{C(Me)}\}_2\text{CC(tert-Bu)}=\text{O}\}_2\text{Y(μ}_2\text{-Cl)}_2\text{Li(THF)}_2
\]

and \n
\[
\{2,6-\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{C(Me)}\}_2\text{CC(tert-Bu)}=\text{O}\}_\text{n}\text{Li(THF)}\_n
\]

Synthesis, Molecular Structures, and Catalytic Activity in ε-Caprolactone Polymerization

G. G. Skvortsov\textsuperscript{a}, A. V. Cherkasov\textsuperscript{a}, D. L. Vorozhtsov\textsuperscript{a}, E. S. Shchegrevina\textsuperscript{b}, and A. A. Trifonov\textsuperscript{a, c, *}

\textsuperscript{a}Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhny Novgorod, Russia

\textsuperscript{b}Nizhny Novgorod State University, Nizhny Novgorod, Russia

\textsuperscript{c}Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 119991 Russia

\*e-mail: trif@iomc.ras.ru

Received May 6, 2020; revised May 27, 2020; accepted June 1, 2020

Abstract—The reaction of lithium β-diketiminate \{2,6-\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{C(Me)}\}_2\text{CH}\text{Li} with benzophenone in toluene at 25°C affords the coordination complex \{2,6-\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{C(Me)}\}_2\text{CH}\text{Li(Ph}_2\text{C}=\text{O}) \_\text{I}(I). New keto-β-diketimine \{2,6-\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{C(Me)}\}_2\text{CHC(tert-Bu)}=\text{O} \_\text{II}(II) is synthesized by the reaction of tert-\text{Bu(C=O)}\text{Cl} with \{2,6-\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{C(Me)}\}_2\text{CH}\text{Li}. The metallation of keto-β-diketimine \text{II with n-butyllithium in THF at 0°C gives lithium keto-β-diketiminate \{2,6-\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{C(Me)}\}_2\text{CC(tert-Bu)}=\text{O}\}_\text{n}\text{Li(THF)}\_n \_\text{III}(III). The exchange reaction of YCl\text{\textsubscript{3}} with compound \text{III (molar ratio 1 : 2, THF)} affords the yttrium bis(keto-diketiminate) complex \{2,6-\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{C(Me)}\}_2\text{CC(tert-Bu)}=\text{O}\}_2\text{Y(μ}_2\text{-Cl)}_2\text{L}-(\text{THF})_2 \_\text{IV}(IV). The molecular structures of complexes \text{I, III, and IV are determined by X-ray diffraction analysis (CIF files CCDC nos. 2001131 \_\text{I}, 2001132 \_\text{III), and 2001133 \_\text{IV}). Complex IV in the crystalline state exists as an ate complex with one LiCl molecule. Complexes \text{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

DOI: 10.1134/S1070328421020007X

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 \textit{rac}-lactide and ε-caprolactone, hydrogenation and hydrosilylation of olefins, and copolymerization of epoxides with \textit{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 polynodentate 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 tri-dentate keto-β-diketiminate ligand \{2,6-\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{C(Me)}\}_2\text{CHC(tert-Bu)}=\text{O} \_\text{II}(II) and the study of possible coordination modes of the \{2,6-\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{C(Me)}\}_2\text{CC(tert-Bu)}=\text{O}\}_- \text{anion with lithium and yttrium cations and the catalytic activity of the diketiminate and ketodiketiminate complexes \{2,6-}
Me₂C₆H₃N=C(Me)₂CH[Li(Ph₃C=O)] (I), {{[2,6-Me₂C₆H₃N=C(Me)]₂CC(tert-Bu)=O[Li(THF)]}, (III), and {{[2,6-Me₂C₆H₃N=C(Me)]₂CC(tert-Bu)=O[LiYCl₂(THF)]} (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 under reduced pressure over metallic sodium. Deuterated pyridine (C₅D₅N) was dried with calcium hydride, degassed, and condensed in vacuo. Benzophenone, ε-caprolactone, C₅D₅N, C₆D₆, and 2,6-dimethylaniline were commercial reagents (Acros). IR spectra were recorded on a Perkin-Elmer Series II CHNS/O Analyser.

Compounds {2,6-Me₂C₆H₃N=CMe}₂CH₂ [11] and YCl₃ [15] were synthesized according to published procedures. Benzophenone, ε-caprolactone, and 2,6-dimethylaniline were commercial reagents (Acros). 1H NMR spectra were detected on Bruker Avance III and MS (EI, 70 eV), m/z (Irel (%)): 390.57 [M]+ (20).

Synthesis of lithium (2,6-dimethylphenyl)(3-(1-(2,6-dimethylphenyl)limino)-5,5-dimethyl-4-oxohex-2-en-2-yl)anilide tetrahydrofuranate (III). n-Butyllithium (4.60 mL, 7.20 mmol, 1.16 M solution in hexane) was added to a solution of {2,6-Me₂C₆H₃N=CMe}₂CH₂ (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-BuOCl (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 Tm = 103°C was isolated as a white powder in a yield of 2.030 g (80%).

For C₁₂H₃₄N₂O (FW = 390.57)
Anal. calcd., % C, 79.96 H, 8.77 N, 7.17
Found, % C, 79.67 H, 8.95 N, 6.87

Synthesis of lithium (2,6-dimethylphenyl)(3-(1-((2,6-dimethylphenyl)limino)-5,5-dimethyl-4-oxohex-2-en-2-yl)anilide tetrahydrofuranate (III). n-Butyllithium (2.40 mL, 2.78 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

For C₁₂H₃₄N₂O Li (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, C₆D₆), δ, ppm: 1.88 (s, 6 H, C₆H₂(CH₃)₂); 2.25 (s, 12 H, C₆H₄(CH₃)₂); 5.05 (s, 1 H, CH); 5.42 (s, 1 H, C₆H₄(CH₃)₂); 6.87–7.08 (m, 16 H, C₆H₅); 7.12 (m, 6 H, C₆H₄(CH₃)₂); 7.18, 7.20, 7.22, 7.24 (s, all 18 H, C₆H₅). 13C NMR (both isomers, 100 MHz, 25°C, CDCl₃), δ, ppm: 39.05 (s, 3 H, C(CH₃)₃); 54.05 (s, 1 H, CH₂); 6.87–7.08 (m, 6 H, C₆H₄(CH₃)₂); 101.8 (CH₃C=O); 123.2, 124.8, 128.1, 128.2, 131.9, 142.8, 158.5, 211.1, 217.4 (C₆H₄(C₆H₃)₂), 26.7, 28.7 (C(CH₃)₂), 46.3, 47.1 (C(CH₃)₂), 68.7 (CH, ketodiimine), 75.8, 77.3, 77.4, 80.3, 80.4, 130.5, 131.6, 149.6, 152.1, 152.4, 159.7, 163.9, 211.1, 217.4, 222.2 (C₆H₄(C₆H₃)₂), 26.6, 28.7 (C(CH₃)₂), 46.3, 47.1 (C(CH₃)₂), 68.7 (CH, ketodiimine), 75.8, 77.3, 77.4, 80.3, 80.4, 130.5, 131.6, 149.6, 152.1, 152.4, 159.7, 211.1, 217.4, 222.2 (C₆H₄(C₆H₃)₂).
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 C₆₀H₈₂N₄O₄Li₂ (FW = 937.17) Anal. calcld., % C, 76.89 H, 8.82 N, 5.98 Found, % C, 76.55 H, 8.89 N, 5.70

1H NMR (400 MHz, 25°C, C₆D₅N), δ, ppm: 1.57 (br.s, 9 H, C(H₂)₃); 1.64 (m, 4 H, β-CH₂, THF); 1.98 (br.s, 6 H, CH₃C=NC); 2.06 (br.s, 12 H, C₆H₃(CH₂)₃); 3.67 (m, 4 H, α-CH₂, THF); 7.00 (t, 2 H, C₆H₅(CH₂)₂); 3JH,HH = 7.3 Hz). 13C NMR (100 MHz, 25°C, C₆D₆), δ, ppm: 19.3 (C₆H₅(CH₂)₂); 23.0 (CH₃C=NC); 26.3 (β-CH₂, THF); 29.3 (C(CH₂)₃); 47.4 (C(CH₂)₃); 68.3 (α-CH₂, THF); 109.0 (CH₃C=C); 122.3, 125.8, 128.8, 131.0, 153.0, 160.5, 211.2, 216.6 (C₆H₃(CH₂)₂, C₆H₃=C, tert-BuC=O).

Synthesis of lithium bis{(2,6-dimethylphenyl)(3-(1-(2,6-dimethylphenyl)iminol(5,5-dimethyl-1-oxohex-2-en-2-yl)anilide[dichloro]yttrate(III) ditetrahydrofuranate (IV). A solution of complex III (0.402 g, 0.43 mmol) in THF (15 mL) was poured to a suspension of YCl₃ (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 C₆₃H₈₀N₄O₄Cl₂LiY (FW = 1147.64) Anal. calcld., % 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

RESULTS AND DISCUSSION

In order to obtain the new diketiminate alkoxide κ³-N₃N₅O₆-ligand of the scorpionate type {[2,6-Me₆C₆H₃N=C(Me)₂]CH₂Ph₂O}⁻, we carried out the reaction of benzophenone with [2,6-Me₆C₆H₃N=CMe₂]CH₂Li synthesized in situ by the metallation of {2,6-Me₆C₆H₃N=CMe₂}CH₂ [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-Me₆C₆H₃N=CMe₂]CH₂Li(Ph₂C=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                            | $P\overline{1}$ | $P2_1/n$    | $P2_1/c$    |
| 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) |
| $\alpha$, deg                          | 93.050(2)  | 90          | 90          |
| $\beta$, deg                           | 91.478(2)  | 107.696(3)  | 107.192(5)  |
| $\gamma$, deg                          | 100.707(2) | 90          | 90          |
| $V$, Å³                                | 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 |
| $\rho$ calc, g/cm³                     | 1.157      | 1.151       | 1.195       |
| $\mu$, mm$^{-1}$                       | 0.069      | 0.071       | 1.045       |
| Scan range over $\theta$, 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 |
| $R_{\text{int}}$                       | 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.

![Scheme 1](image-url)
Table 2. Selected bond lengths ($d$) and bond angles ($\omega$) in compounds I, III, and IV

| Bond | $d$, Å   | Angle       | $\omega$, 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)−C(3)  | 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(2)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 \([2,6-\text{Me}_2\text{C}_6\text{H}_3N=\text{CMe}_2]\text{CH}\)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 \(\kappa^2\)-\(N,N\)-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 \([\{\text{Me}_3\text{SiNCPh}_2\text{CH}\}]\text{Li(Ph}_2\text{CO)}_2\) [27] and is comparable with the Li–O distance (1.860(3) Å) in the lithium triketiminate complex \([\{2,6-\text{Me}_2\text{C}_6\text{H}_3N=\text{CMe}_2]\text{CH}\text{Li(THF)}\) [26]. The O(1)–C(22) bond length is 1.228(2) Å.

The ketoketodiketiminate \(\kappa^3\)-\(N,N,O\)-ligand of the scorpionate type (2,6-\(\text{Me}_2\text{C}_6\text{H}_3N=\text{CMe}_2\text{CH}-(\text{Bu}t\text{C}=\text{O})\) (II) was synthesized by the reaction of \(t\text{ret-Bu(C}=\text{O})\text{Cl}\) with lithium diketiminate \([2,6-\text{Me}_2\text{C}_6\text{H}_3N=\text{CMe}_2]\text{CH}\)Li in toluene and isolated as a white powder in a yield of 80% (Scheme 2). Keto-\(\beta\)-diketimine II was characterized by elemental analysis, NMR and IR spectroscopy, and mass spectrometry.

The study of the \(^1\text{H}\) and \(^{13}\text{C}\) 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 \(^1\text{H}–^{13}\text{C}\) NMR spectrum, CDCl\(_3\)) that the singlet at 5.42 ppm corresponded to the methine proton \(\alpha\text{-C}H\) of the central fragment CHCC of ketodiimine (minor isomer) and the protons of the NH groups of ketoenaminimine appeared as a singlet at 13.12 ppm. It should be mentioned that the \(^{13}\text{C}\) 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 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\(_2\)Cl\(_2\) 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 (\(^1\text{H}, \text{~}^{13}\text{C}\)) and IR spectroscopy suggests that the compound exists in a solution in the ketoenaminimine and ketodiimine forms.

Lithium ketodiketiminate \(\{}\{2,6-\text{Me}_2\text{C}_6\text{H}_3N=\text{C(Me)}_2\text{CC(tert-Bu)=O}\text{Li(THF)}\}\) (III) was synthesized by the metallation of keto-\(\beta\)-diketiminate 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.
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 ¹H 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-Me₂C₆H₃-N=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 ¹H NMR spectrum of complex III give two multiplets at 1.64 and 3.67 ppm attributed to the β- and α-methylene protons. The ⁷Li NMR spectrum of complex III exhibits the single signal at 2.7 ppm (155.5 MHz, 25°С, C₅D₅N).

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 κ₂-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-Me₂C₆H₃-N=C(Me)]₂CC(tert-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 ketoiminates [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 metalcycles 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 YCl₃ 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-Me₂C₆H₃-N=C(Me)]₂CC(tert-Bu)=O]₂Y(μ²-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.
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 \[\text{[2,6-Me}_2\text{C}_6\text{H}_3\text{N=C(Me)}_2\text{CC(terr-Bu)=O}]}_2\text{YCl}_2\text{Li-} (\text{THF})_2\cdot 1/2\text{THF}\cdot 1/4\text{Hex}\ (\text{the molecular structure of complex IV is shown in Fig. 1c}).

Unlike complex III, complex IV exhibits the \(\kappa^2\)-\(N,O\)-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 \(\mu^2\)-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-\(\beta\)-diketiminate ligand in compound IV is nonsymmetrically coordinated by the yttrium atom. 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 \(\beta\)-diketiminate complexes \([\text{HC(2-RC}_2\text{H}_4\text{N=CMe)}_2\text{YCl}_2\text{Li-} (\text{Et}_2\text{O})]_2\) (2.315(6), 2.317(6), 2.3427(19), 2.377(2) Å; \(R = isoPr, tert-Bu\)) [29] and \([\text{HC(PhN=CMe)}_2\text{Y}(\text{2.406(4), 2.404(3) Å})]\) [9]. The \(Y–Cl\) distances are 2.659(2) and 2.676(2) Å and comparable with analogous distances in the \(\beta\)-diketiminate derivatives \([\text{HC(2-RC}_2\text{H}_4\text{N=CMe)}_2\text{YCl}_2\text{Li-(Et}_2\text{O})]_2\) (2.611(2), 2.660(2), 2.6294(6), 2.6169(6) Å; \(R = isoPr, tert-Bu\)) [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 \(\varepsilon\)-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 trans esterification reaction (Table 3, entries 3, 4, 7, 8). When the polymerization of \(\varepsilon\)-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
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 \([{2,6-Me_2C_6H_3N=CMe}_2CH]Li\) 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 \( \text{C}=\text{O} \) bond of benzophenone and no formation of lithium diketiminate alkoxide are observed. Keto-β-diketimine \({[2,6-Me_2C_6H_3N=C(Me)}_2CHC(\text{tert}-\text{Bu})=O \) (II) was synthesized by the reaction of pivaloyl chloride \( \text{tert}-\text{Bu}(C=O)Cl \) with lithium diketiminate \({[2,6-Me_2C_6H_3N=CMe}_2CH]Li\). The reaction of ketodiketimine II with \( n \)-butyllithium afforded the lithium complex \({[{2,6-Me_2C_6H_3N=C(Me)}_2C(\text{tert}-\text{Bu})=O\]Li(THF)} \) (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 \( [{2,6-Me_2C_6H_3N=C(Me)}_2C(\text{tert}-\text{Bu})=O}– \) was synthesized and structurally characterized. Yttrium bis(ketodiketiminate) \( [{2,6-Me_2C_6H_3N=C(Me)}_2CC(\text{tert}-\text{Bu})=O]YCl_2Li-(THF) \) (IV), being an ate complex with one \( \text{LiCl} \) molecule, was synthesized by the exchange reaction of \( \text{YCl}_3 \) 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.

![Fig. 2. \( M_n \) vs \([M_0]/[Cat]_0\). Polymerization of ε-caprolactone. Conditions: catalysts I, III, and IV; toluene (III, THF), 25°C. \([M_0] = 1.0 \text{ mol L}^{-1}\).](image)

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

| Entry | Complex | Solvent | \([M_0]/[Cat]_0\) | \( t \), min | \( M_n^{\text{calc}} \times 10^{-3} \) | \( M_n^{\text{exp}} \times 10^{-3} \) | \( M_w/M_n \) |
|-------|---------|---------|-----------------|-------------|-------------------------------|-------------------------------|-----------------|
| 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, \([M] = 1.0 \text{ mol L}^{-1}\); THF, \([M] = 1.0 \text{ mol L}^{-1}\); \( T = 25°C \). The conversion of the monomer \( M \) was determined by \(^1\text{H} \) NMR and is equal to 100% in all experiments. The molecular weights of the polymers \( M_n^{\text{exp}} \) were determined by gel permeation chromatography using polystyrene standards, and \( M_n^{\text{calc}} \) were calculated by the following equation: \( 114.14 \times [M]/[Ln] \) (\( Y \) 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.

ACKNOWLEDGMENTS

The XRD analyses for complexes I, III, and IV were carried out in the framework of state assignment using the equipment of the Center for Collective Use “Analytical Center of the Institute of Organometallic Chemistry of the Russian Academy of Sciences” at the Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences and supported by the federal target program “Investigation and Developments on Priority Trends of Scientific Technological Complex of Russia for 2014–2020” (project no. RFMEFI62120X0040).

FUNDING

This work was supported by the Russian Science Foundation, project no. 17-73-20262.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

OPEN ACCESS

This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

REFERENCES

1. Ward, B.D., Dubberley, S.R., Maisse-Francois, A., et al., Dalton Trans., 2002, p. 4649.
2. Skinner, M.E.G. and Mountford, P., Dalton Trans., 2002, p. 1694.
3. Hultzsch, K.C., Hampel, F., and Wagner, T., Organometallics, 2004, vol. 23, p. 2601.
4. Zeimentz, P.M., Arndt, S., Elvidge, B.R., and Okuda, J., Chem. Rev., 2006, vol. 106, p. 2404.
5. Skvortsov, G.G., Shavyrin, A.S., Kovylna, T.A., et al., Eur. J. Inorg. Chem., 2019, p. 5008.
6. Trifonov, A.A., Russ. Chem. Rev., 2007, vol. 76, p. 1122.