

Supporting Information

Cationic Group 3 Alkyl Complexes with Isopropyl-substituted Triazacyclononane-amide Ligands: Synthesis, Structure and Thermal Decomposition Processes

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Synthesis of [(iPr)₂TACN-(CH₂)₂NtBu]Y(CH₂SiMe₃)₂ (1).

At ambient temperature, a solution of HL1 (0.32 g, 1.00 mmol) in toluene (2 ml) was added dropwise to a solution of [(Me₃SiCH₂)₃Y(THF)₂] (0.49 g, 1.00 mmol) in toluene (5 ml). The reaction mixture was stirred for 2 hours, after which the volatiles were removed under reduced pressure. The residue was washed with cold pentane (-20 °C, 5 ml) and subsequently dried in vacuum yielding the title compound (0.45 g, 0.78 mmol, 78 %) that provides matching NMR spectra of the previously reported procedure.¹

¹H NMR (300 MHz, 25°C, THF-d₈) δ: 3.81 (sept, *J*_{HH} = 6.6 Hz, 1 H, *i*Pr CH), 3.56 (overlapped, *i*Pr CH), 3.48 (dt, *J*_{HH} = 11.3, 4.4 Hz, 1 H, NCH₂), 3.37 (dt, *J*_{HH} = 12.2, 4.0 Hz, 1 H, NCH₂), 3.28-3.18 (m, 2H, NCH₂), 2.95-2.89 (m, 3H, NCH₂), 2.86 (dd, *J*_{HH} = 11.4, 4.7 Hz, 1 H, NCH₂), 2.78 (m, 2H, NCH₂), 2.68 (m, 2H, NCH₂), 2.61-2.56 (m, 2H, NCH₂), 2.47 (dd, *J*_{HH} = 12.0, 4.5 Hz, 1H, NCH₂), 2.08 (dd, *J*_{HH} = 10.9, 2.9 Hz, 1H, NCH₂), 1.46 (d, *J*_{HH} = 6.6 Hz, 3 H, *i*Pr Me), 1.42 (d, *J*_{HH} = 6.6 Hz, 3 H, *i*Pr Me), 1.23 (s, 9 H, *t*Bu), 1.01 (d, *J*_{HH} = 6.6 Hz, 3 H, *i*Pr Me), 0.97 (d, *J*_{HH} = 6.6 Hz, 3 H, *i*Pr Me), -0.09 (s, 9 H, Me₃SiCH₂), -0.11 (s, 9 H, Me₃SiCH₂), -0.64 (dd, *J*_{HH} = 10.3 Hz, *J*_{YH} = 3.0 Hz, 1 H, YCH₂), -0.96 (dd, *J*_{HH} = 10.5 Hz, *J*_{YH} = 2.2 Hz, 1 H, YCH₂), -1.19 (dd, *J*_{HH} = 10.8 Hz, *J*_{YH} = 3.0 Hz, 1 H, YCH₂), -1.27 (dd, *J*_{HH} = 10.8 Hz, *J*_{YH} = 2.1 Hz, 1 H, YCH₂). ¹³C NMR (125.7 MHz, 25°C, THF-d₈) δ: 59.3 (t, *J*_{CH} =

(1) Bambirra, S.; van Leusen, D.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.*, **2001**, 637.

128.1 Hz, NCH₂), 58.3 (t, $J_{\text{CH}} = 132.7$ Hz, NCH₂), 56.8 (d, $J_{\text{CH}} = 138.4$ Hz, *i*Pr CH), 56.4 (d, $J_{\text{CH}} = 140.7$ Hz, *i*Pr CH), 55.1 (s, *t*Bu C), 54.3 (t, $J_{\text{CH}} = 135.0$ Hz, NCH₂), 53.5 (t, $J_{\text{CH}} = 132.7$ Hz, NCH₂), 53.3 (t, $J_{\text{CH}} = 136.1$ Hz, NCH₂), 46.5 (t, $J_{\text{CH}} = 125.8$ Hz, NCH₂), 43.6 (t, $J_{\text{CH}} = 131.5$ Hz, NCH₂), 43.4 (t, $J_{\text{CH}} = 130.4$ Hz, NCH₂), 34.5 (dt, $J_{\text{YC}} = 37.7$ Hz, $J_{\text{CH}} = 97.1$ Hz, YCH₂), 32.4 (q, $J_{\text{CH}} = 123.5$, *t*Bu Me), 31.8 (t, $J_{\text{YC}} = 36.7$ Hz, $J_{\text{CH}} = 97.3$ Hz, YCH₂), 25.0 (q, $J_{\text{CH}} = 126.3$ Hz, *i*Pr Me), 24.7 (q, $J_{\text{CH}} = 126.3$ Hz, *i*Pr Me), 14.4 (q, $J_{\text{CH}} = 123.5$ Hz, *i*Pr Me), 14.1 (q, $J_{\text{CH}} = 125.7$ Hz, *i*Pr Me), 6.1 (q, $J_{\text{CH}} = 116.2$ Hz, *Me*₃SiCH₂Y), 5.9 (q, $J_{\text{CH}} = 116.2$ Hz, *Me*₃SiCH₂Y).

Synthesis of [(*i*Pr)₂TACN-SiMe₂N*t*Bu]Y(CH₂SiMe₃)₂ (2).

A ambient temperature, a solution of HL2 (0.34 g, 1.00 mmol) in pentane (10 ml) was added dropwise to a solution of Y(Me₃SiCH₂)₃(THF)₂ (0.49 g, 1.00 mmol) in pentane (30 ml). The reaction mixture was stirred for 3 hours (20 °C), after which the volatiles were removed in vacuum. The residue was stripped of remaining THF by stirring with 5 ml of pentane that was subsequently removed under reduced pressure. The resulting sticky solid was then extracted with pentane (20 ml). Cooling the extract to -30 °C produces analytically pure crystalline product in modest yield (0.21 g, 0.34 mmol, 34 %) due to its high solubility. A higher yield (75%) of material, pure by NMR spectroscopy, can be obtained by simple evaporation of the solvent from the reaction mixture, followed by rinsing of the solid with cold pentane (-20 °C, 5 ml) and drying in vacuum.

¹H NMR (300 MHz, -30°C C₆D₅Br) δ: 3.89 (sept br, 1H, *i*Pr CH), 3.55 (sept br, 1H, *i*Pr CH), 3.01 (m, 1H, NCH₂), 2.71 (m, 2 H, NCH₂), 2.49 (m, 1H, NCH₂), 1.86 (m, 2H, NCH₂), 1.73 (m, 2H, NCH₂), 1.56 (s, 9 H, *Nt*Bu Me), 1.43 (m, 2H, NCH₂), 0.97-0.83 (br, 12 H, *i*Pr Me), 0.42 (s, 18 H, Me₃SiCH₂), 0.28 (s, 6 H, Me₂Si), -0.32 (br, 1H, YCH₂), -0.55 (br, 1H, YCH₂), -0.75 (br, 1H, YCH₂), -0.86 (br, 1H, YCH₂).

¹H NMR (300 MHz, 25°C C₆D₆) δ: 2.82 (sept br, 2H, *i*Pr CH), 2.76 (m, 2 H, NCH₂), 2.25 (m, 2 H, NCH₂), 1.86 (m, 2H, NCH₂), 1.73 (m, 2H, NCH₂), 1.56 (s, 9 H, *Nt*Bu), 1.43 (m, 2H, NCH₂), 0.97-0.83 (br, 12 H, *i*Pr Me), 0.42 (s, 18 H, Me₃SiCH₂), 0.28 (s, 6 H, Me₂Si), -0.40 (br, 2 H, YCH₂), -0.56 (dd br, 2 H, YCH₂).

¹³C NMR (75.4 MHz, 25°C, C₆D₆) δ: 55.0 (d, $J_{\text{CH}} = 136.7$, *i*Pr CH), 54.2 (t, $J_{\text{CH}} = 135.7$ Hz, NCH₂), 54.1 (t br, $J_{\text{CH}} = 145.2$ Hz, NCH₂), 53.1 (t br, NCH₂), 52.2 (*Nt*Bu C), 50.8 (t br, $J_{\text{CH}} = 130.5$ Hz, NCH₂), 36.5 (q, $J_{\text{CH}} = 123.2$, *Nt*Bu Me), 33.6 (dt, $J_{\text{CH}} =$

96.3 Hz, $J_{YH} = 37.8$ Hz, YCH_2), 18.5 (q, $J_{CH} = 125.6$ Hz, $NCHMe_2$), 5.0 (q, $J_{CH} = 115.8$ Hz, Me_3SiCH_2), 3.5 (q, $J_{CH} = 117.1$ Hz, Me_2Si).

1H NMR (500 MHz, -50 °C, THF- d_8) δ : 4.01 (sept, $J_{HH} = 6.6$ Hz, 1H, *i*Pr CH), 3.69 (sept, $J_{HH} = 6.6$ Hz, 1H, *i*Pr CH), 3.31 (m, 1 H, NCH_2), 3.10 (m, 1 H, NCH_2), 3.02 (m, 1 H, NCH_2), 2.93 (m, 2H, NCH_2), 2.84 (m, 2H, NCH_2), 2.73 (m, 3 H, NCH_2), 2.60 (m, 2 H, NCH_2), 1.47 (d, $J_{HH} = 6.6$ Hz, 3 H, *i*Pr Me), 1.36 (d, $J_{HH} = 6.6$ Hz, 3 H, *i*Pr Me), 1.32 (s, 9 H, *Nt*Bu), 1.05 (d, $J_{HH} = 6.6$ Hz, 3 H, *i*Pr Me), 1.01 (d, $J_{HH} = 6.6$ Hz, 3 H, *i*Pr Me), 0.33 (s, 3 H, Me_2Si), 0.16 (s, 3 H, Me_2Si), 0.03 (s, 9 H, Me_3SiCH_2), -0.06 (s, 9 H, Me_3SiCH_2), -0.59 (dd, $J_{HH} = 10.5$ Hz, $J_{YH} = 2.7$ Hz, 1 H, YCH_2), -0.79 (dd, $J_{HH} = 10.5$ Hz, $J_{YH} = 2.0$ Hz, 1 H, YCH_2), -1.03 (dd, $J_{HH} = 10.5$ Hz, $J_{YH} = 2.1$ Hz, 1 H, YCH_2), -0.12 (dd, $J_{HH} = 10.4$ Hz, $J_{YH} = 2.2$ Hz, 1 H, YCH_2).

^{13}C NMR (125.7 MHz, -50 °C, THF- d_8) δ : 58.1 (t, $J_{CH} = 136.1$ Hz, NCH_2), 57.1 (d, $J_{CH} = 133.7$, *i*Pr CH), 57.0 (t, $J_{CH} = 138.2$ Hz, NCH_2), 56.6 (t, $J_{CH} = 138.8$ Hz, NCH_2), 56.1 (t, $J_{CH} = 136.0$ Hz, NCH_2), 53.5 (*Nt*Bu C), 44.9 (t, $J_{CH} = 137.9$ Hz, NCH_2), 43.8 (t, $J_{CH} = 135.8$ Hz, NCH_2), 37.7 (q, $J_{CH} = 125.0$, *Nt*Bu Me), 33.1 (dt, $J_{CH} = 95.4$ Hz, $J_{YH} = 34.8$ Hz, YCH_2), 32.8 (dt, $J_{CH} = 94.8$ Hz, $J_{YH} = 35.5$ Hz, YCH_2), 25.7 (q, $J_{CH} = 126.0$ Hz, *i*Pr Me), 24.6 (q, $J_{CH} = 126.0$ Hz, *i*Pr Me), 14.0 (q, $J_{CH} = 125.1$ Hz, *i*Pr Me), 13.8 (q, $J_{CH} = 125.5$ Hz, *i*Pr Me), 6.0 (q, $J_{CH} = 116.7$ Hz, Me_3SiCH_2), 5.5 (q, $J_{CH} = 117.1$ Hz, Me_2Si), 3.9 (q, $J_{CH} = 117.1$ Hz, Me_2Si).

Anal. Calcd for $C_{26}H_{61}N_4Si_3Y$: C, 51.79; H, 10.20; N, 9.29; Y, 14.74. Found: C, 49.21; H, 10.15; N, 8.78; Y, 14.22.

Synthesis of [(*i*Pr) $_2$ TACN-SiMe $_2$ *Nt*Bu]La(CH $_2$ SiMe $_3$) $_2$ (4).

Solid $LaBr_3(THF)_4$ (0.66 g, 1.00 mmol) and $LiCH_2SiMe_3$ (0.28 g, 3.00 mmol) were dissolved in THF (30 mL). The solution was stirred for 30 minutes (RT) after which **L2H** (0.34 g, 1.00 mmol, dissolved in 5 mL THF) was added. The yellowish reaction mixture was stirred for 1 hour, after which the volatiles were removed under reduced pressure. The residue was stripped of remaining THF by stirring twice with 5 ml of pentane (0°C) that was subsequently removed under reduced pressure. The solid was extracted with a hexane/toluene mixture (25 mL each, 0 °C). The filtrate was dried in vacuum affording 0.40 g of the crude product. This material was recrystallized from hexane/toluene (10:1, 5 mL, -30 °C) yielding colorless crystals of the title compound (0.29 g, 44 %).

^1H NMR (500 MHz, 20°C THF- d_8) δ : 3.85 (sept br, 2 H, *i*Pr CH), 3.17 (m, 2 H, NCH₂), 3.00 (m, 2 H, NCH₂), 2.85-2.64 (m, 8 H, NCH₂), 1.35 (s, 9 H, *t*Bu), 1.24 (br, 6 H, *i*Pr Me), 1.17 (br, 6 H, *i*Pr Me), 0.18 (s, 6 H, Me₂Si), -0.10 (s, 18 H, Me₃SiCH₂), -0.82 (s br, 2 H, LaCH₂), -0.87 (s br, 2 H, LaCH₂). ^1H NMR (500 MHz, -60°C THF- d_8) δ : 4.03 (sept, $J_{\text{HH}} = 6.0$ Hz, 1 H, *i*Pr CH), 3.59 (sept, $J_{\text{HH}} = 6.1$ Hz, 1 H, *i*Pr CH), 3.21 (m, 1 H, NCH₂), 3.06-2.90 (m, 4 H, NCH₂), 2.78-2.70 (m, 4 H, NCH₂), 2.62-2.50 (m, 3 H, NCH₂), 1.46 (d, $J_{\text{HH}} = 6.0$ Hz, 3 H, *i*Pr Me), 1.33 (s, 9 H, *t*Bu), 1.28 (d, $J_{\text{HH}} = 6.0$ Hz, 3 H, *i*Pr Me), 1.03 (d, $J_{\text{HH}} = 6.1$ Hz, 3 H, *i*Pr Me), 0.97 (d, $J_{\text{HH}} = 6.1$ Hz, 3 H, *i*Pr Me), 0.28 (s, 3 H, Me₂Si), 0.08 (s, 3 H, Me₂Si), -0.10 (s, 9 H, Me₃SiCH₂), -0.13 (s, 9 H, Me₃SiCH₂), -0.67 (d, $J_{\text{HH}} = 10.5$ Hz, 1 H, LaCH₂), -0.77 (d, $J_{\text{HH}} = 10.5$ Hz, 1 H, LaCH₂), -1.04 (d, $J_{\text{HH}} = 10.5$ Hz, 1 H, LaCH₂), -1.12 (d, $J_{\text{HH}} = 10.5$ Hz, 1 H, LaCH₂). ^{13}C NMR (125.7 MHz, -60°C THF- d_8): δ 58.2 (t, $J_{\text{CH}} = 133.0$ Hz, NCH₂), 57.0 (t, $J_{\text{CH}} = 134.2$ Hz, NCH₂), 55.8 (d, $J_{\text{CH}} = 136.4$ Hz, *i*Pr CH), 55.6 (d, $J_{\text{CH}} = 136.4$ Hz, *i*Pr CH), 55.5 (t, $J_{\text{CH}} = 133.6$ Hz, NCH₂), 52.4 (s, *t*Bu C), 50.3 (t, $J_{\text{CH}} = 97.6$ Hz, LaCH₂), 48.0 (t, $J_{\text{CH}} = 100.8$ Hz, LaCH₂), 44.9 (t, $J_{\text{CH}} = 131.0$ Hz, NCH₂), 43.5 (t, $J_{\text{CH}} = 131.5$ Hz, NCH₂), 43.1 (t, $J_{\text{CH}} = 134.2$ Hz, NCH₂), 36.5 (q, $J_{\text{CH}} = 123.3$, *t*Bu Me), 24.1 (q, $J_{\text{CH}} = 125.2$ Hz, *i*Pr Me), 23.2 (q, $J_{\text{CH}} = 124.5$ Hz, *i*Pr Me), 17.4 (q, $J_{\text{CH}} = 124.0$ Hz, *i*Pr Me), 14.0 (q, $J_{\text{CH}} = 124.0$ Hz, *i*Pr Me), 6.1 (q, $J_{\text{CH}} = 118.2$ Hz, Me₃SiCH₂La), 5.4 (q, $J_{\text{CH}} = 117.5$ Hz, Me₂Si), 5.5 (q, $J_{\text{CH}} = 117.5$ Hz, Me₂Si). The compound is thermally too unstable to be sent out for elemental analysis.

Synthesis of [(*i*Pr)₂TACN-SiMe₂N*t*Bu}Y(CH₂SiMe₃)(THF)][BPh₄](THF) (6).

THF (0.5 mL) was added to a mixture of 100 mg (165 μmol) of [(*i*-Pr)₂-TACN-SiMe₂NBu¹]Y(CH₂SiMe₃)₂ and 73 mg (165 μmol) of [HNMe₂Ph][BPh₄]. The resulting yellowish solution was layered with 2 mL hexanes. Upon standing overnight at ambient temperature, colorless crystals formed. The mother liquor was decanted and the crystals were washed with hexanes. Drying in vacuum yielded 126 mg of the title compound (128 μmol , 78 %).

^1H NMR (300 MHz, 22°C , THF- d_8) δ : 7.25 (d, $^3J = 7.3$ Hz, 8 H, o-H BPh₄), 6.84 (t, $^3J = 7.3$ Hz, 8 H, m-H BPh₄), 6.58 (t, $^3J = 7.3$ Hz, 4 H, p-H BPh₄), 3.22 (br, 2 H, *i*Pr CH), 2.80 (m, 4 H, NCH₂), 2.62-2.47 (m, 8 H, NCH₂), 1.20 (s, 9 H, N*t*Bu), 1.13 (br, 12 H, *i*Pr Me), 0.20 (s, 6H SiMe₂), -0.12 (s, SiMe₄), -0.89 (d, $J_{\text{YH}} = 3.0$ Hz, 2 H, YCH₂). ^1H NMR (500 MHz, -50°C , THF- d_8) δ : 7.23 (br, 8 H, o-H BPh₄), 6.86 (t, $^3J =$

7.0 Hz, 8 H, m-H BPh₄), 6.73 (t, ³J = 7.0 Hz, 4 H, p-H BPh₄), 3.00 (br, 1H, *i*Pr CH), 2.88 (sept, J_{HH} = 6.5 Hz, 1H, *i*Pr CH), 2.73-1.57 (m, 8 H, NCH₂), 2.42 (m, 3 H, NCH₂), 2.23 (m, 1 H, NCH₂), 1.39 (br, 6 H, *i*Pr Me), 1.62 (s, 9 H, *Nt*Bu), 1.01 (d, J_{HH} = 6.5 Hz, 3 H, *i*Pr Me), 0.98 (d, J_{HH} = 6.5 Hz, 3 H, *i*Pr Me), 0.28 (s, 6 H, Me₂Si), -0.04 (s, 9 H, Me₃SiCH₂), -0.06 (s, 9 H, Me₃SiCH₂), -0.86 (d, J_{YH} = 2.9 Hz, 2 H, YCH₂).

¹³C NMR (125.7 MHz, -50 °C, THF-d₈) δ: 165.7 (q, 48.8 Hz, ipso-BPh₄), 137.9 (d, J = 154.0 Hz, o-BPh₄), 126.7 (d, J = 150.5 Hz, m-BPh₄), 123.0 (d, J = 154.1 Hz, p-BPh₄), 57.6 (d, J_{CH} = 135.1, *i*Pr CH), 57.4 (t, J_{CH} = 141.1 Hz, NCH₂), 56.9 (d, J_{CH} = 134.2, *i*Pr CH), 56.2 (t, J_{CH} = 133.0 Hz, NCH₂), 56.3 (*Nt*Bu C), 45.0 (t, J_{CH} = 140.3 Hz, NCH₂), 44.3 (t, J_{CH} = 135.4 Hz, NCH₂), 42.9 (t, J_{CH} = 137.8 Hz, NCH₂), 37.2 (q, J_{CH} = 122.5, *Nt*Bu Me), 37.3 (dt, J_{CH} = 94.1 Hz, J_{YH} = 41.0 Hz, YCH₂), 24.9 (q, J_{CH} = 124.7 Hz, *i*Pr Me), 24.3 (q, J_{CH} = 127.0 Hz, *i*Pr Me), 14.7 (q, J_{CH} = 124.8 Hz, *i*Pr Me), 14.0 (q, J_{CH} = 126.5 Hz, *i*Pr Me), 5.6 (q, J_{CH} = 117.3 Hz, Me₃SiCH₂), 4.5 (q, J_{CH} = 118.1 Hz, Me₂Si), 4.3 (q, J_{CH} = 117.9 Hz, Me₂Si).

Anal. for [C₂₆H₆₀N₄OSi₂Y].[C₂₄H₂₀B].(C₄H₈O) (981.21) calcd: C, 66.10; H, 9.04; N, 5.71. Found: C, 65.42; H, 9.35; N, 5.06.

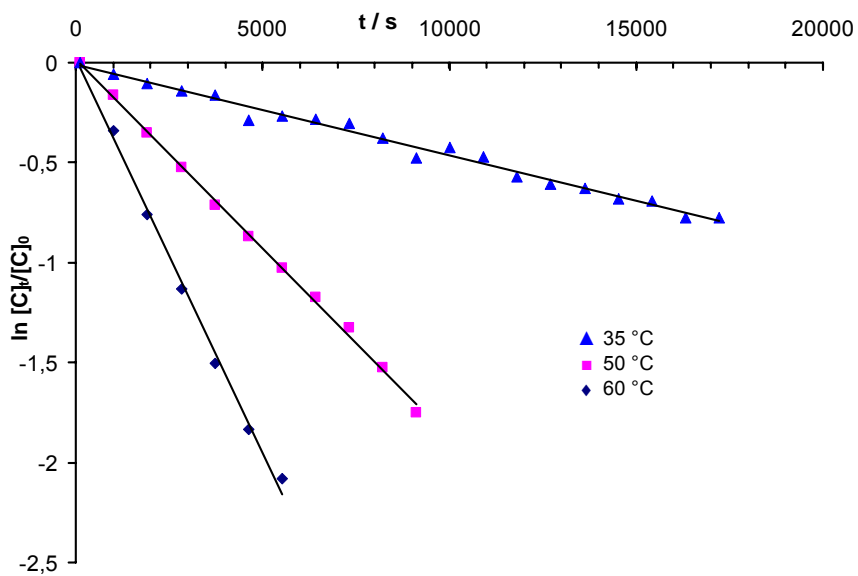


Figure 1. Thermal decomposition of $[(iPr)_2TACN-SiMe_2NtBu]La(CH_2SiMe_3)_2$ (**4**) at different temperatures in THF- d_8 .

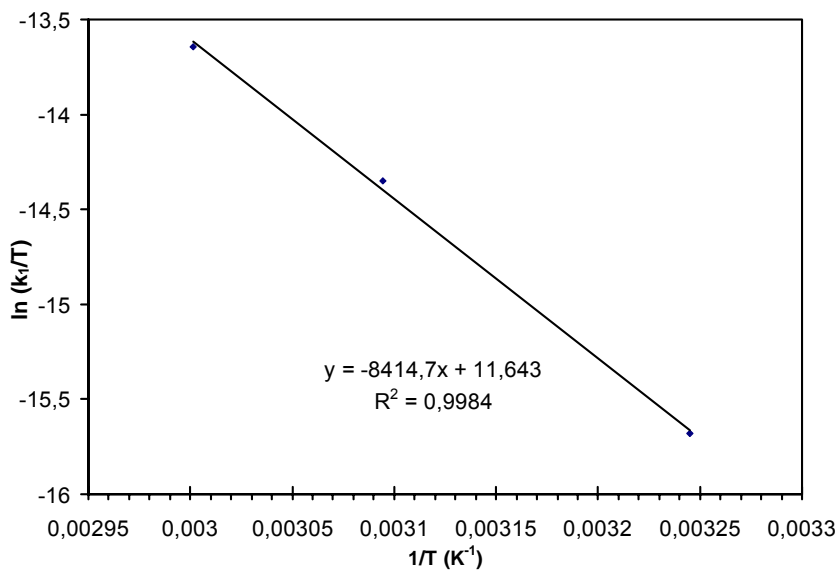


Figure 2. Eyring plot for the thermal decomposition of **4** THF- d_8 .

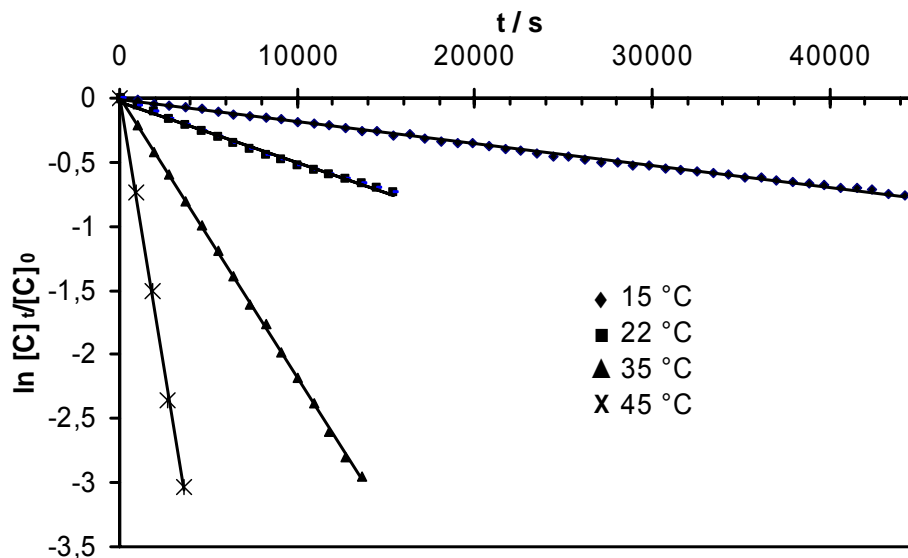


Figure 3. 1st order plot for the thermal decomposition of $\{[(iPr)_2TACN-SiMe_2NtBu]La(CH_2SiMe_3)(THF-d_8)\}^+$ (**8**) at different temperatures to produce $\{[iPrTACN-SiMe_2NtBu]La(THF)\}_2^{2+}$ (**9**) in THF- d_8 .

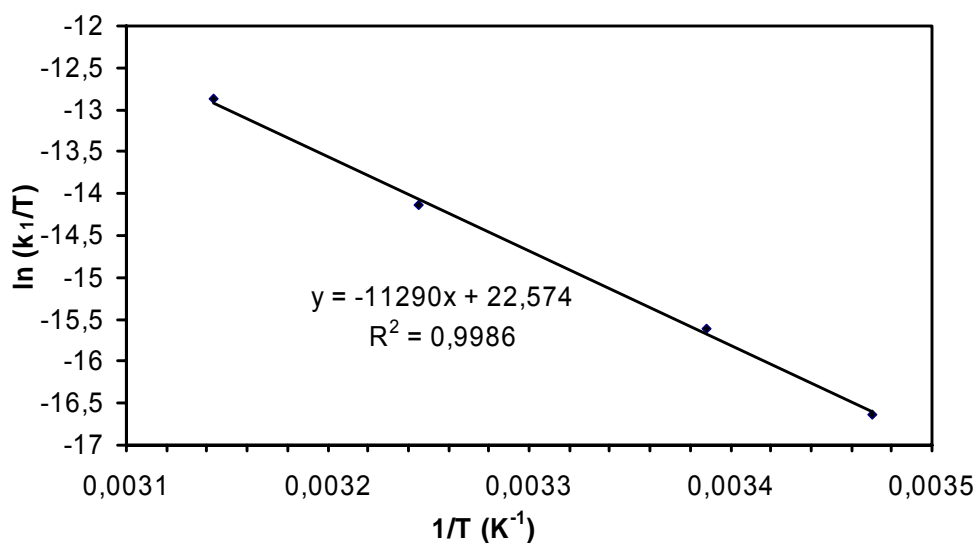


Figure 4. Eyring plot for the decomposition of **8** to produce **9** in THF- d_8 .