# Experimental

## Synthesis and characterization

General: All manipulations and reactions were performed under a purified nitrogen atmosphere using standard Schlenk techniques on a dual manifold Schlenk line. Diethyl ether were distilled from sodium-benzophenone under nitrogen. Dichloromethane was distilled from $CaH_2$ under nitrogen. The ligand transfer reagent compound **1** was prepared according to the reported methods.[1] $^1H$ and $^{13}C$ NMR spectra were recorded with a Bruker DRX-300 spectrometer. Elemental analyses were performed with a Vario EL-III instrument. Melting points were taken with a Sanyo Gallenkamp Variable Heater.

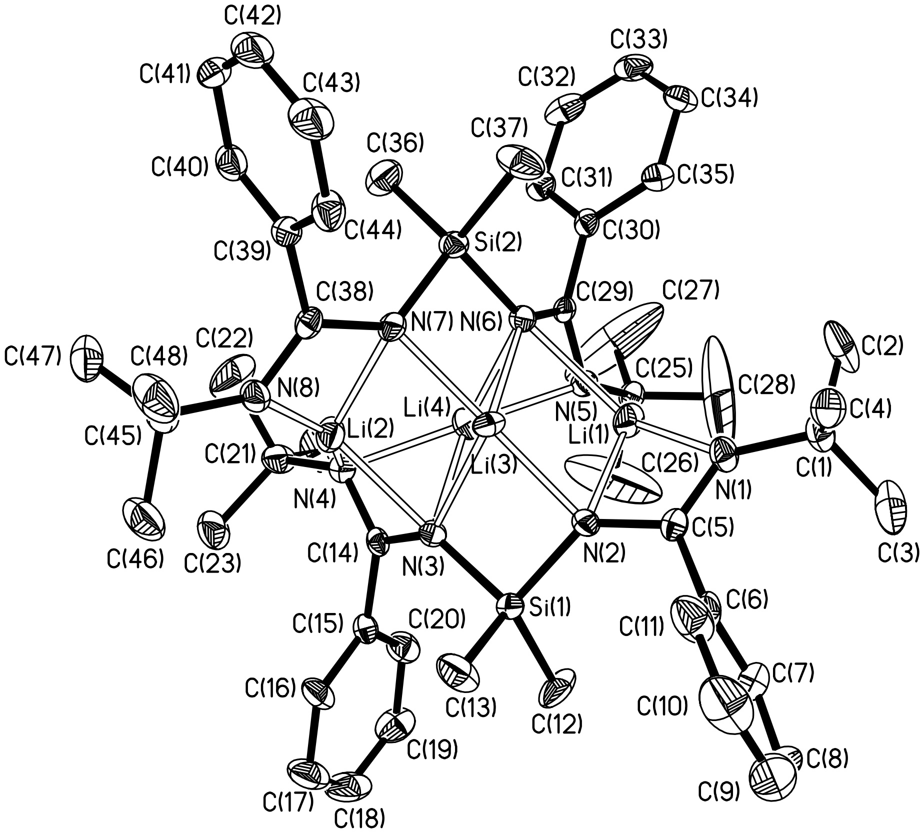
Preparation of **1**: A solution of diamine $SiMe_2[NH(^tBu)]_2$ (2.29 g, 11.34 mmol) in THF (60 $cm^3$) at 0 °C was treated with $LiBu^n$ in hexane (2.8 mol $dm^{-3}$, 8.1 $cm^3$, 22.68 mmol). The reaction mixture was stirred at room temperature for five hours and then PhCN (2.31 $cm^3$, 22.68 mmol) was added at 0 °C. After stirring at room temperature for five hours, the reaction solution was dried in vacuum. Compound **1** was recrystallized in hexane as colorless crystals. Yield: 1.95 g (41 %), mp 177-179 °C. $^1H$ NMR (300 MHz, $C_6D_6$): δ 7.29 (d, $J_{HH}$ = 1.8 Hz, 8H; 2,6-H of phenyls), 7.11 (m, 12H; 3,4,5-H of phenyls), 1.34 (s, 36H; C*Me<sub></sub>*$_3$), -0.13 (s, 12H; Si$Me_2$); $^{13}C$ NMR (75 MHz, $C_6D_6$): δ 175.4 (N-*C*-N), 143.1, 127.3, 127.0 (phenyls), 51.2 (*C*$Me_3$), 33.5 (C$Me_3$), 3.2 (Si$Me_2$); $^7Li$ NMR (117 MHz, $C_6D_6$): δ 2.27, 2.02, 1.85. Anal. Calc. for $C_{48}H_{68}Li_4N_8Si_2$: C, 68.55; H, 8.15; N, 13.32%. Found: C, 68.57; H, 8.18; N, 13.26%.

Preparation of **2**: A solution of $Li_4\{SiMe_2[NC(Ph)N(^tBu)]_2\}_2$ (1.10 g, 1.32 mmol) in $Et_2O$ (20 $cm^3$) was cooled to -78 °C, after which $TiCl_4(thf)_2$ (0.88 g, 2.64 mmol) was added. The mixture was allowed to warm to room temperature. After stirring for 12 hours, the volatiles were removed in vacuum. The residue was extracted with $CH_2Cl_2$ (20 $cm^3$) and filtered. The filtrate was concetrated to give compound **2** as red crystals. Yield: 1.11 g (80%), mp 194-195 °C. $^1H$ NMR (300 MHz, $CD_6Cl_3$): δ 7.83 – 7.14 (m, 10H; phenyls), 1.71 – 0.92 (m, 18H; $^t$Bu), 0.41 – -0.27 (m, 6H; Si$Me_2$); $^{13}C$ NMR (75 MHz, $CD_6Cl_3$): δ 173.5, 161.5 (N-*C*-N), 139.2 – 128.8 (phenyls), 59.5, 58.1 (*C*$Me_3$), 34.4, 33.7, 32.1, 28.3 (C$Me_3$), 8.3, 4.0 (Si$Me_2$). Anal. Calc. for $C_{24}H_{34}Cl_2N_4SiTi$: C, 54.86; H, 6.52; N, 10.66%. Found: C, 54.41; H, 6.57; N, 10.24%.

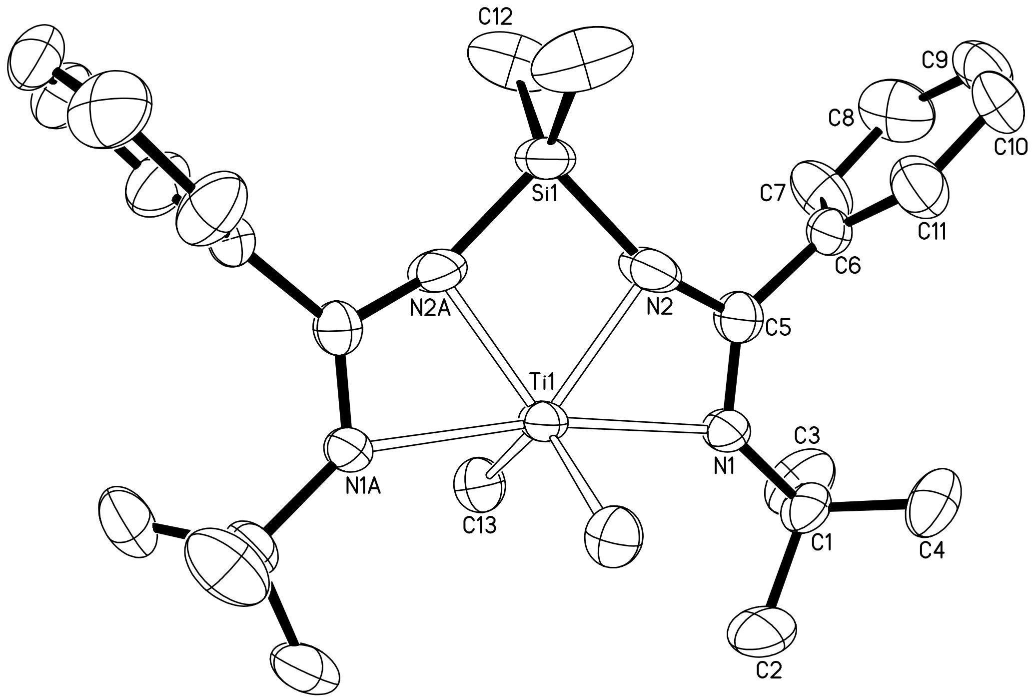
Preparation of **3**: The solution of methyllithium in $Et_2O$ (1.6 mol $dm^{-3}$, 1.98 $cm^3$, 3.16 mmol) was added into the slurry of **2** (0.83 g, 1.58 mmol) in $Et_2O$ (ca 20 $cm^3$) by syringe at -78 °C. The mixture was allowed to warm to room temperature. After stirring for 12 hours, the volatiles were removed in vacuum. The residue was extracted with $CH_2Cl_2$ (20 $cm^3$) and filtered. The filtrate was concetrated to give compound **3** as yellow crystals. Yield: 0.38 g (50%). $^1H$ NMR (300 MHz, $CD_6Cl_3$): δ 7.38 (p, 10H; phenyls), 1.44, 1.41 (d, 18H; $^t$Bu), 1.08 (s, 6H; Ti$Me_2$), -0.21 (s, 6H; Si$Me_2$); $^{13}C$ NMR (75 MHz, $CD_6Cl_3$): δ 171.4 (N-*C*-N), 142.0 (*ipso-C* of phenyl), 131.0 – 129.0 (phenyls), 66.8 (Ti$Me_2$), 58.0 (*C*$Me_3$), 35.2, 34.8 (C$Me_3$), 4.5 (Si$Me_2$). Anal. Calc. for $C_{26}H_{40}N_4SiTi$: C, 64.44; H, 8.32; N, 11.56%. Found: C, 64.21; H, 8.19; N, 11.38%.

**X-ray data collection and crystal structure determination**

The single crystals of **2** and **3** suitable for X-ray diffraction studies were obtained. X-Ray diffraction data were collected with graphite-monochromated Mo-Kα radiation ($\lambda$ = 0.71073 Å) on a Bruker Smart Apex CCD diffractometer. The collected frames were processed with the proprietary software SAINT and an absorption correction was applied (SADABS) to the collected reflections.[2,3] The structures of these molecules were solved by direct methods and expanded by standard difference Fourier syntheses using the software SHELXTL.[4] Structure refinements were made on $F^2$ using the full-matrix least-squares technique. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in their idealized positions and allowed to ride on the respective parent atoms.



Molecular structure of compound **1**. Thermal ellipsoids are set at 30% probability and hydrogen atoms are omitted for clarity.



Molecular structure of compound **3**. Thermal ellipsoids are set at 30% probability and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ti1-N1 = 2.266(4), Ti1-N2 = 2.027(5), Ti1-C13 = 2.124(6), N1-C5 = 1.296(8), N2-C5 = 1.344(7), N2-Si1 = 1.685(5); N1-Ti1-N2 = 60.97(17), N1-Ti1-N1A = 169.6(3), N2-Ti1-N2A = 70.7(3), C13-Ti1-C13A = 125.7(4), N1-C5-N2 = 112.0(5), N2-Si1-N2A = 88.2(4).

**Ethylene polymerization**

General: The polymerizations were performed in a 250 mL autoclave. Compound **2** was dissolved in toluene and transferred into autoclave with a syringe. The solution of MAO in toluene was added with a syringe for activation. While stirring, the ethylene gas was filled into the reactor. After stirring for a definite period of time, the reaction was quenched with 5% HCl/EtOH. The polymer was filtered, washed with ethanol and dried under vacuum.

**Table 1**. Ethylene polymerization by the **2**/MAO system[a]

| Entry | Al/Ti | $T$ [°C] | $P$ [atm] | Productivity[b] | $T_m$[c] | $M_w$[d] | $M_w/M_n$[d] |
|---|---|---|---|---|---|---|---|
| 1 | 2000 | 30 | 1 | no | | | |
| 2 | 2000 | 50 | 1 | no | | | |
| 3 | 5000 | 30 | 1 | no | | | |
| 4 | 5000 | 50 | 1 | trace | | | |
| 5 | 5000 | 50 | 10 | 46 | 132.6 | | |
| 6 | 15000 | 100 | 10 | 1020 | 133.1 | 3.68 | 14 |

[a] Reaction conditions: 5 μmol catalyst, time = 30 min, toluene solvent (100 mL). [b] In units of kg(PE) mol$^{-1}$(Ti) h$^{-1}$. [c] Determined by DSC. [d] In units of $10^5$ g mol$^{-1}$; determined by GPC.

**Table 2**. Ethylene polymerization by the **3**/MAO system[a]

| Entry | Al/Ti | $T$ [°C] | $P$ [atm] | Productivity[b] | $T_m$[c] | $M_w$[d] | $M_w/M_n$[d] |
|---|---|---|---|---|---|---|---|
| 1 | 2000 | 30 | 1 | no | | | |
| 2 | 2000 | 50 | 1 | trace | | | |
| 3 | 5000 | 30 | 1 | no | | | |
| 4 | 5000 | 50 | 1 | trace | | | |
| 5 | 5000 | 50 | 10 | 93 | 133.4 | | |
| 6 | 15000 | 80 | 10 | 1614 | 133.9 | 1.07 | 3.6 |

[a] Reaction conditions: 5 μmol catalyst, time = 30 min, toluene solvent (100 mL). [b] In units of kg(PE) $mol^{-1}$(Ti) $h^{-1}$. [c] Determined by DSC. [d] In units of $10^5$ g $mol^{-1}$; determined by GPC.

**Table 3**. Supplementary polymerization data of **2**/MAO system in 10 atm

| Entry | Al/Ti | t(min) | T(℃) | Productivity(kg(PE) $mol^{-1}$(Ti) $h^{-1}$) | $T_m$(°C) |
|---|---|---|---|---|---|
| 1 | 5000 | 30 | 50 | 46 | 132.6 |
| 2 | 10000 | 30 | 50 | 50 | 132.7 |
| 3 | 15000 | 30 | 50 | 120 | 133.0 |
| 5 | 20000 | 30 | 50 | 98 | 132.5 |
| 6 | 15000 | 30 | 80 | 810 | 132.8 |
| 7 | 15000 | 30 | 100 | 1020 | 133.1 |
| 8 | 15000 | 60 | 100 | 630 | 134.1 |

Entries 1 and 7 are cited from **table 1**. Entry 7 gives the best result of **2**/MAO system. By comparing entry 7 and entry 8, it shows reaction time of 30 minutes is better than 60 minutes.

**Table 4**. Supplementary polymerization data of **3**/MAO system in 10 atm

| Entry | Al/Ti | t(min) | T(℃) | Productivity(kg(PE) $mol^{-1}$(Ti) $h^{-1}$) | $T_m$(°C) |
|---|---|---|---|---|---|
| 1 | 5000 | 30 | 50 | 93 | 133.4 |
| 2 | 10000 | 30 | 50 | 100 | 133.2 |
| 3 | 15000 | 30 | 50 | 650 | 133.5 |
| 5 | 20000 | 30 | 50 | 390 | 132.9 |
| 6 | 15000 | 30 | 80 | 1614 | 133.9 |
| 7 | 15000 | 30 | 100 | 1200 | 133.1 |
| 8 | 15000 | 60 | 80 | 870 | 134.0 |

Entries 1 and 6 are cited from **table 2**. Entry 6 gives the best result of **3**/MAO system. By comparing entry 6 and entry 8, it shows reaction time of 30 minutes is better than 60 minutes.

## References

1 S.-D. Bai, J.-P. Guo, D.-S. Liu, *Dalton Trans.* 2006, 2244.
2 SAINT, Reference manual, Siemens Energy and Automation, Madison, WI, 1994–1996.
3 G. M. Sheldrick, SADABS, Empirical Absorption Correction Program, University of Göttingen, Germany, 1997.

4 G. M. Sheldrick, SHELXTLTM, Reference manual, version 5.1, Siemens, Madison, WI, 1997.