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Chain lithium complexes supported with β-diketiminate ligands containing pyridyl on the carbon framework

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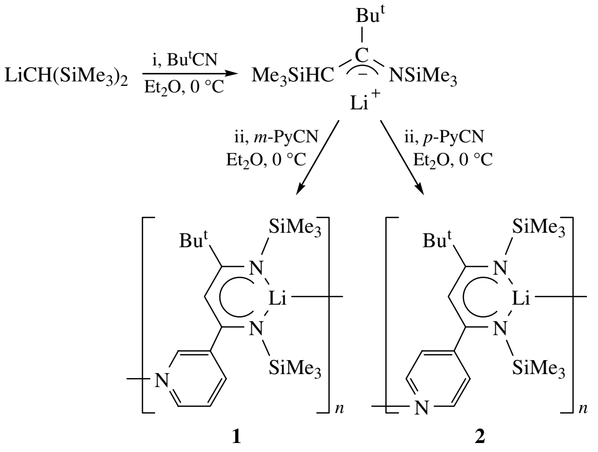
The treatment of $\mathrm{LiCH(SiMe_3)_2}$ with $\mathrm{Bu^tCN}$ followed by the addition of *m*- and *p*-cyanopyridines gave two *tert*-butyl- and pyridyl-substituted β-diketiminato lithium complexes $[\overline{\mathrm{Li(LL}}')_n]$ [$\mathrm{LL}' = \mathrm{N(SiMe_3)C(Bu^t)C(H)C(}$*m*-Py$\mathrm{)NSiMe_3}$ (1) and $\mathrm{LL}' = \mathrm{N(SiMe_3)C(Bu^t)C(H)C(}$*p*-Py$\mathrm{)NSiMe_3}$ (2)], and a one-dimensional polymeric chain could be observed in their crystal structures.

β-Iminoamine compounds[1] have been used as precursors for mono-anionic bidentate ligands,[2] but tremendous attention was paid to the unique ligand system till the past decade.[3] This class of ligands has a number of advantages, such as easy synthesis, variation of substituents and control of steric bulk, as well as strong donor properties. The synthesis, structures and reactions of alkali metal, in particular lithium, 1,3-bis(trimethylsilyl)-1-azaallyl and β-diketiminates have been reported.[4–6] In order to study the steric and electronic effect of the ligand on its metal complexes, bulkier β-diketiminate derivatives have been employed to prepare mononuclear and coordinatively unsaturated complexes.[7–9] However, the variation of substituents attached to the carbon framework of the ligand is rather limited.[10] Thus, the modification of the ligand skeleton can provide an opportunity to add variable functions to the metal complexes and to modulate their coordination chemistry. Here, we report two new β-diketiminate ligands, in which the carbon skeleton is attached to the pyridyl and *tert*-butyl groups: $[\overline{\mathrm{Li(LL}}')]_n$, $\mathrm{LL}' = \mathrm{N(SiMe_3)C(Bu^t)C(H)C(}$*m*-Py$\mathrm{)NSiMe_3}$ (**1**) and $\mathrm{LL}' = \mathrm{N(SiMe_3)C(Bu^t)C(H)C(}$*p*-Py$\mathrm{)NSiMe_3}$ (**2**). As ligand-transfer reagents, the substituted pyridyls provide a potential coordination site so that their crystal structures exhibit a one-dimensional network.



Scheme 1 Synthesis of complexes **1** and **2**.

Bis(trimethylsilyl)methyllithium (3.25 mmol) was treated with trimethylacetonitrile (3.25 mmol) in $\mathrm{Et_2O}$ at 273 K for 30 min. The resulting mixture was warmed to room temperature for 2 h, and *m*-cyanopyridine (3.09 mmol) was added at 273 K, and the mixture was stirred at room temperature for 8 h. The mixture was filtered; the filtrate was concentrated and then cooled to 243 K for two days. Yellow crystals (75%) of **1** were obtained. Similarly to the synthesis of **1** but using *p*-cyanopyridine, compound **2** was prepared as yellow crystals in 79% yield (Scheme 1).†

The probable reaction pathway is shown in Scheme 1. This involves the insertion of $\mathrm{Bu^tCN}$ into the Li–C bond of $\mathrm{Li{-}CH(SiMe_3)_2}$ to give 1,3-bis(trimethylsilyl)-1-azaallyl lithium. An alternative starting with step (ii) is the insertion of *m*- or *p*-PyCN into the Li–C bond of 1-azaallyllithium fragment. Steps (i) and (ii) involve an initial C–C coupling followed by 1,3-migration of the $\mathrm{SiMe_3}$ group from carbon to nitrogen.

Molecular structures of complexes **1** and **2** were determined by crystallographic analysis (Figures 1 and 2, respectively).‡ In contrast to monomeric lithium species with analogous β-diketiminato ligands, **1** and **2** are the first examples displaying a polymeric chain configuration. The unusual configuration was constructed by additional linkages between the nitrogen atom of pyridyl on the backbone to the lithium atom of another neighbouring monomeric unit. This fact underlines the potential of this β-diketiminato ligand offering control of the coordination environment of the metal to an extent that challenges substituted pyridyl. In complexes **1** and **2**, the N atoms in pyridyl groups provide intermolecular bonding to lithium, forming two polymers of tridental coordination environments; the distances of pyridyl N(3)–Li(1) [2.033(6) Å for **1** and 2.030(5) Å for **2**] are longer than that at terminal N–Li [1.924(5) Å for **1** and 1.913(5) Å for **2**].

Crystalline **1** and **2** have lithium in a distorted trigonal pyramidal environment. The lithium atom is coordinated by two

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† *Spectroscopic data for* **1**: ^{1}H NMR (300 MHz, 298 K, $\mathrm{C_6D_6}$) δ: 8.99 (s, 1H, *m*-pyridyl), 8.59 (d, 2H, *m*-pyridyl), 7.09 (s, 1H, *m*-pyridyl) 5.52 (s, 1H, CH), 1.16 (s, 9H, $\mathrm{CMe_3}$), 0.49 (s, 9H, $\mathrm{SiMe_3}$), 0.01 (s, 9H, $\mathrm{SiMe_3}$). ^{13}C NMR (75 MHz, 298 K, $\mathrm{C_6D_6}$) δ: 181.14 (1C of *m*-pyridine ring), 161.55 (1C of diketimine), 149.68 (1C of *m*-pyridine ring), 138.67 (1C of *m*-pyridine ring), 122.84 (1C of *m*-pyridine ring), 99.77 (2C of diketimine), 98.63 (1C of diketimine), 29.41 (3C of $\mathrm{Bu^t}$), 3.85 (3C of $\mathrm{SiMe_3}$), 1.71 (3C of $\mathrm{SiMe_3}$).

For **2**: ^{1}H NMR (300 MHz, 298 K, $\mathrm{C_6D_6}$) δ: 6.43–8.54 (s, 2H, *p*-pyridyl), 7.06 (d, 2H, *p*-pyridyl), 5.48 (s, 1H, CH), 1.49 (s, 9H, $\mathrm{CMe_3}$), 0.51 (s, 9H, $\mathrm{SiMe_3}$), 0.07 (s, 9H, $\mathrm{SiMe_3}$). ^{13}C NMR (75 MHz, 298 K, $\mathrm{C_6D_6}$) δ: 184.69 (1C of *p*-pyridine ring), 162.74 (1C of diketimine), 149.41 (1C of *p*-pyridine ring), 135.54 (1C of *p*-pyridine ring), 123.85 (1C of *p*-pyridine ring), 102.23 (2C of diketimine), 85.12 (1C of diketimine), 31.09 (3C of $\mathrm{Bu^t}$), 3.96 (3C of $\mathrm{SiMe_3}$), 3.41 (3C of $\mathrm{SiMe_3}$).

‡ *Crystal data for* **1**: $\mathrm{C_{18}H_{32}LiN_3Si_2}$, $M = 353.59$, monoclinic, space group $P2_1/n$, $a = 11.398(4)$, $b = 18.283(6)$ and $c = 11.659(4)$ Å, $\beta = 115.690(5)°$, $V = 2189.3(13)$ Å^3, $Z = 4$, $d_\mathrm{calc} = 1.073$ g cm^{-3}, $T = 190(2)$ K, $F(000) = 768$, MoKα radiation ($\lambda = 0.71073$ Å), $\theta_\mathrm{max} = 27.64°$, $\mu = 0.166$ mm^{-1}, 8928 reflections measured, 3845 independent ($R_\mathrm{int} = 0.0675$) and 1749 observed reflections [$I > 2\sigma(I)$], final $R_1 = 0.0545$.

For **2**: $\mathrm{C_{18}H_{32}LiN_3Si_2}$, $M = 353.59$, orthorhombic, space group *Pbca*, $a = 12.470(2)$, $b = 17.688(3)$ and $c = 20.330(4)$ Å, $V = 4484.4(14)$ Å^3, $Z = 8$, $d_\mathrm{calc} = 1.047$ g cm^{-3}, $T = 183(2)$ K, $F(000) = 1536$, MoKα radiation ($\lambda = 0.71073$ Å), $\theta_\mathrm{max} = 27.07°$, $\mu = 0.162$ mm^{-1}, 17508 reflections measured, 3954 independent ($R_\mathrm{int} = 0.0880$) and 1666 observed reflections [$I > 2\sigma(I)$], final $R_1 = 0.0459$.

The data collection was performed on a Bruker Smart CCD area detector diffractometer. Data reduction and absorption were performed with the SMART and SADABS software, respectively. The structure was solved by direct methods and refined by full matrix least-squares techniques on F^2 using SHELXL97.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 255789 and 255790. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2005.

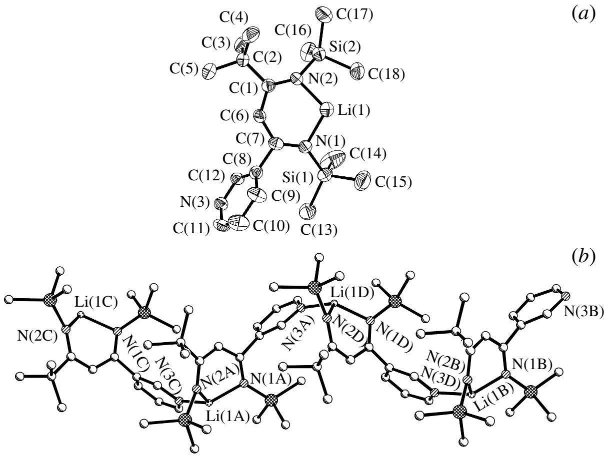

Figure 1 (*a*) The ORTEP drawing (at 50% probability) of complex **1**; (*b*) the one-dimensional chain of complex **1**.

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nitrogen atoms of the β-diketiminate ligand and one nitrogen atom of pyridyl from the neighbouring molecule. There are minor differences in the N(1)–Li(1) and N(2)–Li(1) bond lengths [N(1)–Li(1) is 1.924(5) Å for **1** and 1.913(6) Å for **2**, N(2)–Li(1) is 1.946(5) Å for **1** and 1.927(7) Å for **2**] in two β-diketiminato ligands. The distances between lithium and nitrogen of pyridyls are longer than the Li–N bonds of β-diketiminato in compounds **1** and **2**, respectively. The NCCCN fragment is substantially delocalised and slightly deviated from perfect planarity [mean deviation of 0.031 Å for **1** and 0.028 Å for **2**]. A typical and remarkably similar puckering six-membered LiNCCCN skeleton could be observed in **1** and **2**. The lithium atom is located out of plane and the corresponding distance of lithium to the NCCCN plane is 0.86 Å for **1** or 0.85 Å for **2**.

Comparatively in **1** and **2**, the neutral lithium units associate with back side nitrogen atoms of the pyridyl groups, which make for a less crowded environment to form two zigzag polymeric structures. In the crystal structures of **2**, it is possible to establish the presence of the intramolecular C–H···π interaction between the pyridyl ring and the *tert*-butyl group with the H-centroid distance of 2.85 Å, while in **1** it is absent, which leads to the steric overcrowding of this molecules. The distances of two adjacent central lithium atoms in polymers **1** and **2** are 7.64 and 8.69 Å, respectively, due to the effect of changing the substitution pattern on the pyridyl ring.

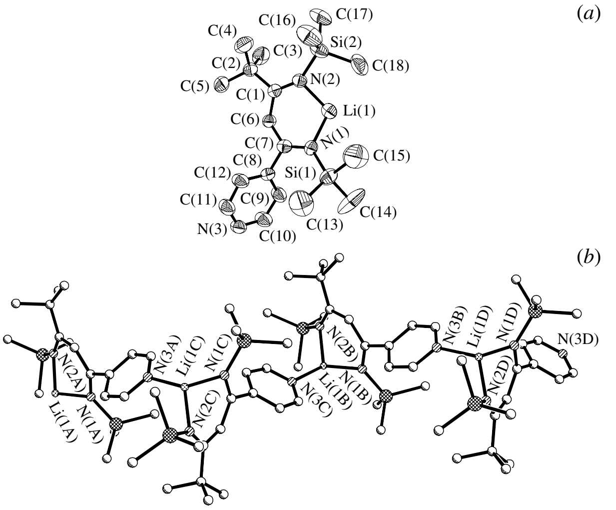

Figure 2 (*a*) The ORTEP drawing (at 50% probability) of complex **2**; (*b*) the one-dimensional chain of complex **2**.

In conclusion, two new β-diketiminate ligands containing a pyridyl group on the carbon framework were developed. Compounds **1** and **2** are new potentially versatile metathesis transfer agents for the synthesis of metal complexes.

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