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# Alkyl-ended *ansa*-bis(amidinate) ligands from aliphatic primary amines and multinuclear lithium derivatives

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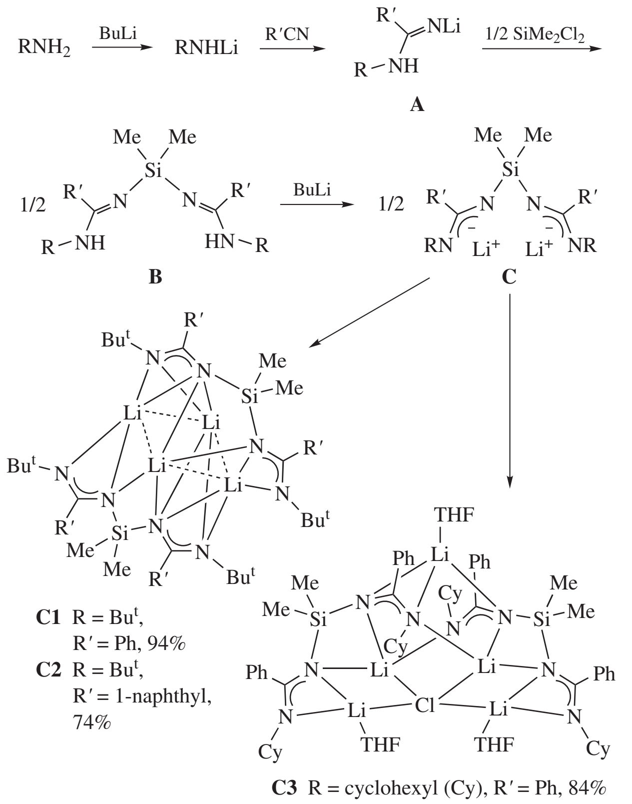
**A practical synthetic pathway to alkyl-ended *ansa*-bis(amidinate) ligands was developed *via* linking the freshly prepared aliphatic group substituted lithium amidinate and the subsequent deprotonation. The lithium complexes prepared by this method were characterized by NMR spectroscopy, elemental analysis and single-crystal X-ray diffraction analysis.**

Amidinate ligands demonstrate a wide range of substitution patterns and steric and electronic features by varying groups attached to the conjugated N–C–N backbone.[1–3] Since Cp[PhC(NTMS)$_2$]ZrCl$_2$ was found active toward ethylene polymerization,[4] tremendous efforts were attracted to the catalysis area of amidinates, covering olefin oligomerization or polymerization, hydroamination, intramolecular hydroamination/cyclization and hydrosilylation.[5–10] The exploration of novel ancillary ligand systems is a longstanding demand in coordination chemistry. As a result, special *ansa*-bis(amidinate) ligands were developed. Linking two anionic ligands together by a covalent bridge can serve as a means of determining the complex geometry and limiting ligand mobility. For example, the stereoregular polymerization of propene catalyzed by the *ansa*-bis(indenyl) complexes belonging to Cp species was reported.[11] In terms of the *ansa*-Cp $\eta^5$:$\eta^5$ ligands, the *ansa*-bis(amidinate) ligands can be regarded as the $\eta^3$:$\eta^3$ alternative system. The latter is more electron-deficient than the former. It is supposedly helpful to enhance the electrophilic behavior of a metal center and then to improve its activity for catalysis. The promising *ansa*-bis(amidinate) ligands can afford both binuclear and mononuclear complexes. They presented several kinds of linking modes including flexible carbon chains,[9(*a*),10(*a*),12] chiral 1,2-cyclohexanyl[8(*b*),13,14] and rigid aromatic ring linkers.[15] What we have explored was a type of silyl linked bis(amidinate) ligands [SiMe$_2${NC(Ph)N(R)}$_2$]$^{2-}$.[16] Herein, we report a newly developed efficient pathway for the alkyl-ended *ansa*-bis(amidinate) ligands and the synthesis and structures of some lithium derivatives.

We found previously that the reactions of lithium silyl linked diamides with benzonitrile afford silyl linked bis(amidinate) ligands, undergoing a special 1,1′,3,3-silyl bridge migration process. However, this method was not multipurpose as we tried to extend more analogous *ansa*-bis(amidinate) species. It was not applicable to prepare alkyl-ended *ansa*-bis(amidinate) ligands. Consequently, we changed the synthetic strategy to try a direct method, and another reaction pathway (Scheme 1) was explored. The corresponding lithium derivatives were prepared as follows: (i) the lithiation of an aliphatic amine with BuLi to give lithium amide; (ii) the addition of one equivalent of nitrile to the lithium amide to yield lithium mono-amidinate **A**; (iii) the coupling of lithium amidinate with half equivalent of SiMe$_2$Cl$_2$ to afford silyl-bridged *ansa*-bis(amidine) **B**; (iv) the lithiation of *ansa*-bis(amidine) to produce corresponding lithium complex **C** with the expected silyl linked bis(amidinate) ligand. By varying the amine and nitrile substituents R and R′, respectively, lithium products **C1**, **C2** and **C3** were obtained in good yields (Scheme 1).[†] They were characterized by NMR spectroscopy, elemental analysis and X-ray diffraction analysis. As the whole process could be summarized as bridging two mono-amidinate moieties, it is obvious that the product array could also be expanded largely by changing the



**Scheme 1** Synthetic route to silyl linked bis(amidinate) ligands.

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[†] All manipulations and reactions were performed under an inert atmosphere of nitrogen using standard Schlenk techniques. Solvents were predried with sodium, distilled from sodium benzophenone (diethyl ether, THF and hexane) and stored over molecular sieves (4 Å). Lithium complexes were prepared using the same procedure. NMR spectra were measured for C$_6$D$_6$ solutions at 300 ($^1$H), 75 ($^{13}$C) and 117 ($^7$Li) MHz.

linker used in the third step from **A** to **B**, besides those two variables R and R′. For examlpe, reagents of carbon-based, phosphorus-based species and some more complicated chain work with two halogen ends can serve as the latent options. It is a distinguished merit of this method. In contrast, the silicon based linker is the only choice for the old method due to the migration process.

Note that the key step of this route is the addition of lithium amide to nitrile to yield mono-amidinate **A**. This addition reaction has been widely used, especially for the N-silylated amides as starting reactants. However, referring to the primary amines, we found this route exclusive to the aliphatic amines, which is consistent with Karsch's report.[17] Attempts to prepare similar aryl-ended *ansa*-bis(amidinate) from aromatic amines were unsuccessful. This route is not applicable to aromatic amines because the nucleophilic attack of related amides to nitrile is uncontrollable (such a tranformation was reported on using *N*-silyl-substituted aromatic amines[18] or on application of Yb-catalyzed process[12(*a*)]). Besides **C1**, **C2** and **C3** reported here, other analogous species and intermediates **A** and **B** were prepared. Though they did not have single crystals suitable for X-ray diffraction analysis, other characterizations and the further utilization could confirm their structures, which also testified to the universal feasibility of the synthetic route shown in Scheme 1.

**C1**, **C2** and **C3** are colourless crystals. The molecule of **C1** (Figure 1)‡ consists of two sets of N–C–N–Si–N–C–N skeletons, which are extending spirally to each other and covering the tetranuclear lithium core. The lithium cluster core displays a quadrilateral geometry with boundaries ranging from 2.4 Å [the Li(3) side] to 2.8 Å [the Li(2) side]. The sum of its four inner angles is 360°, indicating their coplanar arrangement. The distance between inner atoms Li(2) and Li(3) is 2.482(11) Å. Therefore, the three distances from Li(3) to other Li atoms are marginally different. Each metal center possesses a distorted tetrahedral bonding mode. Li(3) is fixed by the four N atoms adjacent to Si. The other three Li atoms are fixed by two amidinate moieties. The central [LiN]$_2$ gives another smaller planar quadrilateral closely to be a rhombus.

**C2** (Figure 2)‡ possesses the same tetranuclear lithium aggregation situation as **C1**. It is almost isostructural to **C1** and their corresponding bond lengths and angles are slightly different. Nevertheless, the molecule of **C2** possesses a $C_2$ symmetry, which

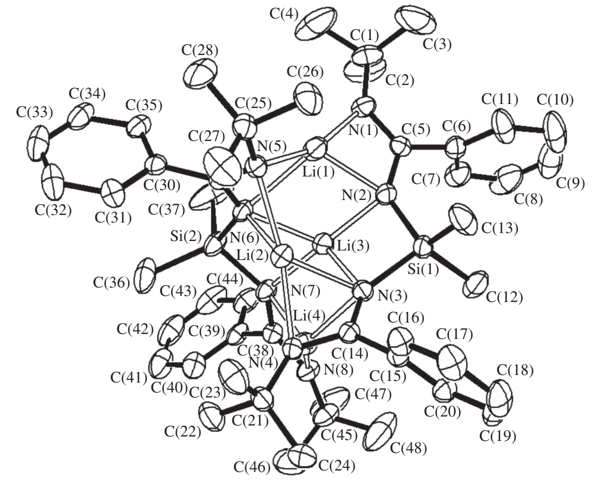

**Figure 1** Molecular structure of compound **C1**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): N(1)–C(5) 1.295(5), N(2)–C(5) 1.355(5), N(2)–Si(1) 1.703(4), Li(1)–N(1) 2.012(8), Li(1)–N(2) 2.062(8), Li(1)–N(5) 2.069(8), Li(1)–N(6) 2.267(9), Li(2)–N(3) 2.108(8), Li(2)–N(4) 2.111(8), Li(2)–N(5) 2.133(8), Li(2)–N(6) 2.095(8), Li(3)–N(2) 1.970(7), Li(3)–N(3) 2.167(8), Li(3)–N(6) 2.173(8), Li(3)–N(7) 2.000(7); selected bond angles (°): N(1)–Li(1)–N(2) 67.3(3), N(1)–C(5)–N(2) 116.8(4), N(2)–Li(3)–N(3) 76.1(3), N(2)–Si(1)–N(3) 95.85(16), N(3)–Li(3)–N(6) 106.4(4), N(6)–Li(2)–N(3) 111.5(4), Li(2)–N(3)–Li(3) 71.0(3), Li(2)–N(6)–Li(3) 71.1(3).

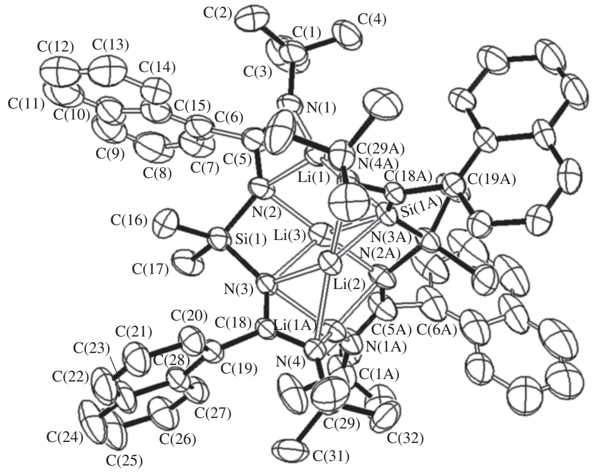

**Figure 2** Molecular structure of compound **C2**. Hydrogen atoms and the disordered naphthyl groups are omitted for clarity. Selected bond distances (Å): N(1)–C(5) 1.287(6), N(2)–C(5) 1.354(5), N(2)–Si(1) 1.702(4), Li(1)–N(1) 2.007(8), Li(1)–N(2) 2.022(7), Li(1)–N(3A) 2.266(8), Li(1)–N(4A) 2.068(8), Li(2)–N(3) 2.094(6), Li(2)–N(4) 2.163(4), Li(3)–N(2) 1.991(4), Li(3)–N(3) 2.180(7); selected bond angles (°): N(1)–Li(1)–N(2) 68.3(2), N(1)–C(5)–N(2) 117.7(4), N(2)–Li(3)–N(3) 75.37(18), N(2)–Si(1)–N(3) 96.17(16), N(3)–Li(2)–N(3A) 112.5(4), N(3)–Li(3)–N(3A) 106.0(4), Li(2)–N(3)–Li(3) 70.7(3). Symmetry code: –*x* + 1, *y*, –*z* + 1/2.

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*The preparation of* **C2** *(typical procedure)*. A solution of BuLi (2.5 mol dm$^{-3}$, 3.8 ml, 9.52 mmol) in hexane was added to a stirred solution of Bu$^t$NH$_2$ (1.01 ml, 9.52 mmol) in Et$_2$O (~30 ml) using a syringe at 0 °C. The reaction mixture was warmed to room temperature and stirred for 3 h; then, 1-naphthonitrile (1.31 ml, 9.52 mmol) was added with a syringe at 0 °C. The reaction mixture was warmed to room temperature and stirred for 4 h; then, SiMe$_2$Cl$_2$ (0.58 ml, 4.76 mmol) was added with a syringe at 0 °C. After stirring at room temperature for 4 h, the mixture was filtered. A solution of BuLi (2.5 mol dm$^{-3}$, 3.8 ml, 9.52 mmol) in hexane was added to the filtrate at 0 °C. The reaction mixture was warmed to room temperature, stirred for 3 h, and concentrated to give colourless crystals of **C2**.

For **C1**: yield 93.5%. $^1$H NMR, $\delta$: 7.29 (d, 8H, 2,6-H$_{\mathrm{Ph}}$), 7.11 (m, 12H, 3,4,5-H$_{\mathrm{Ph}}$), 1.34 (s, 36H, CMe$_3$), –0.13 (s, 12H, SiMe$_2$). $^{13}$C NMR, $\delta$: 175.4 (N–C–N), 143.1, 127.3 and 127.0 (Ph), 51.2 (*C*Me$_3$), 33.5 (C*Me*$_3$), 3.2 (SiMe$_2$). $^7$Li NMR, $\delta$: 2.27, 2.02, 1.85. Found (%): C, 68.57; H, 8.18; N, 13.26. Calc. for C$_{48}$H$_{68}$Li$_4$N$_8$Si$_2$ (%): C, 68.55; H, 8.15; N, 13.32.

For **C2**: yield 1.82 g (73.7%). $^1$H NMR, $\delta$: 8.551–7.166 (m, 28H, naphth), 1.56–0.967 (m, 36H, 2CMe$_3$), –0.67, –1.11 (d, 6H, SiMe$_2$). $^{13}$C NMR, $\delta$: 66.7 (N–C–N), 142.5–125.0 (naphth), 52.7 (*C*Me$_3$), 34.3, 34.1, 32.7 (C*Me*$_3$), 3.8, 3.5 (SiMe$_2$). Found (%): C, 73.55; H, 7.18; N, 10.92. Calc. for C$_{64}$H$_{76}$Li$_4$N$_8$Si$_2$ (%): C, 73.82; H, 7.36; N, 10.76.

For **C3**: yield 84.1%. $^1$H NMR, $\delta$: 7.37–7.09 (m, 20H, Ph), 3.69 (s, 16H, OCH$_2$ of THF), 1.60 [s, 16H, 3,4-(CH$_2$)$_2$ of THF], 1.93–0.92 (m, 44H, Cy), –0.001 (s, 12H, SiMe$_2$). $^{13}$C NMR, $\delta$: 141.7–127.3 (Ph), 68.35 (OCH$_2$ of THF), 26.17 [3,4-(CH$_2$)$_2$ of THF], 56.22, 37.63, 26.75, 25.46 (Cy), 4.22 (SiMe$_2$). Found (%): C, 67.55; H, 8.41; N, 8.86. Calc. for C$_{72}$H$_{108}$ClLi$_5$N$_8$O$_4$Si$_2$ (%): C, 67.77; H, 8.53; N, 8.78.

‡ *Crystal data for* **C1**: C$_{48}$H$_{68}$Li$_4$N$_8$Si$_2$, $M$ = 841.04, monoclinic, space group $P2_1/n$, $a$ = 11.7377(11), $b$ = 21.728(2) and $c$ = 21.2696(19) Å, $\beta$ = 99.599(2)°, $V$ = 5348.5(8) Å$^3$, $Z$ = 4, $d_{\mathrm{calc}}$ = 1.044 g cm$^{-3}$, $\mu$(MoK$\alpha$) = = 0.103 mm$^{-1}$, $T$ = 238(2) K, $R[I > 2\sigma(I)]$ = 0.0808, GOF = 1.028.

*Crystal data for* **C2**: C$_{64}$H$_{76}$Li$_4$N$_8$Si$_2$, $M$ = 1041.27, monoclinic, space group $C2/c$, $a$ = 20.312(6), $b$ = 18.046(5) and $c$ = 18.102(5) Å, $\beta$ = = 93.725(5)°, $V$ = 6621(3) Å$^3$, $Z$ = 4, $d_{\mathrm{calc}}$ = 1.045 g cm$^{-3}$, $\mu$(MoK$\alpha$) = = 0.095 mm$^{-1}$, $T$ = 238(2) K, $R[I > 2\sigma(I)]$ = 0.0864, GOF = 1.023.

*Crystal data for* **C3**: C$_{72}$H$_{108}$ClLi$_5$N$_8$O$_4$Si$_2$, $M$ = 1275.99, triclinic, space group $P\bar{1}$, $a$ = 14.7172(8), $b$ = 15.9395(8) and $c$ = 18.3343(10) Å, $\alpha$ = 115.1730(10)°, $\beta$ = 98.1710(10)°, $\gamma$ = 99.4350(10)°, $V$ = 3730.1(3) Å$^3$, $Z$ = 2, $d_{\mathrm{calc}}$ = 1.136 g cm$^{-3}$, $\mu$(MoK$\alpha$) = 0.134 mm$^{-1}$, $T$ = 200(2) K, $R[I > 2\sigma(I)]$ = 0.0642, GOF = 1.021.

CCDC 933506–933508 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2013.

does not occur in **C1**. The two-fold rotational axis is located on the inner line crossing Li(2) and Li(3). **C2** differs from **C1** on the substitution of naphthyl for phenyl, which causes another notable feature in **C2**. The C–C single bond between naphthyl and C atom of N–C–N unit can rotate to some extent, while it cannot act as a $C_2$ axis for the naphthyl group. Additionally, the naphthyl plane is almost perpendicular to the [NCN] plane; these factors will lead to different orientation combinations when two naphthyl groups anchored on the N–C–N–Si–N–C–N skeleton. It is predictable that the *cis*- or *trans*-like isomerization caused by the same or opposite directions of two naphthyl groups exists in **C2**. Figure 2 only displays the *trans*-like situation for a clear view. In fact, the naphthyl group attached on C(5) has a disordered counterpart, which is *cis* to the naphthyl group attached at C(18). Though the ligand in **C2** molecule has both *cis* and *trans* forms, as found in Group IV metal complexes, it will merely adopt a *cis* form in the Ti complex and a *trans* form in Zr and Hf complexes.

**C3** was prepared in the same way as **C1**, while the only change was the starting amine used. Cyclohexylamine was used for synthesizing **C3**. It caused a significant change in their molecular structures. **C3** (Figure 3)[‡] is a pentanuclear lithium species. Correspondingly, there are two bianionic *ansa*-bis(amidinate) ligands and one chloride ion in it. Overall, the composition of **C3** could be thought of as the similar components in **C1** plus a LiCl moiety and three THF molecules. The terminal cyclohexyl groups adopt a typical chair-like configuration. Two N–C–N–Si–N–C–N skeletons tend to be close to each other with one of their ends. The other two ends are much wider, and the chloride ion is settled at the middle position between the two N ends. All the lithium metal centers are embedded in the interior space enclosed by two *ansa*-bis(amidinate) ligands. Each lithium ion is tetracoordinated in a tetrahedral geometry. They are arranged in a unique sequence of 1, 2 and 2. On the top side of the molecule of **C3**, there is a THF molecule attached to the lithium ion, which is free from the chloride ion. The bottom two lithium ions are separated by the chloride ion and both are covered with one THF molecule from opposite sides. Besides the bottom two lithium ions, the chloride ion is also bound by two lithium ions in the middle layer. A resulting quadrilateral [Li(3)–Li(4)–Cl(1)–Li(5)] in the core has four inner angles summed to 360°, which reflects the coplanar relationship of the corresponding four atoms. The lengths of Li–Cl bonds vary from 2.31 to 2.43 Å.

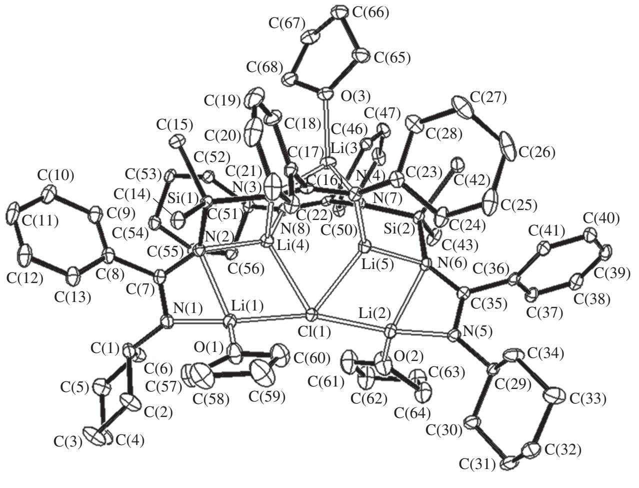

**Figure 3** Molecular structure of compound **C3**. Hydrogen atoms and a solvated THF molecule are omitted for clarity. Selected bond distances (Å): N(1)–C(7) 1.313(4), N(2)–C(7) 1.346(4), Si(1)–N(2) 1.715(2), Li(1)–O(1) 1.928(6), Li(1)–N(1) 1.997(6), Li(1)–N(2) 2.123(5), Cl(1)–Li(1) 2.319(5), Li(3)–O(3) 1.943(5), Li(3)–N(7) 2.073(5), Li(3)–N(4) 2.174(5), Li(3)–N(3) 2.188(5), Li(4)–N(8) 2.000(5), Li(4)–N(2) 2.034(5), Li(4)–N(3) 2.144(5), Cl(1)–Li(4) 2.428(5); selected bond angles (°): N(1)–Li(1)–N(2) 67.00(18), N(1)–C(7)–N(2) 117.7(2), N(2)–Li(4)–N(3) 77.54(18), N(2)–Si(1)–N(3) 98.64(11), Li(5)–Cl(1)–Li(4) 71.21(16), Cl(1)–Li(4)–Li(3) 107.6(2), Li(5)–Li(3)–Li(4) 64.28(18), Cl(1)–Li(5)–Li(3) 116.9(2).

By comparing the molecular structures of **C1**, **C2** and **C3**, we can see that **C1** is closely similar to **C2** in the arrangement of lithium ions and ligands, while they are quite different from **C3**. Three lithium complexes adopt two different types of aggregation in a crystalline state. According to ligand changes in substituents on the same skeleton, the different aggregation is obviously caused by the terminal group, which is originated from the primary amine used. Meanwhile, it reflects that the terminal group has a notable impact on the property of corresponding ligand and its compatibility to metal ions.

In conclusion, a newly developed synthetic method with direct and efficient features for alkyl-ended *ansa*-bis(amidinate) ligands is reported. It has a wide range of product array as there are three variable sites, which can also result in numerous combinations of steric and electronic properties in ligands and complexes. The chain-like skeleton with the bianionic property of ligands causes the lithium derivatives to demonstrate the similar multinuclear feature.

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