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Synthesis of four-membered bissilylene-linked bisamidines

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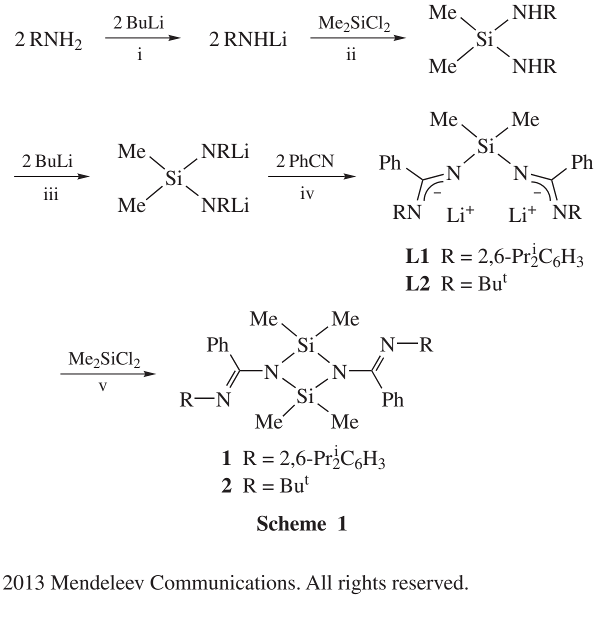
Reaction of dilithium derivatives of *N,N'*-(dimethylsilanediyl)diamines, $Me_2Si[N(Li)R]_2$ with benzonitrile followed by treatment with Me_2SiCl_2 afforded 1,3-bis[1-(*N*-R-imino)-1-phenylmethyl]-1,3,2,4-diazadisiletidines, the neutral four-membered bissilylene-linked bisamidines, whose structure was established by X-ray diffraction.

The exploration of ancillary ligand systems supporting catalytically active metal centres is a long-standing demand in the coordination chemistry. Amidinates represent an important class in the array comparable to the cyclopentadienyl system.[1,2] They are four-electron, monoanionic and N-donor bidentate chelates, providing a great diversity by variation of substituents on the conjugated N–C–N backbone. Their steric and electronic properties are easily tunable to meet the requirements of different metal centres.[3] The coordination chemistry of amidinates towards various metals was well studied in the past few decades and amidinate complexes proved to be promising,[4–6] among which *ansa*-bis(amidinates)[7–11] attracted increasing attention. We have explored[12] a convenient synthetic pathway to the silylene-linked bis(amidinate) ligands, $[SiMe_2\{NC(Ph)N(R)\}_2]^{2-}$, from which the Group IV complexes indicating the η^3:η^3 environment analogous to the '*ansa*-metallocene' (the latter are known as good catalysts for ethylene polymerization[13–15]). Amidines are convenient precursors of monoanionic amidinate ligands, as well as cationic amidinium species. On the other hand, dianionic amidinates located at organosilicon centres, namely *ansa*-bisamidines, are potentially useful to form polymers with $[(R)N–C(Ph)–N]^{2-}$ linkages, mimicking O^{2-} bridges in silicones or silicates in one-, two- or three-dimensional frameworks. This inspired us to extend the research of bissilylene *ansa*-bisamidines based on silylene-linked bisamidinate ligands.



Scheme 1

In the present communication (Scheme 1), lithium complexes **L1** and **L2** of formula $Li_2\{Me_2Si[NC(Ph)N(R)]_2\}$ (R = = 2,6-$Pr^i_2C_6H_3$ or Bu^t) were prepared as follows: (i) lithiation of an amine with BuLi to give lithium amide; (ii) coupling of the lithium amide with half equivalent of Me_2SiCl_2 to afford the silylene-bridged diamine; (iii) lithiation of the diamine to give lithium diamide; (iv) addition of benzonitrile to yield the linked bis(amidinate) after an interesting 1,1′,3,3′-migration of the dimethylsilyl bridge.[12] New compounds **1** and **2** were obtained upon final treatment of lithium complexes **L1** and **L2** with $SiMe_2Cl_2$ [see (v), Scheme 1].[†] Similar results on bisilicon-centred aliphatic-group-ended neutral amidines were reported by Karsch *et al.*[16] The synthetic way they used was to treat the lithium amidinates with one equivalent of $SiMe_2Cl_2$, and NEt_3 was then added to neutralize the evolving HCl. However, such a procedure led to four-, six- and eight-membered products depending on substrate. In our method, both the aliphatic-group-ended and the aromatic-

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[†] All manipulations and reactions were performed under an inert atmosphere of nitrogen using standard Schlenk techniques. Solvents were predried over sodium, distilled from sodium-benzophenone (diethyl ether, THF and toluene) and stored over molecular sieves (4Å). Dichloromethane was distilled from CaH_2. Anionic precursors **L1** and **L2** were prepared according to the reported procedure.[12]

*1,3-Bis{1-[*N*-(2,6-diisopropylphenyl)imino]-1-phenylmethyl}-1,3,2,4-diazadisiletidine* **1**: Me_2SiCl_2 (0.11 ml, 0.91 mmol) was added to a solution of **L1** (0.70 g, 0.91 mmol) in Et_2O (30 ml) at 0 °C and the reaction mixture was warmed to room temperature and stirred overnight, then the solvent was removed *in vacuo*, and the residue was extracted with CH_2Cl_2. Compound **1** was recrystallized from toluene as colourless crystals (yield 0.41 g, 56%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.14–6.85 (m, 16H, Ph), 3.05 (m, 4H, C*H*Me$_2$), 1.19–0.96 (m, 24H, CH*Me*$_2$), 0.38 (s, 12H, SiMe$_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 139.1 (N–C–N), 129.3–123.0 (Ph), 29.0, 25.3, 22.7 (Pr^i), 2.2 (SiMe$_2$). Found (%): C, 74.66; H, 8.21; N, 8.38. Calc. for $C_{42}H_{56}N_4Si_2$ (%): C, 74.95; H, 8.39; N, 8.32.

*1,3-Bis[1-(*N*-tert-butylimino)-1-phenylmethyl]-1,3,2,4-diazadisiletidine* **2**: Me_2SiCl_2 (0.36 ml, 2.92 mmol) was added to a solution of **L2** (1.23 g, 2.92 mmol) in THF (30 ml) at 0 °C and the reaction mixture was warmed to room temperature and stirred overnight, then the solvent was removed *in vacuo*, and the residue was extracted with CH_2Cl_2. The extract was filtered and concentrated to give compound **2** as colourless crystals (yield 1.19 g, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.22–7.08 (m, 10H, Ph), 0.89 (s, 18H, Bu^t), 0.02 (s, 12H, SiMe$_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 141.4 (N–C–N), 129.8–127.5 (Ph), 53.3 (*C*Me$_3$), 32.9, 31.7, 29.4 (C*Me*$_3$), 1.7 (SiMe$_2$). Found (%): C, 66.93; H, 8.54; N, 12.12. Calc. for $C_{26}H_{40}N_4Si_2$ (%): C, 67.19; H, 8.67; N, 12.05.

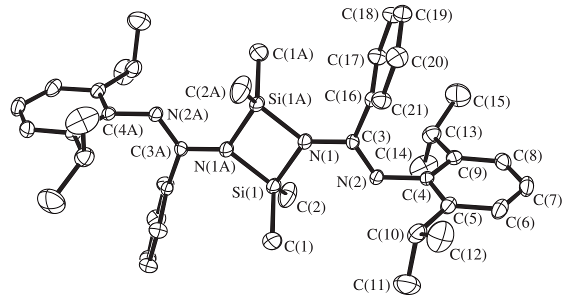

Figure 1 Molecular structure of compound **1**. Selected bond lengths (Å) and bond angles (°): Si(1)–N(1) 1.751(2), N(1)–Si(1A) 1.7495(19), N(1)–C(3) 1.377(3), N(2)–C(3) 1.281(3), N(2)–C(4) 1.425(3); N(1A)–Si(1)–N(1) 83.34(10), Si(1A)–N(1)–Si(1) 96.66(10), Si(1)–N(1)–C(3) 126.26(15), Si(1A)–N(1)–C(3) 136.90(16), N(1)–C(3)–N(2) 118.5(2), N(2)–C(3)–C(16) 126.54(19), N(1)–C(3)–C(16) 114.95(18). Symmetry codes: (i) $-x+1/2$, $-y+1/2$, $-z$.

group-ended species can be synthesized, whereas the products are only four-membered.

The X-ray-analyzable single crystals of **1** (Figure 1)[‡] were obtained by crystallization from toluene. The molecule of compound **1** is centrosymmetric and each amidine unit is tetrasubstituted. For the N–C–N framework, the distance of C(3)–N(1) [1.377(3) Å] is much longer than that of C(3)–N(2) [1.281(3) Å], suggesting a non-conjugated system. Generally, trisubstituted amidines exist as four (*E-anti*, *E-syn*, *Z-syn* and *Z-syn*) tautomeric forms.[17,18] In compound **1**, both phenyl groups are on the same side of C–N double bond. Therefore, it could be classified as the *E* type. The molecule exhibits a rhombus $[SiN]_2$ core, with sides of 1.75 Å (av.) long. The diagonally opposite two C–N double bonds are almost located in the plane of the rhombus. The terminal bulky phenyl plane crosses the rhombus plane in angle of 81.51°. Corresponding angle between the inner phenyl plane and the rhombus plane is 79.59°.

As for analogue **2** with *tert*-butyl groups (Figure 2),[‡] its single crystals were grown from CH_2Cl_2. The different compatibility of **1** and **2** with solvents was presumably due to the alternation of terminal substituents. On the other hand, the different electronic properties of terminal groups have made an apparent impact on the linkages between them and the $[SiN]_2$ core. For **1**, the N(1)–C(3)–N(2)–C(4) chain could serve as a conjugated bridge due to the influence from the aromatic 2,6-$Pr^i_2C_6H_3$ group. The similar property is weakened in the corresponding chain of **2**, since Bu^t is an electron-donating group. Moreover, the Bu^tN= group in compound **2** is less bulky than the 2,6-$Pr^i_2C_6H_3N$= one in compound **1**. Consequently, the flank could rotate along the connecting N–C single bond axis and disorder occurs in the crystal structure of **2**. Recently, Tacke and coworkers reported a series of bis(benzamidinate)silicon(IV) complexes (SiN_4X_2 skeletons), in which each amidinate ligand bit Si in κ^2 fashion and Si was hexacoordinate.[19] In contrast, both **1** and **2** demonstrate the κ^1 amidinate ligand and tetracoordinate Si centre.

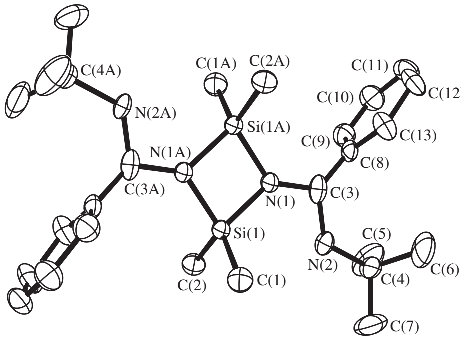

Figure 2 Molecular structure of compound **2**. Selected bond lengths (Å) and bond angles (°): Si(1)–N(1) 1.750(2), N(1)–Si(1A) 1.751(2), N(1)–C(3) 1.372(3), N(2)–C(3) 1.414(11), N(2)–C(4) 1.505(9); N(1A)–Si(1)–N(1) 83.44(10), Si(1A)–N(1)–Si(1) 96.56(10), Si(1)–N(1)–C(3) 130.7(2), Si(1A)–N(1)–C(3) 132.8(2), N(1)–C(3)–N(2) 105.9(4), N(2)–C(3)–C(8) 128.1(4), N(1)–C(3)–C(8) 125.9(4). Symmetry codes: (i) $-x+1$, $-y+2$, $-z$.

In summary, we successfully developed a universal synthetic pathway from aliphatic or aromatic amines to the bissilylene *ansa*-bisamidines μ-$[RN(Ph)C{-}N]_2(SiMe_2)_2$ possessing a four-membered core.

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[‡] *Crystal data for* **1**: $C_{42}H_{56}N_4Si_2$, $M = 673.09$, monoclinic, space group $C2/c$, $a = 27.789(2)$, $b = 9.2265(8)$ and $c = 16.4715(13)$ Å, $\beta = 96.475(2)°$, $V = 4196.3(6)$ Å^3, $Z = 4$, $d_{calc} = 1.065$ g cm^{-3}, μ(MoKα) = 0.116 mm^{-1}, $T = 238(2)$ K, $R[I > 2\sigma(I)] = 0.0498$, GOF = 1.030.

Crystal data for **2**: $C_{26}H_{40}N_4Si_2$, $M = 464.80$, triclinic, space group $P\bar{1}$, $a = 6.4846(6)$, $b = 10.6886(10)$ and $c = 11.2487(10)$ Å, $\alpha = 69.8640(10)°$, $\beta = 85.8130(10)°$, $\gamma = 76.7310(10)°$, $V = 712.45(11)$ Å^3, $Z = 1$, $d_{calc} = 1.083$ g cm^{-3}, μ(MoKα) = 0.143 mm^{-1}, $T = 238(2)$ K, $R[I > 2\sigma(I)] = 0.0599$, GOF = 1.046.

CCDC 905707 and 905708 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/data_request/cif. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2013.