Twice silicon-induced C–H activation and tautomerisation of a β -diketiminato ligand and formation of new types of N-heterocyclic silanes[†]

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Received 9th October 2008, Accepted 21st November 2008 First published as an Advance Article on the web 8th December 2008 DOI: 10.1039/b820285k

Unexpected formation of the novel dianionic N,C-chelate ligand L_D^{2-} {HC[C(Me)-NR][C(NHR)=CH]}²⁻ occurs by a twice silicon-assisted C–H bond activation of a terminal methyl group on a β -diketiminato ligand backbone, starting from the corresponding lithium β -diketiminide and silicon tetrabromide to give the new *N*-heterocyclic dibromosilanes 2 and 3.

Monoanionic, chelating β -diketiminato ligands L_{A}^{-} (Scheme 1) are valuable supporting ligands for the development of new molecular catalysts containing metals even in unusual low oxidation states.^{1,2} The fascinating variety of the latter complexes stems from the relatively strong coordination ability of the resonance-stabilised β -diketiminato ligand L_{A}^{-} to metal centres along with their tuneable steric congestion. Additionally, the β -diketiminato ligand can undergo rearrangements in its metal complexes such as metal-mediated ring contraction or C–H bond activation. Striking examples for ring contractions are shown by the partial reductive C–N bond fission of the C₃N₂ backbone in β -diketiminato complexes,^{3a-e} which more recently led to the isolation of a cyclopentadienide analogue with divalent germanium.^{3f} Furthermore, unexpected C–H activation on a methyl group of the backbone of the β -diketiminato ligand afforded remarkable



Scheme 1 β -Diketiminato (L_{A}^{-}) and the related mono- and dianionic chelate ligands L_{B}^{-} , $L_{C}^{2-}/(L_{C}^{2-})^{2}$, and L_{D}^{2-} .

complexes containing the new related ligands L_{B}^{-} , $[L_{B}-H]^{2-}$ and L_{C}^{2-} , respectively (Scheme 1).⁴ Recently, we described a simple one-pot synthesis of a *N*-heterocyclic dibromosilane $L_{C}SiBr_{2}$ containing the dianionic ligand L_{C}^{2-} (R = 2,6-diisopropylphenyl, DIPP).^{5a} The latter dibromosilane results from the reaction of the corresponding $L_{A}Li$ salt with SiBr₄ in the presence of tetramethylethylenediamine (TMEDA) as an auxiliary base. Its debromination leads to a new type of stable silylene $L_{C}Si:^{5a}$ with zwitterionic character owing to the contribution of the resonance form (L_{C}^{2-})' on the electronic ground state (Scheme 1).^{4f,5}

We now learned that sterically less demanding substituted lithium β -diketiminides L_ALi react with SiBr₄ in the absence of TMEDA to give a new type of N-heterocyclic dibromosilane containing the novel dianionic N,C-ligand L_D^{2-} (Scheme 1). In fact, reaction of the lithium β -diketiminide L_ALi 1 (R = 2,6dimethylphenyl, DMP) with SiBr₄ in the molar ratio of 1:1 in diethyl ether at -40 °C furnishes the new dibromosilanes 2 and 3, containing the N,C-chelate ligand L_{D}^{2-} , along with 4 which is the HBr adduct of $L_A H$ (Scheme 2). In contrast, the similar conversion in the presence of TMEDA affords the dibromosilane 5 which can be isolated in the form of colorless crystals in 63% yield. Its ¹H, ¹³C and ²⁹Si NMR spectroscopic data⁶ show similar features with those observed for the L_cSiBr₂ derivative reported previously.^{5a} In addition, the structure of 5 has been confirmed by a single crystal diffraction analysis (Fig. 1).7 Despite of the presence of the less bulkier DMP group at nitrogen in 2, the metric features are practically identical with those of L_cSiBr₂.^{5a}



Scheme 2 Synthesis of compounds 2–5.

The isolation of **2** and **3** has been achieved by fractional crystallisation in n-hexane at -20 °C. Since the bromide salt **4** is insoluble in hydrocarbon solvents it can be easily separated from **2** and **3** and isolated in 21% yield. Compound **2** results in the form of colorless crystals in 38% yield, whereas **3** is accessible as colourless crystals in only 9% yield. Apparently, L_ALi has a dual

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[†] Electronic supplementary information (ESI) available: Additional experimental details. CCDC reference numbers 705079–705081. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b820285k



Fig. 1 Molecular structure of 5. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms, except for those at C1, are omitted for clarity. Selected bond lengths [pm] and angles [°]: Br1-Si1 220.7(1), Br2-Si1 221.7(1), Si1-N2 169.2(3), Si1-N1 169.7(3), C1-C2 136.9(5), C2-C3 145.5(5), C3-C4 133.1(5), C4-C5 149.0(6), C2-N1 141.9(5), C4-N2 143.8(5), N2-Si1-N1 107.14(15), N2-Si1-Br1 110.0(1), N1-Si1-Br1 113.67(13), N2-Si1-Br2 114.0(1), N1-Si1-Br2 110.16(11), Br1-Si1-Br2 102.02(4).

function and acts as a nucleophile and a base (HBr scavenger) at the same time which is evident by formation of $[L_AH HBr] 4$. Thus, a larger molar ratio of L_ALi (mole ratio of L_ALi :SiBr₄ = 3:2) increases the yield of **2** to 43%. Correspondingly, the yield of **3** is somewhat reduced owing to the higher reactivity of SiBr₄ towards the stronger nucleophile L_ALi versus **2**.

The composition and constitution of the compounds **2** and **3** were proven by elemental analysis and NMR spectroscopy (¹H, ¹³C, and ²⁹Si).⁶ The ¹H NMR spectrum of **2** reveals two characteristic doublets at 4.25 and 4.76 ppm with ⁴J_{HH} = 2.7 Hz corresponding to the α - and the γ -H atoms on the C₄NSi ring, respectively, while the broad singlet at 4.47 ppm belongs to the N-H proton of the terminal amino group. Likewise, two doublets are observed in the ¹H NMR spectrum of **3** at 5.22 and 5.96 ppm (⁴J_{HH} = 3.0 Hz) which can be assigned to the α - and the γ -H atoms on the C₄NSi ring, respectively. The ¹H-decoupled ²⁹Si NMR spectrum of **2** shows a singlet at -31.6 ppm, while that of **3** exhibits two singlets at -31.2 and -66.1 ppm corresponding to the Si atom in the C₄NSi ring *versus* that of the exocyclic SiBr₃ group.

The structures of **2** and **3** were established by single-crystal Xray diffraction analyses as shown in Fig. 2 and Fig. 3, respectively.⁷ Both structures consist of an almost planar six-membered SiNC₄ ring, featuring an exocyclic amino group with the nitrogen atom nearly within the plan of the six-membered SiNC₄ ring. Despite of the difference of the amino groups, the interatomic parameters of the SiNC₄ ring in **2** and **3** are practically identical. The endocyclic C–C bond distance alternation in **2** [135.4(4) (C2-C3), 143.9(4) pm (C3-C4), 136.5(4) pm (C4-C5)] suggests only little π conjugation, and the same is true for the corresponding butadienelike moiety in **3**. Interestingly, the C4-C5 distance in **2** and **3** is much shorter than the corresponding one in the related L_BPCl⁺ complex [149.5(5) pm],^{4e} indicating reduced C–C π -bond character in the latter.

How could one explain the formation of **2** and **3**? Although their mechanism is still unknown, it is reasonable to assume that the initial step is a nucleophilic substitution at silicon to give LiBr and the SiBr₃-substituted bis-imine **I** as an reactive intermediate (Scheme 3). Precedents for related species with substitution at the γ -C ring atom have previously been reported for reactions employing germanium⁸ and phosphorus chlorides.⁹ It has been suggested that both steric congestion and the unfavourable bite



Fig. 2 Molecular structure of **2**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms, except for those at C1, C3, C5 and N2, are omitted for clarity. Selected bond lengths [pm] and angles [°]: Si1-N1 171.8(3), Si1-C5 177.7(3), Si1-Br1 222.0(1), Si1-Br2 223.8(1), N1-C2 140.1(4), N2-C4 137.5(4), C1-C2 149.0(4), C2-C3 135.4(4), C3-C4 143.9(4), C4-C5 136.5(4), N1-Si1-C5 106.41(14), N1-Si1-Br1 110.82(9), C5-Si1-Br1 115.00(11), N1-Si1-Br2 111.14(9).



Fig. 3 Molecular structure of 3. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms, except for those at C1, C3, and C5, are omitted for clarity. Selected bond lengths [Å] and angles [°]:Br1-Si1 222.2(2), Br2-Si1 222.8(2), Br3-Si2 219.0(2), Br4-Si2 218.6(2), Br5-Si2 218.6(2), Si1-N1 171.7(6), Si1-C5 179.6(7), Si2-N2 170.1(6), N1-C2 141.0(9), N2-C4 144.8(8), C1-C2 149.1(9), C2-C3 136.0(10), C3-C4 142.9(9), C4-C5 134.4(9), N1-Si1-C5 105.0(3), N1-Si1-Br1 111.4(2), C5-Si1-Br1 112.8(3), N1-Si1-Br2 112.5(2), C5-Si1-Br2 113.8(3), Br1-Si1-Br2 101.68(9).

angle of the six-membered β -diketiminate ring are mostly responsible for this outcome.^{9a} In a next step, intramolecular N \rightarrow Si coordination in the bis-imine I favours in the presence of the bases L_ALi and/or L_AH deprotonation of a β -methyl group affording the corresponding azaallylide-like intermediate II (Scheme 3). The latter undergoes rearrangement and subsequent Br⁻ elimination to give the *N*-heterocyclic dibromosilane III with a terminal imino group. A similar rearrangement of an phosphorus analogue with C,N-chelation has recently been reported by Cowley and coworkers.^{4e,9d} Remarkably, 1,3-H migration (tautomerisation) from the α -C atom of the CH₂-Si ring moiety to the imido nitrogen



Scheme 3 Proposed mechanism for the formation of 2 via the reactive intermediates I, II, and III.

centre in **III** is favoured by the α -Si effect¹⁰ leading to the formation of **2**. In other words, the formation of **2** involves a double C–H bond activation induced by silicon. Apparently, **3** results from silylation of **2** with SiBr₄ under HBr elimination.

In summary, silylation of $L_A Li 1$ with SiBr₄ in the presence or absence of TMEDA as auxiliary base leads to remarkably different products: While the *N*-heterocyclic dibromosilane **5** is formed in the presence of TMEDA, the same conversion without TMEDA affords the distinct product **2** and its SiBr₃-derivative **3** along with the HBr adduct of $L_A H$. Both **2** and **3** are promising precursors for novel isolable *N*-heterocyclic silylenes. Respective investigations are in progress.

Acknowledgements

Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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- 6 Spectroscopic data for 2: ¹H NMR (200.13 MHz, C₆D₆, 298 K): δ 1.40 (s, 3 H, NCMe), 2.11 (s, 6 H, 2,6-Me₂C₆H₃), 2.31 (s, 6 H, 2,6- $Me_2C_6H_3$), 4.25 (d, 1 H, ${}^4J_{HH} = 2.7$ Hz, α -CH), 4.47 (s, 1 H, NH), 4.76 (d, ${}^{1}\text{H}, {}^{4}\text{J}_{\text{HH}} = 2.7 \text{ Hz}, \gamma \text{-CH}$), 6.91–7.02 (m, br, 6 H, 2,6-Me₂C₆H₃). ¹³C{¹H} NMR (100.61 MHz, C₆D₆, 298 K): δ 18.2–22.6 (Me), 78.12(α-C), 100.4 (γ -C), 125.6–155.2 (NCMe, NCCH₂, 2,6-Me₂C₆H₃). ²⁹Si{¹H} NMR (79.49 MHz, C₆D₆, 298 K): δ-31.4 (s). EI-MS: m/z (%): 492.3(5, $[M]^+$), 476.9 (6, $[M - Me]^+$, 371.8 (7, $[M - NHR]^+$, R = 2,6-Me₂C₆H₃), $306.2 (35, [M - SiBr_2]^+), 291.1 (30.0, [M - SiBr_2 - Me]^+), 187.1(100, [M - SiBr_2 - Me]^+)), 187.1(100, [M - SiBr_2 - Me]^+)))$ [HSiBr₂]⁺). Elemental analysis (%) calcd for C₂₁H₂₄N₂SiBr₂: C, 51.23; H, 4.91; N, 5.69. Found: C, 50.82; H, 4.70; N, 5.44. Spectroscopic data for 3: 1H NMR (200.13 MHz, C₆D₆, 298 K): δ 1.36 (s, 3 H, NCMe), 2.21 (s, 6 H, 2,6-Me₂C₆H₃), 2.28 (s, 6 H, 2,6-Me₂C₆H₃), 5.22 (d, 1 H, ${}^{4}J_{HH} = 3.0$ Hz, α -CH), 5.96 (d, 1H, ${}^{4}J_{HH} = 3.0$ Hz, γ -CH), 6.81–6.90 (m, br, 6 H, 2,6-Me₂C₆ H_3). ¹³C{¹H} NMR (100.61 MHz, C₆D₆, 298 K): δ 19.3–22.7 (Me), 92.7 (α-C), 101.1 (γ-C), 128.6– 153.7 (NCMe, NCCH₂, 2,6-Me₂C₆H₃). ²⁹Si{¹H} NMR (79.49 MHz, C_6D_6 , 298 K): δ -31.2 (s, SiBr₂), -66.1 (s, SiBr₃). EI-MS: m/z (%): 759.6(55, [M]⁺), 744.6 (21, [M – Me]⁺, 679.7 (35, [M-Br]⁺), 491.9 (14, [M-SiBr₃]⁺), 477.0(13, [M-SiBr₃-Me]⁺), 371.7(13, [M-SiBr₃-NHR]⁺, $R = 2,6-Me_2C_6H_3$). Elemental analysis (%) calcd for $C_{21}H_{23}N_2Si_2Br_5$: C, 33.23; H, 3.05; N, 3.69. Found: C, 33.05; H, 3.21; N, 3.70. Spectroscopic data for 4: ¹H NMR (200.13 MHz, C₆D₆, 298 K):δ 1.89 (s, 12 H, 2,6-Me₂C₆H₃), 2.61 (s, 6 H, NCMe), 4.10 (s, 1 H, γ-CH), 6.72-6.98 (m, br, 6 H, 2,6-Me₂C₆H₃), 11.45 (s, 2H, NH); EI-MS: m/z (%): 307.1 (9, $[M - Br]^+$), 187.1 (100, $[M - NC_6H_3Me_2]^+$. Spectroscopic data for 5: ¹H NMR (200.13 MHz, C₆D₆, 298 K): δ 1.32 (s, 3 H, NCMe), 2.39 (s, 6 H, 2,6-Me₂C₆H₃), 2.49 (s, 6 H, 2,6-Me₂C₆H₃), 3.56 (s, 1 H, NCCH₂), 3.97 (s, 1 H, NCCH₂), 5.36 (s, 1 H, γ-CH), 6.87-7.14 (m, br, 6 H, 2,6- $Me_2C_6H_3$). ¹³C{¹H} NMR (100.61 MHz, C₆D₆, 298 K): δ 20.1, 20.2, 21.2 (NCMe, 2,6-Me₂C₆H₃), 87.5 (NCCH₂), 105.9 (γ-C), 129.2-144.7 (NCMe, NCCH₂, 2,6-Me₂C₆H₃). ²⁹Si{¹H} NMR (79.49 MHz, C₆D₆, 298 K):δ-55.1 (s). EI-MS: m/z (%): 492.8 (7, [M]⁺), 491.8 (20, [M-H]⁺, 476.9 (100, $[M - Me]^+$). Elemental analysis (%) calcd for C₂₁H₂₄N₂SiBr₂: C, 51.23; H, 4.91; N, 5.69. Found: C, 51.08; H, 4.96; N, 5.99.
- 7 Crystal data for 2:† $C_{21}H_{24}Br_2N_2Si$, M = 492.33, monoclinic, space group $P2_1/a$, a = 14.9450(4), b = 8.2720(2), c = 17.7852(4) Å, $\beta =$ $104.903(3)^{\circ}$. V = 2124.73(9) Å³, Z = 4, $\rho_{calc} = 1.539$ Mg m⁻³, μ (Mo $K\alpha$) = 3.879 mm⁻¹, 13787 collected reflections, 3731 crystallographically independent reflections [$R_{int} = 0.0370$], 2656 reflections with I > $2\sigma(l), \ \theta_{\text{max}} = 25.00^{\circ}, \ R(F_{\circ}) = 0.0305 \ (I > 2\sigma(l)), \ wR(F_{\circ}^{2}) = 0.0708$ (all data), 240 refined parameters. Crystal data for 3: C₂₁H₂₃Br₅N₂Si₂, M = 759.14, orthorhombic, space group $P2_12_12_1$, a = 11.1177(5), b = 13.9333(7), c = 16.9301(4) Å. V = 2622.6(2) Å³, $Z = 4, \rho_{calc} =$ 1.923 Mg m⁻³, μ (Mo K α) = 7.766 mm⁻¹, 13453 collected reflections, 4586 crystallographically independent reflections [$R_{int} = 0.0687$], 3015 reflections with $I > 2\sigma(l)$, $\theta_{\text{max}} = 25.00^\circ$, $R(F_\circ) = 0.0410$ $(I > 2\sigma(l))$, $wR(F_o^2) = 0.0690$ (all data), 276 refined parameters, Flack parameter: 005(14). Crystal data for 5: $C_{21}H_{24}Br_2N_2Si$, M = 492.33, orthorhombic, space group $Pna2_1$, a = 18.7680(4), b = 7.8976(2), c = 14.2285(5) Å. $\bar{V} = 2108.98(10)$ Å³, Z = 4, $\rho_{calc} = 1.551$ Mg m⁻³, μ (Mo K α) = 3.908 mm⁻¹, 11209 collected reflections, 3592 crystallographically independent reflections [$R_{int} = 0.0431$], 2875 reflections with $I > 2\sigma(l)$, $\theta_{\text{max}} = 25.00^{\circ}, R(F_{\circ}) = 0.0294 (I > 2\sigma(l)), wR(F_{\circ}^{2}) = 0.0521 \text{ (all data)},$ 240 refined parameters, Flack parameter: 008(8). Crystals of 2, 3, and 5 were each mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data of compounds 2, 3 and 5 were collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K (Mo-Kα radiation, $\lambda = 0.71073$ Å). CCDC 705079–705081.
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