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Stable bidentate silylene adducts of alkaline-earth amides

Xiaofei Sun,[a] Alexander Hinz,[a] Michael T. Gamer,[a] and Peter. W. Roesky*[a]

Dedicated to Prof. D. Fenske on the occasion of his 80th birthday

The coordination chemistry of silylenes is known for a vast number of elements of all blocks of the periodic table. However, only a handful of examples of silylene complexes have been reported for heavy alkaline-earth elements, which is mainly attributed to the "hard-soft" mismatch between the "hard" metal center and the "soft" silicon donor. Herein, we report the synthesis and characterization of a series of alkaline-earth silylene complexes comprising a bidentate pyridyl-amido-silylene ligand. The isolated Ca, Sr and Ba complexes show considerably increased stability in comparison to other known alkaline-earth silylene complexes. The molecular structures of all three complexes are essentially similar. Interestingly, depending on the central metal, the ^{1}H NMR chemical shifts of the *ortho*-H atom show unexpected large differences. DFT computations were conducted to elucidate this trend in the NMR resonances.

Over the past decades, a great variety of silylenes have been reported in the literature.[1] The coordination chemistry of silylenes is of continuing interest and has been studied toward elements from all blocks of the periodic table.[2] By now, silylenes have become indispensable building blocks spanning different fields in coordination and organometallic chemistry, homogenous catalysis and main group chemistry.[3] Despite the richness of contribution in this field, the number of alkaline-earth silylene complexes is still limited. The first examples (**A**–**D**, Figure 1) have only appeared in 2015,[4] almost 30 years after Jutzi's report on the first divalent silicon species.[5] The scarcity is mainly due to the "hard-soft" mismatch between the "hard" alkaline-earth metals and the "soft" silylene donors.[6] Therefore, the bonding of neutral silylenes toward highly electropositive alkaline-earth elements remains challenging. Following the first report by Blom and Driess,[4] our group reported the synthesis of the bis(silylene) calcium complex **E** in 2020.[7] By taking advantage of the chelating nature of the pincer-type bis(silylene) ligand, the successful coordination toward the Ca center was achieved. In this contribution, we investigate the coordination of the bidentate ligand $[\mathrm{L^{Ph}SiN}]$[8] (N=2-(methylamino)pyridine) comprising a rather "hard" pyridine and a "soft" silylene toward heavy alkaline-earth metal amides.

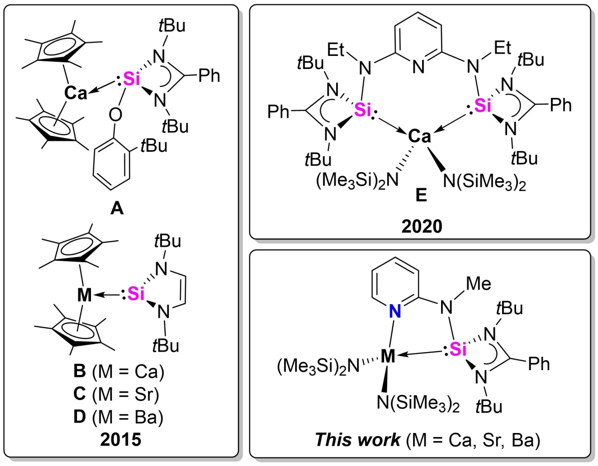
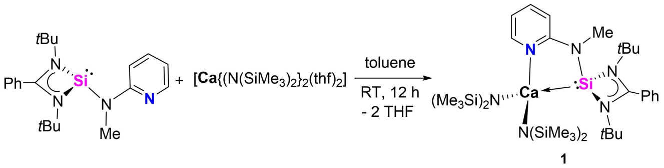


Figure 1. Alkaline-earth silylene complexes.[4,7]

Formation of a calcium complex bearing the bidentate pyridyl-amido-silylene ligand $[\mathrm{L^{Ph}SiN}]$ was first targeted. The THF-coordinated calcium silylamide complex $[\mathrm{Ca\{N(SiMe_3)_2\}_2(thf)_2}]$ was chosen as suitable starting material due to the vacant coordination site that can be generated *in situ* by decoordination of the THF molecules.

Stirring the two species in toluene at room temperature for 12 h led to the formation of the silylene complex **1** (Scheme 1), which could be isolated in analytically pure form as colorless solid in 72% yield. Single crystals suitable for X-ray diffraction analysis were obtained from a highly concentrated toluene solution at room temperature. In the ^{1}H NMR spectrum, three



Scheme 1. Synthesis of the calcium silylene complex **1**.

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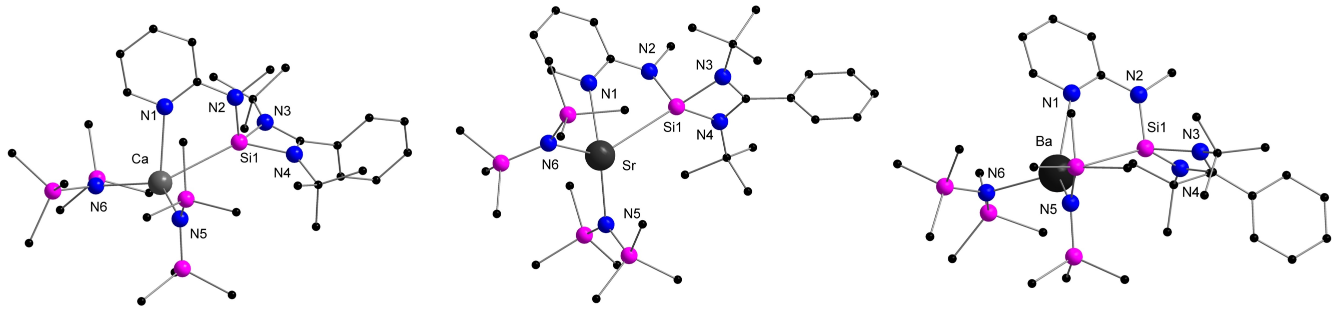


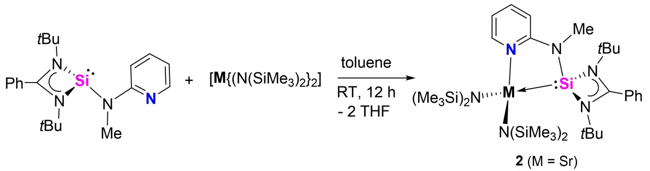
Figure 2. Molecular structures of **1** (left), **2** (middle) and **3** (right) in the solid state. H atoms are omitted for clarity. Selected bond length [Å] and angles [°] in **1**: Ca–Si1 3.0632(8), Ca–N1 2.489(2), Ca–N5 2.317(2), Ca–N6 2.300(2); Si1–Ca–N1 63.00(5), Si1–Ca–N5 104.47(5), Si1–Ca–N6 131.04(5), N1–Ca–N5 115.14(7), N1–Ca–N6 97.46(7), N5–Ca–N6 124.15(7). In **2**: Sr–Si1 3.2573(9), Sr–N1 2.685(3), Sr–N5 2.437(3), Sr–N6 2.458(3); Si1–Sr–N1 59.47(6), Si1–Sr–N5 104.48(7), Si1–Sr–N6 137.57(7), N1–Sr–N5 132.43(9), N1–Sr–N6 94.21(9), N5–Sr–N6 117.33(9). In **3**: Ba–Si1 3.391(4), Ba–N1 2.912(6), Ba–N5 2.577(10), Ba–N6 2.603(10); Si1–Ba–N1 55.4(2), Si1–Ba–N5 123.8(2), Si1–Ba–N6 115.0(3), N1–Ba–N5 98.4(3), N1–Ba–N6 135.7(3), N5–Ba–N6 116.5(4).

singlet signals were found at δ 2.41, 0.97 and 0.53 ppm, assignable to the NMe, *t*Bu and $SiMe_3$ protons, respectively. In the aromatic region, well-defined signals for the pyridine and phenyl groups were detected. All THF signals of the starting material $[Ca\{N(SiMe_3)_2\}_2(thf)_2]$ disappeared, indicating the successful displacement of THF by $[L^{Ph}SiN]$ and exclusive formation of complex **1**. Two signals were detected in the $^{29}Si\{^1H\}$ NMR spectrum (δ −5.5 ppm and −14.6 ppm), for the silylene and silyl groups, respectively. The coordination of the divalent silicon atom toward the Ca center led to a downfield-shifted signal (δ −5.5 ppm) compared to that of the free silylene (δ −12.0 ppm). The molecular structure was unambiguously determined by X-ray diffraction analysis and is depicted in Figure 2 (left). Complex **1** crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ and the geometry around the calcium center is distorted tetrahedral ($\tau = 0.74$).[9] The Ca–Si(II) bond length of 3.0632(8) Å is comparable to that found in the structurally related divalent Yb silylene complex (Yb–Si(II) 3.0766(7) Å),[10] which is consistent with the very close ionic radii of Ca^{2+} and Yb^{2+}.[11] The calcocene silylene complex **B** (3.2732(5) Å) and the bis(silylene) ligated Ca silylamide **E** (3.1646(8) and 3.2080(9) Å) have considerably longer Ca–Si(II) bonds (Figure 1). This indicates a significantly stronger interaction between Ca and Si(II) in complex **1**. In comparison to **E**, which could only be obtained at low temperatures (below −30 °C), and readily decomposes through Si(II)–N bond cleavage at higher temperatures, the replacement of the bidentate bis(silylene) by the bidentate mono(silylene) comprising only one amido-pyridine moiety has led to increased thermal stability. Although **1** is highly sensitive toward air and moisture, it is stable in the solid state as well as in solution (toluene or C_6D_6) for at least several weeks.

Molecular complexes with M–Si (M = Sr, Ba) bonds are exceptionally scarce, most of them are bearing tetravalent silanide substituents.[12] The first and only examples of heaviest stable alkaline-earth (Sr, Ba) silylene complexes **C** and **D**[4b] are not stable at room temperature, as they were found to decompose into the respective 1,4-diazabuta-1,3-diene M(II) complexes and Si(0). With the aim of synthesizing stable Sr and Ba silylene complexes, again, we employed silylamides $[M\{N(SiMe_3)_2\}_2]$ (M = Sr, Ba) as starting materials. Reaction of $[M\{N(SiMe_3)_2\}_2]$ with $[L^{Ph}SiN]$ (1:1 molar ratio) afforded the corresponding Sr and Ba silylene complexes **2** and **3** in good yields (75% and 79%), respectively (Scheme 2). The identities of both species were confirmed by a combination of ^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$ NMR spectroscopy, IR spectroscopy and X-ray diffraction analysis.

$^{29}Si\{^1H\}$ NMR studies show that the chemical shift of the silylene silicon nucleus of the Sr complex **2** (δ −5.1 ppm) is comparable to that of complex **1** (δ −5.5 ppm) and that of the Ba complex **3** is detected at a slightly lower field (δ −0.3 ppm). Single crystals were obtained from concentrated toluene solutions at room temperature and their molecular structures are shown in Figure 2 (**2**: middle; **3**: right). Although both molecules are isostructural to **1**, they crystallize in different space groups. The Sr complex **2** crystallizes in the centrosymmetric orthorhombic space group *Pbca* and the Ba analogue **3** in the non-centrosymmetric monoclinic space group *Cc*. Both metal centers are distorted tetrahedrally coordinated by the Si(II) and N atoms of the silylene ligand and two amido nitrogen atoms ($\tau = 0.64$ for **2** and $\tau = 0.71$ for **3**).[9]

As expected, due to the similar ionic radii of Sr^{2+} and Eu^{2+},[11] there is only little variation in the bonding parameters of **2** in comparison with the analogues divalent europium complex.[10] The Sr–Si(II) bond length of 3.2573(9) Å is some-



2 (M = Sr)
3 (M = Ba)

Scheme 2. Synthesis of the strontium and barium silylene complexes **2** and **3**.

what longer than the Sr–Si(II) bond lengths in the Sr silanides, $[Sr(thf)_3\{Si(SiMe_3)_3\}_2]$ (3.196 Å) and $[Sr(tmeda)(thf)(Si(SiMe_3)_3)]$ (3.223 Å, tmeda = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine),[12a] which is consistent with the larger ionic radius of Si^{2+} compared to Si^{4+}. The Ba–Si(II) bond length in complex **3** (3.391(4) Å) is significantly longer. This nicely correlates to the increasing ionic radii from Ca^{2+} to Ba^{2+}.[11] Moreover, as the ionic radii grow gradually from Ca^{2+} to Ba^{2+} (for six-coordinate metal centers: Ca: 1.00 Å, Sr: 1.18 Å, Ba: 1.35 Å),[11] the elongation of the respective M–Si bond is smaller than that of the M–N bonds, which reflects the more pronounced "hard-soft" mismatch between the increasingly soft metal center with the soft silicon versus the hard nitrogen donor. The silylene complexes of the heaviest alkaline-earth elements Sr and Ba are also stable at room temperature both in the solid state and in solution for several weeks. To the best of our knowledge, complexes **2** and **3** are the first examples of thermally stable Sr and Ba silylene complexes, as no decomposition could be detected after prolonged storage of the solution.

Interestingly, when comparing the ^{1}H NMR spectra of all three complexes **1**–**3**, we noticed that all proton signals (except the signal of the *ortho*-H of pyridine) are only marginally shifted compared with each other by maximum 0.04 ppm, which indicates that the different metal centers have little effect on the chemical environment of the H-atoms.

In sharp contrast, the *ortho*-^{1}H of the pyridine becomes more shielded as the signal is upfield shifted from Ca (δ 9.09 ppm) to Sr (δ 8.86 ppm) to Ba (δ 8.45 ppm, Figure 3). While this resonance in the Ba compound **3** is comparable to that of the non-coordinated pyridyl-silylene (δ 8.49 ppm), the corresponding signals for the Sr compound **2** and the Ca compound **1** are considerably downfield-shifted. This is in accord with a decrease in shielding upon coordination of metal sites. The comparison to the free ligand might suffer from rotation of the pyridyl moiety which could influence its ^{1}H NMR resonances. The overall shift by 0.63 ppm is remarkably large and matches with the trend observed for the *ortho*-^{13}C NMR shift in their respective ^{13}C NMR spectra (**1** δ 148.1 ppm; **2** δ 146.7 ppm; **3** δ 145.2 ppm). This increased shielding might be explained by the increasing "softer" nature from Ca^{2+} to Ba^{2+}, which lead to a decreased interaction with the rather "harder" pyridine moiety. Therefore, the pyridine nitrogen atom is more electron rich in **3**, which in turn can shield the neighbor C–H moiety more efficiently. The observed NMR-spectroscopic data in ^{1}H and $^{13}C\{^1H\}$ are qualitatively reproduced by DFT computations: The predicted ^{1}H NMR shifts decrease in the sequence **1** (δ 9.40 ppm) > **2** (δ 9.36 ppm) > **3** (δ 8.06 ppm), and the ^{13}C NMR shifts of the attached C atom behave accordingly (**1** δ 148.4 ppm; **2** δ 148.2 ppm; **3** δ 143.4 ppm). This is unusual, as frequently, the heavier the metal atom, the more downfield-shifted the ^{1}H NMR resonances in close proximity are.[13] In an attempt to rationalize the divergent behavior in the series of silylene complexes, NBO and AIM analyses were carried out (Table 1). The computed natural charges on the metal ion, the pyridyl moiety and the silylene donor differ only marginally. The computed Ba–Si and Ba–N bond lengths show differences to the experimentally observed ones, but the trend is clear: The heavier the metal ion, the smaller the difference between the two types of contacts is. It decreases along the sequence **1** (0.48 Å) > **2** (0.44 Å) > **3** (0.37 Å). The natural occupancies of the donor lone pairs of Si and N is again relatively unchanged within the series. As expected, the Wiberg Bond Index (WBI) for both bond types decrease slightly, the heavier the metal atom is, indicating lower covalency of the interaction. The second order perturbation theory calculations show a stronger interaction with Si, but a weaker interaction with N the heavier the metal ion is. Topologically, the interactions become weaker the heavier the central atom is.

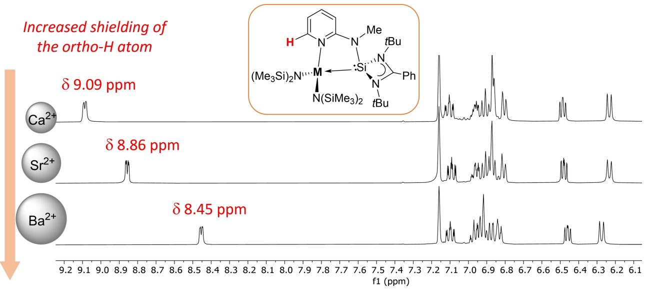


Figure 3. Stacked cut-out of the ^{1}H NMR spectra of complexes **1** (top), **2** (middle) and **3** (bottom).

This can be interpreted in the way that the bidentate ligand has a hard (pyridine) and a soft (silylene) coordination site. The interaction of both donor atoms with the metal ion becomes weaker, the heavier the metal ion is. This is more pronounced for the hard donor N. Consequently, less electron density is shared with the metal ion, and the pyridine moiety, most notably on the *ortho*-C and *ortho*-H atom is more shielded, which is reflected in the observed and computed NMR resonances.

Table 1. Summary of computed data.

	$1^{Calcd.}$	$2^{Calcd.}$	$3^{Calcd.}$
M–N [Å]	2.53	2.73	2.98
M–Si [Å]	3.01	3.17	3.35
Δ [Å]	0.48	0.44	0.37
q(M) [e]	1.78	1.80	1.80
q(N) [e]	-0.66	-0.65	-0.63
q(C) [e]	0.07	0.07	0.07
q(H) [e]	0.23	0.23	0.21
q(Si) [e]	1.08	1.07	1.08
N_{LP} [e]	1.89	1.89467	1.89
PTB [kcal/mol]	4.03	2.46	1.67
WBI	0.04	0.0245	0.02
Si_{LP} [e]	1.88	1.88689	1.89
PTB [kcal/mol]	15.36	17.52	17.70
WBI	0.11	0.095	0.08
M–N (ρ)	2.86E-02	2.42E-02	2.02E-02
M–N (∇_ρ)	1.29E-01	9.61E-02	7.00E-02
M–Si (ρ)	2.11E-02	2.03E-02	1.92E-02
M–Si (∇_ρ)	5.42E-02	4.83E-02	4.32E-02

PTB = 2nd order pertubation theory analysis stabilization energy.

In summary, we succeeded in the preparation and characterization of a series of stable heavy alkaline-earth (Ca, Sr, Ba) silylene complexes. By using the pyridyl-amido-functionalized silylene [L^{Ph}SiN], the chelating ability of this bidentate ligand allows the successful coordination toward the highly electropositive metal centers. The complexes were characterized by X-ray diffraction analysis, NMR and IR spectroscopy. The isolated Ca, Sr and Ba complexes show considerably increased stability in comparison to other known alkaline-earth silylene complexes. Interestingly, depending on the central metal, the chemical shifts of the *ortho*-H atom show unexpected large differences.

Experimental Section

All air- and moisture-sensitive manipulations were performed under dry N_2 or Ar atmosphere using standard Schlenk techniques or in an argon-filled MBraun glovebox, unless otherwise stated. Et_2O, *n*-pentane, and toluene were dried using an MBraun solvent purification system (SPS-800) and degassed. THF and was distilled under nitrogen from potassium benzophenone ketyl. C_6D_6 was dried over Na–K alloy and degassed by three freeze-pump-thaw cycles. [L^{Ph}SiN] (L^{Ph} = PhC(N*t*Bu)$_2$)[8] [Ca{N(SiMe$_3$)$_2$}$_2$(thf)$_2$][14] and [M{N(SiMe$_3$)$_2$}$_2$][15] (M = Sr, Ba) were prepared according to the literature procedures. All other chemicals were obtained from commercial sources and used without further purification. Elemental analyses were carried out with an Elementar vario MICRO cube. NMR spectra were recorded on Bruker spectrometers (Avance III 300 MHz, Avance 400 MHz or Avance III 400 MHz). Chemical shifts are referenced internally using signals of the residual protio solvent (^{1}H) or the solvent (^{13}C{^{1}H}) and are reported relative to tetramethylsilane (^{1}H, ^{13}C{^{1}H}), or externally relative to tetramethylsilane (^{29}Si). All NMR spectra were measured at 298 K. The multiplicity of the signals is indicated as s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet and br = broad. Assignments were determined based on unambiguous chemical shifts, coupling patterns and ^{13}C-DEPT experiments or 2D correlations. Infrared (IR) spectra were recorded in the region 4000–400 cm^{-1} on a Bruker Tensor 37 FTIR spectrometer equipped with a room temperature DLaTGS detector, a diamond attenuated total reflection (ATR) unit and a nitrogen-flushed chamber. In terms of their intensity, the signals were classified into different categories (vs = very strong, s = strong, m = medium, w = weak, and sh = shoulder).

*Synthesis of **1***: To a mixture of [Ca{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] (0.100 g, 0.198 mmol) and [L^{Ph}SiN] (0.073 g, 0.198 mmol) was condensed toluene (10 mL) at −88 °C, and the resulting mixture was stirred at room temperature for 12 h. All volatiles were removed under reduced pressure. The resulting solid was washed with cold *n*-pentane (5 mL) and dried *in vacuo* for 10 min, affording the title compound as a white solid. Crystals suitable for X-ray diffraction analysis were obtained from a concentrated toluene solution at room temperature. Yield: 0.104 g (0.143 mmol), 72 %. Anal. Calcd. for $C_{33}H_{66}N_6Si_5Ca$ (727.44 g/mol): C, 54.49; H, 9.15; N, 11.55. Found: C, 54.74; H, 8.72; N, 11.09. ^{1}H NMR (400.3 MHz, C_6D_6): (ppm) = 9.09 (dd, $^3J_{HH}$ = 5.3 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, CH_{py}), 7.11 (dt, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, CH_{py}), 6.98-6.80 (m, 5H, CH_{Ph}), 6,49 (ddd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 5.3 Hz,$^4J_{HH}$ ≈ 1.0 Hz 1H, CH_{py}), 6.24 (d, $^3J_{HH}$ = 8.6 Hz, 1H, CH_{py}), 2.41 (s, 3H, NCH_3), 0.97 (s, 18H, C(CH_3)$_3$), 0.53 (s, 36H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (100.67 MHz, C_6D_6): δ (ppm) = 169.1 (NCN), 163.3 (C_{py}), 148.1 (C_{py}), 140,7 (C_{py}), 132.0 ($C_{q\ Ph}$), 130.4 (C_{Ph}), 129.4 (C_{Ph}), 128.4 (C_{Ph}), 128.0 (C_{Ph}), 127.8 (C_{Ph}), 114.4 (C_{py}), 108.7 (C_{py}), 54.6 (C(CH_3)$_3$), 31.3 (C(CH_3)$_3$), 30.3 (NCH_3), 6.5 (Si(CH_3)$_3$). ^{29}Si{^{1}H} NMR (79.52 MHz, C_6D_6): δ (ppm) = −5.5 (N*Si*N), −14.6 (*Si*Me$_3$). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2955 (vs), 2166 (w), 1646 (m), 1599 (vs), 1563 (sh), 1481 (vs), 1440 (m), 1415 (m), 1363 (m), 1315 (m), 1237 (s), 1201 (s), 1117 (m), 1036 (vs), 928 (w), 866 (s), 818 (vs), 758 (s), 705 (m), 680 (m), 658 (w), 629 (w), 589 (w), 526 (w), 484 (w), 430 (w).

*Synthesis of **2***: To a mixture of [Sr{N(SiMe$_3$)$_2$}$_2$] (0.100 g, 0.245 mmol) and [L^{Ph}SiN] (0.088 g, 0.245 mmol) was condensed toluene (10 mL) at −88 °C, and the resulting mixture was stirred at room temperature for 12 h. All volatiles were removed under reduced pressure. The resulting solid was washed with cold *n*-pentane (5 mL) and dried *in vacuo* for 10 min, affording the title compound as a white solid. Crystals suitable for X-ray diffraction analysis were obtained from a concentrated toluene solution at room temperature. Yield: 0.143 g (0.184 mmol), 75 %. Anal. Calcd. for $C_{33}H_{66}N_6Si_5Sr$ (774.98 g/mol): C, 51.15; H, 8.58; N, 10.84. Found: C, 51.22; H, 8.28; N, 10.53. ^{1}H NMR (400.3 MHz, C_6D_6): δ (ppm) = 8.86 (ddd, $^3J_{HH}$ = 5.2 Hz, $^4J_{HH}$ = 2.0 Hz, $^4J_{HH}$ = 0.7 Hz, 1H, CH_{py}), 7.09 (ddd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, CH_{py}), 6.98-6.79 (m, 5H, CH_{Ph}), 6.48 (ddd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 5.2 Hz,$^4J_{HH}$ ≈ 0.9 Hz 1H, CH_{py}), 6.23 (d, $^3J_{HH}$ = 8.6 Hz, 1H, CH_{py}), 2.40 (s, 3H, NCH_3), 0.96 (s, 18H, C(CH_3)$_3$), 0.51 (s, 36H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (100.67 MHz, C_6D_6): δ (ppm) = 167.3 (NCN) 163.3 (C_{py}), 146.7 (C_{py}), 140,5 (C_{py}), 132.2 ($C_{q\ Ph}$), 130.4 (C_{Ph}), 129.4 (C_{Ph}), 128.4 (C_{Ph}), 128.0 (C_{Ph}), 127.7 (C_{Ph}), 114.7 (C_{py}), 108.7 (C_{py}), 53.6 (C(CH_3)$_3$), 31.3 (C(CH_3)$_3$), 30.2 (NCH_3), 6.3 (Si(CH_3)$_3$). ^{29}Si{^{1}H} NMR (79.52 MHz, C_6D_6): δ (ppm) = −5.1 (N*Si*N), −16.8 (*Si*Me$_3$). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2959 (s), 2903 (sh), 2869 (sh), 1645 (m), 1605 (m), 1577 (sh), 1477 (s), 1419 (s), 1358 (sh), 1329 (w), 1290 (w), 1250 (s), 1205 (sh), 1158 (w), 983 (vs), 838 (vs), 797 (sh), 772 (sh), 703 (w), 583 (w), 472 (w).

*Synthesis of **3***: To a mixture of [Ba{N(SiMe$_3$)$_2$}$_2$] (0.100 g, 0.198 mmol) and [L^{Ph}SiN] (0.073 g, 0.198 mmol) was condensed toluene (10 mL) at −88 °C, and the resulting mixture was stirred at room temperature for 12 h. All volatiles were removed under reduced pressure. The resulting solid was washed with cold *n*-pentane (5 mL) and dried *in vacuo* for 10 min, affording the title compound as a white solid. Crystals suitable for X-ray diffraction analysis were obtained from a concentrated toluene solution at room temperature. Yield: 0.144 g (0.143 mmol), 79 %. Anal. Calcd. for $C_{33}H_{66}N_6Si_5Ba$ (824.69 g/mol): C, 48.06; H, 8.07; N, 10.19. Found: C, 47.87; H, 7.49; N, 9.70. ^{1}H NMR (400.3 MHz, C_6D_6): δ (ppm) = 8.45 (dd, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, CH_{py}), 7.10 (ddd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.9 Hz, 1H, CH_{py}), 6.99-6.82 (m, 5H, CH_{Ph}), 6,46 (ddd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 5.1 Hz,$^4J_{HH}$ ≈ 1.0 Hz 1H, CH_{py}), 6.26 (d, $^3J_{HH}$ = 8.6 Hz, 1H, CH_{py}), 2.42(s, 3H, NCH_3), 0.97 (s, 18H, C(CH_3)$_3$), 0.49 (s, 36H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (100.67 MHz, C_6D_6): δ (ppm) = 166.4 (NCN) 163.3 (C_{py}), 145.2 (C_{py}), 140.2 (C_{py}), 132.4 ($C_{q\ Ph}$), 130.3 (C_{Ph}), 129.4 (C_{Ph}), 128.3 (C_{Ph}), 128.1 (C_{Ph}), 127.8 (C_{Ph}), 114.8 (C_{py}), 108.7 (C_{py}), 53.5 (C(CH_3)$_3$), 31.3 (C(CH_3)$_3$), 30.3 (NCH_3), 6.0 (Si(CH_3)$_3$). ^{29}Si{^{1}H} NMR (79.52 MHz, C_6D_6): δ (ppm) = −0.3 (N*Si*N), −18.8 (*Si*Me$_3$). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2960 (vs), 2901 (sh), 2869 (sh), 1645 (s), 1602 (vs), 1546 (w), 1478 (s), 1445 (m), 1420 (m), 1385 (m), 1357 (s), 1329 (w), 1291 (m), 1249 (s), 1204 (m), 1157 (w), 1140 (w), 981 (vs), 838 (s), 770 (m), 754 (m), 744 (m), 701 (m), 493 (w).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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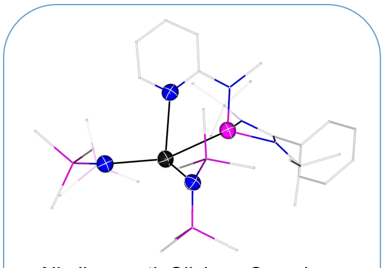

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Stable bidentate silylene adducts of alkaline-earth amides