N-Aryl substituted heterocyclic silylenes†

Lingbing Kong, Jianying Zhang, Haibin Song and Chunming Cui*

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Two N-aryl substituted five-membered heterocyclic silylenes and their nickel complexes have been isolated and structurally characterized.

Since the first stable N-heterocyclic silylene (**A**) was reported by West in 1994,[1] several other types of cyclic silylenes have also been reported (Chart 1).[2,3] Among them, the five-membered heterocyclic silylenes, silicon analogues of the "Arduengo type" carbenes, are particularly attractive synthetic targets due to their fundamental interest and potential applications in transition metal catalysis[3] like N-heterocyclic carbenes (NHCs).[4] However, compared to a large number of isolable NHCs,[5] only a handful of analogous silylenes with *tert*-butyl and neopentyl substituents on the ring nitrogen atoms have been fully characterized. It appears surprising that few successful efforts[6] have been dedicated to the synthesis, structural characterization and reactivity of other N-substituted heterocyclic silylenes, probably due to the lack of reliable synthetic methods.[3b] Nevertheless, there is still a great demand for new N-heterocyclic silylenes for the understanding of the effects of steric and electronic factors on the stability, structure and reactivity of this family of silylenes.[3a,b] We, therefore, proposed to extend the synthesis and structural characterization of this series of N-aryl substituted silylenes since the steric and electronic effects on the phenyl rings can be tuned as required as shown by N-aryl substituted NHCs. The substituents on the phenyl rings and their different orientations have substantial effects on the properties of the carbenes themselves and their metal complexes.[5b] Herein, we report the synthesis and structures of the N-heterocyclic silylenes **4** and **5** with bulky aryl substituents on the ring nitrogen atoms and their corresponding nickel cyclooctadiene complexes. They represent the first structurally characterized five-membered heterocyclic silylenes with flanking N-aryl groups.

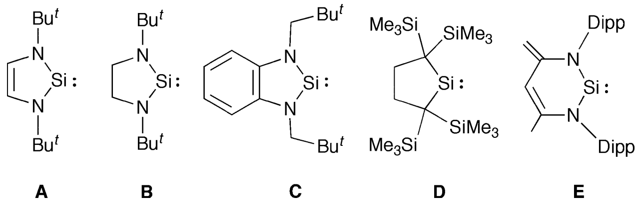
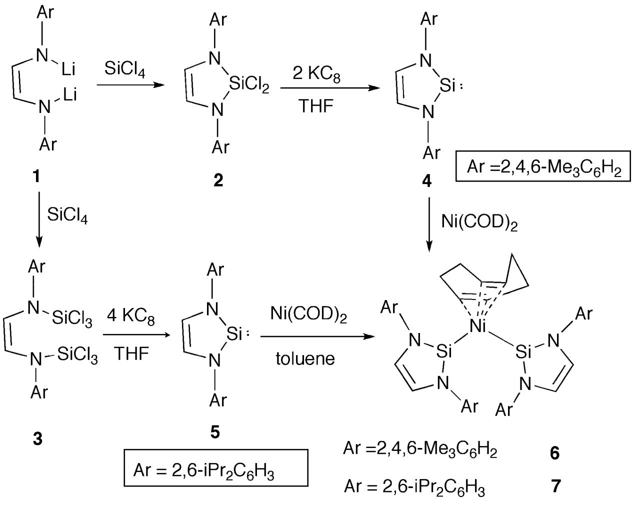


Chart 1

The aryl-substituted heterocyclic silylene **4**‡ was finally obtained as yellow crystals in *ca.* 43% yield by reduction of the corresponding dichloride **2**[6a] in THF at low temperature (from −78 to −30 °C) after various reducing conditions had been examined (Scheme 1). Similar reduction of **3**[6b] yielded **5** as yellow crystals in *ca.* 64% yield while reduction with six equiv. of KC_8 resulted in the formation of extremely air-sensitive orange materials, which have not been identified definitely at present. **5** was previously obtained by reduction of the corresponding silicon dichloride, but has not been structurally characterized.[6a] We found that easily available **3** is an excellent precursor for **5**,[6b] giving good and reproducible yields. The formation of **5** might involve the elimination of $(SiCl_2)_n$. However, we were unable to identify the insoluble materials due to the complicated composition. Previous unsuccessful efforts for the synthesis of crystalline N-aryl (phenyl, *p*-tolyl and mesityl) substituted heterocyclic silylenes[3b] suggested that the reduction conditions were important in the isolation of these N-aryl substituted silylenes. Both **4** and **5** do not decompose at 80 °C in C_6D_6 solution. The two compounds were fully characterized by ^1H, ^{13}C and ^{29}Si NMR spectroscopy, elemental analysis and X-ray single crystal analysis. The ^1H NMR spectra of **4** and **5** show a resonance for the five-membered ring protons at δ 6.29 and 6.47 ppm, respectively. Their ^{29}Si resonances in C_6D_6 fall at δ 77.8 ppm for **4** and 76.7 for **5**, quite close to that for **A** (δ = 78.3 ppm), indicating the formation of the N-heterocyclic silylenes.



Scheme 1

Single crystals of **4** were obtained from *n*-hexane at −40 °C. The structure is shown in Fig. 1 with selected bond parameters. The five-membered SiN_2C_2 central ring is essentially planar (the average deviation from the plane = 0.0015 Å) with the Si–N bond lengths of 1.750(2) and 1.743(2) Å, comparable to those found in **A**. The flanking mesityl rings are substantially twisted with

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State Key Laboratory and Institute of Elemento-organic Chemistry, Nankai University, Tianjin, 300071, People's Republic of China. E-mail: cmcui@nankai.edu.cn; Fax: +86-22-23503461; Tel: +86-22-23503461

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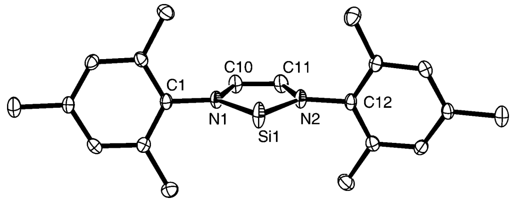

Fig. 1 Ortep drawing of **4** with 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–N1 1.750(2), Si1–N2 1.743(2), N1–C10 1.390(3), N1–C1 1.442(3), N2–C11 1.388(3), N2–C12 1.442(3), C10–C11 1.339(3)N1–Si1–N(2) 87.53(10), C10–N1–C1 120.96(19), C10–N1–Si1 113.30(16), C1–N1–Si1 125.70(16), C11–N2–C12 121.29(19), C11–N2–Si1 113.56(16), C12–N2–Si1 125.15(16).

respect to the SiN_2C_2 ring with the interplane angles of 89.0° and 105.3°. The N–C and C–C distances in the SiN_2C_2 ring are in the range of their representative values in aromatic systems, indicating the electron delocalization in the C_2N_2 plane. The N–Si–N angle of 87.53(10)° is slightly open in comparison with the calculated value for the N-phenyl substituted silylene (86.0°).[8] The wide Si1–N1–C1 and Si1–N2–C12 angles (125.70(16) and 125.15(16)°) leave the Si atom unprotected, suggesting that the π-electron donation from the nitrogen lone pairs is a major stabilizing factor.

Compound **5** crystallizes in the monoclinic system space group *C*2. The structure was modelled as consisting of disordered central C_2N_2Si atoms. The structure of **5** is shown in Fig. 2. The Si–N bond lengths (1.761(4) and 1.774(4) Å) are very close to those found in **4**, and longer than those in the corresponding dichloride (1.701(1) and 1.703(1) Å).[6a] The short N1–C25 and N2–C26 bond length (1.420(4) and 1.379(4) Å) and the long C25–C26 double bond length (1.391(7) Å) indicate the delocalization of the π-electrons on the central N1C25C26N2 plane. The N(1)–Si(1)–N(2) angle (87.50(17)°) is in line with that in **4**. Similar to **4**, **5** also features the wide Si–N–C(aryl) angles (127.8(3) and 127.4(2)°).

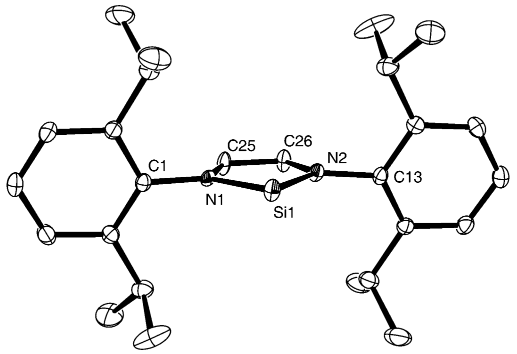

Fig. 2 Ortep drawing of **5** with 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–N1 1.761(4), Si1–N2 1.774(4), C25–N1 1.420(4), C26–N2 1.379(4), C25–C26 1.391(7)N1–Si1–N2 87.50(17), C25–N1–Si1 113.4(3), C26–N2–Si1 114.9(3), C25–C26–N2 111.9(3), C26–C25–N1 112.3(3), C1–N1–C25 118.9(3), C1–N1–Si1 127.8(3), C13–N2–Si1 127.4(2).

The twists of the aryl groups and wide Si–N–C(aryl) angles observed in **4** and **5** indicate that the divalent silicon atom is not efficiently protected by the flanking aryl groups. These structural features imply that the other silylenes of this type with less hindered groups might also be accessible provided that suitable synthetic routes were available. It is evident that the donation of the lone pairs on the nitrogen atoms to the divalent silicon atom is predominantly responsible for the stability of **4** and **5**.

It is anticipated that the steric effects afforded by N-substituents would be crucial to the geometry and coordination environments of the corresponding metal silylene complexes. It has been shown that the reactions of **A**, **B** and **C** with $Ni(COD)_2$ resulted in the formation of homoleptic trigonal planar Ni(**A**)$_3$ and Ni(**B**)$_3$ and tetrahedral Ni(**C**)$_4$ complexes, respectively.[7] To access the coordinative properties of the N-aryl heterocyclic silylenes, their reactions with $Ni(COD)_2$ were investigated for comparison. The reactions in THF at ambient temperature yielded **6** and **7** as yellow crystals, irrespective of the amount of the silylenes employed. The formation of **6** and **7** indicates that the steric bulkiness of the flanking aryl substituents of **4** and **5** may prevent the third silylene approaching the nickel atom. Complexes **6** and **7** were characterized by ^1H and ^{13}C NMR spectroscopy, elemental analysis and X-ray single-crystal analysis in the case of **7**.[7] The ^1H, ^{13}C NMR spectra of **6** and **7** clearly indicate the existence of one COD ligand and two silylene ligands. Single crystals of **7** were obtained from toluene at –40 °C. The structure of **7** was shown in Fig. 3 with selected bond lengths and angles. The molecule has a crystallographic C_2 axis. The two silylene ligands are coordinated to the Ni atom with the Si–Ni–Si angle of 101.91(4)°. The Ni–Si bond lengths (2.1395(8) Å) are shorter than those in Ni(**A**)$_2$(CO)$_2$ (2.207(2) and 2.216(2) Å) and slightly shorter than those found in trigonal Ni(**A**)$_3$ and Ni(**B**)$_3$ (2.144–2.175 Å. The Ni–C distances (2.130–2.146 Å) are very close to those in $Ni(COD)_2$ (2.11–2.13 Å).[9]

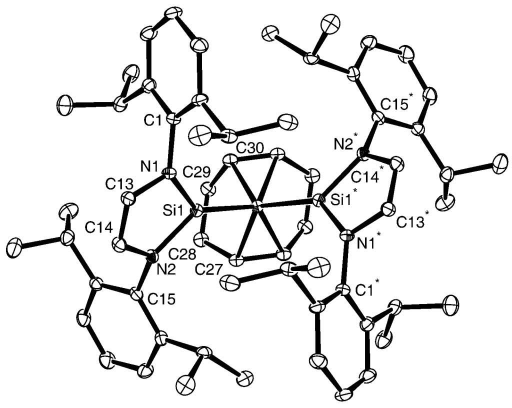

Fig. 3 Ortep drawing of **7** with 30% probability. §Hydrogen atoms and one toluene molecule have been omitted for clarity. Selected bond length and angles Selected bond lengths (Å) and angles (deg): Ni1–Si1 2.1395(8), Ni1–C27 2.130(3), Ni1–C30 2.146(2), Si1–N1 1.754(2), Si1–N2 1.754(2), N1–C13 1.410(3), N2–C14 1.394(3), N1–C1 1.452(3), C13–C14 1.330(3)Si1*–Ni1–Si1 101.91(4), C27–Ni1–C27* 99.89(13), C27–Ni1–Si1 98.40(7), C27–Ni1–C30 84.59(9), N2–Si1–N1 88.08(10), C13–N1–Si1 112.36(15), C1–N1–Si1 130.84(16), C14–N2–Si1 112.86(16), C15–N2–Si1 126.76(17). * 1 – *x*, *y*, 1.5 – *z*.

In summary, we have established suitable conditions for the reliable synthesis of the two N-aryl substituted heterocyclic silylenes **4** and **5** in good yield and structurally characterized them for the first time. The synthetic conditions may be applied to the other N-substituted silylenes so that the steric and electronic effects on the stability of this family of silylenes could be experimentally realized. Initial examination shows that the two silylenes could be used as ligands for transition metal complexes. These results showed that N-substituents may have significant effects on the structure of the silylene metal complexes. The reactivity studies of **4** and **5**, especially their transition metal complexes, and the synthesis of the other N-substituted heterocyclic silylenes are currently in progress.

Acknowledgements

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Notes and references

‡ **4**: A solution of **2** (1.95 g, 5.0 mmol) in THF (70 mL) was added to a suspension of potassium graphite (1.35 g, 10.0 mmol) at −78 °C. The reaction mixture was stirred for 4 d at low temperature. The volatiles were removed, and the residue was extracted with *n*-hexane (80 mL). After filtration, the yellow filtrate was concentrated and stored at −40 °C overnight to yield yellow crystals of **4** (0.69 g, 43.1%). M.p. 110–112 °C. ^{1}H NMR (C_6D_6): δ 2.17 (s, 6H, *p*-C*H*$_3$), 2.25 (s, 12H, *o*-C*H*$_3$), 6.29 (s, 2H, NC*H*), 6.83 (m, 4H, Ar*H*), ^{13}C NMR (C_6D_6): δ 18.5 (*p*-CH$_3$), 21.0 (*o*-CH$_3$), 124.4 (H*C*CH), 129.3, 134.8, 135.8, 140.3 (Ar*C*). ^{29}Si NMR (C_6D_6): δ 77.8. Anal. found for $C_{20}H_{24}N_2Si$: C 74.92, H 7.41, N 8.68. Calc. C 74.95, H 7.55, N 8.74. **5**: It was prepared similarly to **4** and obtained as yellow crystals (0.49 g, 60.8%). M.p. 131 °C. ^{29}Si NMR (C_6D_6): δ 76.7. Anal. found for $C_{26}H_{36}N_2Si$: C, 76.51, H, 8.66, N, 6.81. Calc. C 77.17, H 8.97, N 6.92. **6**: A solution of **4** (0.64 g, 2.0 mmol) and Ni(COD)$_2$] (0.27 g, 1.0 mmol) in THF (50 mL) was stirred for 24 h at room temperature. The solvents were removed, and the remaining solid was crystallized from toluene at −40 °C to yield yellow crystals of **6** (0.43 g, 53%). M.p. 192 °C (dec). ^{1}H NMR (C_6D_6): δ 1.35 (m, 4H, C*H*$_2$), 1.97 (m, 4H, C*H*$_2$), 2.05 (s, 12H, *p*-C*H*$_3$), 2.20 (s, 24H, *o*-C*H*$_3$), 3.93 (s, 4H, C*H*), 6.18 (s, 4H, NC*H*), 6.79 (s, 8H, Ar*H*). ^{13}C NMR (C_6D_6): δ 18.5 (*p*-*C*H$_3$), 20.9 (*o*-*C*H$_3$), 32.1 (*C*H$_2$), 79.5 (*C*H), 123.3 (H*CC*H), 129.2, 135.3, 135.5, 141.1 (Ar–*C*). Anal. found for $C_{48}H_{60}N_4NiSi_2$: C 71.52, H 7.86, N 6.92. Calc. C 71.36, H 7.49, N 6.94. **7**: it was prepared similarly to **6** and obtained as yellow crystals (0.68 g, 64%). M.p. 232 °C (dec). ^{1}H NMR (C_6D_6): δ 0.36 (d, 6H, CH*Me*$_2$), 1.04 (d, 6H, CH*Me*$_2$), 1.23 (t, 12H, CH*Me*$_2$), 1.32 (t, 12H, CH*Me*$_2$), 1.32 (m, 4H, C*H*$_2$), 1.38 (d, 12H, CH*Me*$_2$), 2.10 (s, 3H, Ph*C*H$_3$), 2.26 (m, 2H, CH$_2$), 2.59 (m, 2H, C*H*$_2$), 3.10 (m, 2H, C*H*Me$_2$), 3.17 (m, 2H, C*H*Me$_2$), 3.53 (m, 2H, C*H*Me$_2$), 3.77 (m, 2H, C*H*Me$_2$), 3.90 (m, 2H, C*H*), 4.51 (m, 2H, C*H*), 6.06 (d, 2H, *H*CC*H*), 6.16 (d, 2H, *H*CC*H*), 7.02–7.35 (m, 17H, Ar-*H*). ^{13}C NMR (C_6D_6): δ 23.3, 23.8, 24.0, 26.7, 27.3, 27.6, 27.8, 28.1, 28.3, 28.5, 30.0, 30.2 (CHMe$_2$), 34.0, 35.0 (CH$_2$), 80.4, 80.9 (CH),21.4, 125.7, 128.5, 129.3, 137.9 (toluene-C), 123.6, 123.9, 124.0, 124.8 (HCCH), 125.1, 125.4, 140.8, 141.2, 146,3, 146,4, 147.1, 147.2 (Ar–C). Anal. found $C_{67}H_{92}N_4NiSi_2$: C 75.34, H 8.74, N 5.22. Calc. C 75.32, H 8.68, N 5.24.

§ The X-ray data were collected on a Bruker Smart-CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 113 K. The structure was solved by direct methods (SHELXS-97)[10] and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97).[11] Crystal data for **4**: $C_{20}H_{24}N_2Si$, Fw = 320.50, monoclinic, space group $P2_1/c$, $a = 8.2595(17)$, $b = 13.842(3)$, $c = 16.171(3)$ Å, $\beta = 97.06(3)°$, $V = 1834.9(6)$ Å^3, Z = 4, $\rho_{\text{calcd}} = 1.160$ g cm^{-3} 13 920 reflections, 3234 unique (Rint = 0.0642)$R1$ = 0.0631 ($I > 2\sigma(I)$), $wR2$ = 0.1694 (all data). **5**: $C_{26}H_{36}N_2Si$, Fw = 404.66, monoclinic, space group $C2$, $a = 20.089(4)$, $b = 6.4762(13)$, $c = 20.030(4)$ Å, $\beta = 102.71(3)°$, $V = 2576.3$ (9) Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.043$ g cm^{-3} 15 860 reflections, 6011 unique (Rint = 0.0408) $R1$ = 0.0489 ($I > 2\sigma(I)$), $wR2$ = 0.1315 (all data). **7**·C_7H_8: $C_{67}H_{92}N_4NiSi_2$, Fw = 1068.34, orthorhombic, space group $Pbcn$, $a = 13.558(3)$, $b = 18.331(4)$, $c = 24.290(5)$ Å, $V = 6037(2)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.175$ g cm^{-3} 38 920 reflections, 5323 unique (Rint = 0.0684) $R1$ = 0.0684 ($I > 2\sigma(I)$), $wR2$ = 0.1772 (all data).

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