

**Abnormal Carbene-Silicon Halide Complexes**

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Abnormal Carbene-Silicon Halide Complexes

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Reaction of the anionic N-heterocyclic di-carbene (NHDC), [C{[N(2,6-Prⁱ₂C₆H₃)]₂CHCl}]_n (1), with SiCl₄ gives the trichlorosilyl-substituted (at the C4 carbon) N-heterocyclic carbene complex (7). Abnormal carbene-SiCl₄ complex (8) can be conveniently synthesized by combining 7 with HCl·NEt₃. In addition, 7 may react with CH₂Cl₂ in warm hexane, giving the abnormal carbene-complexed SiCl₃⁺ cation (9). The nature of bonding in 9 was probed with complementary DFT computations.

Low-oxidation-state main-group chemistry has made enormous strides over the past few decades.¹⁻⁷ Sterically demanding ligands have usually been employed to stabilize these unusual main-group species. N-heterocyclic carbenes, as potent σ-donor ligands, have played a major role in these recent advances.⁵⁻¹³ For instance, a series of unusual zero-oxidation-state E_n (n = 1, E = C,¹⁴⁻¹⁶ Si,¹⁷⁻¹⁹ Ge,^{20,21} n = 2, E = B,²² C,^{23,24} Si,^{25,26} Ge,²⁷ Sn,²⁸ P,^{29,30} As,³¹ and Sb³²) species have been isolated via carbene-stabilization. These syntheses usually involve alkali (or alkaline earth) metal reduction of the corresponding carbene-complexed EX_n (X = halides). Notably, both N-heterocyclic carbenes (NHC, I in Fig. 1) and cyclic (alkyl)(amino)carbenes³³ (CAAC, IV in Fig. 1) have been extensively utilized in stabilizing these highly reactive main group species.^{7,11}

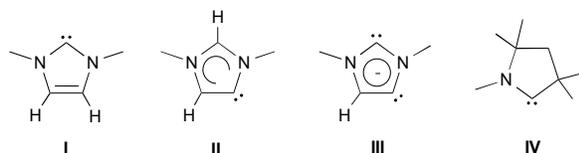
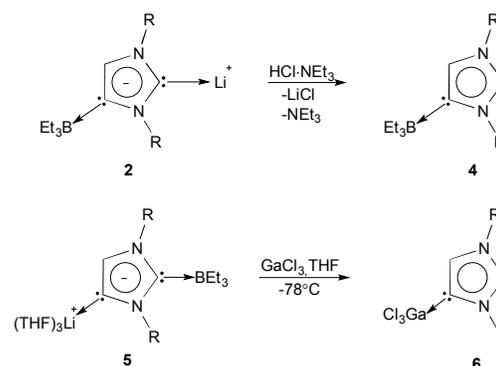


Fig. 1 Imidazole-based carbenes (I-III) and CAAC (IV)

However, *abnormal* N-heterocyclic carbene (*α*NHC, II in Fig.

1)-based low-oxidation-state main group chemistry remains largely undeveloped.³⁴

Since Crabtree's seminal discovery of the first *α*NHC-based transition metal complexes,³⁵ have been actively utilized in organometallic synthesis and catalysis.³⁶⁻³⁸ It is generally accepted that *α*NHCs, possesses stronger σ-donation capability than normal NHCs. Considering the fragile nature of *α*NHCs (compared to NHCs), Bertrand's isolation of the first stable *α*NHC represents a remarkable breakthrough in this field.^{39,40} In contrast to the rapidly developing normal NHC-based low-oxidation-state silicon chemistry, the literature reveals a paucity of studies on *α*NHC-based complexes.^{41,42} This may be largely due to the lack of convenient access to the corresponding *α*NHC-silicon halide precursors (To the best of our knowledge, *α*NHC-based SiCl₂ and SiH₂Cl₂ complexes represent the rare examples of this type).^{41,42} Thus, development of new synthetic routes of *α*NHC-silicon halides is important. Herein, we report the syntheses,⁴³ structures,⁴³ and computations⁴³ of SiCl₃-substituted (at the C4 carbon) NHC (7), and its abnormal carbene derivatives [*α*NHC:SiCl₄ (8) and *α*NHC₂SiCl₃⁺Cl⁻ (9)].



Scheme 1 NHDC-based synthesis of 4 and 6.

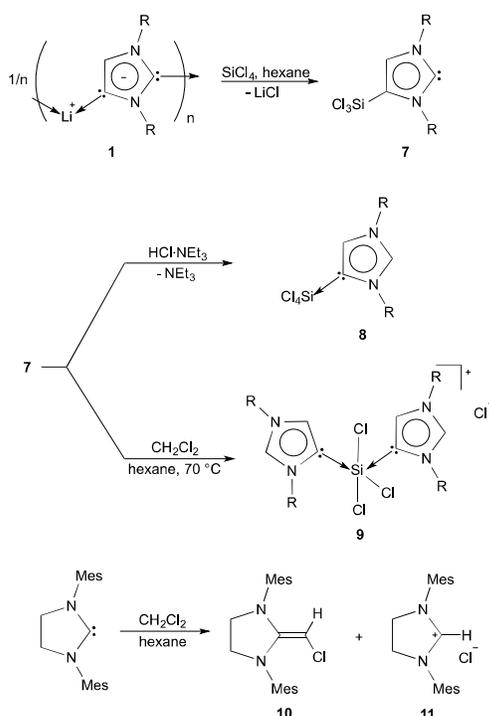
The anionic N-heterocyclic dicarbene (NHDC, III in Fig. 1) contains both C2 and C4 carbene centres.^{34,44} The first such anionic NHDC ligand (1) was synthesized by this laboratory *via*

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C4-lithiation of a NHC ligand $[\text{C}\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{CH}_2\}_2]$, which exhibits a polymeric chain structure.^{45,46} Recently, Lavallo synthesized a series of multi-anionic NHDC ligands, which contain one or two flanking anionic carborane groups.^{47,48} It is noteworthy that NHDC **1** has proven a unique platform from which α NHC-based group **12** and **13** complexes may be conveniently synthesized.⁴⁹⁻⁵¹ When **1** is combined with group **13** and **12** alkyls (*i.e.*, BEt_3 and ZnEt_2), respectively, only the corresponding C2-lithiated NHDC- BEt_3 (**2**) and - ZnEt_2 (**3**) adducts are isolated. Reactions of **2** or **3** with electrophiles gave the corresponding α NHC-based borane (**4**) and zinc complexes, respectively, *via* salt elimination (the **2**-to-**4** transformation is shown in Scheme 1; R = 2,6-diisopropylphenyl).^{49,50} Interestingly, **5**, the THF-solvated C4-lithiated isomer of **2**, reacts with GaCl_3 at low temperature to give an abnormal carbene- GaCl_3 adduct (**6** in Scheme 1).⁵¹ Notably, the syntheses of these α NHC-based group **12** and **13** complexes involve anionic NHDC-based precursors (such as **2** and **5**).



Scheme 2 NHDC-based synthesis of 7-9.

Now we report that α NHC-silicon halides (**8** and **9**) may be conveniently synthesized through a neutral trichlorosilyl-substituted N-heterocyclic carbene (**7**). The 1:1 reaction of **1** with SiCl_4 gives **7** (77.0% yield) (Scheme 2; R = 2,6-diisopropylphenyl). The addition of excess SiCl_4 does not result in the complexation of another SiCl_4 to the C2 carbon of the imidazole ring in **7**. While α NHC: SiCl_4 (**8**) was synthesized (95.9% yield) by combining **7** with $\text{HCl}\cdot\text{NEt}_3$ (in a 1:1 ratio), α NHC $_2\text{SiCl}_3^+\text{Cl}^-$ (**9**) was isolated as pale yellow crystalline solid (75.6% yield) by reaction **7** with excess CH_2Cl_2 (Scheme 2). The formation of **8** involves protonation of the C2 carbon of **7** and

addition of the Cl^- anion to the silicon centre in **7**. Although the mechanism remains obscure, the formation of **9** may be initiated from the reaction of the C2 carbene centre of **7** with CH_2Cl_2 . Indeed, CH_2Cl_2 has been reported to react with the NHC ligand $[\text{C}\{\text{N}(\text{Mes})\text{CH}_2\}_2]$, giving mono-chloro-olefin (**10**) and the imidazolium salt (**11**) (Scheme 2).⁵² The presence of mono-chloro-olefin byproduct in our case remains obscure since the sticky residue could not be characterized. The ^{29}Si NMR chemical shifts of **8** (-103.6 ppm) and **9** (-102.6 ppm) are comparable to that (-108.9 ppm) for $\text{L}\cdot\text{SiCl}_4$ (L = $[\text{C}\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{CH}_2\}_2]$),²⁵ which, however, shift dramatically upfield with compared to that (-13.5 ppm) for **7**.

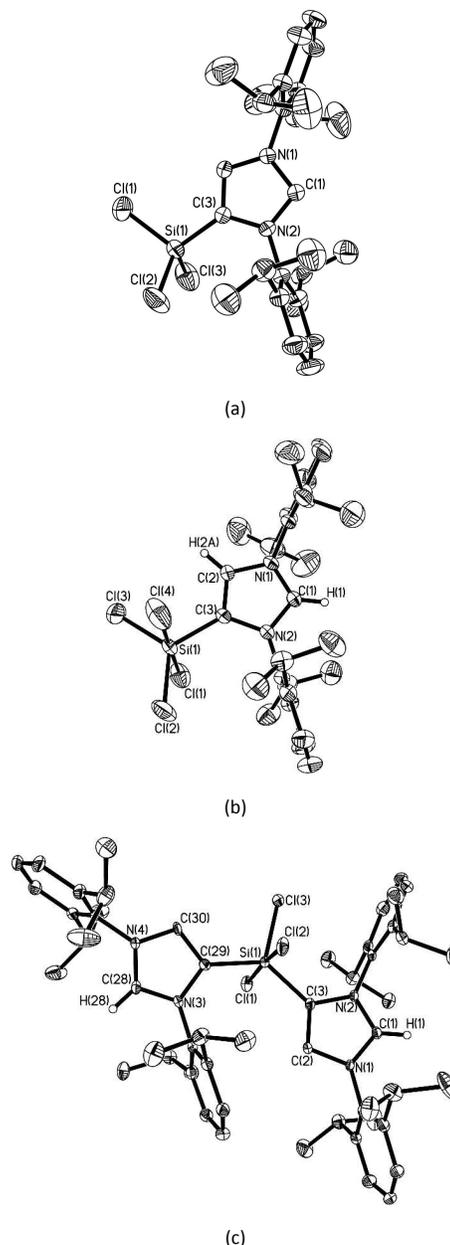


Fig. 2 Molecular structures of (a) **7**, (b) **8** and (c) **9**. Thermal ellipsoids represent 30% probability; hydrogen atoms on carbon are omitted for clarity, except for those at C(1) and C(2) of **8** and C(1) and C(28) of **9**. Selected bond distances (Å) and angles (deg) are

as follows. For **7**, Si(1)–C(3) 1.819(3), Si(1)–Cl(1) 2.0109(15), C(3)–Si(1)–Cl(1) 108.06(11), C(3)–Si(1)–Cl(2) 113.61(12), C(3)–Si(1)–Cl(3) 113.28(12). For **8**, Si(1)–C(3) 1.885(4), Si(1)–Cl(1) 2.191(2), Si(1)–Cl(2) 2.0552(19), Si(1)–Cl(3) 2.064(2), Si(1)–Cl(4) 2.201(2); C(3)–Si(1)–Cl(1) 90.52(14), C(3)–Si(1)–Cl(2) 123.18(15), C(3)–Si(1)–Cl(3) 114.70(15), Cl(2)–Si(1)–Cl(3) 122.11(8), Cl(1)–Si(1)–Cl(4) 179.35(9). For **9**, Si(1)–C(3) 1.896(5), Si(1)–C(29) 1.893(5), Si(1)–Cl(1) 2.2209(19), Si(1)–Cl(2) 2.2475(19), Si(1)–Cl(3) 2.0529(18); C(3)–Si(1)–C(29) 131.8(2), Cl(1)–Si(1)–Cl(2) 172.44(8), C(3)–Si(1)–Cl(3) 119.26(15), C(29)–Si(1)–Cl(3) 108.89(16), Cl(1)–Si(1)–Cl(3) 89.19(16).

Compound **7** crystallizes in the monoclinic space group $P_{2_1/n}$. The asymmetric unit contains two molecules of **7** and two THFs (Fig. 2; for clarity, only one molecule of **7** is shown). In **7**, the silicon atom is bound to the C4 carbon and adopts a distorted tetrahedral geometry. The $122.6(3)^\circ$ C(1)–N(1)–C(16) and $121.9(3)^\circ$ C(1)–N(2)–C(4) angles of **7** are only marginally smaller than those (123.52° , av) in the $[\text{C}\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{CH}_2\}]_2$ carbene ligand.⁵³ However, the fact that the C2 carbene centre of **7** is not inclined to bind another SiCl_4 may be ascribed to the steric and electronic effects of the trichlorosilyl substituent.

Regarding **8**, the H(1) atom residing at C(1) was located from difference Fourier map (Fig. 2). And the silicon centre adopts a trigonal bipyramidal geometry as a result of the equatorial coordination of the αNHC ligand. While the Si–C $_{\alpha\text{NHC}}$ bond distance [1.885(4) Å] for **8** is approximately 0.04 Å shorter than that [1.928(2) Å] in its normal carbene isomer $\text{L}:\text{SiCl}_4$ (L = $[\text{C}\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{CH}_2\}]_2$),²⁵ the Si–Cl bond distances [2.0552(19)–2.201(2) Å] for **8** compare well to those [2.0696(6)–2.1892(5) Å] in the latter. Both the Si–C bond [1.819(3) Å] and the Si–Cl bonds [2.002(2)–2.011(2) Å] in **7** are obviously shorter than those in **8**, $\text{L}:\text{SiCl}_4$ (L = $[\text{C}\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{CH}_2\}]_2$),²⁵ and **9** [$d_{\text{Si-C}} = 1.895(5)$ Å, av; $d_{\text{Si-Cl}} = 2.0529(18)$ – $2.2475(19)$ Å], respectively.

Single crystal X-ray structural analysis shows that in the solid state two neighbouring 9^+ (*i.e.*, $\alpha\text{NHC}_2\text{SiCl}_3^+$) fragments are connected via C $_{\text{NHC}}\text{--H}\cdots\text{Cl}^-$ hydrogen bonds [C $_{\text{NHC}}\cdots\text{Cl}^-$ distance = 3.267(5) Å, av; C $_{\text{NHC}}\text{--H}\cdots\text{Cl}^-$ bond angles = $165(5)^\circ$ and $171(5)^\circ$],⁵⁴ which result in the supramolecular assembly of **9** as a long chain. The five-coordinate silicon atom in **9** adopts a trigonal bipyramidal geometry with two carbene carbon atoms residing at the equatorial positions (Fig. 2). DFT computations on the simplified model $\alpha\text{NHC}_2\text{SiCl}_3^+$ ($\alpha\text{NHC} = [\text{HC}\{\text{N}(\text{Ph})_2\text{CHC}:\}]$ [**9-Ph**]⁺) show that two isomeric structures (as shown in Fig. 3) may exist.⁴³ The carbon atoms of the two carbene ligands may reside at the axial position (Fig. 3a) or at the equatorial position (Fig. 3b). The [**9-Ph**]⁺-a isomer is merely 0.05 kcal/mol in energy lower than [**9-Ph**]⁺-b isomer. The equatorial coordination of carbene ligands in **9** (in the solid state) may be ascribed to the steric bulk of the carbene ligands and the packing effects in crystals.

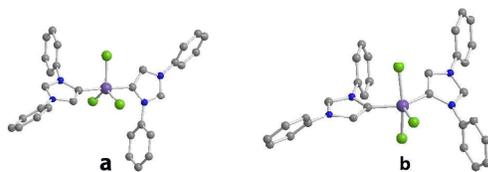


Fig. 3 The optimized isomeric structures [(a) αNHCs at the axial position; (b) αNHCs at the equatorial position] of the simplified model [**9-Ph**]⁺.

The axial Cl(1)–Si(1)–Cl(2) bond angle in **9** [$172.44(8)^\circ$] is about 10° larger than that in [**9-Ph**]⁺-b (163.27°). Meanwhile, the equatorial C(3)–Si(1)–C(29) bond angle in **9** [$131.8(2)^\circ$] is about 8° smaller than that in [**9-Ph**]⁺-b (139.62°). Thus, the trigonal bipyramidal geometry around the silicon atom in [**9-Ph**]⁺-b is more distorted than that for **9**. The axial Si–Cl bond distances of **9** (2.234 Å, av) are between those for **8** (2.196 Å, av) and those for [**9-Ph**]⁺-b (2.270 Å, av). The Si–Cl $_{\text{eq}}$ bond distance for **9** [2.0529(18) Å] compares well with that in [**9-Ph**]⁺-b (2.078 Å) and those in **8** (2.060 Å, av). In [**9-Ph**]⁺-a model, one Si–Cl $_{\text{eq}}$ bond (2.175 Å) is somewhat longer than the other two (2.143 Å). And the C–Si–C axis in [**9-Ph**]⁺-a is almost linear (the C–Si–C bond angle = 176.07°). Notably, the Si–C $_{\text{NHC}}$ bond distances in [**9-Ph**]⁺-a (1.982 Å) are obviously longer than those in [**9-Ph**]⁺-b (1.918 Å) and in **9** (1.895 Å, av). Natural bond orbital (NBO) analysis shows that the silicon atoms in [**9-Ph**]⁺-a and -b conformational isomers bear +1.33 and +1.38 positive charges, respectively.

Conclusions

The anionic NHDC ligand (**1**) has been utilized in preparing trichlorosilyl-substituted NHC ligand (**7**). Compound **7** may be employed in synthesizing abnormal carbene-silicon halide complexes (**8** and **9**). Compounds **8** and **9** provide a unique platform to access αNHC -based low-oxidation-state silicon chemistry, which is being explored in this group.

Acknowledgements

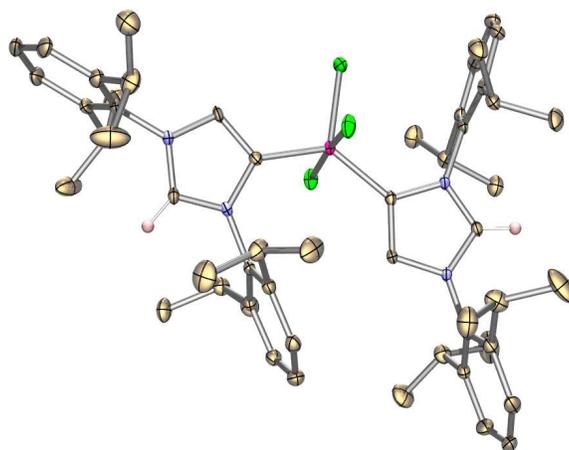
We are grateful to the National Science Foundation for support: CHE-1265212(G.H.R., Y.W.) and CHE-1361178 (H.F.S.).

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Graphic for Table of Contents



Reaction of the anionic NHDC ligand, $[\text{:C}\{\text{[N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{]}_2\text{CHCl}\text{I}}\}_n$ (**1**), with SiCl_4 gives the trichlorosilyl-substituted NHC ligand (**7**). Abnormal carbene- SiCl_4 complex (**8**) can be conveniently synthesized by combining **7** with $\text{HCl}\cdot\text{NEt}_3$. Meanwhile, **7** may react with CH_2Cl_2 in warm hexane, giving the abnormal carbene-complexed SiCl_3^+ cation (**9**). The structure and bonding of **9** have also been probed by DFT computations.