# 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), \([\text{NHC}]_{2}\), with SiCl\(_4\) gives the trichlorosilyl-substituted (at the C4 carbon) N-heterocyclic carbene complex (7). Abnormal carbene-SiCl\(_4\) complex \((8)\) can be conveniently synthesized by combining 7 with HCl-NET\(_3\). In addition, 7 may react with CH\(_2\)Cl\(_2\) in warm hexane, giving the abnormal carbene-complexed SiCl\(_3\) 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 α-donor ligands, have played a major role in these recent advances.\(^5\)\(^-\)\(^7\) 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;\(^27\)\(^-\)\(^28\) n = 3, E = P,\(^29\)\(^,\)\(^30\) As,\(^31\)\(^-\)\(^32\) and Sb\(^33\)\(^-\)\(^34\)) species have been isolated via carbene-stabilization. These syntheses usually involve alkali (or alkaline earth) metal reduction of the corresponding carbene-complexed E\(_n\) (X = halides). Notably, both N-heterocyclic carbenes (NHC, I in Fig. 1) and cyclic (alkyl)(amino)carbenes\(^35\) (CAAC, IV in Fig. 1) have been extensively utilized in stabilizing these highly reactive main group species.\(^7\)\(^,\)\(^11\)

![Imidazole-based carbenes (I-III) and CAAC (IV)](image)

However, abnormal N-heterocyclic carbene (αNHC, II in Fig. 1)-based low-oxidation-state main group chemistry remains largely undeveloped.\(^34\)

Since Crabtree’s seminal discovery of the first αNHC-based transition metal complexes,\(^35\) have been actively utilized in organometallic synthesis and catalysis.\(^36\)\(^-\)\(^38\) It is generally accepted that αNHCs possess stronger α-donation capability than normal NHCs. Considering the fragile nature of αNHCs (compared to NHCs), Bertrand’s isolation of the first stable αNHC 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 αNHC-based complexes.\(^41\)\(^,\)\(^42\) This may be largely due to the lack of convenient access to the corresponding αNHC-silicon halide precursors. (To the best of our knowledge, αNHC-based SiCl\(_3\) and SiH\(_2\)Cl\(_2\) complexes represent the rarest examples of this type).\(^41\)\(^,\)\(^42\) Thus, development of new synthetic routes of αNHC-silicon halides is important. Herein, we report the syntheses,\(^3\)\(^4\)\(^3\)\(^-\)\(^43\) and computations\(^43\) of SiCl\(_3\)-substituted (at the C4 carbon) NHC (7), and its abnormal carbene derivatives \([\alpha\text{NHC-SiCl}_4\] (8) and \([\alpha\text{NHC-SiCl}_3\text{Cl}]^+\) (9)).

Table 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
C4-lithiation of a NHC ligand [:C{N(2,6-Pr$_2$C$_6$H$_3$)CH}]$_2$, which exhibits a polymeric chain structure. Recently, Lavallo synthesized a series of multi-anionic NHDC ligands, which contain one or two flanking anionic carborane groups. It is noteworthy that NHDC 1 has proven a unique platform from which anHBC-based group 12 and 13 complexes may be conveniently synthesized. 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 anHBC-based borane (4) and zinc complexes, respectively, via salt elimination (the 2-to-4 transformation is shown in Scheme 1; R = 2,6-diisopropylphenyl). 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). Notably, the syntheses of these anHBC-based group 12 and 13 complexes involve anionic NHDC-based precursors (such as 2 and 5).

Now we report that anHBC-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 anHBC:SiCl$_4$ (8) was synthesized (95.9% yield) by combining 7 with HCl-NEt$_3$ (in a 1:1 ratio), anHBC$_2$SiCl$_3$Cl (9) was isolated as pale yellow crystalline solid (75.6% yield) by reaction 7 with excess CH$_2$Cl$_2$ (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$_2$Cl$_2$. Indeed, CH$_2$Cl$_2$ has been reported to react with the NHC ligand [:C{N(Mes)CH}]$_2$, giving mono-chloro-olefin (10) and the imidazolinium salt (11) (Scheme 2). 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 L:SiCl$_4$ (L = [:C{N(2,6-Pr$_2$C$_6$H$_3$)CH}]$_2$), which, however, shift dramatically upfield with compared to that (-13.5 ppm) for 7.

![Scheme 2 NHDC-based synthesis of 7-9.](image)

**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
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°) C(1)-N(1)-C(16) and 121.9(3°) C(1)-N(2)-C(4) angles of 7 are only marginally smaller than those (123.52°, av) in the \([\text{C(N}(2,6-\text{Pr}_2\text{C}_6\text{H}_3)\text{CH}_3])\] carbene ligand.\(^{53}\) However, the fact that the C2 carbene centre of 7 is not inclined to bond 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 aNHCl ligand. While the Si-C\(_\text{eq}\) 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 L:SiCl\(_{\text{eq}}\) (L: = \([\text{:C}{\text{N}}(2,6-\text{Pr}_2\text{C}_6\text{H}_3)\text{CH}]\)).\(^{25}\) The Si-Cl bond distances [2.0552(19)–2.0212(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, L:SiCl\(_4\) (L: = \([\text{C(N}(2,6-\text{Pr}_2\text{C}_6\text{H}_3)\text{CH}_3])\)).\(^{25}\) And 9 [d\(_{\text{Si-Cl}}\) = 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., aNHCl\(_2\)SiCl\(_4\)) fragments are connected via C\(_\text{NHCl}\)–H···Cl hydrogen bonds [C\(_\text{NHCl}\)–H···Cl bond angles = 165(5)° and 171(5)°],\(^{54}\) 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 aNHCl\(_2\)SiCl\(_4\) (aNHCl = \([\text{HC(N}(\text{Ph})_2}\text{CH}_3])\) \([\text{9-Ph}]^+\) show that two isomeric structures (as shown in Fig. 3) may exist.\(^{45}\) The carbon atoms of the two carbene ligands may reside at the axial position (Fig. 3a) or at the equatorial position (Fig. 3b). The \([\text{9-Ph}]^+\)-a isomer is merely 0.05 kcal/mol in energy lower than \([\text{9-Ph}]^+\)-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.

The axial Cl(1)-Si(1)-Cl(2) bond angle in 9 [172.44(8)°] is about 10° larger than that in \([\text{9-Ph}]^+\)-b (163.27°). Meanwhile, the equatorial Cl(3)-Si(1)-Cl(29) bond angle in 9 [131.8(2)°] is about 8° smaller than that in \([\text{9-Ph}]^+\)-b (139.62°). Thus, the trigonal bipyramidal geometry around the silicon atom in \([\text{9-Ph}]^+\)-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 \([\text{9-Ph}]^+\)-b (2.270 Å, av). The Si-Cl\(_{\text{eq}}\) bond distance for 9 [2.0529(18) Å] compares well with that in \([\text{9-Ph}]^+\)-b (2.078 Å) and those in 8 (2.060 Å, av). In \([\text{9-Ph}]^+\)-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 \([\text{9-Ph}]^+\)-a is almost linear (the C-Si-C bond angle = 176.07°). Notably, the Si-C\(_\text{NHCl}\) bond distances in \([\text{9-Ph}]^+\)-a (1.982 Å) are obviously longer than those in \([\text{9-Ph}]^+\)-b (1.918 Å) and in 9 (1.895 Å, av). Natural bond orbital (NBO) analysis shows that the silicon atoms in \([\text{9-Ph}]^+\)-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 NHCl 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 aNHCl-based low-oxidation-state silicon chemistry, which is being explored in this group.

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Notes and references

Reaction of the anionic NHDC ligand, \([\text{[:C}{[\text{N}(2,6-\text{Pr}^i\text{C}_6\text{H}_3)]_2\text{CHCl}]_n}\) (1), with SiCl\(_4\) gives the trichlorosilyl-substituted NHC ligand (7). Abnormal cabene-SiCl\(_4\) complex (8) can be conveniently synthesized by combining 7 with HCl\(\cdot\)NEt\(_3\). Meanwhile, 7 may react with CH\(_2\)Cl\(_2\) 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.