



Cite this: *Dalton Trans.*, 2016, **45**, 5941

Received 5th October 2015,
Accepted 17th November 2015

DOI: 10.1039/c5dt03894d

www.rsc.org/dalton

Abnormal carbene–silicon halide complexes†

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Reaction of the anionic N-heterocyclic dicarbene (NHDC), $[\text{C}\{\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)_2\text{CHCl}\}_n]^-$ (**1**), with SiCl_4 gives the trichlorosilyl-substituted (at the C4 carbon) N-heterocyclic carbene complex (**7**). Abnormal carbene– SiCl_4 complex (**8**) may be conveniently synthesized by combining **7** with $\text{HCl}\cdot\text{NEt}_3$. In addition, **7** may react with CH_2Cl_2 in warm hexane, giving the abnormal carbene-complexed SiCl_3^+ cation (**9**). The nature of the 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 ($n = 1$, $\text{E} = \text{C}$,^{14–16} Si ,^{17–19} Ge ;^{20,21} $n = 2$, $\text{E} = \text{B}$,²² C ,^{23,24} Si ,^{25,26} Ge ,²⁷ Sn ,²⁸ P ,^{29,30} As ,³¹ and Sb ³²) species have been isolated *via* carbene-stabilization. These syntheses usually involve alkali (or alkaline earth) metal reduction of the corresponding carbene-complexed EX_n ($\text{X} = \text{halides}$). Notably, both N-heterocyclic carbenes (NHC, **I** in Fig. 1) and cyclic (alkyl)(amino)carbenes³³ (CAAC, **IV** in Fig. 1) have been exten-

sively utilized in stabilizing these highly reactive main group species.^{7,11} However, abnormal N-heterocyclic carbene (aNHC, **II** in Fig. 1)-based low-oxidation-state main group chemistry remains largely undeveloped.³⁴

Since Crabtree's seminal discovery of the first aNHC-based transition metal complexes,³⁵ aNHC ligands have been actively utilized in organometallic synthesis and catalysis.^{36–38} It is generally accepted that aNHCs, possesses stronger σ -donation capabilities than normal NHCs. Considering the reactive nature of aNHCs (compared to NHCs) Bertrand's isolation of the first stable aNHC 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 aNHC-based complexes.^{41,42} This may be largely due to the lack of convenient access to the corresponding aNHC–silicon halide precursors (to the best of our knowledge, aNHC-based SiCl_2 and SiH_2Cl_2 complexes represent the rare examples of this type).^{41,42} Thus, development of new synthetic routes of aNHC–silicon halides is important. Herein, we report the syntheses,⁴³ structures,⁴³ and computations⁴³ of SiCl_3 -substituted (at the C4 carbon) NHC (**7**), and its abnormal carbene derivatives [aNHC: SiCl_4 (**8**) and aNHC₂ $\text{SiCl}_3^+\text{Cl}^-$ (**9**)].

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 $[\text{C}\{\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)_2\text{CH}\}_2]^-$, 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 aNHC-based group 12 and 13 complexes may be conveniently synthesized.^{49–51} When **1** was 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 $-\text{ZnEt}_2$ (**3**) adducts were isolated. Reactions of **2** or **3** with electrophiles gave the corresponding aNHC-based borane (**4**) and zinc complexes, respectively, *via* salt elimination (the 2-to-4 transformation is shown in Scheme 1; $\text{R} = 2,6\text{-diisopropyl-}$

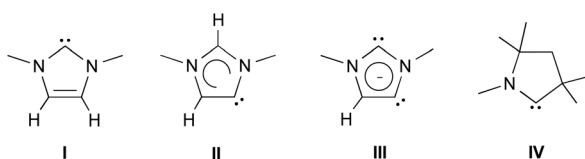


Fig. 1 Imidazole-based carbenes (I–III) and CAAC (IV).

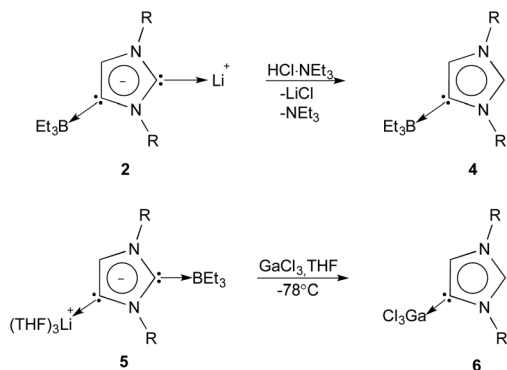
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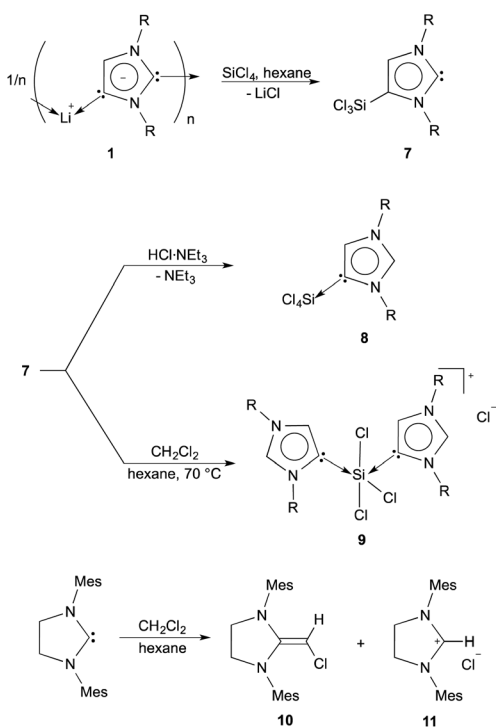
† Electronic supplementary information (ESI) available: Synthetic and computational details and structural and spectral characterization. Crystallographic details in .cif format. CCDC 1425407–1425409. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt03894d

phenyl).^{49,50} Interestingly, **5**, the THF-solvated C4-lithiated isomer of **2**, reacts with GaCl₃ at low temperature to give an abnormal carbene–GaCl₃ adduct (**6** in Scheme 1).⁵¹ Notably, the syntheses of these aNHC-based group 12 and 13 complexes involve anionic NHDC-based precursors (such as **2** and **5**).

Herein we report that aNHC–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 SiCl₄ gave **7** (77.0% yield) (Scheme 2; R = 2,6-diisopropylphenyl). The addition of excess SiCl₄ did not result in the complexation of another SiCl₄ to the C2 carbon of the imidazole ring in **7**. While aNHC : SiCl₄ (**8**) was synthesized (95.9% yield) by combining **7** with HCl·NEt₃ (in a 1 : 1 ratio),



Scheme 1 NHDC-based synthesis of **4** and **6**.



Scheme 2 NHDC-based synthesis of **7–9** and the reported preparation of **10** and **11**.

aNHC₂SiCl₃⁺Cl[−] (**9**) was isolated as pale yellow crystalline solid (75.6% yield) by reaction **7** with excess CH₂Cl₂ (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 CH₂Cl₂. Indeed, CH₂Cl₂ has been reported to react with the NHC ligand [C{N(Mes)CH₂}₂], giving mono-chloro-olefin (**10**) and the imidazolium salt (**11**) (Scheme 2).⁵² The presence of the mono-chloro-olefin byproduct in our case remains obscure since the sticky residue could not be characterized. The ²⁹Si NMR chemical shifts of **8** (−103.6 ppm) and **9** (−102.6 ppm) are comparable to that (−108.9 ppm) for L:SiCl₄ (L = [C{N(2,6-Prⁱ₂C₆H₃)CH₂}₂]),²⁵ which, however, shift dramatically upfield with compared to that (−13.5 ppm) for **7**.

Compound **7** crystallizes in the monoclinic space group *P2₁/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)° 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 [C{N(2,6-Prⁱ₂C₆H₃)CH₂}₂] carbene ligand.⁵³ However, the fact that the C2 carbene centre of **7** is not inclined to bind another SiCl₄ 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 aNHC ligand. While the Si–C_{aNHC} 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:SiCl₄ (L = [C{N(2,6-Prⁱ₂C₆H₃)CH₂}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**, L:SiCl₄ (L = [C{N(2,6-Prⁱ₂C₆H₃)CH₂}₂]),²⁵ and **9** [*d*_{Si–C} = 1.895(5) Å, av; *d*_{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.*, aNHC₂SiCl₃⁺) fragments are connected *via* C_{NHC}–H⋯Cl[−] hydrogen bonds [C_{NHC}⋯Cl[−] distance = 3.267(5) Å, av; C_{NHC}–H⋯Cl[−] bond angles = 165(5)° and 171(5)°],⁵⁴ which results 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 aNHC₂SiCl₃⁺ (aNHC = [HC{N(Ph)₂CHC:] ([**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^{−1} 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.

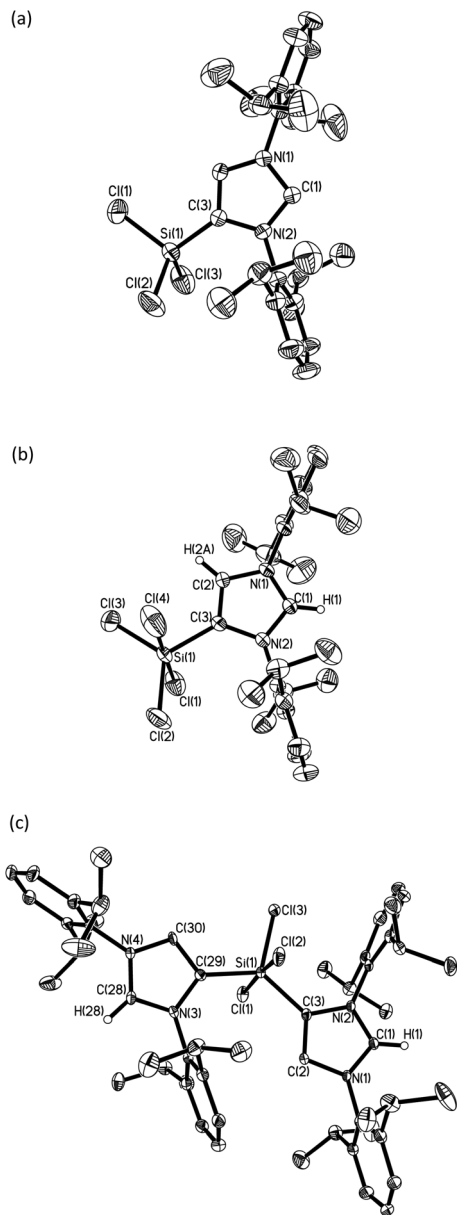


Fig. 2 Molecular structures of (a) **7**, (b) **8** and (c) **9**. Thermal ellipsoids represent 30% probability; hydrogen atoms on carbon are omitted for clarity, except for those at C(1) and C(2) of **8** and C(1) and C(28) of **9**. Selected bond distances (Å) and angles (°) are as follows. For **7**, 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)–C(3) 89.19(16).

The axial Cl(1)–Si(1)–Cl(2) bond angle in **9** [172.44(8)°] 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)°] is about 8° smaller than that in [9-Ph]⁺-**b** (139.62°). Thus, the

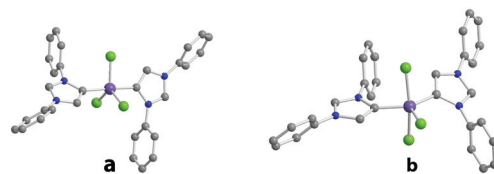


Fig. 3 The optimized isomeric structures [(a) aNHCs at the axial position; (b) aNHCs at the equatorial position] of the simplified model [9-Ph]⁺.

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_{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_{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_{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 aNHC-based low-oxidation-state silicon chemistry, which is presently being explored in this laboratory.

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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