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Facile access to silyl-functionalized N-heterocyclic olefins with $HSiCl_3$†

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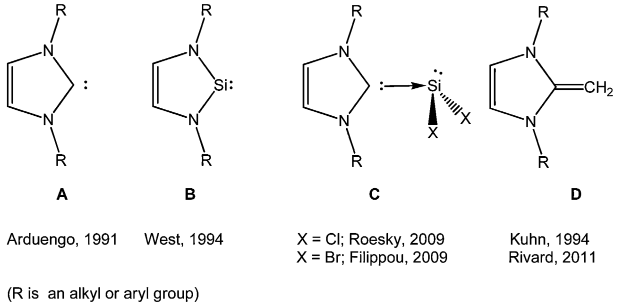
N-heterocyclic olefins (NHOs), $IPrCH_2$ (1) and $SIPrCH_2$ (2) ($IPrCH_2$ = $\{N(2,6\text{-}iPr_2C_6H_3)CH\}_2CCH_2$ and $SIPrCH_2$ = $\{N(2,6\text{-}iPr_2C_6H_3)CH_2\}_2CCH_2$), react with $HSiCl_3$ and afford $IPrCH(SiHCl_2)$ (3) and $SIPrCH(SiHCl_2)$ (4), respectively. Compounds 3 and 4 have been isolated in almost quantitative yield. Interestingly, treatment of the silylene $IPr{\cdot}SiCl_2$ with 1 also affords 3, where silylene insertion into a C–H bond is observed. Computational analysis shows a high energy barrier for silylene insertion, therefore a protonation–deprotonation mechanism is more likely.



Scheme 1 NHC (**A**), NHSi (**B**), NHC stabilized silylenes (**C**), and NHO (**D**).

Investigation of intriguing properties, reactivity and applications of the compounds with low-valent main group elements is an active area of current research.[1–4] Among group 14 elements, carbenes and silylenes are the most studied reactive species.[5] They insert into σ-bonds or undergo oxidative cycloaddition reactions with unsaturated organic compounds to form tetravalent derivatives of carbon and silicon.[2–6] Carbenes were believed to be non-isolable highly reactive intermediates. This situation changed when Bertrand *et al.* reported a phosphino stabilized carbene[7] in 1989. In 1991, Arduengo and co-workers reported the first thermally stable carbene as a N-heterocyclic carbene (NHC) (Scheme 1**A**).[8] However, it took almost three years to isolate a silicon analogue of a NHC. In 1994, West and co-workers succeeded in isolating the first stable N-heterocyclic silylene (NHSi) (Scheme 1**B**).[9] Now, a number of stable carbenes and silylenes with variable structural motifs are known and can be readily synthesized.[2–4]

The electron richness and structure of the NHCs provide a unique class of σ-donor ligands. NHCs have found widespread applications not only as ligands in transition-metal catalysis and organometallic chemistry, but also as organocatalysts in their own right.[10,11] Furthermore, NHCs have been found to be very efficient neutral ligands in stabilizing highly reactive main group species.[3,4,12] Among dihalosilylenes, some trapping reactions of condensed $SiCl_2$ with acetylene and benzene were already carried out by Timms in 1968.[13] In 2009, the first monomeric dihalosilylenes were reported, which were stabilized by a NHC (Scheme 1**C**).[14,15] Besides the classical method for preparing compounds with low-valent main group elements using alkali metals, a novel route was also disclosed to prepare NHC-stabilized dichlorosilylene (Scheme 1**C**; X = Cl).[14] Reductive dehydrochlorination of $HSiCl_3$ with a NHC affords a NHC stabilized dichlorosilylene.[14] Silylene **C** (X = Cl) has been found to be a strong σ-donor ligand for transition metals.[16,17] Silylene **C** (X = Cl) behaves as a Lewis base and some Lewis acid–base adducts of **C** with boranes have also been isolated.[18,19]

N-heterocyclic olefin (NHO) (Schemes 1**D** and 2) and its Lewis acid–base adducts were reported by Kuhn *et al.* in 1994.[20] Scheme 2 illustrates various mesomeric forms (**a**, **b**, and **c**) of a NHO. Therefore, NHO (**D**) can be considered as a lighter congener of **C**. Interest in this seemingly unusual molecule aroused very recently. Rivard and co-workers have used NHOs (Scheme 2) with sterically demanding substituents and have isolated interesting compounds with low-valent Ge and Sn.[21a] Recently, NHOs have been shown to stabilize interesting boron compounds.[21c,d]

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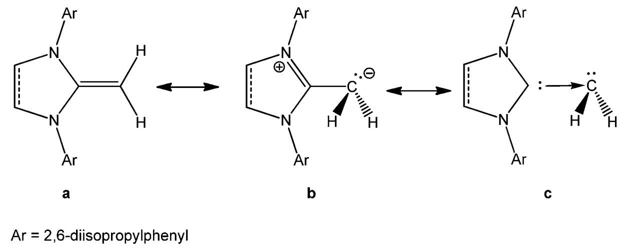
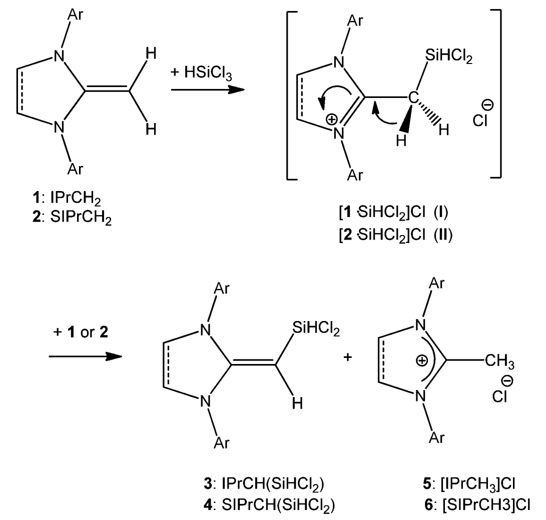
† Electronic supplementary information (ESI) available: General experimental procedures, X-ray crystallographic information on compound **3**, cartesian coordinates (in Å) and total BP86/def2-TZVP energies (in au, noncorrected zero-point vibrational energies included) of all stationary points discussed. CCDC 951884. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc45652h



Scheme 2 Different mesomeric forms of a NHO.



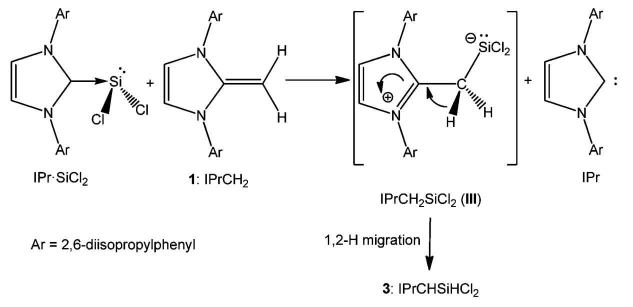
($IPrCH_2$ = {(N(2,6-$i$$Pr_2C_6H_3$)CH}$_2CCH_2$ and $SIPrCH_2$ = {(N(2,6-$i$$Pr_2C_6H_3$)$CH_2$}$_2CCH_2$)

Scheme 3 Synthesis of compounds **3** and **4**.

Surprisingly, the chemistry of NHOs with silicon has not been explored so far.

Here, we report on the facile formation of silyl-functionalized NHOs **3** and **4** (Scheme 3) by the reaction of NHOs **1** and **2** with $HSiCl_3$. Compound **3** can also be prepared by the reaction of NHC stabilized dichlorosilylene IPr·$SiCl_2$ with **1** (Scheme 4).

Compounds **3** and **4** have been prepared in almost quantitative yield by the reaction of a NHO (**1** or **2**) with $HSiCl_3$ (Scheme 3). The insoluble side products **5** and **6** can be readily isolated by filtration and can be recycled to form NHOs **1** and **2**. Compounds **3** and **4** crystallize as colourless crystals and are soluble in common organic solvents. Formation of compounds **3** and **4** can be readily observed from their NMR spectra.[22] The ^1H NMR spectrum of each of the compounds **3** and **4** shows a doublet for the SiH proton accompanied by silicon satellite signals (J_{Si-H} = 291.13 Hz (**3**) and J_{Si-H} = 295.67 Hz (**4**)). Imidazoline ring NCH protons in **3** are magnetically non-equivalent, and each appears as a doublet. Similarly, NCH_2 protons of **4** exhibit a multiplet. Olefinic CH proton each in compounds **3** and **4** appears as a doublet due to coupling with the SiH proton. ^{13}C NMR spectra of the compounds **3** and **4** show resonances consistent with their ^1H NMR spectral data.[22] The resonances are shifted downfield when compared with those of respective NHO **1** or **2**. Each of the compounds **3** (δ −9.83 ppm) and **4** (δ −7.15 ppm) shows a signal in the ^{29}Si NMR spectrum, which is consistent with those observed for four-coordinate organosilicon compounds.[2–4] The EI-mass spectrum of **3** exhibits the molecular ion peak at 500 (m/z).



Scheme 4 Proposed mechanism for the formation of **3**.

Base induced disproportionation of $HSiCl_3$ to generate dichlorosilylene is well known.[14,23] Use of NHO as a Lewis base has been shown by Kuhn, Rivard and others.[20,21] We decided to use NHO as a base to generate silylene with $HSiCl_3$.[14] In analogy with the reaction of NHCs and $HSiCl_3$,[14] dehydrochlorination of $HSiCl_3$ with a NHO base and subsequent silylene insertion into a C–H bond of NHO to afford **3** or **4** were assumed. However, computational analysis shows a high energy barrier for $SiCl_2$ insertion (Fig. 1).[22] Therefore, formation of adducts **I** and **II** and subsequent deprotonation with the second molecule of the NHO base to afford **3** and **4** seem more plausible (Scheme 3).

We also carried out the reaction of IPr·$SiCl_2$ (IPr = {(N(2,6-$iPr_2C_6H_3$)CH}$_2$C:)) with **1**. Formation of compound **3** with the liberation of free IPr was readily observed from the ^1H and ^{29}Si NMR spectral studies (Scheme 4). However, in this case, high solubility of **3** and IPr in common organic solvents impedes their separation. In general, silylenes insert into the O–H, Si–H, S–H, C–Cl, and metal–hydrogen bonds.[24] Insertion of a thermally stable silylene into a C–H bond is rather rare.[25] Irrespective of the mechanism involved, reaction of IPr·$SiCl_2$ with **1** to afford **3** is a clear silylene insertion into a C–H bond (Scheme 4). In this case, formation of an intermediate (**III**) and subsequent 1,2-hydrogen migration to give **3** are plausible. However, the role of IPr as a proton transfer agent *via* protonation–deprotonation cannot be ruled out.

Suitable single crystals of **3** for X-ray diffraction studies were grown from a saturated benzene solution at room temperature

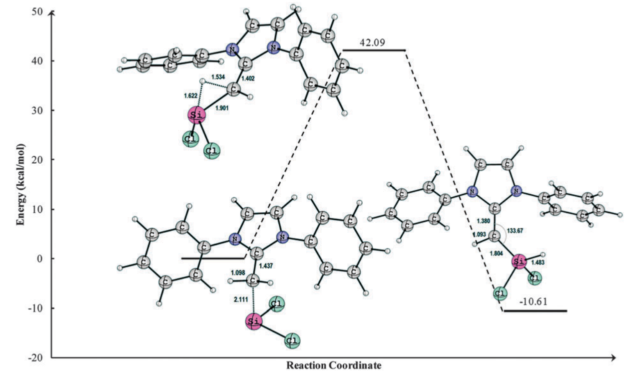


Fig. 1 Calculated energy profiles at BP86/def2-TZVP for the silylene insertion into a C–H bond. Values are the electronic energy (corrected with the ZPVE) given in kcal mol^{-1}.[22]

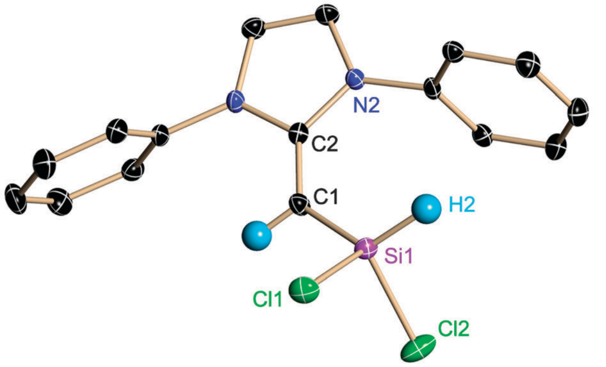


Fig. 2 Thermal ellipsoid representation of the molecular structure of **3**; anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms (except the CHSiH part) and isopropyl groups on phenyl rings are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–Cl1 2.082(1), Si1–Cl2 2.081 (1), Si1–C1 1.776(2), C1–C2 1.379(2); Cl1–Si1–Cl2 101.66(3), Cl1–Si1–C1 107.59(6), Cl2–Si1–C1 115.66(6).

by the slow diffusion of *n*-hexane. Compound **3** crystallizes in the triclinic space group $P\bar{1}$. The molecular structure of **3** is shown in Fig. 2. Solid state structure of compound **3** reveals the formation of a silyl-functionalized NHO with a $SiHCl_2$ group. Silyl-functionalized-NHO **3** features a distorted tetrahedral geometry at the four-fold coordinated silicon atom. The average Si–Cl bond length of 2.08 Å is consistent with those measured for the compounds with four-coordinate silicon.[26]

In this communication, we have presented direct access to silyl-functionalized NHOs **3** and **4** in almost quantitative yield by the reaction of **1** and **2** with $HSiCl_3$. The only side products **5** and **6** are insoluble and can be easily separated. Computational analysis shows a high energy barrier for silylene insertion, therefore a protonation–deprotonation mechanism is more likely. Reaction of IPr·$SiCl_2$ with **1** to yield **3** shows formal silylene insertion into a C–H bond. Easy separation of the products and the use of commercially available $HSiCl_3$ instead of silylene IPr·$SiCl_2$ and facile access to silyl-functionalized NHOs **3** and **4** by the reaction of **1** and **2** with $HSiCl_3$ are more appealing. Further studies on the chemistry of **3** and **4** are currently in progress and the results will be published in due course.

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