Facile access to silyl-functionalized N-heterocyclic olefins with HSiCl_3^+ Cite this: *Chem. Commun.*, 2013, **49**, 9440Received 25th July 2013,
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N-heterocyclic olefins (NHOs), IPrCH_2 (1) and SIPrCH_2 (2) ($\text{IPrCH}_2 = \{\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\text{CH}_2\}_2\text{CCH}_2$ and $\text{SIPrCH}_2 = \{\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\text{CH}_2\}_2\text{CCH}_2$), react with HSiCl_3 and afford $\text{IPrCH}(\text{SiHCl}_2)$ (3) and $\text{SIPrCH}(\text{SiHCl}_2)$ (4), respectively. Compounds 3 and 4 have been isolated in almost quantitative yield. Interestingly, treatment of the silylene IPr-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.

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 carbene⁷ in 1989. In 1991, Arduengo and co-workers reported the first thermally stable carbene as a N-heterocyclic carbene (NHC) (Scheme 1A).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 1B).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

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

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 1C).^{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 1C; 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 1D 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

Ar = 2,6-diisopropylphenyl

Scheme 2 Different mesomeric forms of a NHO. (IPrCH₂ = {(N(2,6-*i*-Pr₂C₆H₃)CH₂)₂CCH₂} and SiPrCH₂ = {(N(2,6-*i*-Pr₂C₆H₃)CH₂)₂CCH₂})**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 HSiCl₃. Compound 3 can also be prepared by the reaction of NHC stabilized dichlorosilylene IPr-SiCl₂ 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 HSiCl₃ (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

Ar = 2,6-diisopropylphenyl

Scheme 4 Proposed mechanism for the formation of 3.

compounds 3 and 4 shows a doublet for the SiH proton accompanied by silicon satellite signals ($J_{\text{Si-H}} = 291.13$ Hz (3) and $J_{\text{Si-H}} = 295.67$ Hz (4)). Imidazoline ring NCH protons in 3 are magnetically non-equivalent, and each appears as a doublet. Similarly, NCH₂ 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. ¹³C 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 ($\delta -9.83$ ppm) and 4 ($\delta -7.15$ ppm) shows a signal in the ²⁹Si 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*).

Base induced disproportionation of HSiCl₃ 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 HSiCl₃.¹⁴ In analogy with the reaction of NHCs and HSiCl₃,¹⁴ dehydrochlorination of HSiCl₃ 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 SiCl₂ 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-SiCl₂ (IPr = {(N(2,6-*i*-Pr₂C₆H₃)CH₂)₂C:}) with 1. Formation of compound 3 with the liberation of free IPr was readily observed from the ¹H and ²⁹Si 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-SiCl₂ 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 CH₂ part) and isopropyl groups on phenyl rings are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–C1 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 SiHCl₂ 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 HSiCl₃. 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–SiCl₂ 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 HSiCl₃ instead of silylene IPr–SiCl₂ and facile access to silyl-functionalized NHOs **3** and **4** by the reaction of **1** and **2** with HSiCl₃ 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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