Journal Name

ARTICLE TYPE

A Facile Access to a Novel NHC-Stabilized Silyliumylidene Ion and Its C-H Activation of Phenylacetylene

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Taking advantage of two N-heterocyclic carbenes (NHCs), novel silyliumylidene ions 1a and 1b are prepared by a facile one-pot reaction of the corresponding dichlorosilanes with three equivalents of NHCs. For the first time, a C-H insertion
10 **reaction at phenylacetylene by a novel silyliumylidene ion is reported. The treatment of *m*-terphenyl substituted silyliumylidene ion 1a with three equivalents of phenylacetylene results into the formation of *m*-terphenyl substituted 1-alkenyl-1,1-dialkynylsilane 2.**

15 Silylium ions [R_3Si^+], heavier analogue of carbenium ions, are among the strongest Lewis acids. It took a deliberate effort of over half a century towards their successful isolation.[1] In general, the factors like specially designed non-coordinating counter
20 anions, donor free solvents and kinetically stabilizing bulky substituents were crucial towards the isolation of free silylium ions.[2] The trivalent silicon centre in silylium ions is highly electrophilic and now Lewis acid catalysis as well as C-F bond activation are the most prominent applications of silylium ions.[3]
25 On the other hand, silylenes [R_2Si:], heavier analogues of carbenes, have attracted much attention in past 20 years and are now enjoying their interesting reactivities and potential applications in transition metal catalysis.[4]
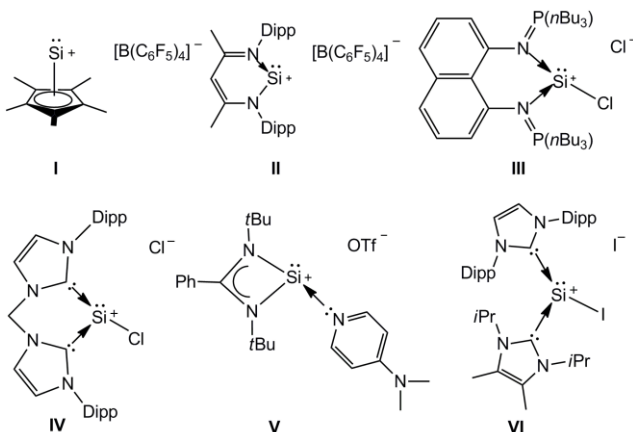
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Chart 1. Examples of Isolable Silyliumylidene Ions.

Meanwhile, silyliumylidene ions [$RSi:^+$] bear the best combined character of both silylium ion and silylenes. For example, the
50 electrophilicity is more pronounced since the silicon centre possesses four valence electrons, two vacant orbitals and a lone pair of electrons. Consequently the isolation of silyliumylidene ions gets even more challenging.[5] Several silyliumylidene cations, however, have been reported in the previous ten years.[6-11]

55 This has been achieved either by employing well-designed ligand or multistep synthetic methods. For example, the seminal work in this field is reported by Jutzi for silyliumylidene ion **I**, thanks to the stabilization effect of pentamethylcyclopentadienyl ligand.[6] Driess and co-workers utilized intramolecular stabilization effect
60 for the isolation of the silicon(II) cation **II**[7] which also possess the aromatic stabilization. The same group later on, reported on the synthesis of **III**[8] and **IV**[9] by the incorporation of especially designed bisiminophosphorane and bis *N*-heterocyclic carbene ligands, respectively. Moreover, So and coworkers reported on
65 the synthesis of a silyliumylidene ion **V** stabilized by a DMAP and the amidinate ligand.[10] It should also be mentioned that Filippou and co-workers reported on the striking example of silyliumylidene **VI** stabilized by two NHCs in a three step synthetic methodology starting from SiI_4.[11a]
70 Despite their interesting character, the reactivity study of silyliumylidenes is still in its infancy.[12] For example, the catalytic behavior of **I** in the controlled degradation of ether,[13] the remarkable synthesis of a silylone from **IV**[9] and activation of elemental sulfur from **III**[8] and **V**[10] remain as the highlights of the
75 reactivity of silyliumylidene ions. Herein we report the C-H insertion at the phenylacetylene with a novel silyliumylidene ion synthesized in a facile single step methodology.

The computational studies performed by Müller suggested a stable silyliumylidene ion substituted with the kinetically
80 stabilizing terphenyl group at silicon-center.[14] This prompted us to employ the terphenyl substituent towards the synthesis of a novel silyliumylidene ion. On the other hand, N-heterocyclic carbenes (NHCs) are employed as external donor to provide the desired stabilization for the low-valent silicon compounds.[11,15-17]
85 Thus, we employed two NHCs parallel to the methodology used by Filippou towards the isolation of NHC-stabilized chlorosilylene.[16b] Interestingly, we have found that the target *m*-terphenyl substituted silyliumylidene ion **1a** stabilized by two NHCs can be obtained in a very facile one step experimental
90 procedure (Scheme 1). In addition, we have also employed the triisopropylphenyl substituent at the silicon centre in order to generalize this convenient synthesis (Scheme 1). The synthetic methodology involves the addition of a solution of three equivalents of ^{Me4}NHC (^{Me4}NHC = 1,3,4,5-tetramethylimidazol-
95 2-ylidene) to a solution of the corresponding dichlorosilane *m*-$TerSiHCl_2$[18] for the synthesis of **1a** as well as $TippSiHCl_2$[19] for the synthesis of **1b** (*m*-Ter = 2,6-$Mes_2C_6H_3$, Mes = 2,4,6-trimethylphenyl, Tipp = 2,4,6-triisopropylphenyl). Compound **1a** is obtained by slow stirring of reaction mixture only during the
100 addition of the NHC at room temperature. Overnight standing of the reaction mixture results into the yellow-orange crystals of **1a** which are obtained in 54% yield based on ^1H NMR spectrum. Compound **1b**, however, is synthesized by slow addition of NHC

to a heated solution of TippSiHCl$_2$ in benzene at 50°C. Consequently, the solution is separated from the imidazolium salt and the solvent is reduced in volume and allowed to stand overnight at room temperature. Compound **1b** is obtained as bright yellow crystalline product in 45 % yield.
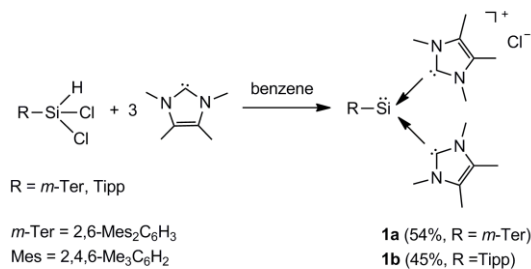
Scheme 1. Synthesis of the silyliumylidenes **1a** and **1b**.

The ^{1}H NMR spectrum of **1a** and **1b** at room temperature displays one set of signals for the respective *m*-terphenyl and Tipp groups as well as the two coordinated NHCs. Additionally, for **1a**, four broad singlets (corresponding to the N-*Me* and C-*Me* protons of NHCs, the 3,5-*Mes* protons and the ortho-*Me* protons of the mesityl group) observed at room temperature split into two singlets each at -20 °C. On the other hand, the ^{1}H NMR spectrum of **1b** does not show a similar broadening of the chemical shifts as seen for **1a**. The ^{13}C NMR resonance for the carbene-carbons for **1a** and **1b** are observed at 160.3 ppm and 159.7 ppm as singlets, in the ^{13}C NMR spectrum, respectively. One sharp signal was observed at -68.85 ppm for **1a** in the ^{29}Si NMR spectrum, whereas the ^{29}Si NMR spectrum of **1b** displayed a chemical shift at -69.50 ppm as a singlet. These are downfield shifted than that of **V** (δ = -82.3 ppm),[10] but upfield shifted than that of **IV** (δ = -58.4 ppm)[9]. The calculated value of ^{29}Si NMR resonances of **1a** and **1b** (δ = -67.32 ppm and -68.55 ppm, respectively, B3LYP/6-31G(d)[C,N,H]/6-311G(3d)[Si]) are in good agreement with the experimental values.
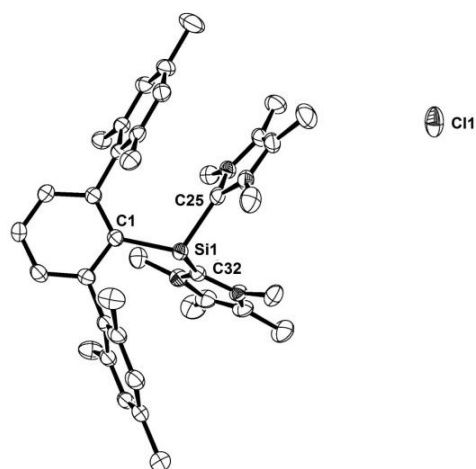

Figure 1. Molecular structure of **1a**. Thermal ellipsoids represent 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si(1)-C(1) 1.9355(19), Si(1)-C(32) 1.9481(19), Si(1)-C(25) 1.9665(19), C(1)-Si(1)-C(32) 105.06(8), C(1)-Si(1)-C(25) 111.36(8), C(32)-Si(1)-C(25) 93.78(8).

Compound **1a** crystallizes in monoclinic space group *P*2$_1$/*c* as separated ion pairs (the shortest Si-Cl distance is 6.234 Å). Molecular structure of **1a** is depicted in Figure 1. The silicon centre is three fold coordinated to the two *N*-heterocyclic

carbenes and *ipso* carbon (C1) of the *m*-terphenyl group. The sum of the bond angles around the Si1 atom is 310.2°. The Si-C bond distances in **1a** for the coordinated NHCs are almost identical [1.948(19) and 1.967(19) Å] to the Si-C bonds of the coordinated NHCs in **VI** [SiI(NHC^{iPr2Me2})NHC^{dipp})I]I [1.947(2) and 1.967(2) Å for Si-C (NHC^{dipp}) and Si-C (NHC^{iPr2Me2}), respectively (NHC^{iPr2Me2} = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, NHC^{dipp} = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene).[11a] Scheme 2 presents the possible mesomeric structures for compounds **1a** and **1b.** A zwitterionic structure, where the positive charge is dispersed over the two NHC backbones, and a donor-acceptor stabilized silicon(II) cation which is more appropriate description of **1** based on the high degree of pyramidalization observed for **1a** (310.2°).[20]
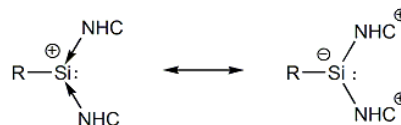
Scheme 2. Zwitterionic and donor-acceptor stabilized canonical structures for **1a** (R = m-Ter) and **1b** (R = Tipp).

Furthermore, DFT calculations for the cationic part of **1a** and **1b** were carried out at B3LYP/6-31G(d) level of theory. The HOMO of **1a** shows mainly the lone pair orbital at the silicon centre, whereas the LUMO of **1a** is dispersed over the NHC skeletons (Figure 2). Molecular orbitals of **1b** are similar to that of **1a** (Supporting Information). The NBO charge clearly shows that the silicon centre bears positive net charge (+0.798 for **1a** and +0.804 for **1b**).
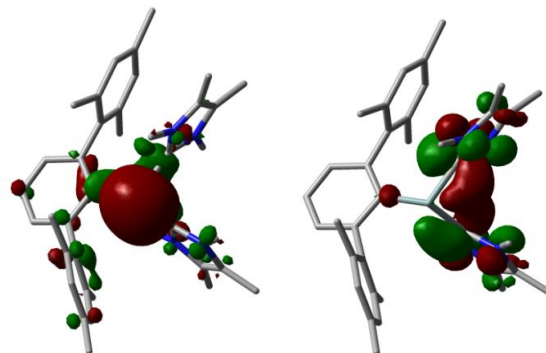

Figure 2: Molecular orbitals of **1a**, HOMO (left, -6.92 eV) and LUMO (right, -3.37 eV).

Silylenes undergo cycloaddition reaction with internal alkynes[21,22] and terminal alkynes[22] as well as activate C-H bonds in terminal alkynes[17,23]. It is of note that Müller has predicted the potential of silyliumylidene ions towards C-H activation through the generation of a silylium ion by proton abstraction form solvent by an intermediate silyliumylidene.[24] We have therefore embarked on reactivity investigation of the silyliumylidene **1a** with the terminal alkyne. Interestingly, the unprecedented reactivity of the silyliumylidene **1a** towards phenylacetylene was observed. The reaction of **1a** with three equivalents of phenylacetylene in acetonitrile yields the *m*-terphenyl substituted 1-alkenyl-1,1-dialkynylsilane **2** in 68% yield, solely as the *Z*-isomer. Compound **2** was fully characterized by multinuclear NMR spectrometry, ESI-HRMS as well as single crystal X-ray analysis. The ^{1}H-NMR of **2** displays one set of signals for the *m*-terphenyl group, the alkynyl substituents and the alkenyl substituent. The ethylene (Si-C*H*=C*H*-Ph) protons are observed

as doublets at 5.16 and 6.97 ppm. In the ^{13}C NMR spectrum of **2**, the ethylyne carbon resonances (Si-$C\equiv C$-Ph) appear at 90.9 and 106.7 ppm, whereas the ethylene carbon chemical shifts (Si-$CH=CH$-Ph) are observed at 126.5 and 145.3 ppm. The ^{29}Si-
5 NMR chemical shift of **2** is observed at -62.28 ppm as a sharp singlet, which is downfield shifted in comparison to that of precursor **1a** (δ = -68.85 ppm). In addition, this value fits well with the calculated value (δ = -59.02 ppm, B3LYP/6-31G(d)[C,N,H]/6-311G(3d)[Si]). Furthermore, DFT calculations
10 [RI-B97-D/cc-pVTZ(SMD=acetonitrile)//RI-B97-D/6-31G* level of theory] were performed to suggest a plausible mechanism for the formation of **2** as a *Z*-isomer as the sole product (see supporting information). According to the DFT calculations, the formation of *E*-isomer bears high activation barriers and therefore
15 the formation of *E*-isomer is kinetically not favored (for details see also the Supporting Information).
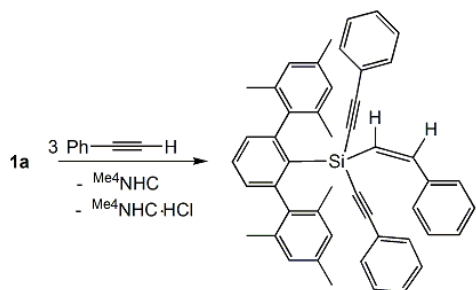
20 **Scheme 3.** Reaction of **1a** with three equivalents of phenylacetylene.

Compound **2** crystallize in monoclinic space group C2/c and molecular structure is shown in Figure 3. The central silicon possess distorted tetrahedral geometry with two alkylyne groups
25 (C33-C34 and C41-C42) and one alkylene group (C25-C26) terminally coordinated to the silicon, whereas the maximum steric room is occupied by the umbrella shaped *m*-terphenyl substituent on the silicon. The broadest angle at the Si centre is displayed between C(terphenyl)-Si-C(alkylene) as 115.03°. The
30 alkylene substituent (C25-C26) reveals *Z*-configuration at the C=C double bond in contrast to the *E*-configuration of 1-alkenyl-1-alkynylsilole reported by Cui and co-workers.[17] Another feature to be compared with the 1-alkenyl-1-alkynylsilole is the Si-C bond lengths. While the Si-C(alkynyl) bonds (1.82(15) Å and
35 1.83(15) Å) of **2** are similar to those of the 1-alkenyl-1-alkynylsilole (1.83(2) Å), however the Si-C(alkenyl) bond (1.87(25) Å) is slightly longer than that of 1-alkenyl-1-alkynylsilole (1.83(2) Å) which leads back to electronic interaction of silicon and butadiene in the silole ring.[17]
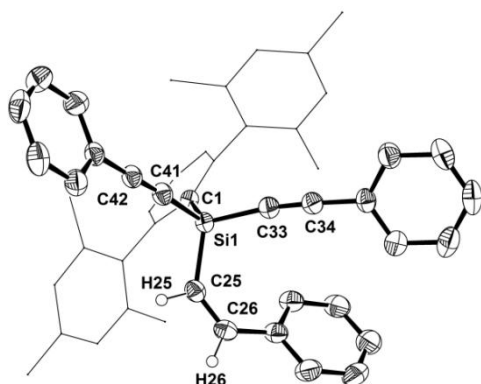

Figure 3. Molecular structure of **2**. Thermal ellipsoids represent 50% probability level. Hydrogen atoms (except those on C25 and C26) are
60 omitted for clarity. Selected bond lengths [Å] and angles [°]: Si(1)-C(33) 1.8281(15), Si(1)-C(41) 1.8320(16), Si(1)-C(25) 1.8713(15), Si(1)-C(1) 1.8913(15), C(33)-Si(1)-C(41) 106.92(7), C(33)-Si(1)-C(25) 107.83(7), C(41)-Si(1)-C(25) 103.26(7), C(33)-Si(1)-C(1) 112.34(6), C(41)-Si(1)-C(1) 110.80(7), C(25)-Si(1)-C(1) 115.03(7).

65 In conclusion, we report on the synthesis of novel *m*-terphenyl and Tipp substituted silyliumylidene ions **1a** and **1b** stabilized by two NHCs through a facile synthetic route. This striking one pot reaction will be further generalized by employing various substituents at the silicon center in our laboratories. In addition,
70 the promising reactivity of **1a** is evident from its reaction with phenylacetylene leading to the C-H insertion product **2**. Both compounds **1a** and **2** are characterized by multinuclear NMR as well as single-crystal X-ray diffraction analysis. Moreover, DFT calculations are performed to establish the energy pathway for the
75 formation of **2** from **1a**, which rationalizes the formation of *Z*-isomer in this reaction. Further reactivity studies on **1a** and **1b** are currently under investigation and will be reported in due course.

Notes and references

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