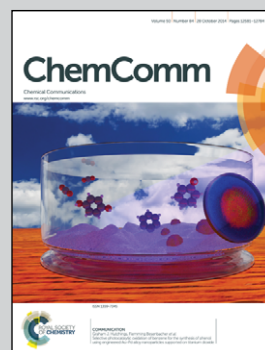


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A facile access to a novel NHC-stabilized silyliumylidene ion and C–H activation of phenylacetylene

A facile one-pot synthetic route for the synthesis of donor stabilized silyliumylidene ions has been devised. Additionally, an unusual C–H insertion product was isolated from the reaction of NHC-stabilized arylsilyliumylidene ion with three equivalents of phenylacetylene.

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A facile access to a novel NHC-stabilized silyliumylidene ion and C–H activation of phenylacetylene†

Syed Usman Ahmad,^a Tibor Szilvási^b and Shigeyoshi Inoue^{*a}

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 reaction of phenylacetylene by a novel silyliumylidene ion is reported. The treatment of *m*-terphenyl substituted silyliumylidene ion **1a** with three equivalents of phenylacetylene results in the formation of *m*-terphenyl substituted 1-alkenyl-1,1-dialkynylsilane **2**.

Silylium ions [R_3Si^+], heavier analogues 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 anions, donor free solvents and kinetically stabilized 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 On the other hand, silylenes [$R_2Si:$], heavier analogues of carbenes, have attracted much attention in the past 20 years and show interesting reactivities and potential applications in transition metal catalysis.⁴

Meanwhile, silyliumylidene ions [RSi^+] bear the best combined character of both silylium ions and silylenes. For example, the 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 past ten years (Chart 1).^{6–11} This has been achieved either by employing well-designed ligands or multi-step synthetic methods. For example, the seminal work

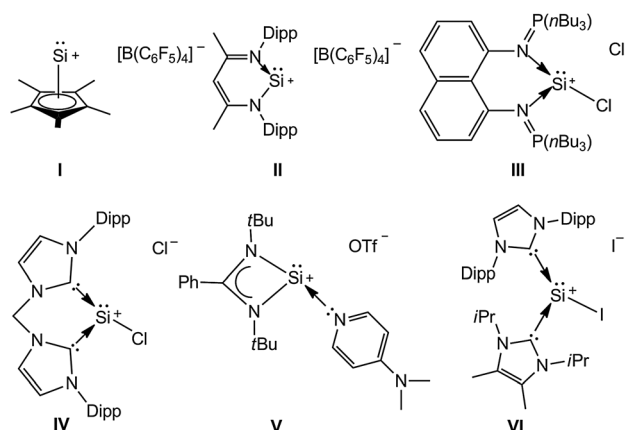


Chart 1 Examples of isolable silyliumylidene ions.

in this field is reported by Jutzi for silyliumylidene ion **I**, thanks to the stabilization effect of the pentamethylcyclopentadienyl ligand.⁶ Driess and co-workers utilized the intramolecular stabilization effect for the isolation of the silicon(II) cation **II**⁷ which also shows 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 the synthesis of silyliumylidene ion **V** stabilized by 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 SiH_4 .^{11a}

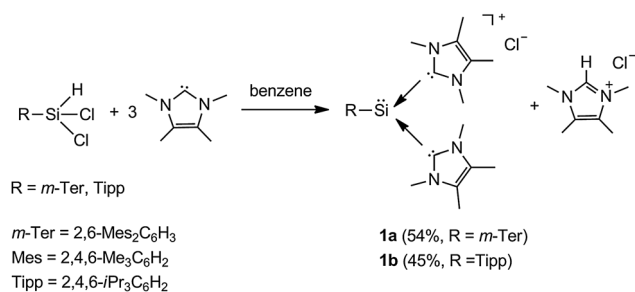
Despite their interesting character, the reactivity study of silyliumylidenes is still in its infancy.¹² For example, the catalytic behavior of **I** in the controlled degradation of ether,¹³ the remarkable synthesis of a silylone from **IV**⁹ and activation of elemental sulfur from **III**⁸ and **V**¹⁰ remain as the highlights of the reactivity of silyliumylidene ions. Herein we report the C–H insertion in phenylacetylene using a novel silyliumylidene ion synthesized in a facile single step methodology.

^a Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, Sekr. C2, 10623 Berlin, Germany. E-mail: shigeyoshi.inoue@tu-berlin.de

^b Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Szent Gellért tér 4, 1111, Budapest, Hungary

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Scheme 1 Synthesis of silyliumylidenes **1a** and **1b**.

The computational studies performed by Müller suggested a stable silyliumylidene ion substituted by the kinetically stabilizing terphenyl group at the silicon-center.¹⁴ This prompted us to employ the terphenyl substituent for the synthesis of a novel silyliumylidene ion. On the other hand, N-heterocyclic carbenes (NHCs) are employed as external donors to provide the desired stabilization for the low-valent silicon compounds.^{11,15–17} 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 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 ^{Me}NHC (^{Me}NHC = 1,3,4,5-tetramethylimidazol-2-ylidene) to a solution of the corresponding dichlorosilane *m*-TerSiHCl₂¹⁸ for the synthesis of **1a** as well as TippSiHCl₂¹⁹ for the synthesis of **1b** (*m*-Ter = 2,6-Mes₂C₆H₃, Mes = 2,4,6-trimethylphenyl, Tipp = 2,4,6-triisopropylphenyl). Compound **1a** is obtained by slow stirring of the reaction mixture only during the addition of the NHC at room temperature. Overnight standing of the reaction mixture results in the yellow-orange crystals of **1a** which are obtained in 54% yield based on the ¹H NMR spectrum. Compound **1b**, however, is synthesized by slow addition of NHC to a heated solution of TippSiHCl₂ 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 a bright yellow crystalline product in 45% yield.

The ¹H 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 ¹H NMR spectrum of **1b** does not show a similar broadening of the chemical shifts as seen for **1a**. The ¹³C NMR resonances for the carbene-carbons of **1a** and **1b** are observed at 160.3 ppm and 159.7 ppm as singlets, in the ¹³C NMR spectrum, respectively. One sharp signal was observed at –68.85 ppm for **1a** in the ²⁹Si NMR spectrum, whereas the ²⁹Si NMR spectrum of **1b** displayed a chemical shift at –69.50 ppm as a singlet. These are downfield shifted compared to **V** (δ = –82.3 ppm),¹⁰

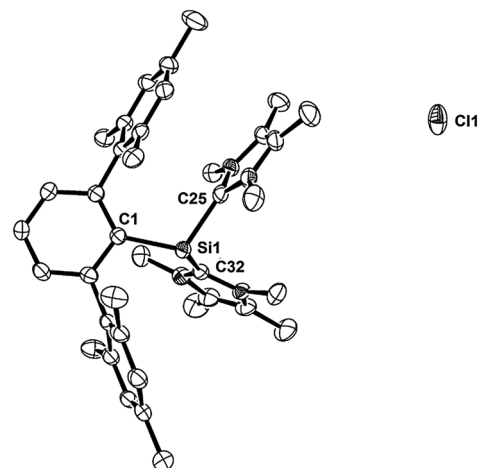


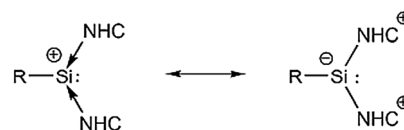
Fig. 1 Molecular structure of **1a**. Thermal ellipsoids represent the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si(1)–C(1) 1.9355(19), Si(1)–C(32) 1.9481(19), Si(1)–C(25) 1.9665(19), C(1)–Si(1)–C(32) 105.06(8), C(1)–Si(1)–C(25) 111.36(8),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

but upfield shifted compared to **IV** (δ = –58.4 ppm).⁹ The calculated values of ²⁹Si 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.

Compound **1a** crystallizes in the monoclinic space group *P*₂₁/*c* as separated ion pairs (the shortest Si–Cl distance is 6.234 Å). The molecular structure of **1a** is depicted in Fig. 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** [Si(NHC^{*i*Pr₂Me₂})(NHC^{*dipp*})]I [1.947(2) and 1.967(2) Å] for Si–C (NHC^{*dipp*}) and Si–C (NHC^{*i*Pr₂Me₂}), respectively (NHC^{*i*Pr₂Me₂} = 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 of compounds **1a** and **1b**. A donor–acceptor stabilized silicon(II) cation is the mesomeric structure based on the high degree of pyramidalization observed for **1a** (310.21).²⁰ The other mesomeric form is the zwitterionic structure, where the positive charge is dispersed over the two NHC backbones.

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 (Fig. 2). Molecular orbitals of **1b** are similar to that of



Scheme 2 Zwitterionic and donor–acceptor stabilized canonical structures of **1a** (R = *m*-Ter) and **1b** (R = Tipp).



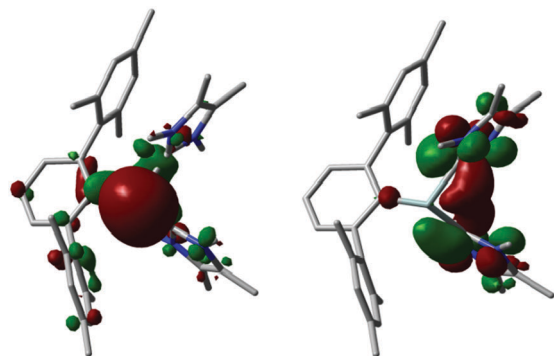


Fig. 2 Molecular orbitals of **1a**, the HOMO (left, -6.92 eV) and the LUMO (right, -3.37 eV).

1a (ESI^+). The NBO charge clearly shows that the silicon centre bears positive net charge ($+0.798$ for **1a** and $+0.804$ for **1b**).

Silylenes undergo cycloaddition reaction with internal alkynes^{21,22} and terminal alkynes²² 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 from 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 (Scheme 3). Compound **2** was fully characterized by multinuclear NMR spectroscopy, ESI-HRMS as well as single crystal X-ray analysis. The ^1H -NMR of **2** displays one set of signals for the *m*-terphenyl group, the alkynyl substituents and the alkenyl substituent. The ethylene ($\text{Si}-\text{CH}=\text{CH}-\text{Ph}$) protons are observed as doublets at 5.16 and 6.97 ppm. In the ^{13}C NMR spectrum of **2**, the ethylene carbon resonances ($\text{Si}-\text{C}\equiv\text{C}-\text{Ph}$) appear at 90.9 and 106.7 ppm, whereas the ethylene carbon chemical shifts ($\text{Si}-\text{CH}=\text{CH}-\text{Ph}$) are observed at 126.5 and 145.3 ppm. The ^{29}Si -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** ($\delta = -68.85$ ppm). In addition, this value fits well with the calculated value ($\delta = -59.02$ ppm, B3LYP/6-31G(d)[C,N,H]/6-311G(3d)[Si]). Furthermore, DFT calculations [RI-B97-D/cc-pVTZ(SMD = acetonitrile)//RI-B97-D/6-31G* level of theory] were performed to suggest a plausible mechanism

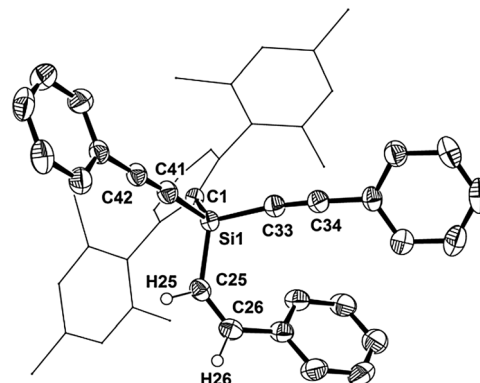


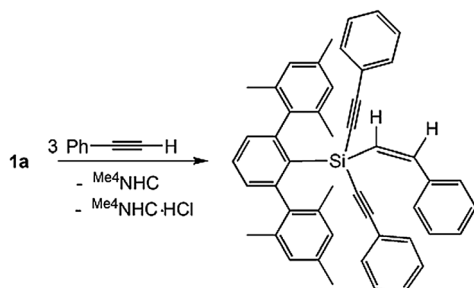
Fig. 3 Molecular structure of **2**. Thermal ellipsoids represent 50% probability level. Hydrogen atoms (except those on C25 and C26) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si(1)–C(33) 1.8281(15), Si(1)–C(41) 1.8320(16), Si(1)–C(25) 1.8713(15), Si(1)–C(1) 1.8913(15), C(33)–Si(1)–C(41)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

for the formation of **2** as a *Z*-isomer as the sole product (see ESI^+). According to the DFT calculations, the formation of the *E*-isomer requires high activation barriers and therefore the formation of the *E*-isomer is kinetically not favored (for details see also the ESI^+).

Compound **2** crystallizes in the monoclinic space group $C2/c$ and the molecular structure is shown in Fig. 3. The central silicon possesses a distorted tetrahedral geometry with two alkynyl groups (C33–C34 and C41–C42) and one alkenyl 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 alkenyl 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 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

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, 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 formation of **2** from **1a**, which rationalizes the formation of the *Z*-isomer in this reaction. Further reactivity studies on **1a** and **1b** are ongoing and will be reported in due course.

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Scheme 3 Reaction of **1a** with three equivalents of phenylacetylene.

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