

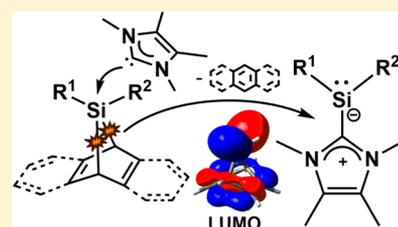
Activation of 7-Silanorbornadienes by N-Heterocyclic Carbenes: A Selective Way to N-Heterocyclic-Carbene-Stabilized Silylenes

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S Supporting Information

ABSTRACT: The synthesis of hydridosilylenes Ter(H)Si : **3a** (Ter: 2,6-bis(2,4,6-trimethylphenyl)phenyl) and $\text{Ter}^*(\text{H)Si}$: **3b** (Ter*: 2,6-bis(2,4,6-triisopropylphenyl)phenyl) stabilized by the N-heterocyclic carbene (NHC) ImMe_4 is reported. The synthesis of stabilized hydridosilylenes **3** was accomplished by a previously unknown NHC-induced fragmentation of silanorbornadiene derivatives. Structural studies of the stabilized silylenes **3** and of its $\text{Fe}(\text{CO})_4$ complex **12** accompanied by a theoretical analysis of their bonding situation indicate that stabilized silylenes such as **3** can be regarded as neutral silyl anion equivalents. A computational investigation of the reaction course indicate a virtual one-step reaction between the NHC and the silanorbornadiene. A theoretical assessment of the scope and limitations of this reaction suggests that it is general and can be used also for the synthesis of other carbene analogues such as gerylenes and phosphinidenes.



INTRODUCTION

Recent progress in the chemistry of carbenes and their analogues is certainly one of the mainsprings for the renaissance of main group chemistry during the last years.¹ For their synthesis, either reductive processes applying dihalides as precursors or α -elimination reactions are utilized.² The latter process includes the classical decomposition of small cyclic systems^{1c} and also the landmark synthesis of silylenes by photolytic decomposition of trisilanes.³ A third classical synthetic route to transient carbene analogues, such as silylenes, gerylenes, or phosphinidenes is the thermal or photolytic decomposition of the corresponding 7-element-norbornadiene via concerted loss of an aromatic unit.⁴ Besides this destructive use of these bicyclic systems, their particular bonding situation is of interest.⁵ In the case of 7-silanorbornadienes, we recently showed that β -SiC hyperconjugation between the strained Si–C bond and the C=C double bonds is structurally relevant and explains the elongated bonds between the bridgehead carbon atoms and the bridging silicon atom (Si–C: 190.6–196.8 pm).⁶ In addition, the bridging silicon atoms in 7-silanorbornadienes are unusually deshielded with ²⁹Si NMR resonances at very low field ($\delta^{29}\text{Si} = 98\text{--}32$). According to a molecular orbital (MO) analysis of the parent 7-silanorbornadiene **1**, the reason for this unusual low field ²⁹Si NMR chemical shift is a low-lying LUMO located mainly at the silicon atom (see Figure 1).⁶ This molecular orbital is of antibonding character in respect of both Si–C bonds. This suggests that electron donation into this orbital by an external electron donor or nucleophile weakens the Si–C bonds further and finally leads to the fragmentation of the 7-silanorbornadiene into silylene (H_2Si) and benzene.⁷ The need for a strong nucleophile in this reaction is also of benefit for the isolation of the silylene, as it will form donor–acceptor type complexes with the nucleophile. Therefore, we

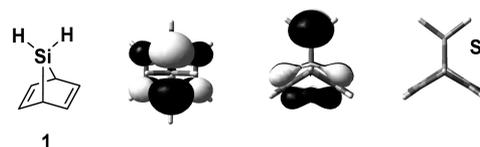
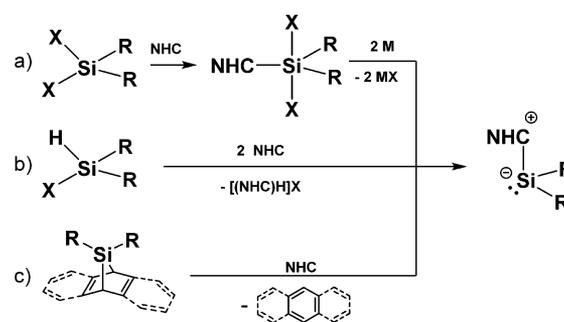


Figure 1. Calculated surface diagram of the LUMO of 7-silanorbornadiene **1** in two different orientations (at B3LYP/6-31G(d), isodensity value 0.05, from ref 6a).

reasoned that reaction of 7-silanorbornadienes with strong nucleophiles such as N-heterocyclic carbenes (NHC) should result in the formation of stabilized silylenes. During the past decade, the synthesis and isolation of a large number of NHC-stabilized carbene analogues has been reported.^{2,8} Reduction of hypercoordinated NHC-substituted silicon halides (Scheme 1a) and NHC-assisted α -elimination of HX from hydridosilicon

Scheme 1. Synthetic Routes to NHC-Stabilized Silylenes

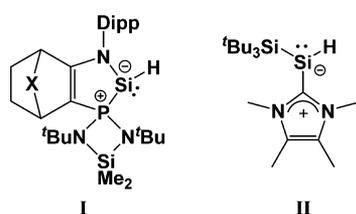


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halides (Scheme 1b) are established synthetic approaches to NHC-stabilized silylenes.⁹ If correct, our assumption will add a third general synthesis to this scheme, the NHC-induced, concerted cleavage of two activated Si–C bonds from a tetraorganosubstituted silicon(IV) precursor to give the stabilized silicon(II) compound (Scheme 1c). Here we will describe the experimental verification of this hypothesis for NHC-stabilized hydridosilylenes **3**. Hydridosilylenes represent an intriguing class of compounds, as they combine the properties of carbene analogues with those of the Si–H functionality. Only two examples for donor-stabilized hydridosilylene, **I** and **II**, are known and the Kato and Baccareo group disclosed for the phosphine stabilized silylene **I** an interesting hydrosilylation chemistry (Chart 1).^{10,11} In addition, we will

Chart 1. Hydridosilylenes Stabilized by Lewis Base Interaction^{10,a}



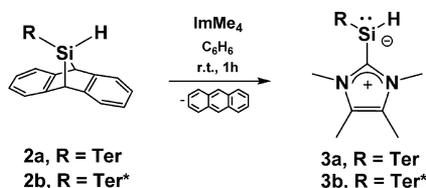
^aDipp: 2,6-diisopropylphenyl, X: CH₂; –CH₂–CH₂–.

present the results of a computational study which suggest that the NHC-induced fragmentation reaction is general and can be used also for the synthesis of other stabilized main group carbene analogues.

RESULTS AND DISCUSSION

Synthesis and Characterization. As starting point for the experimental investigation, we used terphenylsubstituted dibenzosilanorbornadienes **2** which were prepared according to a modified protocol reported by Tokitoh and co-workers.¹² The synthesized silanorbornadienes **2** were fully characterized and can be easily identified by their specific low field ²⁹Si resonances (**2a**: δ²⁹Si = 31.6; **2b**: δ²⁹Si = 31.5) and by the ¹H NMR data of the bridgehead methine groups (**2a**: δ¹H = 2.82; **2b**: δ¹H = 2.70).^{12b} Reaction of silanorbornadienes **2** with 1 equiv of 1,3,4,5-tetramethylimidazol-2-ylidene (ImMe₄)¹³ in benzene at room temperature occurred immediately as indicated by an intense yellow color of the reaction mixture (Scheme 2). Control of the reaction mixture after 1 h by ¹H NMR and ²⁹Si NMR spectroscopy showed the complete consumption of silanorbornadienes **2** and, in each case, the formation of only one new silicon-containing species **3** along

Scheme 2. Reaction of Silanorbornadienes **2** with ImMe₄ To Give NHC-Substituted Hydridosilylenes **3**^a

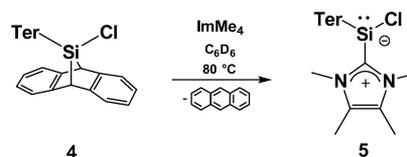


^aTer = 2,6-Bis(2,4,6-trimethylphenyl)phenyl. Ter* = 2,6-Bis(2,4,6-triisopropylphenyl)phenyl. ImMe₄ = 1,3,4,5-Tetramethylimidazol-2-ylidene.

with anthracene. The newly formed species **3** are characterized by strongly high-field shifted ²⁹Si NMR signals (**3a**: δ²⁹Si = –87.6; **3b**: δ²⁹Si = –80.5) which in the ¹H coupled ²⁹Si NMR spectra gives doublets with surprisingly small ¹J(SiH) coupling constants (**3a**: ¹J(SiH) = 103 Hz; **3b**: ¹J(SiH) = 105 Hz). At that point, the reaction is quantitative according to the NMR spectroscopic data and the obtained reaction mixture can be used for subsequent reactions. For isolation of pure stabilized silylenes **3**, the anthracene byproduct was removed by sublimation (*p* = 2 × 10^{–6} mbar and *T* = 110 °C) and the residue was recrystallized from a hexane/toluene mixture to obtain crystalline material. This purification procedure resulted in a significant decrease of the isolated yield (28% (**3a**), 31% (**3b**)). The products were identified as NHC-stabilized hydridosilylenes **3** by multinuclear NMR methods. Particularly informative proved to be ¹H/¹⁵N HMBC spectroscopy of these compounds as it showed in both cases a clear correlation between the signals of the Si–H hydrogen protons (**3a**: δ¹H = 4.00; **3b**: δ¹H = 3.88) and those of the nitrogen atoms (**3a**: δ¹⁵N = 178.4; **3b**: δ¹⁵N = 179.2) of the imidazolylidene substituent. This demonstrates the direct connectivity between the carbene- and the silylene units and finds further support by the high field shifted ¹³C resonances of the carbene carbon atoms (**3a**: δ¹³C = 169.1; **3b**: δ¹³C = 168.5) which appears in the typical region for NHC-stabilized silylenes.^{2a,b,f,10b} The IR spectra of both compounds **3** show a strong band for the Si–H stretch vibration at $\tilde{\nu}$ = 1970 cm^{–1} which is shifted to lower energy compared to Si–H stretch vibrations in regular Si(IV) hydrides ($\tilde{\nu}$ (Si–H) = 2200–2100 cm^{–1}) but compares well with IR data from related stabilized hydridosilylenes **I** and **II**.¹⁰

We noted no reaction of silanorbornadienes **2** with carbenes of only slightly increased steric hindrance or other strong nucleophiles. For example, 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (ImiPr₂Me₂) did not react with silanorbornadienes **2** in toluene even at elevated temperatures (*T* = 60 °C). Similarly, no reaction was observed with triethylphosphine or with 4-dimethylaminopyridine. There are also clear restrictions for this reaction regarding the substrate. That is, reaction of 7-chloro-7-silanorbornadiene **4** with ImMe₄ needs longer reaction times and higher temperatures (Scheme 3). The formed NHC-

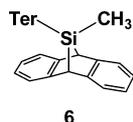
Scheme 3. Reaction of Silanorbornadiene **4** with ImMe₄ To Give NHC-Substituted Chlorosilylene **5**^a



^aTer = 2,6-Bis(2,4,6-trimethylphenyl)phenyl. ImMe₄ = 1,3,4,5-Tetramethylimidazol-2-ylidene.

stabilized chlorosilylene **5** was clearly identified by NMR spectroscopy and by comparison to literature data (**5**: δ²⁹Si = 1.7).^{2f} At the applied reaction conditions, decomposition of the chlorosilylene **5** is already a significant follow-up process and prevented its isolation before complete consumption of the starting material. The methylsubstituted 7-silanorbornadiene **6** showed no reaction with ImMe₄ even at elevated temperatures (Chart 2).

From both stabilized hydridosilylenes **3** crystals suitable for X-ray diffraction analysis were obtained by recrystallization from hexane/toluene (**3a**) and hexane (**3b**) (see Figure 2 for

Chart 2^a

^aTer = 2,6-Bis(2,4,6-trimethylphenyl)phenyl.

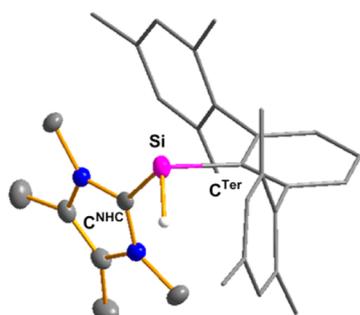


Figure 2. Molecular structure of stabilized hydridosilylene **3a** in the crystal. (Thermal ellipsoids at 50% probability, all hydrogen atoms but the Si–H hydrogen are omitted. The Ter substituent is shown in the wireframe modus.) Pertinent structural data (bond lengths [pm], bond angles [°]): Si–C^{NHC} 195.06(21), Si–C^{Ter} 194.73(21), Si–H 144(2), H–Si–C^{NHC} 92.734(816), C^{Ter}–Si–C^{NHC} 98.848(89), H–Si–C^{Ter} 98.205(768).

the molecular structure of **3a**). The key structural parameter around the silicon atoms indicate a trigonal pyramidal coordination environment for the silicon atoms with Si–C bonds of nearly equal lengths to the carbene substituent and to the terphenyl group (Si–C^{NHC}: 195.06(21) pm (**3a**), 195.55(13) pm (**3b**); Si–C^{Ter}: 194.73(21) pm (**3a**), 192.92(18) pm (**3b**)) and sums of the bond angles around silicon $\Sigma\alpha(\text{Si})$ of approximately 290° (**3a**: $\Sigma\alpha(\text{Si}) = 289.8^\circ$; **3b**: $\Sigma\alpha(\text{Si}) = 293^\circ$). This coordination is similar to that found for other by Lewis base interaction stabilized hydridosilylenes such as **I** and **II**, and for isoelectronic NHC-stabilized cationic Si(II) compounds and also for trichlorogermanates(**II**).^{2i,10,14}

DFT Calculations on the Electronic Structure of NHC-Stabilized Silylenes 3. Density functional computations at the M06-2X/6-311+G(d,p) level provided further insight into the electronic structure of hydridosilylenes **3**.¹⁵ This level of theory provided gas phase molecular structures which are in all relevant structural parameter very close to the experimental solid state molecular structures (largest deviation between heavy atom distances less than 2%). Moreover, calculations of the NMR parameter based on the DFT-optimized molecular structures agree sufficiently with the experimentally determined ones (**3a**: $\delta^{29}\text{Si}^{\text{calc}} = -86$, $^1\text{J}(\text{SiH})^{\text{calc}} = 91$ Hz; **3b**: $\delta^{29}\text{Si}^{\text{calc}} = -83$, $^1\text{J}(\text{SiH})^{\text{calc}} = 101$ Hz). Therefore, a more detailed bonding analysis for the stabilized silylenes **3** and a series of model compounds **7–10** based on the structural results of the DFT computations is appropriate. At first, we note that the calculated heterolytic bond dissociation energy D_E of the Si–C^{NHC} bond is for both cases substantial (**3a**: $D_E = 216$ kJ mol⁻¹; **3b**: 206 kJ mol⁻¹). Not unexpected, the calculated Si–C bond lengths and corresponding Wiberg bond indices (WBI)¹⁶ according to a natural bond order (NBO) analysis for NHC-stabilized hydridosilylenes **3a** and **7** differ significantly from those computed for the Si=C double bond in silene **9**, the expected product from the reaction of carbene and silylene (see **Figure 3**). They are, however, remarkably close to the same

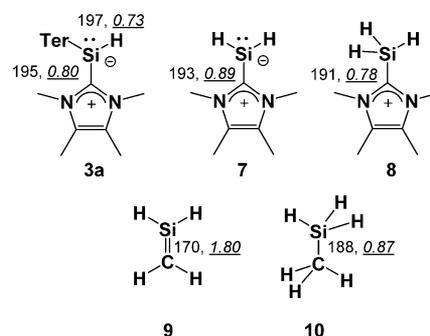
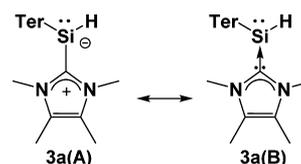


Figure 3. Comparison of calculated Si–C bond lengths (pm) and their Wiberg bond indices of compounds **3a**, **7–10** according to a NBO analysis (M06-2X/cc-pvtz//M06-2X/6-311+G(d,p)).

parameter calculated for the Si–C bonds of silane **10** and silylimidazolium cation **8**. In addition, the two Si–C bonds in compound **3a** are very close in their calculated bond lengths and in their WBIs. Obviously, this fact does not justify a different phenomenological bond description for these two bonds and therefore favors the formulation of an ylidic Lewis structure **3a(A)** for NHC-stabilized hydridosilylene **3a** over the donor–acceptor type description **3a(B)**.¹⁷

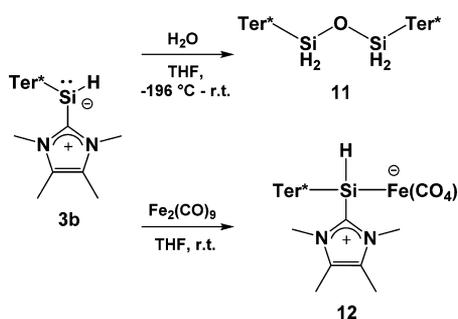
Scheme 4. Resonance Structures of NHC-Stabilized Hydridosilylene **3a**^a



^aTer = 2,6-Bis(2,4,6-trimethylphenyl)phenyl.

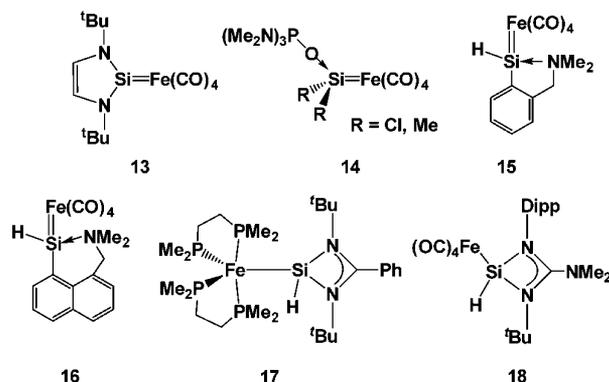
Characteristic for stabilized hydridosilylenes **3** and also for **I** and **II** are relatively small Si–H coupling constants $^1\text{J}(\text{SiH})$ of 85–105 Hz, which is approximately half of the size for a $^1\text{J}(\text{SiH})$ in tetracoordinated silanes such as **2** (**2a**: $^1\text{J}(\text{SiH}) = 207$ Hz; **2b**: $^1\text{J}(\text{SiH}) = 209$ Hz) or **10** ($^1\text{J}(\text{SiH}) = 194$ Hz).^{10,12b,18} A further computational analysis of the calculated spin–spin coupling constants for hydridosilylene **3a** and silane **10** reveals that the unusually small $^1\text{J}(\text{SiH})$ coupling constant in **3a** (calculated, 91 Hz; experimental, 103 Hz) is a consequence of the strongly reduced Fermi contact (Fc) term (calculated for **3a**: 92 Hz; for **10**: 201 Hz). This result suggests an only small 3s(Si)-orbital participation to the Si–H bond in **3a**, in agreement with the results of an NBO analysis that indicates a contribution of the 3s(Si) orbitals to the Si–H bond of only 16% (**10**: 24%). In consequence, the silicon lone pair in **3a** shows a high 3s-orbital character (54%).

Reactivity Studies. Hydridosilylenes **3** are highly reactive and in solution also thermolabile. The Ter* substituted compound **3b** turned out to be the less sensitive one, therefore further reactivity studies were done with this compound. Reaction with excess water in THF gives cleanly the tetrahydridodisiloxane **11** (**Scheme 5**). Disiloxane **11** was fully characterized by multinuclear NMR and by IR spectroscopy. Particular informative for its identification are the specific NMR resonances for the SiH₂ groups ($\delta^1\text{H} = 4.17$, $^1\text{J}(\text{SiH}) = 227.3$ Hz, $\delta^{29}\text{Si} = -31.5$).

Scheme 5. Some Selected Reactions of NHC-Stabilized Hydridosilylene 3b^a

^aTer* = 2,6-Bis(2,4,6-triisopropylphenyl)phenyl.

The analysis of the bonding situation in NHC-stabilized hydridosilylenes **3** suggests that they are able to act as strong σ -donors in organometallic transition metal complexes. This prediction was tested by the reaction of silylene **3b** with $\text{Fe}_2(\text{CO})_9$, which led to the isolation of the iron complex **12** in moderate yields (Scheme 5). Complex **12** was identified initially by NMR and IR spectroscopy. Also in this case the $^{29}\text{Si}/^1\text{H}$ NMR parameter of the Si–H group are of particular relevance for its structure ($\delta^1\text{H} = 5.75$, $^1J(\text{SiH}) = 189$ Hz, $\delta^{29}\text{Si} = -11.1$). The characteristically high field shifted ^{13}C NMR resonance of the NHC-substituent at $\delta^{13}\text{C} = 157.7$ and the correlation between its two magnetically nonequivalent nitrogen atoms and the Si–H hydrogen atom ($^1\text{H}/^{15}\text{N}$ HMBC, $\delta^{15}\text{N} = 171.8$ and 183.8) indicated the coordination of the NHC-substituent to the silicon atom. The rotation around the carbene C–Si bond is hindered which leads to the non-equivalence of the nitrogen atoms and to broad signals in ^1H NMR for the N-Me groups. In addition, a cross peak in the $^1\text{H}/^{13}\text{C}$ HMBC spectrum showed the correlation between the Si–H hydrogen atom and the carbonyl carbon atoms of the iron tetracarbonyl fragment ($\delta^{13}\text{C} = 217.6$) providing evidence for the direct connection between the iron fragment and the silylene unit. Therefore, the general constitution of the iron complex **12** is already provided by the NMR results. A closer comparison with NMR data reported for related iron complexes with stabilized hydridosilylenes, **13–18** (Chart 3), revealed however that the ^{29}Si resonance of complex **12** is significantly high field shifted ($\delta^{29}\text{Si} = -11.1$ (**12**) vs $\delta^{29}\text{Si} =$

Chart 3. Iron Complexes of Silylenes and Stabilized Hydridosilylenes^a

^aDipp: 2,6-diisopropylphenyl.

60–112 (**13–18**),¹⁹ suggesting a different bonding situation in complex **12**. This was further substantiated by the results of an X-ray diffraction analysis of pale violet crystals which were obtained from a saturated toluene solution of complex **12** at -30 °C. The molecular structure of complex **12** (Figure 4)

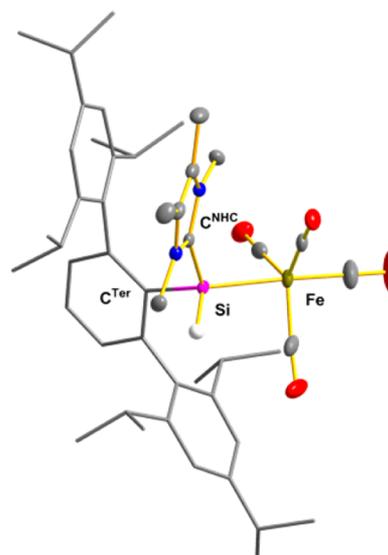


Figure 4. Molecular structure of complex **12** in the crystal. (Thermal ellipsoids at 50% probability, all hydrogen atoms but the Si–H hydrogen omitted. The Ter* substituent is shown in the wireframe modus.) Pertinent structural data (bond lengths [pm], bond angles [deg]): Si–C^{NHC} 194.48(18), Si–C^{Ter} 192.67(18), Si–H 138(2), Fe–Si 232.68(6).

shows that the silylene ligand is located at the apical position of the trigonal bipyramidal coordination polyhedron of the iron atom. In that position π -backbonding from the iron to the silicon atom is excluded by orbital symmetry. This is in contrast to the experimental structures of iron silylene complexes such as **13** and **17**,^{19a,c} where the silylene ligand occupies an equatorial position and forms very short Fe–Si bonds.^{15b} The silicon atom in complex **12** adopts a tetrahedral coordination environment with nearly equidistant carbene and terphenyl substituents (Si–C^{NHC} 194.48(18) pm; Si–C^{Ter} 192.67(18) pm). Most notable is however the long Si–Fe bond (232.68(6) pm) in complex **12**. This value is significantly larger than expected for a Si=Fe double bond (216 pm, based on theoretical assessment of covalent radii)²⁰ and also larger than that found in complexes **13–18** (Si–Fe: 218–228 pm).¹⁹ It reaches the expected value for a regular Si–Fe single bond (232 pm) and can be best compared with Si–Fe distances of silyl substituted iron complexes (i.e., $\text{Cp}(\text{CO})_2\text{FeSiPh}_2\text{Me}$: Fe–Si 234 pm).²¹ Therefore, the NHC-stabilized hydridosilylene **3b** behaves from a structural point of view in complex **12** as anionic silyl ligand and not as silylene ligand.

DFT Calculations on the Mechanism and Thermochemistry. We used quantum mechanical calculations at the DFT M06-2X/6-311+G(d,p) level to suggest a possible reaction mechanism for the studied fragmentation reaction and to investigate the substituent effects which control this reaction. The calculations predict a strong thermodynamic driving force for the reaction of the parent silanorbornadiene **1** with ImMe_4 to give the NHC-stabilized silylene **7** and benzene ($\Delta E = -145$ kJ mol⁻¹, $\Delta G^{298} = -142$ kJ mol⁻¹). According to the calculations the first step along the reaction coordinate

(Figure 5) is the exothermic formation of an encounter complex **19** from the reactants ($\Delta E = -62$ kJ mol⁻¹, $\Delta G^{298} =$

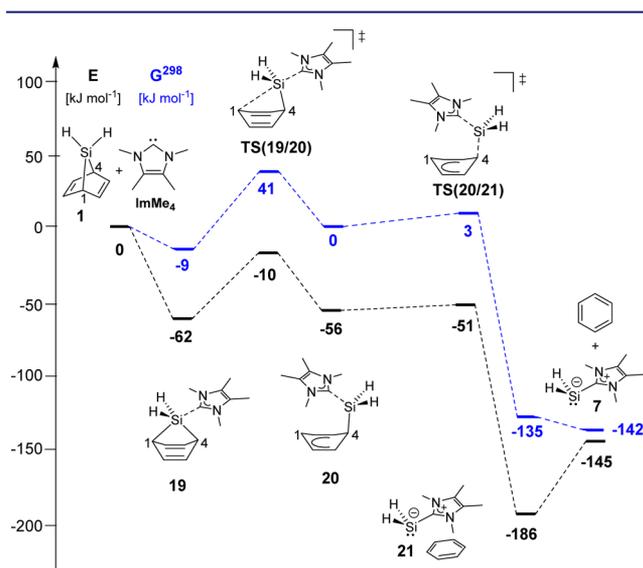


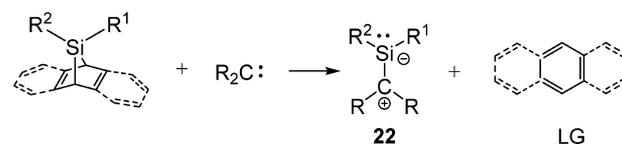
Figure 5. Calculated potential energy surface for the reaction of silanorbornadiene **1** with ImMe₄ (at M06-2X/6-311+G(d,p), relative electronic energies *E* in black, and free enthalpies at 298 K, *G*²⁹⁸, in blue letters).

−9 kJ mol⁻¹). The alternative dissociative process to give silylene, SiH₂, and benzene is endothermic ($\Delta E = 93$ kJ mol⁻¹, $\Delta G^{298} = 32$ kJ mol⁻¹). This suggests that this reaction channel is not favored and that the reaction proceeds along the associative bimolecular path via the complex **19**. The structure of complex **19** is dominated by the HOMO (carbene)/LUMO (silanorbornadiene) interaction, which predicts an attack of the nucleophile at the silicon atom orthogonal to the plane of the SiH₂ group (see the Supporting Information for the calculated structures). Due to this interaction the silicon carbon bonds are further weakened which results in their significant lengthening (Si–C: 208.6 and 199.4 pm (**19**) vs 192.2 pm (**1**)). Subsequently, the product complex, **21**, between benzene and the NHC-stabilized silylene **7** is formed in virtual one step. This reaction is connected with an energetic barrier of $\Delta E^\ddagger = 52$ kJ mol⁻¹ ($\Delta G^{298\ddagger} = 50$ kJ mol⁻¹), which is in qualitative agreement with the fragmentation of the heavily substituted silanorbornadienes **2** at room temperature. The calculations predicted also a second intermediate **20**, which is however located in a very shallow valley on the PES. The barrier for the forward reaction is extremely small ($\Delta E^\ddagger = 5$ kJ mol⁻¹; $\Delta G^{298\ddagger} = 3$ kJ mol⁻¹, Figure 5) which denies intermediate **20** any chemical significance. The product complex **21** is lower in energy than the isolated products benzene and silylene **7** by 41 kJ mol⁻¹ but its dissociation into the final products is favored by entropy ($\Delta G^{298} = -7$ kJ mol⁻¹ in favor of benzene and the stabilized silylene **7**).

In order to extend the scope of the fragmentation reaction, we tested computationally the thermochemistry of the reaction given in Scheme 6 for different aromatic leaving groups (LGs), for several carbenes of varying electron demand and for different substituents R¹ and R². The results are given in detail in the Supporting Information; here we provide only the main conclusions.

Not unexpected, we found that the thermodynamic driving force for the formation of the carbene stabilized silylene **22**

Scheme 6. General Equation for the Fragmentation of Silanorbornadienes by Reaction with Carbenes^a

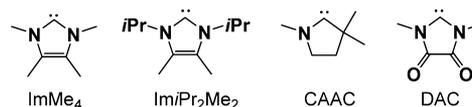


^aLG: Leaving group.

increases significantly with the stability of the leaving group LG. For example, for our standard reaction using R¹ = Ter, R² = H, and as carbene reactant ImMe₄, we calculated for benzene as leaving group a reaction energy which is by 131 kJ mol⁻¹ higher than that predicted for anthracene. In fact, the experimentally realized fragmentation using anthracene as the leaving group is according to our calculations a borderline case as the model reaction is actually thermoneutral ($\Delta E = 3$ kJ mol⁻¹; $\Delta G^{298} = -2$ kJ mol⁻¹).

The electronic situation of the applied carbene has a significant impact on the thermodynamics of the fragmentation reaction. We tested four carbenes of variable π -acceptor ability (Chart 4). This includes the NHCs, ImMe₄ and Im*i*Pr₂Me₂, the

Chart 4. Types of Carbenes Included in the Computational Study^a

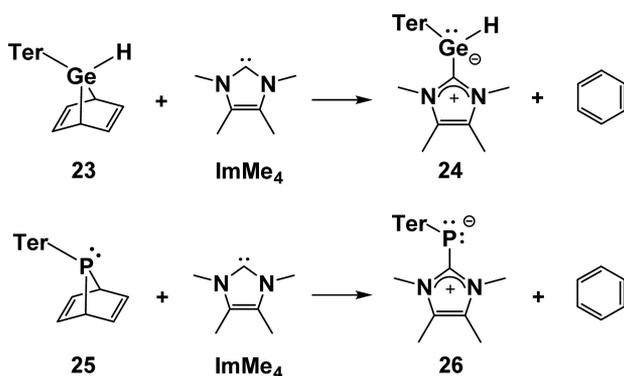


^aCAAC: Cyclic alkylaminocarbene. DAC: Diamido carbene.

CAAC carbene, and the DAC carbene as a close model for the Bielawski type carbene.^{1,j,k,22} The increasing π -acceptor ability of the carbene favors the formation of the stabilized silylene **22**. Again quoting our standard system (R¹ = Ter, R² = H, LG = C₆H₆), the exothermicity of the fragmentation reaction increases from $\Delta E = -115$ kJ mol⁻¹ calculated for Im*i*Pr₂Me₂ to $\Delta E = -159$ kJ mol⁻¹ for the DAC carbene. This clearly reflects the stronger Si–C linkage in the stabilized silylene **22** due to enhanced π -backbonding. The substituents R¹ and R² at silicon also influence the thermodynamics of the fragmentation reaction. For the generation of hydrogen-substituted stabilized silylenes **22** (R² = H, LG = C₆H₆) using ImMe₄ as carbene reactant, the calculations predict that aryl substituents R¹ which are more electron rich than the Ter group favor the formation of silylene **22**. Particular favorable are substitution by the 2,6-di*iso*-propylphenyl (Dipp) or Si(SiMe₃)₃ groups, which provide 39 (Dipp) and 33 kJ mol⁻¹ (Si(SiMe₃)₃) additional stabilization. This is encouraging for future experimental investigations since both substituents are large and could be a useful substitute for the Ter group, also in respect of kinetic stabilization of the reactive stabilized silylene **22**. In contrast, replacement of the Ter group by alkyl substituents of different size leads to less exothermic fragmentation reactions. In respect of terphenyl substituted stabilized silylenes **22** (R¹ = Ter, LG = C₆H₆, R₂C: = ImMe₄), it is noteworthy that of all tested substituents the hydrogen atom is the most efficient one. Replacement by any other group tested gave less exothermic fragmentation reactions. The reason for that could be the steric overcrowding at the silylene product. Important in view of the experimental investigations is that substitution with chlorine

atoms and with methyl groups reduces the exothermicity of the reaction by 10 (Cl) and 37 kJ mol⁻¹ (CH₃). This is in agreement with the sluggish reaction of the chloro-substituted compound **4** and the inertness of methylsilanorbornadiene **6** found in our experiments. Finally, we tested the NHC-induced fragmentation reaction for possible generation of other carbene analogues such as germylenes and phosphinidenes (Scheme 7).

Scheme 7. Hypothetical Fragmentation Reaction of 7-Germanorbornadiene **23 and 7-Phosphanorbornadiene **25** with ImMe₄^a**



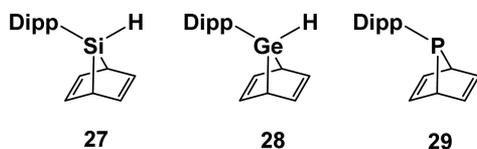
^aTer = 2,6-Bis(2,4,6-trimethylphenyl)phenyl.

With ImMe₄ as reactant and benzene as leaving group, the calculations predict a strong thermodynamic driving force for the formation of both stabilized carbene analogues, germylene **24** and phosphinidene **26** (**24**: $\Delta E = -172$ kJ mol⁻¹, **26**: $\Delta E = -235$ kJ mol⁻¹). These fragmentation reactions are calculated to be significantly more exothermic than calculated for the corresponding silylene (**22** (R¹ = Ter, R² = H, LG = C₆H₆, R₂C: = ImMe₄) $\Delta E = -128$ kJ mol⁻¹), which suggests that this reaction could be also a suitable synthetic approach for these stabilized carbene analogues.

SUMMARY AND CONCLUSION

We have introduced a previously unknown synthetic approach to stabilized silylenes using the NHC-induced fragmentation of

Chart 5^a



^aDipp = 2,6-diiso-propylphenyl.

silanorbornadiene derivatives. This reaction allowed the synthesis and characterization of two stabilized hydridosilylenes **3**. The analysis of structural data and a computational investigation of the electronic situation in these hydridosilylenes suggested that these silicon(II) compounds can be regarded as neutral silyl anion equivalents. Although the scope of the formation reaction shown in Scheme 6 seems to be limited in particular for anthracene as leaving group, the results of a systematic theoretical survey of the thermodynamics of the equations given in Schemes 6 and 7 indicate significantly better prospects for other leaving groups and for other elements. Using these computational results as guideline for future

investigations of the NHC-induced fragmentation reaction, 7-heteronorbornadienes such as **27–29** come into focus as valuable synthetic targets as precursor for stabilized carbene analogues (Chart 5). Currently, we are investigating the synthesis of these class of compounds in our laboratories.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b02824.

- Calculated compounds from Table S2 (XYZ)
- Calculated compounds from Table S4 (XYZ)
- Calculated compounds from Table S5 (XYZ)
- Calculated compounds from Table S6 (XYZ)
- Calculated compounds from Table S7 (XYZ)
- Calculated compounds from Table S9 (XYZ)
- Calculated compounds from Table S10 (XYZ)
- Calculated compounds from Table S11 (XYZ)
- Calculated compounds from Table S12 (XYZ)
- Calculated compounds from Table S14 (XYZ)
- Crystallographic data for compound **3a** (CIF)
- Crystallographic data for compound **12** (CIF)
- Crystallographic data for compound **3b** (CIF)
- Crystallographic data for compound **6** (CIF)

Experimental and theoretical characterization, including preparation of all compounds of interest and computational details (PDF)

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Notes

The authors declare no competing financial interest.

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