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Preparation of a stable disilane amidinium heterocycle and attempted syntheses of an inorganic *N*-heterocyclic carbene

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ABSTRACT

The cyclic disilane amidinium salt [(Me$_2$SiNDipp)$_2$CH]OTf (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$; OTf = OSO$_2$CF$_3^-$) was obtained in high yield, and attempts to generate the *N*-heterocyclic carbene [(Me$_2$SiNDipp)$_2$C:] via deprotonation with numerous bases exclusively gave ring-opened products of the general form: R–SiMe$_2$–SiMe$_2$N(Dipp)–CH=NDipp (R = carbon-, nitrogen- or oxygen-based nucleophiles). Although this approach was not directly successful in generating silicon-based *N*-heterocyclic carbenes, judicious manipulation of the ring-bound substituents might enable the future synthesis of new inorganic carbenes to transpire.

1. Introduction

Since their discovery [1], *N*-heterocyclic carbenes (NHCs) have adopted a prominent role as versatile ligands in coordination chemistry and are now replacing more traditional electron pair donors, such as phosphines, for various applications [2]. As a result, there has been considerable progress in modifying the electronic and steric properties of this general ligand class by changing the substituents at either the intraring carbon or nitrogen atoms, including the development of carbene systems where the σ-donor site is found at alternate positions along the *N*-heterocyclic carbene backbone [3].

A less explored method of tuning the σ-donor/π-acceptor strength of an *N*-heterocyclic carbene is to incorporate inorganic elements within an NHC framework. Important breakthroughs in this area include the synthesis of phosphorus-containing cyclic carbenes, such as heterocycle **A** by Grubbs et al. [4], and the preparation of boron-containing carbenes by the groups of Bertrand and Roesler (**B**–**D**) (Chart 1) [5]. Despite these advances, the development of new inorganic element-based NHCs has been somewhat slow due to the significant synthetic challenges stemming from the high degrees of reactivity inherent to many inorganic compounds.

In this paper we describe our efforts to obtain an *N*-heterocyclic carbene with a disilane backbone (compound **E** in Chart 1). The initial goal of this project was to promote increased σ-donor ability relative to pre-existing NHCs via the placement of electron-donating silicon and tin atoms within a carbene heterocycle. Of note, we recently reported the heavier Group 14 element analogs of the target carbene **E**, wherein the carbene carbon in the heterocycle is replaced by Ge or Sn [i.e., (Me$_2$SiNDipp)$_2$E; E = Ge and Sn; Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$] [6,7].

2. Results and discussion

2.1. Preparation of an amidinium heterocycle containing a disilane backbone

The incorporation of inorganic elements within the backbone of an *N*-heterocyclic carbene (NHC) represents a relatively new concept, and provides an added dimension with respect to tuning the donor/acceptor properties of an *N*-heterocyclic carbene [4,5,8]. In order to progress toward a cyclic carbene with a tetramethyldisilane (–Me$_2$Si–SiMe$_2$–) backbone, we modeled our synthetic strategy after a general method used previously to generate NHCs with heterocycles containing phosphorus and boron atoms [4,5].

The requisite disilane amidinium salt [(Me$_2$SiNDipp)$_2$CH]OTf (OTf = OSO$_2$CF$_3^-$) (**1**) was prepared from the cyclocondensation of ClSiMe$_2$SiMe$_2$Cl with the silylformamidine, DippN=CHN(Dipp)

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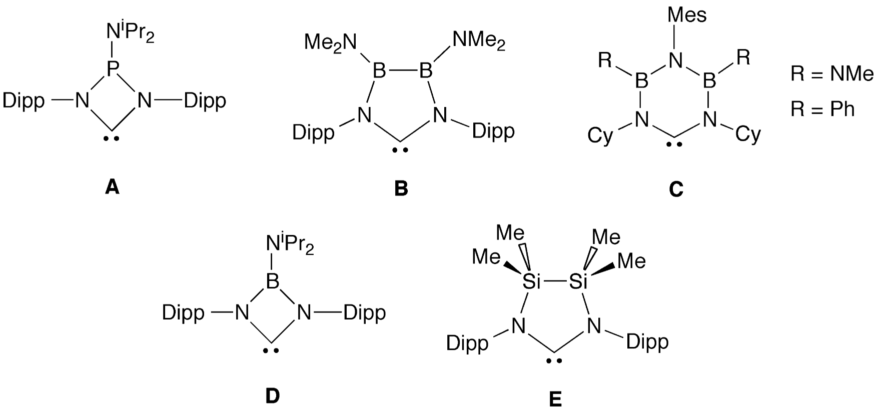
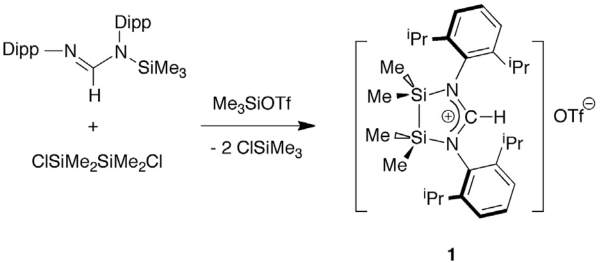


Chart 1. Various known inorganic element-containing NHCs (**A**–**D**) and the target species (**E**) discussed in this paper; Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$.

SiMe$_3$, in the presence of Me$_3$SiOTf (Eq. (1)). The potential NHC precursor, **1**, was isolated as a thermally stable white solid (Mp = 245–250 °C) in a nearly quantitative yield and was structurally authenticated by single-crystal X-ray crystallography (Fig. 1).



(1)

As shown in Fig. 1, [(Me$_2$SiNDipp)$_2$CH]OTf (**1**) contains a cationic NSiSiNC heterocycle with a nearly planar arrangement of the constituent ring atoms. Interestingly, both SiMe$_2$ units within the tetramethyldisilane backbone in **1** are locked in mutually eclipsed geometries [N(1)–Si(1)–Si(2)–N(2) torsion angle = 5.08(6)° in **1**] with narrow intraring N–Si–Si angles of *ca.* 90°. The adjacent N(1)–C(1)–N(2) angle in the imidazolium cation was determined to be 120.46(14)°, suggesting the presence of sp^2-hybridization at C(1); significant N–C–N π-bonding is also present within this imidazolium heterocycle as manifested by average C–N bond lengths [1.326(3) Å] that are shorter than typical C–N single bonds. For comparison, the related intraring C–N bond lengths within the imidazolium triflate salt [(HCNDipp)$_2$CH]OTf average to 1.329(5) Å [9]. Lastly, the aryl groups in **1** are significantly canted forward to form a steric pocket about the proximal imidazolium carbon centers, C(1). The ^{19}F{^{1}H} NMR spectrum of **1** in CDCl$_3$ is consistent with the presence of a weakly interacting OTf anion in solution (δ −78.3 ppm; *c.f.* [^{n}Bu$_4$N]OTf, δ −78.7 ppm) [10]. However significant Si···O contacts between the imidazolium ring in **1** and the OTf anion were detected in the solid state [2.8090(16) and 2.8534(17) Å] with the triflate anion located directly below the cationic ring; these Si–O distances lie within the sum of the van der Waals radii for O and Si (3.52 Å) [11]. The observed metrical parameters in **1** attest to a low degree of steric protection provided by the methyl substituents attached to the silicon atoms, thus enabling weak cation–anion contacts to exist.

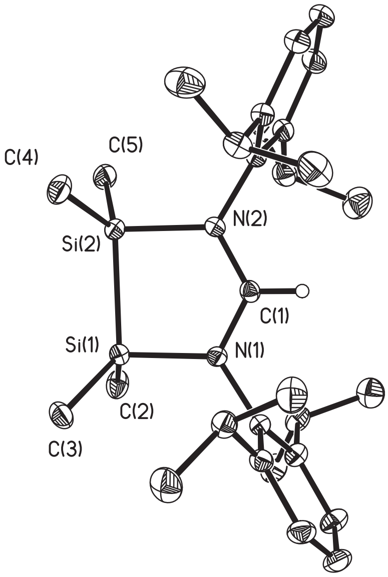


Fig. 1. Molecular structure (30% probability level) of the [(Me$_2$SiNDipp)$_2$CH]$^+$ cation in **1** with all hydrogen atoms except the imidazolium proton at C(1) omitted for clarity. Selected bond lengths [Å] and angles [°]: Si(1)–Si(2) 2.2976(7), Si(1)–N(1) 1.8485(14), Si(2)–N(2) 1.8496(15), N(1)–C(1) 1.330(2), N(2)–C(1) 1.323(2), Si(1)···O(2) 2.8090(16), Si(1)···O(2)′ 2.8534(17); N(1)–C(1)–N(2) 120.46(14), N(1)–Si(1)–Si(2) 90.71(5), N(2)–Si(2)–Si(1) 90.34(5). O(2) is related to the triflate oxygen O(2)′ by the symmetry operation −*x*, −*y*, 1 − *z* through the 0, 0, 1/2 inversion center.

2.2. Attempted deprotonation of 1 to afford an N-heterocyclic carbene

With the desired cyclic disilane amidinium salt **1** in hand, we explored various methods of accessing the target carbene [(Me$_2$SiNDipp)$_2$C:] via deprotonation of the ring-bound hydrogen atom at C(1) (Fig. 1). Our first deprotonation attempt involved treatment of **1** with the commonly used hindered base K[N(SiMe$_3$)$_2$]. This reaction yielded a new product as a colorless and moisture-sensitive solid, however ^{1}H NMR spectroscopic analysis revealed that a downfield-positioned singlet at 7.39 ppm was present in C$_6$D$_6$, indicating that the N=C*H*–N unit remained intact. In addition, the expected resonance for a carbenic carbon of an NHC was not located in the ^{13}C{^{1}H} NMR spectrum (>180 ppm) [1]. These data, in conjunction with the appearance of two inequivalent SiMe$_2$ environments in the ^{1}H and ^{13}C{^{1}H} NMR spectra, suggested that nucleophilic attack of the ring structure in **1** by the [N(SiMe$_3$)$_2$] anion had transpired. Single-crystal X-ray crystallography later identified the product as the ring-opened species (Me$_3$Si)$_2$NSiMe$_2$SiMe$_2$N(Dipp)C(H)=NDipp (**2**) (Scheme 1, Fig. 2).

The metrical parameters in **2** are consistent with the molecular structure presented in Scheme 1. Specifically, planar coordination environments are observed about N(1) and N(3) [angle sum = 359.0(3) and 359.94(17)°, respectively], while the Si–N