Synthesis and Reactivity of Boryl Substituted Silaimines

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Synthesis and Reactivity of Boryl Substituted Silaimines

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Abstract

Reactions of two N-heterocyclic silylenes with a boron azide have given the first *N*-boryl substituted silaimines, $(HCNR)_2Si{=}N\{B(DipNCH)_2\}$ (R = Dip or Bu^t, Dip = 2,6-diisopropylphenyl) which are either monomeric or dimeric in the solid state. The compounds shows divergent reactivity with CO_2, in that the bulkier silaimine undergoes a [2+2] cycloaddition with CO_2 to form $(HCNDip)_2Si\{OC(=O)N[B(DipNCH)_2]\}$ under mild conditions, while the smaller silaimine undergoes a bond metathesis reaction with CO_2, affording the boron isocyanate, $(HCNDip)_2B(NCO)$, and a known oxo-bridged silicon(IV) system. Both silaimines add H_2O across their Si=N bonds to give the boryl-aminosilanols, $(HCNR)_2Si(OH){-}(H)N\{B(DipNCH)_2\}$. The larger silaimine does not react with the bulky boron azide $(HCNDip)_2BN_3$, whereas the smaller system undergoes a [3+2] cycloaddition reaction with the azide to give spirocyclic borasilatetrazoline, $(HCNBu^t)_2Si\{[(HCNDip)_2B]NN\}_2$. Overall, the reactivity of the prepared *N*-boryl substituted silaimines is similar to that reported for other silaimines. However, the steric differences between the two Si=N bonded compounds plays a definitive role in the outcomes of their reactions with the small molecule substrates studied.

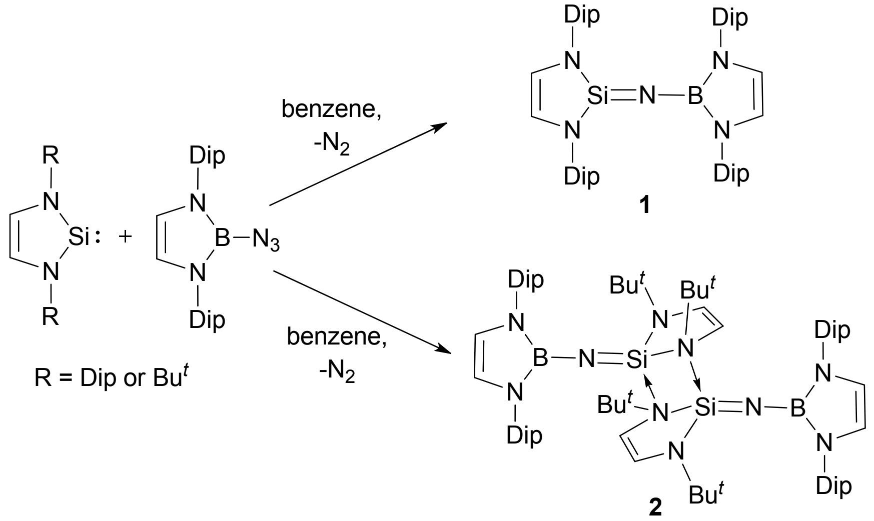
Introduction

In contrast to the widely explored chemistry of imines, $R_2C{=}NR$,[1] that of the silicon analogues of these species, *viz.* silaimines $R_2Si{=}NR$, has developed only since Wiberg and co-workers' preparation of the first stable silaimine in 1985.[2] Since that time, scores of stable silaimines have been come forward, which can be three- or four-coordinate at silicon, and which can be substituted at silicon or nitrogen with a range of heteroatom donor ligands, e.g. guanidinates, amidinates, halides, amides, silyls, siloxides, and deprotonated β-diketiminates.[3-6] Silaimines have proved markedly more reactive than their imine counterparts, largely because of the very polarised nature of their Si=N bonds. Of most relevance to the current study is their well demonstrated reactivity towards unsaturated small molecule substrates,[3-6] which is typically not shared by less reactive imines.

Our interest in silaimines sprung from a recent study in which one of us reported the reaction of the first isolated 2-coordinate, acyclic silylene, :Si{B(DipNCH)$_2$}{N(SiMe$_3$)(Dip)} (Dip = 2,6-diisopropylphenyl), with CO_2. This afforded the bulky boryl substituted silaimine, {(HCNDip)$_2$B}(Me$_3$SiO)Si=NDip, *via* O-atom abstraction from CO_2, and concomitant silyl migration.[7] While this compound represents the first acyclic silamine that is coordinated by a boryl group at silicon, to the best of our knowledge there are no known structurally authenticated examples of silaimines coordinated by a boryl group at nitrogen. These seemed worthy targets as the vacant *p*-orbital on the boron atom of boryl fragments could possibly change the electronics and reactivity of silaimines, relative to those of their *N*-alkyl or *N*-aryl substituted counterparts. Here we describe the synthesis of the first *N*-boryl substituted silaimines and describe their reactivity towards, CO_2, H_2O and a boron azide.

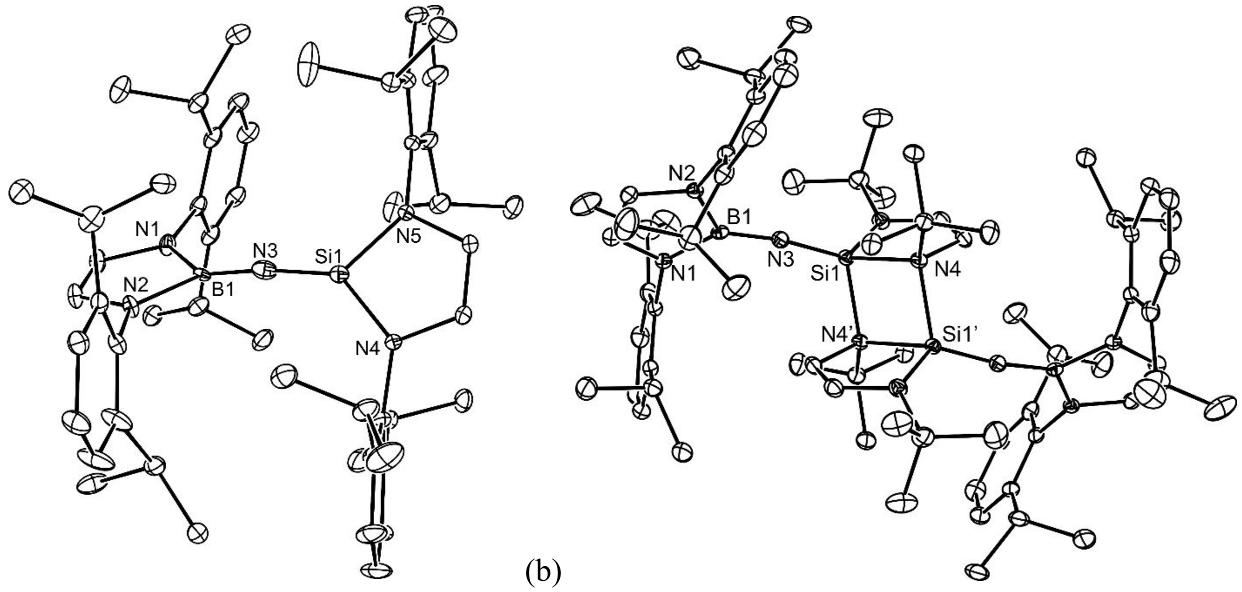
Results and Discussion

One synthetic route to silaimines that has proved useful involves reaction of N-heterocyclic silylenes with organo-azides.[3a] Given the availability of the bulky boron azide, (HCNDip)$_2$BN$_3$,[8] we similarly investigated its treatment with two N-heterocyclic silylenes, :Si(RNCH)$_2$ (R = Dip[9] or Bu^t [10]). Both reactions proceeded cleanly at room temperature to afford high isolated yields (86% and 88% respectively), of the *N*-boryl substituted silaimines, **1** and **2**, as colourless crystalline solids (Scheme 1). The compounds are indefinitely stable in the solid state and solution at room temperature, when kept under an inert atmosphere. Their $^{11}B\{^1H\}$ NMR spectra each exhibit singlet resonances at *ca.* δ 21 ppm, indicating similar three-coordinate boron environments in the compounds. Singlet resonances were observed in the $^{29}Si\{^1H\}$ NMR spectra of **1** (δ -48.0 ppm) and **2** (δ -57.6 ppm), the latter of which lies between signals previously reported for three- and four-coordinate silaimines derived from N-heterocyclic silylenes, e.g. (HCNDip)$_2$Si=N(C$_6$H$_3$Mes$_2$-2,6) (^{29}Si: δ -49.0 ppm, Mes = mesityl)[3a] and (HCNBu^t)$_2$(THF)Si=NC(C$_6$H$_5$)$_3$ (^{29}Si: δ -66.6 ppm).[3d] The heaviest ions detected in the EI mass spectra of the compounds correspond to the monomeric silaimines.



Scheme 1. The synthesis of silaimines **1** and **2**.

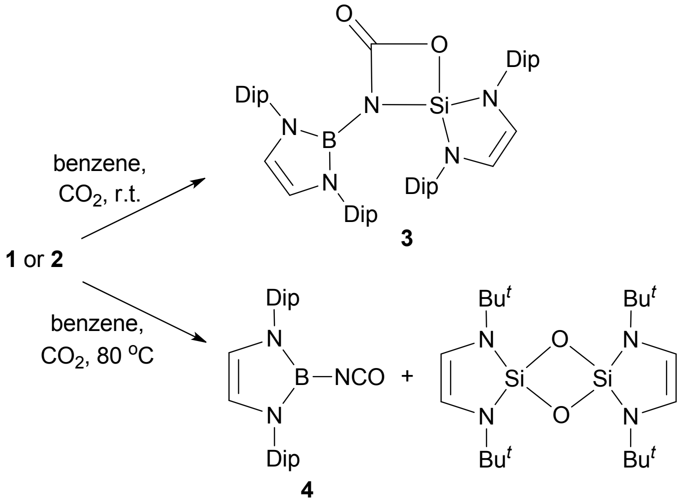
The X-ray crystal structures of **1** and **2** were determined, and their molecular structures are depicted in Figure 1. That for **1** shows it to be monomeric with three-coordinate trigonal planar silicon and boron centres. The Si-N distance in the compound, 1.502(2) Å, is at the lower end of the range for Si=N double bonds,[3-6,11] but close to that in the closely related compound, $(HCNDip)_2Si{=}N(C_6H_3Mes_2\text{-}2,6)$ (1.533(2) Å).[3a] Interestingly, the degree of bending at the imine *N*-centre is small (Si-N-B 172.7(2)°), but again similar to the equivalent angle in $(HCNDip)_2Si{=}N(C_6H_3Mes_2\text{-}2,6)$ (176.7(2)°).[3a] Moreover, the exocyclic B-N distance in **1** (1.284(3) Å) is the shortest for any compound incorporating the boryl ligand, $-B(DipNCH)_2$,[11] and may well indicate a degree of π-bonding in this linkage. However, because of Si/B crystallographic site disorder modelled in the crystal structure of **1**, bond lengths within the Si-N-B fragment should be considered as tentative. In contrast to **1**, silaimine **2** is dimeric, associating through long intermolecular Si-N interactions (1.904(2) Å). This leads to a distorted tetrahedral silicon centre and a $Si\text{-}N_{imine}$ bond (1.573(2) Å) that is longer than that in **1**, but shorter than the Si-N distance in the related four-coordinate silaimine, $(HCNBu^t)_2(THF)Si{=}NC(C_6H_5)_3$ (1.599(4) Å).[3d] Despite an equivalent, nearly linear Si-N-B fragment in **2** (171.5(2)°), the exocyclic B-N distance in the compound (1.396(4) Å) is more than 0.1 Å longer than that in **1**, and reminiscent of a single bond.



(a) (b)

Figure 1. Molecular structures of (a) **1** and (b) **2** (20% thermal ellipsoids are shown; hydrogen atoms omitted). See crystallographic discussion for relevant metrical parameters.

With compounds **1** and **2** in hand, we were keen to investigate their reactivity toward a variety of small molecules. Both compounds exhibited no reaction with H_2, CO or HBpin (pin = pinacolato), even when the reaction mixtures were heated at 60 °C for several hours. In contrast, treatment of a benzene solution of **1** with 1 atmosphere of CO_2 at room temperature resulted in the formation of the [2+2] cycloadduct, **3**, which was isolated in a 72 % yield after work-up (Scheme 2). The compound is stable in benzene solutions at 80 °C for 12 hours. It is of note that closely related [2+2] cycloadducts of CO_2 with a guanidinate coodinated silaimine and a metalla-silaimine have previously been reported.[12,13] A different outcome resulted from the reaction of **2** with an excess of CO_2. That is, no reaction occurred at room temperature, but upon heating the reaction mixture at 80 °C for 14 hours, the silaimine was consumed and a mixture of the boron isocyanate, **4**, and the known oxo-bridged silicon(IV) species, $\{(HCNDip)_2Si(\mu\text{-}O)\}_2$,[10] were formed. It is conceivable that this reaction proceeds *via* an intermediate [2+2] cycloadduct similar to **3**, which then cleaves to give the observed products. However, following the reaction by NMR spectroscopy revealed no signals that might correspond to any intermediate, implying that if there is an intermediate in the reaction, it is too short lived to be observed.



Scheme 2. Synthesis of compounds **3** and **4**.

In solution, compound **3** exhibits a signal at δ -49.2 ppm in its ^{29}Si{^{1}H} NMR spectrum, which is considerably downfield of the resonance for the related guanidinato-silaimine/CO_2 cycloadduct, $\{Me_2NC(NDip)_2\}(Me_3SiO)Si\{OC(=O)N(SiMe_3)\}$ (δ -120.0 ppm).[12] A strong C=O stretching band is present in the FTIR spectrum of the compound at ν = 1804 cm^{-1}. An X-ray crystallographic analysis of the compound shows it to be monomeric in the solid state (Figure 2), and to contain a planar four-membered SiOCN ring with an exocyclic C=O moiety, as is the case in the two other silaimine/CO_2 cycloadducts that have been structurally authenticated.[12,13] The bond lengths within that ring, which is coordinated by boryl and 1,4-diazabutadiendiyl fragments, are all consistent with single bond interactions. A representation of the molecular structure of **4** is depicted in Figure 2. The compound possesses a linear NCO fragment with a slightly bent BNC unit (159.4(1)°), similar to the situation in the related N-heterocyclic carbene coordinated boron isocyanate complex, $\{(HCNDip)_2C\}(H)_2B(NCO)$ (166.6(2)°).[14]

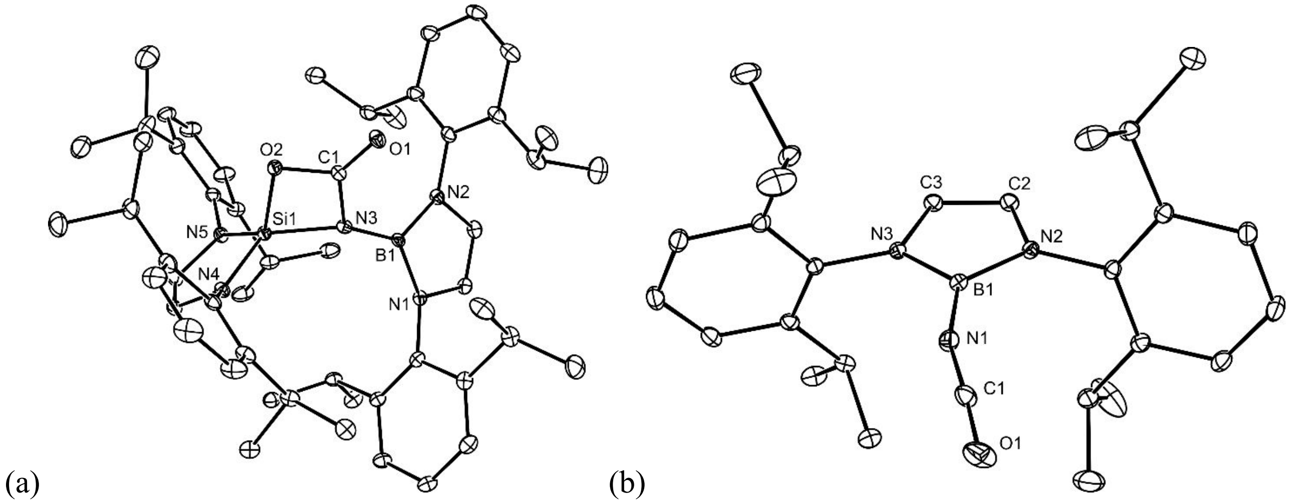
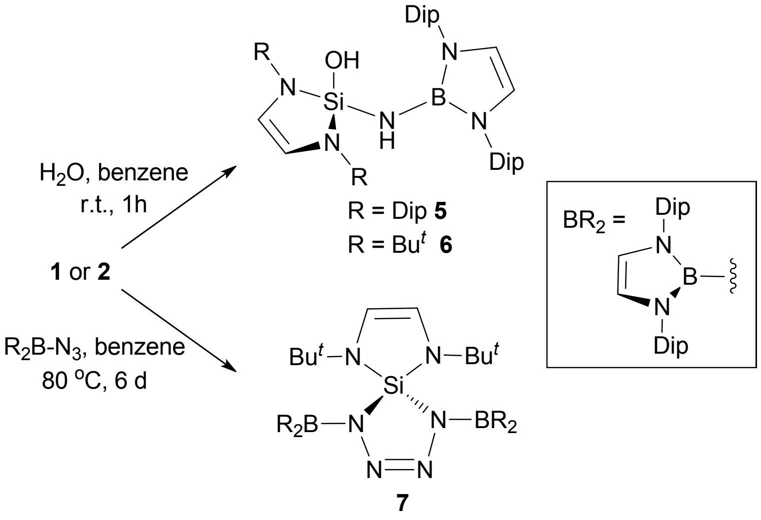


Figure 2. Molecular structures of (a) **3** and (b) **4** (20% thermal ellipsoids are shown; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°) for **3**: Si(1)-O(2) 1.693(2), Si(1)-N(3) 1.755(3), O(1)-C(1) 1.191(4), C(1)-O(2) 1.379(4), C(1)-N(3) 1.410(4), B(1)-N(3) 1.440(4), Si(1)-O(2) 1.693(2), Si(1)-N(3) 1.755(3), O(1)-C(1) 1.191(4), C(1)-O(2) 1.379(4), C(1)-N(3) 1.410(4), B(1)-N(3) 1.440(4), O(2)-Si(1)-N(3) 78.48(11), O(1)-C(1)-N(3) 131.5(3), O(2)-C(1)-N(3) 102.9(2), C(1)-O(2)-Si(1) 91.04(16), C(1)-N(3)-Si(1) 87.53(17). Selected bond lengths (Å) and angles (°) for **4**: O(1)-C(1) 1.1763(16), N(1)-C(1) 1.1703(16), N(1)-B(1) 1.4374(17), C(1)-N(1)-B(1) 159.40(12), N(1)-C(1)-O(1) 176.80(15).

For sake comparison with silaimines devoid of boryl substituents, the reactivity of **1** and **2** towards H_2O and the boron azide, $(HCNDip)_2BN_3$, was explored here. With respect to the former substrate, water is known to add across the Si=N double bond of silaimines, yielding aminosilanols.[3a] Both **1** and **2** behave similarly in that when benzene solutions of the compounds were treated with stoichiometric amounts of water, their B-N linkages remained intact, and good isolated yields of **5** and **6** were obtained as colourless crystalline solids after work-up (Scheme 3). To the best of our knowledge, these compounds represent the first examples of structurally characterized borylaminosilanols. Isolated, or *in situ* generated, silaimines are also well known to react with organoazides, RN_3, to give silatetrazolines, $R_2Si(RNN)_2$, *via* [3+2] cycloaddion reactions.[15] In contrast, compound **1** was found to be unreactive towards the azide $(HCNDip)_2BN_3$, even at elevated temperatures over extended periods. As this could be due to the steric bulk of both the silaimine and the azide substrate, attention then turned to the less hindered silaimine **2**. Although this also did not react with the boron azide at ambient temperature, a reaction did occur over 6 days at 80 °C to give a moderate isolated yield of the spirocyclic borasilatetrazoline, **7** (Scheme 3), presumably *via* a [3+2] cycloaddition reaction. As was the case with **5** and **6**, compound **7** appears to have no precedent in the literature.



Scheme 3. Synthesis of compounds **5**-**7**.

In the solution state compounds **5**-**7** exhibit resonances in their ^{29}Si{^{1}H} NMR spectra (**5**: δ -51.9 ppm; **6**: δ -47.4 ppm; **7**: δ -43.0 ppm) that have similar chemical shifts to each other, and that of the silaimine precursor **2**. Moreover, the signals in their ^{11}B{^{1}H} NMR spectra (**5**: δ 22.4 ppm; **6**: δ 22.3 ppm; **7**: δ 23.6 ppm) are typical of three-coordinate boron centres in compounds bearing the $(HCNDip)_2BN$ fragment, e.g. :Si{N(SiMe$_3$)[B(DipNCH)$_2$]}$_2$ (δ 23.7 ppm).[16] All of **5**-**7** were crystallographically characterised, but given the similarities between **5** and **6**, only the molecular structures of **5** and **7** are depicted in Figure 3. The B-N, Si-N and Si-O distances of the former are consistent with single bonds, while its silicon centre possess a distorted tetrahedral geometry (*cf.* the related aminosilanol (HCNDip)$_2$Si(OH)-N(H)(C$_6$H$_3$Mes$_2$-2,6)).[3a] The structure of **7** shows it to be similar to previously reported spirocyclic silatetrazolines, e.g. (HCNBu^t)$_2$Si(RNN)$_2$ (R = SiPh$_3$),[15d] in that it exhibits a heavily distorted tetrahedral geometry at silicon, and alternating N-N single and double bonds over the N_4 fragment of the compound. The level of steric protection provided by the boryl substituents to the central spirocyclic unit is clearly evident from its molecular structure.

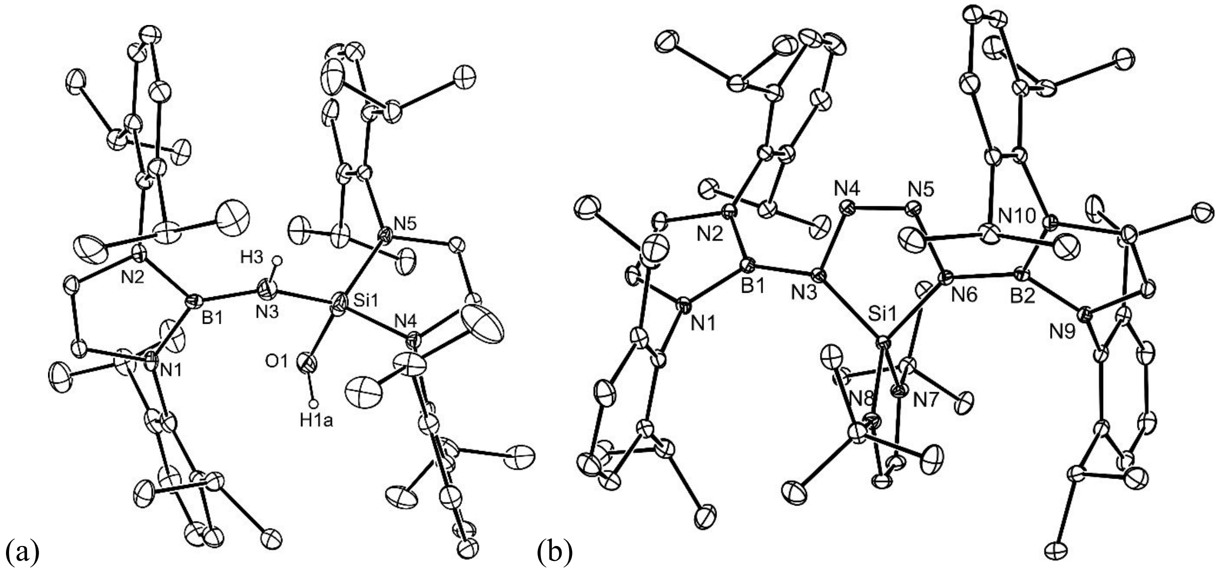


Figure 3. Molecular structures of (a) **5** and (b) **7** (20% thermal ellipsoids are shown; hydrogen atoms, except hydroxyl and amino protons, omitted). Selected bond lengths (Å) and angles (°) for **5**: Si(1)-N(3) 1.588(5), Si(1)-O(1) 1.947(6), B(1)-N(3) 1.394(8), N(3)-Si(1)-O(1) 100.8(3), B(1)-N(3)-Si(1) 146.7(5). Selected bond lengths (Å) and angles (°) for **7**: Si(1)-N(6) 1.7490(10), Si(1)-N(3) 1.7505(10), B(1)-N(3) 1.4718(16), B(2)-N(6) 1.4656(16), N(3)-N(4) 1.4106(14), N(4)-N(5) 1.2547(15), N(5)-N(6) 1.4069(14), Si(1)-N(6) 1.7490(10), Si(1)-N(3) 1.7505(10), B(1)-N(3) 1.4718(16), B(2)-N(6) 1.4656(16), N(3)-N(4) 1.4106(14), N(4)-N(5) 1.2547(15), N(5)-N(6) 1.4069(14), N(7)-Si(1)-N(8) 92.64(5), N(6)-Si(1)-N(3) 88.48(5), N(4)-N(3)-Si(1) 110.72(7), N(5)-N(4)-N(3) 114.95(10), N(4)-N(5)-N(6) 114.87(10), N(5)-N(6)-Si(1) 110.97(7).

Conclusion

The preparation of the first examples of *N*-boryl substituted silaimines have been described. The more hindered molecule **1** is monomeric, whereas the smaller silaimine is dimeric in the solid state. The compounds shows divergent reactivity with CO_2, in that **1** undergoes a [2+2] cycloaddition with CO_2 to form a four-membered SiCON heterocycle in product **3** under mild conditions. In contrast, compound **2** undergoes a bond metathesis reaction affording a boron isocyanate **4**, and a known oxo-bridged silicon(IV) system. Both silaimines add H_2O across their Si=N bonds to give the borylaminosilanols **5** and **6** at ambient temperature. The larger silaimine does not react with the bulky boron azide used in this study, whilst smaller **2** undergoes a [3+2] cycloaddition reaction with the azide to give spirocyclic borasilatetrazoline, **7**. Overall, the reactivity of the prepared *N*-boryl substituted silaimines is similar to that reported for organo- and amido-substituted silaimines, though the steric differences between the two Si=N bonded compounds plays a definitive role in the outcomes of their reactions with the small molecule substrates studied.

Electronic supplementary information (ESI) available: Experimental procedures and characterisation data for all new compounds. Crystal data, details of data collections and refinements. CCDC numbers: 1936046-1936052. For ESI and crystallographic data in CIF format see DOI: 10.xxxxxxx

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Graphical Abstract

Synthesis and Reactivity of Boryl Substituted Silaimines

K. Yuvaraj and Cameron Jones*

Two bulky *N*-boryl substituted silaimines have been prepared and their reactivity toward a number of small molecule substrates examined (e.g. see picture, Dip = 2,6-diisopropylphenyl). Steric differences between the two Si=N bonded compounds play a definitive role in the outcomes of these reactions.