Facile Activation of Inert Small Molecules using a 1,2-Disilylene

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Facile Activation of Inert Small Molecules using a 1,2-Disilylene

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Abstract

Reactions of the known amidinate stabilised 1,2-disilylene, [{ArC(NDip)$_2$}Si]$_2$ **1** (Dip = 2,6-diisopropylphenyl, Ar = 4-$C_6H_4Bu^t$) with a series of inert, unsaturated small molecule substrates have been carried out. Compound **1** reduces Bu^{t}NC: to give the singlet biradicaloid 1,3-disilacyclobutanediyl [{ArC(NDip)$_2$}Si(μ-CNBu^t)]$_2$ **3**, which can be oxidised by 1,2-dibromoethane to give [{ArC(NDip)$_2$}(Br)Si(μ-CNBu^t)]$_2$ **4**. Disilylene **1** reduces two molecules of ethylene to give an unprecedented disilabicylo[2.2.0]hexane, [{ArC(NDip)$_2$}Si(μ-C_2H_4)]$_2$ **5**. In contrast, only one molecule of ethylene inserts in the Ge–Ge bond of the digermylene analogue of **1**, *viz.* [{ArC(NDip)$_2$}Ge]$_2$ **6**, leading to the formation of the bis(germylene), [{ArC(NDip)$_2$}Ge]$_2$(μ-C_2H_4) **7**. Compound **1** reduces CO_2, generating CO, and the oxo/carbonate-bridged disilicon(IV) system, {ArC(NDip)$_2$}Si(μ-CO_3)$_2$(μ-O)Si{(NDip)$_2$CAr} **10**, while its reaction with N_2O proceeds *via* generation of N_2, and a hydrogen abstraction process, to give the oxo/hydroxy disilicon(IV) species, [{ArC(NDip)$_2$}(HO)Si(μ-O)]$_2$ **11**. This study highlights new small molecule activation chemistry for 1,2-disilylenes, which could lead to further adoption of compound **1** as a potent reducing reagent for the transformation of inert unsaturated molecules into value added products.

Introduction

The application of low oxidation state s- and p-block compounds to the activation of enthalpically strong small molecules (e.g. H_2, N_2, CO, C_2H_4, NH_3, CO_2 etc.) is now well established.[1] Interest in this area has blossomed in recent years, largely because such reactive main group systems are increasingly viewed as potential sustainable alternatives to the often toxic and expensive transition metal complexes which have dominated small molecule activations, and associated organic synthetic transformations. In this respect, low oxidation state silicon compounds have been particularly well studied, primarily due to the low cost, low toxicity and high earth abundance of silicon. Moreover, low oxidation silicon compounds are typically very reactive, more so than their heavier group 14 analogues, which lends them to the reductive activation of inert substrates. Examples of low oxidation state silicon compound types that have proved effective in this realm include silylenes, :SiR_2; 1,2-disilylenes, RSi(:)–(:)SiR; disilynes, RSi≡SiR; and bis(silylenes), RSi(:)–(organic linker)–(:)SiR.[2]

The low oxidation state silicon compound most pertinent to the current study is Roesky's amidinate chelated 1,2-disilylene, $[\{PhC(NBu^t)_2\}Si]_2$, which was first reported in 2009.[3] This compound has been extensively exploited for the activation of an array of small molecule substrates, yielding a multitude of novel organo-silicon products.[2,4] Despite the synthetic versatility of $[\{PhC(NBu^t)_2\}Si]_2$, it is perhaps surprising that only one other structurally characterised amidinate chelated 1,2-disilylene, $[\{ArC(NDip)_2\}Si]_2$ **1** (Dip = 2,6-diisopropylphenyl, Ar = 4-$C_6H_4Bu^t$), has been described in the literature (Figure 1).[5] It is noteworthy, however, that a small number of other 1,2-disilylenes are known,[2,6] and have showed reactivity related to that of $[\{PhC(NBu^t)_2\}Si]_2$. While the further chemistry of **1** is sparse,[7] we have recently showed that it reacts cleanly with CO under ambient conditions to give an unprecedented example of an "abnormal" N-heterocyclic silylene, **2** (Figure 1), which is functionalised by an oxysilylene fragment.[8] The ability of this compound to act as a chelating ligand towards transition metal fragments has been demonstrated. Given that no similar chemistry has been described for the related disilylene, $[\{PhC(NBu^t)_2\}Si]_2$, we were keen to explore reactions of **1** with other unsaturated substrates, in order to investigate if other differences between the reactivity of **1** and $[\{PhC(NBu^t)_2\}Si]_2$ exist. The results of those studies are reported herein.

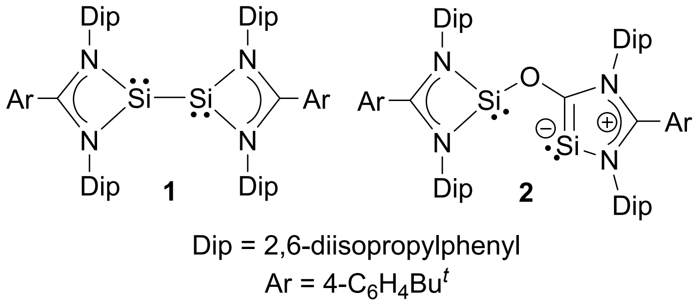
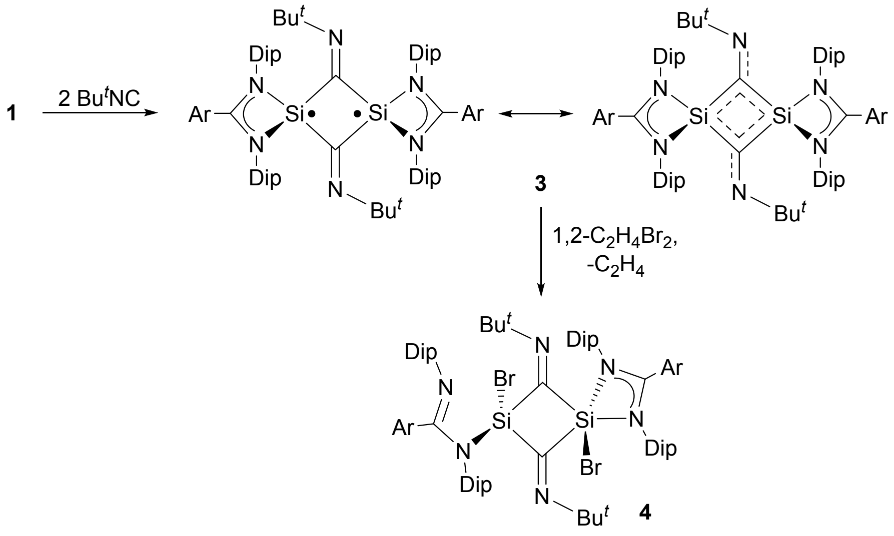


Figure 1. 1,2-disilylene **1** and "abnormal" N-heterocyclic silylene **2**.

Results and Discussion

Reaction with Bu^{t}NC:

In light of the fact that isonitriles are isolobal with CO, and for sake of comparison with the synthesis of **2**, the reaction between disilylene **1** and the isonitrile, Bu^{t}NC:, was carried out. This proceeded rapidly at room temperature to give a moderate isolated yield (50 %) of the dark red crystalline, 1,3-disilacyclobutanediyl **3**, after work-up (Scheme 1). As far as we are aware, the reactivity of Roesky's 1,2-disilylene towards isonitriles has not been reported,[9] though So an co-workers have described an analogous disilacyclobutanediyl, LSi(μ-CNDip)$_2$SiL (L = [PhC(NBu^t)$_2$]$^-$), as arising from a lower yield reductive C=N bond cleavage reaction between [{PhC(NBu^t)$_2$}Si]$_2$ and the carbodiimide, DipNCNDip.[10] DFT calculations revealed a model of that system to have singlet biradicaloid character, which is implied in the isostructural analogue **3**. To provide some experimental evidence for this proposal, compound **3** was reacted with 1,2-dibromoethane, which gave a moderate isolated yield of the yellow-orange compound, **4**. Such halogen abstraction processes are well known for reactions between silicon radicals and organo-halides.[11]



Scheme 1. Synthesis of compounds **3** and **4**.

Compound **3** is diamagnetic in solution, and exhibits a singlet resonance at δ -46.3 ppm in its ^{29}Si NMR spectrum (*cf.* δ -39.9 ppm for LSi(μ-CNDip)$_2$SiL[3]). Interestingly, the aliphatic signals in the room temperature ^{1}H NMR spectrum of **3** are very broad. Cooling *d*$_8$-toluene samples of the compound resolved the spectrum between -40 and -60 °C, thus showing it to display eight isopropyl methyl and four isopropyl methine signals (see ESI for more details). This is what would be expected for the solid-state structure of **3** (see below) being retained in solution. It is possible that the signal broadness at room temperature results from rotation of the NBu^t units at a speed that is similar to the NMR timescale. The solution state ^{1}H and ^{13}C NMR spectra of diamganetic **4** are complex, and are consistent with the asymmetric solid-state structure of the compound. For example, eight isopropyl methine signals were observed in each spectrum. The low solubility of **4** in common deuterated solvents prevented the acquisition of an interpretable ^{29}Si NMR spectrum.

Both **3** and **4** were crystallographically characterised, and their molecular structures are depicted in Figures 2 and 3, respectively. Compound **3** is isostructural to LSi(μ-CNDip)$_2$SiL, and shows it to have a central, planar Si$_2$C$_2$ four-membered ring, with nearly identical Si-C distances. These lie between those normally seen for single (1.87 Å) and double (1.70 Å) bonds,[12] as do the C-N distances of the bent bridging CNBu^t units, which are close to coplanar with the Si$_2$C$_2$ ring. All of these features are strongly suggestive of significant electronic delocalisation over the Si$_2$C$_2$N$_2$ core of the molecule. The bulky amidinate ligands chelate the tetrahedral Si centres, forming SiN$_2$C four-membered rings which subtend dihedral angles of 80.5° with the Si$_2$C$_2$ plane. The trans-annular Si···Si distance (2.5020(9) Å) is well outside that expected for Si-Si single bonds (*ca.* 2.35 Å).[13]

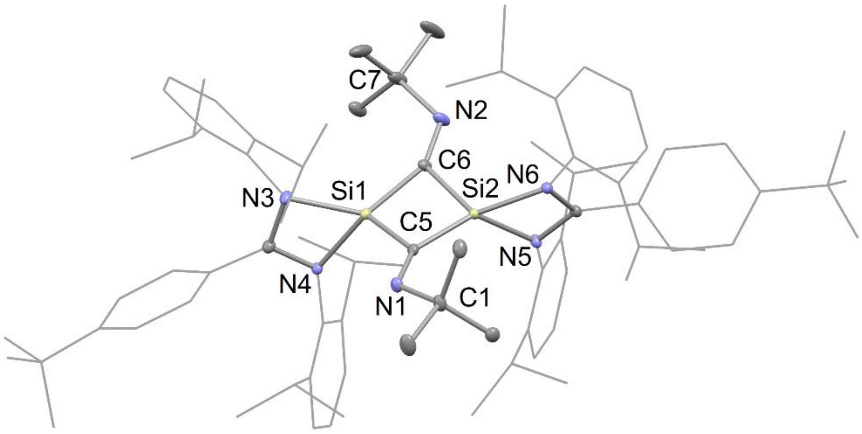


Figure 2. Molecular structure of **3**. Thermal ellipsoids drawn at the 25 % probability level. Hydrogen atoms omitted. Aryl groups displayed as wireframe for clarity. Selected bond lengths (Å) and angles (°): Si(1)-C(6) 1.833(3), Si(1)-C(5) 1.843(2), Si(1)-N(4) 1.874(2), Si(1)-N(3) 1.893(2), Si(2)-C(6) 1.837(3), Si(2)-C(5) 1.840(3), Si(2)-N(6) 1.879(2), Si(2)-N(5) 1.881(2), N(1)-C(5) 1.311(3), N(2)-C(6) 1.315(4), C(6)-Si(1)-C(5)92.62(11), C(6)-Si(2)-C(5) 92.62(12), Si(2)-C(5)-Si(1) 85.59(11), Si(1)-C(6)-Si(2) 85.96(11), C(5)-N(1)-C(1) 119.8(2), C(6)-N(2)-C(7) 120.0(3).

In the solid state, compound **4** also displays a Si_2C_2 four-membered ring, though the Si-C bond lengths are significantly longer than those in **3**, and more akin to single bonded interactions. Moreover, the cyanide C-N bond lengths are shorter than those in **3**, and close to what would be expected for double bonds. Therefore, and as opposed to the situation for **3**, there appears to be little electronic delocalisation over the $Si_2C_2N_2$ core of the compound. This is fully consistent with the oxidation of the silicon centres of **3** with bromine. However, in the product **4**, one amidinate chelates distorted trigonal bipyramidal Si(1), while the other acts as an electronically localised κ^1-N-iminoamide ligand towards tetrahedral Si(2). The difference between the ligating modes of the amidinate units probably arises from the steric bulk of those units, discounting both amidinates acting as chelating ligands.

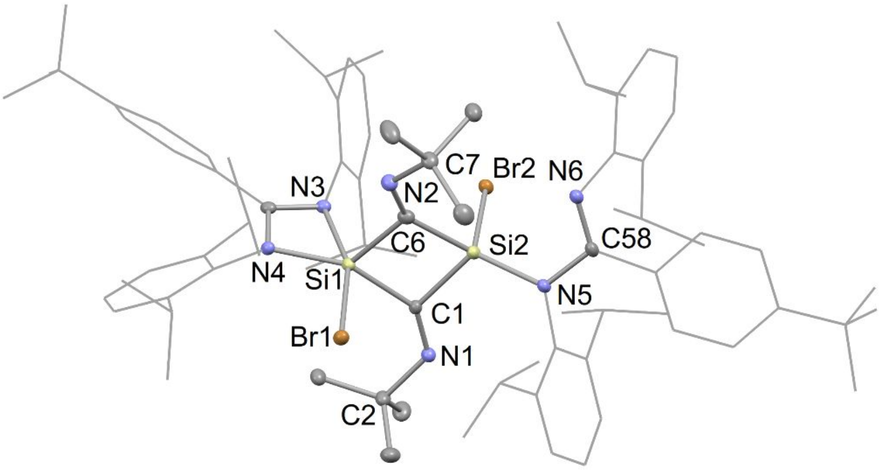


Figure 3. Molecular structure of **4**. Thermal ellipsoids drawn at the 25 % probability level. Hydrogen atoms omitted. Aryl groups displayed as wireframe for clarity. Selected bond lengths (Å) and angles (°): Br(1)-Si(1) 2.3808(6) Si(1)-C(6) 1.917(2), Si(1)-C(1) 1,.934(2), N(1)-C(1) 1.262(3), C(1)-Si(2) 1.925(2), Br(2)-Si(2) 2.2277(15), Si(2)-C(6) 1.953(2), N(2)-C(6) 1.277(3), C(6)-Si(1)-C(1) 87.19(9), C(6)-Si(1)-Br(1) 93.30(7), C(1)-Si(1)-Br(1) 90.53(6), C(1)-Si(2)-C(6) 86.45(9), C(1)-Si(2)-Br(2) 101.78(8), C(6)-Si(2)-Br(2) 101.91(8), C(1)-N(1)-C(2) 124.01(18), C(6)-N(2)-C(7) 124.2(2).

In order to understand the electronic structure of **3**, and to make further comparisons with LSi(μ-CNDip)$_2$SiL, DFT calculations (B3PW91) were carried out on the full molecule in the gas phase, both as a singlet state and a triplet state species. The geometry of the singlet state molecule optimised to be very close to that of the compound in the solid state, and is 10.51 kcal/mol more stable that the triplet state. The electronic structure of singlet biradicaloid **3** is very similar to that described for its parent version (*viz.* {HC(NH)$_2$}Si(μ-CNH)$_2$Si{(NH)$_2$CH}),[10] so will not be described in detail here. However, like that compound, the HOMO of **3** (Figure 4) is delocalised over the Si$_2$C$_2$N$_2$ core, with significant Si-N σ* and C-N π* orbital character. This situation is fully consistent with the Si-C and C-N interactions being intermediate between single and double bonds, as also suggested by the crystallographic data.

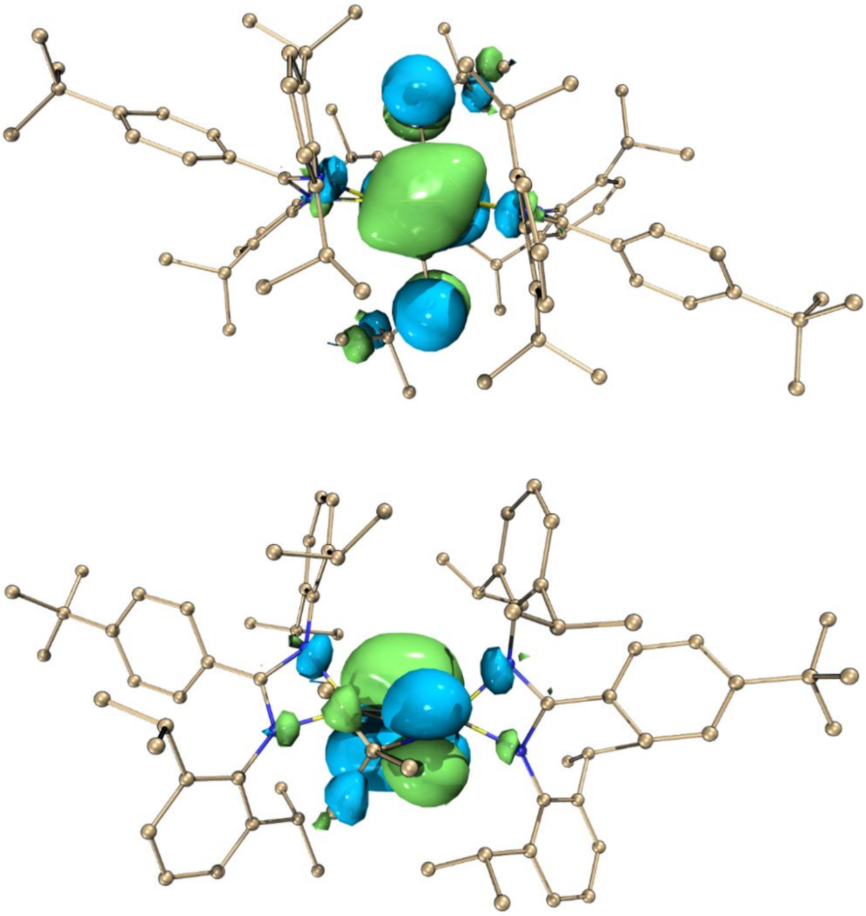


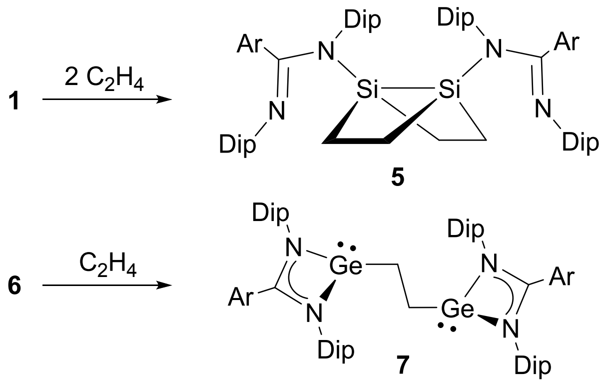
Figure 4. Representation of the HOMO of **3** viewed from above (top), and side-on to (bottom), the Si_2C_2 ring.

Reaction with C_2H_4

Ethylene is widely used as a chemical feedstock in numerous industrial processes, which involve its oxidation, reduction, oligomerisation, polymerisation etc.[14] Because of the importance of its synthetic transformations, it is not surprising that the activation of ethylene by low oxidation state main group compounds is extensively studied.[1,2] Notwithstanding this, we are not aware of any reports on the activation of ethylene using amido-1,2-disilylenes (including Roesky's), though ethylene activations involving silylenes, disilynes, disilenes and bis(silylenes) have yielded a variety of product types.[2]

When a hexane solution of 1,2-disilylene **1** was stirred under one atmosphere of ethylene at room temperature, the solution changed from deep blue to orange in colour over 1 hour. Subsequent work up led to the formal [2+2+2] cycloadduct, **5**, in moderate isolated yield, as an orange crystalline solid (Scheme 2). While **5** represents the first example of a disilabicylo[2.2.0]hexane derived from ethylene activation, a handful of germanium and tin analogues have been reported.[15,16] As has been suggested for those systems, the mechanism of formation of **5** could involve an initial [2+1] cycloaddition of ethylene to one or both of the Si centres of the disilylene, yielding three-membered silirane rings, followed by rearrangement to the final product.

For sake of comparison, a solution of the germanium analogue of **1**, *viz.* $[\{\mathrm{ArC(NDip)_2}\}\mathrm{Ge}]_2$ **6**,[5] was placed under an atmosphere of ethylene. This did not lead to a bicyclic species similar to **5**, but instead to insertion of ethylene into the Ge−Ge bond of **6**, and formation of the ethylene bridged bis(germylene), **7** in moderate isolated yield as a yellow-orange crystalline solid. This compound is reminiscent of the bulky amido-substituted, ethylene bridged bis(germylene) $\mathrm{L^\dagger Ge(C_2H_4)GeL^\dagger}$ ($\mathrm{L^\dagger}$ = $\mathrm{N(SiPr^{\mathit{i}}_3)[C_6H_2\{C(H)Ph_2\}_2Pr^{\mathit{i}}\text{-}2,6,4]}$).[17] It seems likely that **6** does not react with two equivalents of ethylene, whereas **1** does, because of the already demonstrated lower reactivity of the digermylene.[8]



Scheme 2. Synthesis of compounds **5** and **7.**

The ^{29}Si NMR spectrum of **5** exhibits a singlet resonance at δ 30.0 ppm, which is *ca.* 67 ppm upfield of that for **1** (δ 96.9 ppm). This is consistent with the increase in oxidation state of the silicon centres in **5**, and can be compared to the chemical shifts for somewhat related 1,4-disila-Dewar benzenes, e.g. δ -26.3 ppm for $\mathrm{(MeBu^{\mathit{t}}_2Si)Si(\mu\text{-}C_2Et_2)_2Si(SiBu^{\mathit{t}}_2Me)}$.[18] The ^{1}H and ^{13}C NMR spectra of **5** are suggestive of a more symmetrical structure for the molecule than it has in the solid state (see below). For example, there is only one isopropyl methine resonance in each spectrum. It is possible that this arises due to a fluxional process in solution, whereby the imine arms of the amidinate ligands rapidly coordinate/dissociate on the NMR timescale, giving rise to a more symmetrical averaged structure, in which both amidinate N-centres are coordinated to the Si centres. With that said, the ^{29}Si NMR chemical shift for the silicon centres is outside the normal region for 5-coordinate silicon, so the N···Si interactions in the purported average structure would have to be weak. Attempts to probe the fluxional process for **5** using variable temperature NMR studies were not successful, due to the low solubility of the compound in non-coordinating deuterated solvents at temperatures below -20 °C. The NMR spectra for the bis(germylene) compound **7** are reminiscent of its solid-state structure.

The solid-state molecular structures of **5** and **7** are depicted in Figures 5 and 6, respectively. Compound **5** is the first crystallographically characterised disilabicyclo[2.2.0]hexane, in which the two silicon centres have heavily distorted tetrahedral geometries. The silicon atoms are bridged by two ethylene fragments, while retaining a single Si–Si bond that is shorter than that in **1** (2.4885(15) Å). The two four-membered Si_2C_2 rings are puckered with respect to each other (dihedral angle = 68.3°), and the Si_2C_4 core is ligated in a κ^1-fashion by two electronically localised imino-amide ligands. The geometry of **5** is closely comparable to previously reported amido-digermabicylo[2.2.0]hexanes.[15] In contrast to **5**, the Ge–Ge bond in bis(germylene) **7** has been cleaved, and both pyramidal Ge atoms are coordinated by bidentate, electronically localised amidinate ligands, and one bridging ethylene unit. Accordingly, the Ge centres are formally in the +2 oxidation state, and possess stereochemically active lone pairs of electrons. This is comparable to the situation in the amido bis(germylene), $L^{\dagger}Ge(C_2H_4)GeL^{\dagger}$.[17]

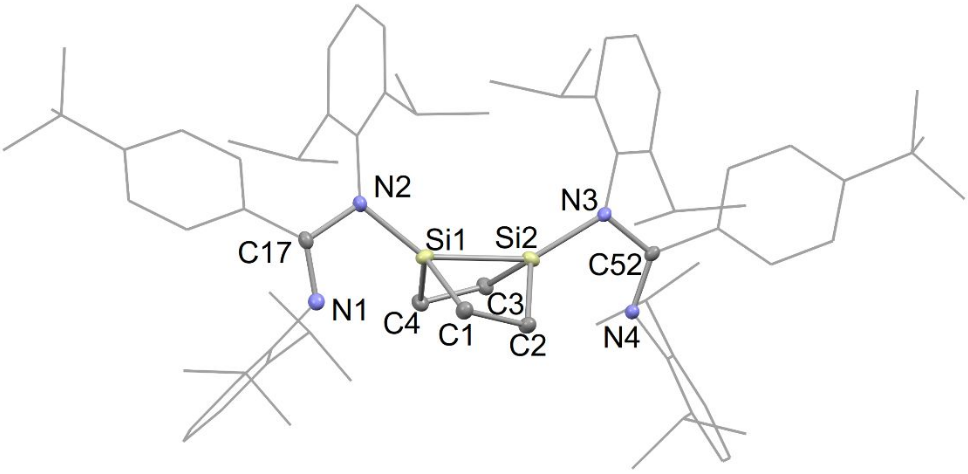


Figure 5. Molecular structure of **5**. Thermal ellipsoids drawn at the 25 % probability level. Hydrogen atoms omitted. Aryl groups displayed as wireframe for clarity. Selected bond lengths (Å) and angles (°): Si(1)-N(2) 1.7861(18), Si(1)-C(1) 1.873(2), Si(1)-C(4) 1.917(2), Si(1)-Si(2) 2.3731(9), C(1)-C(2) 1.569(3), Si(2)-N(3) 1.7900(18), Si(2)-C(3) 1.865(2), Si(2)-C(2) 1.915(2), C(3)-C(4) 1.565(3),

N(2)-Si(1)-C(1) 122.85(10), N(2)-Si(1)-C(4) 117.85(10), N(2)-Si(1)-Si(2) 142.82(7), N(3)-Si(2)-C(3) 121.80(9), N(3)-Si(2)-C(2) 117.25(10), N(3)-Si(2)-Si(1) 144.15(6).

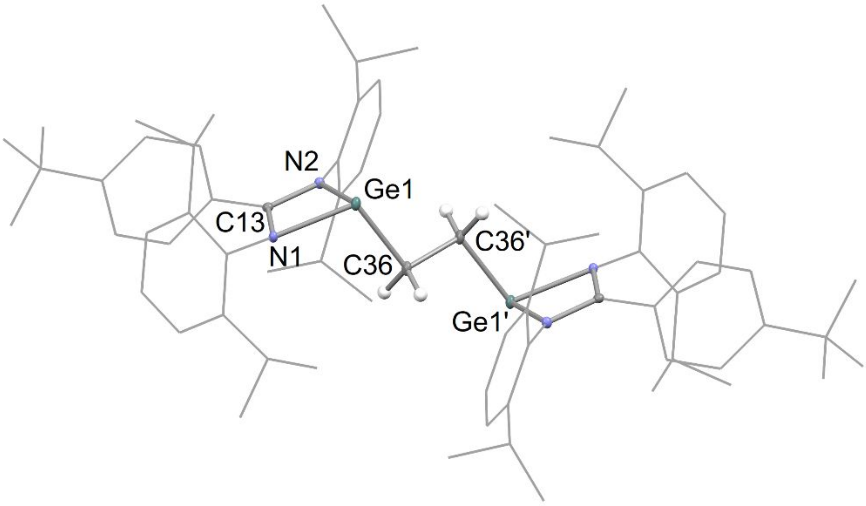


Figure 6. Molecular structure of **7**. Thermal ellipsoids drawn at the 25 % probability level. Hydrogen atoms omitted. Aryl groups displayed as wireframe for clarity. Selected bond lengths (Å)

and angles (°): Ge(1)-C(36) 1.999(2), Ge(1)-N(2) 2.0276(16), Ge(1)-N(1) 2.0393(17), C(36)-C(36)' 1.551(4), N(2)-Ge(1)-N(1) 64.52(7), C(36)'-C(36)-Ge(1) 105.74(19).

Reactions with CO_2 and N_2O

A considerable amount of research has been directed towards the transition metal free activation of CO_2 and N_2O, *en route* to value added products. This has included many studies on the use of low oxidation state main group compounds for the activation of both gasses.[1,2] Although success has been had in this arena for low-valent silicon compounds, there are only two reports of reductive activations involving base stabilised amido-1,2-disilylenes. Baceiredo and Kato's phosphine stabilised disilylene reduces CO_2 to CO to give aminosilicate **8**, in which the silicon centres are bridged by one carbonate and two oxo units (Figure 7).[6] Roesky's amidinato disilylene reduces N_2O to N_2, yielding compound **9**, which features two disiloxane rings, bridged by oxygen atoms.[19] These results prompted us to explore the reactivity of **1** towards CO_2 and N_2O.

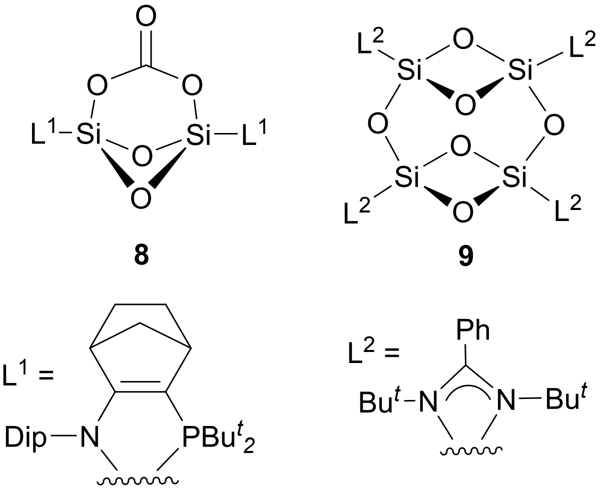
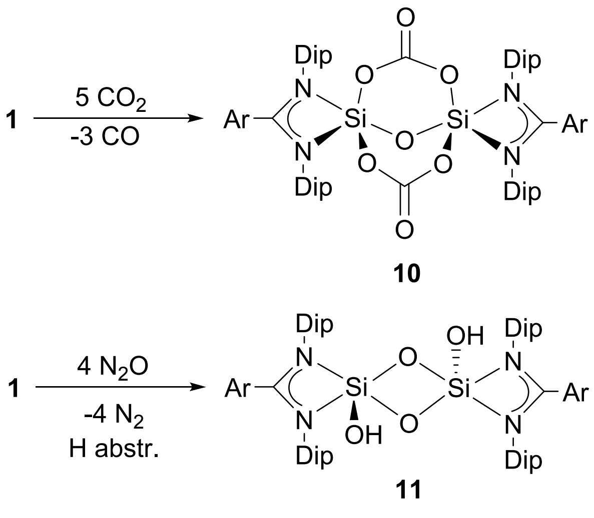


Figure 7. Previously reported products arising from reactions of amido-1,2-disilylenes with CO_2 (**8**) and N_2O (**9**).

A toluene solution of **1** was placed under an atmosphere of dry CO_2, which led to loss of the deep blue colour of the disilylene over *ca.* 1 hour, yielding a colourless solution. Work-up provided a moderate isolated yield of compound **10**, as a colourless crystalline material (Scheme 3). It seems reasonable that the mechanism of formation of **10** is similar to that proposed for **8**.[6] That is, the disilylene reduces three molecules of CO_2 to give a tri-oxo disilicon(IV) intermediate, which reacts with two further molecules of CO_2 to give the oxo-dicarbonate product **10**. Further evidence for this proposal is the evolution of a gaseous by-product in the reaction, presumed to be CO. It is noteworthy that other low-valent silicon and germanium compounds are known to reduce CO_2 to CO,[2,20] and in some cases the group 14 oxo-products can trap excess CO_2 to form carbonate products, as in the formation of **10**.[2,21]

Although tri-oxo intermediate was not observed, and could not be isolated from the reaction of **1** with CO_2, it was thought that reaction of **1** with N_2O, an excellent atomic oxygen source, might lead to the isolation of the oxo-intermediate. However, treatment of a hexane solution of **1** with an excess of dry N_2O gas led to the formation of the oxohydroxy silicon(IV) compound **11** as a colourless crystalline solid, in moderate isolated yield (Scheme 3). The mechanism of formation of **11** is unknown at this stage, though it could involve net reduction of four molecules of N_2O, in conjunction with abstraction of hydrogen from the amidinate ligand or adventitious moisture, though moisture was rigorously excluded from the reaction. Abstraction of hydrogen from the reaction solvent was ruled out, as when the reaction was carried out in C_6D_6, the hydroxy signal appeared in the ^{1}H NMR spectrum of the reaction mixture. It is worth mentioning that related reactions of terphenyl substituted digermynes with N_2O, can similarly proceed *via* hydrogen abstraction, and formation of terminal germanium hydroxide species.[22]



Scheme 3. Synthesis of compounds **10** and **11**.

The solution-state ^{1}H and ^{13}C NMR spectra of **10** and **11** are consistent with their proposed structures. Of most note is the presence of a hydroxide proton singlet resonance at δ 2.64 ppm in the ^{1}H NMR spectrum of **11**. The ^{29}Si NMR spectra of the compounds display signals at fields (**10**: δ -121.1 ppm; **11**: δ -102.4 ppm) typical for five-coordinate silicon, and comparable with the spectra recorded for the related compounds **8** (δ -100.7 and -101.6 ppm for two diastereomers)[6] and **9** (δ -111.0 ppm).[19] A strong C=O stretching band at $\nu = 1756$ cm^{-1} is present in the infra-red spectrum of **10**, close to that found for the related carbonate bridged disilicon compound, $Cp^*_2Si(\mu\text{-}CO_3)_2SiCp^*_2$ ($\nu = 1760$ cm^{-1}; $Cp^* = [C_5Me_5]^-$).[23]

The molecular structure of **10** (Figure 8) reveals it to be a silicon(IV) compound, in which each five-coordinate silicon centre is chelated by an amidinate ligand, and both are bridged by two carbonates and one oxo group. The Si···Si separation (2.820(2) Å) is well outside of what would be expected for a bonding interaction. The structure of compound **11** (Figure 9) also shows it to be a five-coordinate disilicon(IV) compound, but in this case, the silicon centres are chelated by amidinate ligands, coordinated by a terminal hydroxide, and bridged by oxo-groups. The Si···Si separation in the compound (2.448(2) Å) is markedly shorter than that in **10**, but comparable to such separations in related compounds with central Si_2O_2 four-membered rings, e.g. 2.503 Å in $L(Bu^tO)Si(\mu\text{-}O)_2Si(OBu^t)L$ ($L = [PhC(NBu^t)_2]^-$).[24]

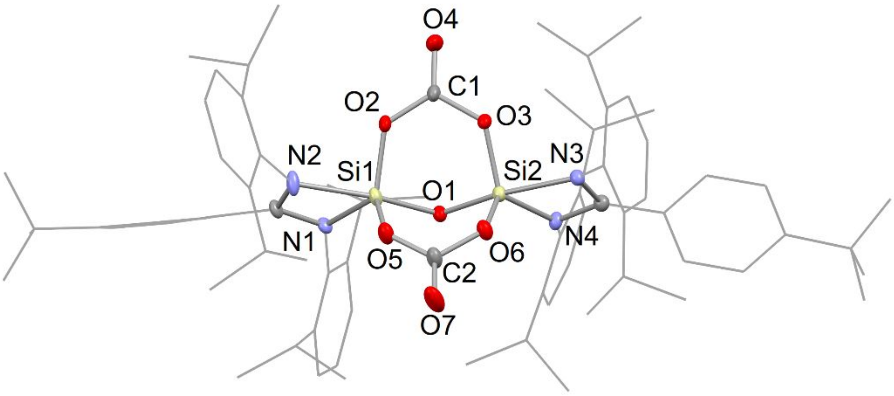


Figure 8. Molecular structure of **10**. Thermal ellipsoids drawn at the 25 % probability level. Hydrogen atoms omitted. Aryl groups displayed as wireframe for clarity. Selected bond lengths (Å) and angles (°): Si(1)-O(1) 1.660(5), Si(1)-O(5) 1.666(5), Si(1)-O(2) 1.678(5), O(1)-Si(2) 1.659(5), C(1)-O(4) 1.190(9), Si(2)-O(3) 1.679(5), Si(2)-O(6) 1.692(5), C(2)-O(7) 1.195(9), O(1)-Si(1)-O(5) 96.5(3), O(1)-Si(1)-O(2) 97.9(2), O(5)-Si(1)-O(2) 115.9(3), O(1)-Si(1)-N(2) 170.1(3), O(1)-Si(2)-O(3) 96.6(2), O(1)-Si(2)-O(6) 97.9(2), O(3)-Si(2)-O(6) 115.1(3), O(1)-Si(2)-N(3) 169.9(3).

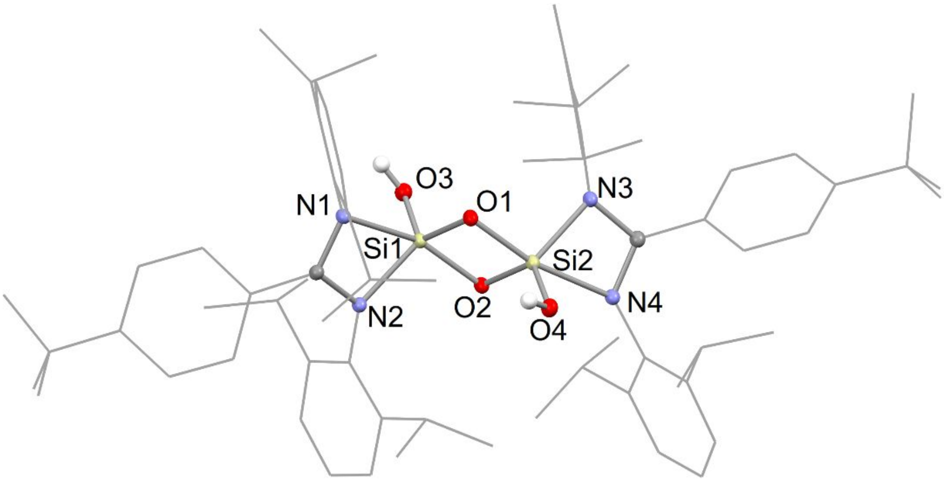


Figure 9. Molecular structure of **12**. Thermal ellipsoids drawn at the 25 % probability level. Hydrogen atoms, except hydroxide protons, omitted. Aryl groups displayed as wireframe for clarity. Selected bond lengths (Å) and angles (°): Si(1)-O(3) 1.6459(13), Si(1)-O(1) 1.6515(11), Si(1)-O(2) 1.7126(10), O(1)-Si(2) 1.7156(10), Si(2)-O(4) 1.6524(13), Si(2)-O(2) 1.6536(11), O(3)-Si(1)-O(1) 120.13(6), O(3)-Si(1)-O(2) 101.07(6), O(1)-Si(1)-O(2) 86.80(5), Si(1)-O(1)-Si(2) 93.26(5), O(4)-

Si(2)-O(2) 122.75(6), O(4)-Si(2)-O(1) 99.60(6), O(2)-Si(2)-O(1) 86.63(5), Si(2)-O(2)-Si(1) 93.30(5).

Conclusion

Reactions of a previously reported amidinate stabilised 1,2-disilylene **1** with a series of inert, unsaturated small molecule substrates have been described. The disilylene reduces Bu^{t}NC: to give the singlet biradicaloid 1,3-disilacyclobutanediyl **3**, which is readily oxidised by 1,2-dibromoethane. This outcome differs to that from the reaction of **1** with CO (isolobal to Bu^{t}NC:), which has previously been shown to yield abnormal N-heterocyclic silylene, **2**. Compound **1** activates two molecules of ethylene, giving rise to the first example of a disilabicylo[2.2.0]hexane, **5**. In contrast, only one molecule of ethylene is activated by the less reactive germanium analogue of **1**, leading to the formation of the bis(germylene), **7**. Disilylene **1** reduces CO_2, generating CO, and the oxo/carbonate-bridged disilicon(IV) system, **10**, while its reaction with N_2O proceeds *via* generation of N_2, and an apparent hydrogen abstraction process, to give the oxo/hydroxy disilicon(IV) species, **11**. This study has described small molecule activations, initiated by 1,2-disilylene **1**, that have either not been reported for Roesky's more widely explored 1,2-disilylene, or have led to different outcomes to those communicated for that compound. There is considerable scope to further develop the chemistry of highly reactive 1,2-disilylene **1**, which is a goal we have embarked upon.

Electronic supplementary information (ESI) available: Experimental procedures, characterisation data for all new compounds, and details of computational studies. Crystal data, details of data collections and refinements. CCDC numbers: 2154622-2154627. For ESI and crystallographic data in CIF format see DOI: 10.xxxxxxx

Conflict of Interest

The authors declare no conflict of interest.

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References

1. Selected reviews: (a) C. Wheetman, S. Inoue, *CatChemCat*, 2018, **10**, 4213; (b) T. Chu, G. I. Nikonov, *Chem. Rev.*, 2018, **118**, 3608; (c) T. J. Hadlington, M. Driess, C. Jones, *Chem. Soc. Rev.*, 2018, **47**, 4176; (d) P. P. Power, *Acc. Chem. Res.*, 2011, **44**, 627; (e) M. Asay, C. Jones, M. Driess, *Chem. Rev.*, 2011, **111**, 354; (f) D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.*, 2011, **2**, 389; (g) P. P. Power, *Nature*, 2010, **463**, 171; (h) C. Jones, *Nat. Rev. Chem.*, 2017, **1**, 0059; (h) S. Fujimori, S. Inoue, *J. Am. Chem. Soc.*, 2022, **144**, 2034.
2. Selected reviews: (a) C. Shan, S. Yao, M. Driess, *Chem. Soc. Rev.*, 2020, **49**, 6733; (b) R. Tacke, T. Ribbeck, *Dalton Trans.*, 2017, **46**, 13628; (c) B. Blom, M. Stoelzel, M. Driess, *Chem. Eur. J.*, 2013, **19**, 40; (c) S. S. Sen, S. Khan, P. P. Samuel, H. W. Roesky, *Chem. Sci.*, 2012, **3**, 659; (d) F. Hanusch, L. Groll, S. Inoue, *Chem. Sci.*, 2021, **12**, 2001; (e) V. Y. Lee, A. Sekiguchi, *Organometallic Compounds of Low-Coordinate Si, Ge, Sn and Pb*. Wiley, Chichester, 2010; (f) A. Sekiguchi, M. Ichinohe, R. Kinjo, *Bull. Chem. Soc. Jpn.*, 2006, **79**, 825; (f) S. Fujimori, S. Inoue, *Eur. J. Inorg. Chem.*, 2020, **2020**, 3131.
3. S. S. Sen, A. Jana, H. W. Roesky, C. Schulzke, *Angew. Chem. Int. Ed.*, 2009, **48**, 8536.
4. Y. Ding, S. K. Sarkar, M. Nazish, S. Muhammed, D. Lüert, P. N. Ruth, C. M. Legendre, R. Herbst-Irmer, P. Parameswaram, D. Stalke, Z. Yang, H. W. Roesky, *Angew. Chem. Int. Ed.*, 2021, **60**, 27206, and references therein.

5. C. Jones, S. J. Bonyhady, N. Holzmann, G. Frenking, A. Stasch, *Inorg. Chem.*, 2011, **50**, 12315.
6. D. Gau, R. Rodriguez, T. Kato, N. Saffon-Merceron, A. de Cózar, F. P. Cossío, A. Baceiredo, *Angew. Chem. Int. Ed. Engl.*, 2011, **50**, 1092.
7. A. Sidiropoulos, A. Stasch, C. Jones, *Main Group Met. Chem.*, 2019, **42**, 121.
8. P. Garg. A. Carpentier, I. Douair, D. Dange, Y. Jiang, K. Yuvaraj, L. Maron, C. Jones, *Angew. Chem. Int. Ed.*, accepted manuscript online. DOI:10.1002/anie.202201705
9. N.B. Related activations of isonitriles have been reported for amidinate coordinated bis(silylenes), which do not possess Si-Si bonds. See for example: (a) Y. Wang, A. Kostenko, T. J. Hadlington, M.-P. Luecke, S. Yao, M. Driess, *J. Am. Chem. Soc.*, 2019, **141**, 626; (b) Y. Xiong, S. Yao, T. Szilvasi, A. Ruzicka, M. Driess, *Chem. Commun.*, 2020, **56**, 747.
10. S.-H. Zhang, H.-W. Xi, K. H. Lim, Q. Meng, M.-B. Huang, C.-W. So, *Chem. Eur. J.*, 2012, **18**, 4258.
11. C. Chatgilialoglu, *Chem. Rev.*, 1995, **95**, 1229.
12. N. Wiberg, G. Wagner, G. M_ller, *Angew. Chem. Int. Ed. Engl.*, 1985, **24**, 229.
13. P. Pyykkö, M. Atsumi, *Chem. Eur. J.*, 2009, **15**, 186.
14. L. Kniel, O. Winter, K. Stork, *Ethylene, keystone to the petrochemical industry*, Dekker, New York, 1980.
15. (a) T. Sasamori, T. Sugahara, T. Agou, K. Sugamata, J.-D. Guo, S. Nagase, N. Tokitoh, *Chem. Sci.*, 2015, **6**, 5526; (b) T. J. Hadlington, J. Li, M. Hermann, A. Davey, G. Frenking, C. Jones, *Organometallics*, 2015, **34**, 3175; (c) T. Ohtaki, W. Ando, *Organometallics,* 1996, **15**, 3103; (d) J. A. Kelly, M. Juckel, T. J. Hadlington, I. Fernandez, G. Frenking, C. Jones, *Chem. Eur. J.*, 2019, **25**, 2773; (e) O. T. Summerscales, C. A. Caputo, C. E. Knapp, J. C. Fettinger, P. P. Power, *J. Am. Chem. Soc.*, 2012, **134**, 14595.
16. Y. Peng, B. D. Ellis, X. Wang, J. C. Fettinger, P. P. Power, *Science*, 2009, **325**, 1668.
17. T. J. Hadlington, M. Hermann, G. Frenking, C. Jones, *Chem. Sci.*, 2015, **6**, 7249.

18. N. Nakata, T. Oikawa, T. Matsumoto, Y. Kabe, A. Sekiguchi, *Organometallics*, 2005, **24**, 3368.

19. S. S. Sen, G. Tavcar, H. W. Roesky, D. Kratzert. J. Hey, D. Stalke, *Organometallics*, 2010, **29**, 2343.

20. J. Li, M. Hermann, G. Frenking, C. Jones, *Angew. Chem. Int. Ed.*, 2012, **51**, 8611.

21. K. Junold, M. Nutz, J. A. Baus, C. Burschka, C. Fonseca Guerra, F. M. Bickelhaupt, R. Tacke, *Chem. Eur. J.*, 2014, **20**, 9319.

22. C. Cui, M .M. Olmstead, J. C. Fettinger, G. H. Spikes, P. P. Power, *J. Am. Chem. Soc.*, 2005, **127**, 17530.

23. P. Jutzi, D. Eikenberg, A. Möhrke, B. Neumann, H.-G. Stammler, *Organometallics*, 1996, **15**, 753.

24. R. Azhakar, K. Propper, B. Dittrich, H. W. Roesky, *Organometallics*, 2012, **31**, 7586.