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Equilibrium between a cyclotrisilene and an isolable base adduct of a disilenyl silylene

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In organic chemistry, compounds with adjacent alkene and carbene functionalities (vinyl carbenes) are studied widely as fleeting intermediates and in the coordination sphere of transition metals. Stable derivatives of vinyl carbenes remain elusive, including the corresponding heavier group 14 homologues. Here we report the isolation and full characterization of a base-stabilized silicon version of a vinyl carbene that features a silicon–silicon double bond as well as a silylene functionality, coordinated by an *N*-heterocyclic carbene (NHC). In solution, the intensely green disilenyl silylene adduct exists in equilibrium with the corresponding silicon analogue of a cyclopropene and free NHC, which was quantified by nuclear magnetic resonance spectroscopy and ultraviolet–visible spectroscopy. The reversibility of this process raises exciting possibilities for the preparation of extended conjugated π systems of silicon.

Formally, the double bond of alkenes is constituted by the covalent interaction of two electron-deficient carbene fragments[1]. The interaction between silylenes, the silicon version of carbenes, to form disilenes is considerably weaker, which explains the prominent role of silylenes as transient intermediates in industrial silicon chemistry[2]. Although stable representatives of disilenes[3] and silylenes[4,5] are now known in the hundreds, compounds that contain both structural motifs in the same molecule remain hypothetical. In fact, the simultaneous presence of double-bond and carbene functionalities is difficult to achieve even in carbon chemistry[6]. One of the simplest conceivable examples is the elusive vinyl carbene, which has been characterized in ultracold matrices[7], by trapping reactions[8] and as ligands in transition-metal complexes[9]. Under standard conditions, however, it almost instantly isomerizes to cyclopropene, even in the presence of coordinating bases such as pyridines[10]. The silicon version of vinyl carbene, disilenyl silylene, has been subject to computational studies[11], but as yet has not been observed. The stabilization of Si(II) species by the coordination of strong bases to the vacant *p* orbital at the silicon centre is a powerful concept[12,13]. Since the isolation of disilicon coordinated by *N*-heterocyclic carbenes (NHCs), **I**[14], the use of NHCs as stabilizing ligands has become a popular strategy for the isolation of otherwise unstable low-coordinate silicon compounds (Fig. 1), particularly silylenes such as **II**[15], **III**[16] and **IV**[17].

We now report the isolation and full characterization of a disilenyl silylene stabilized by an NHC as a coordinating base. In solution, the disilenyl silylene adduct coexists in equilibrium with the isomeric cyclotrisilene (the heavier analogue of a cyclopropene) and free NHC, which mirrors the postulated gas-phase equilibrium in the case of the corresponding carbon compounds at elevated temperatures[18,19]. Our findings demonstrate full reversibility of such a process in the condensed phase at room temperature. The relatively weak binding of the NHC to an unsaturated silylene centre suggests the application of such strong electron donors as catalytic additives to silicon deposition processes in solution, for example from silane precursors[20]. In addition, the availability of a stable disilenyl silylene reveals new synthetic avenues in the emerging field of conjugated systems that incorporate coordinatively unsaturated silicon atoms[21].

Results and discussion

Combination of the cyclotrisilene **1** with NHC **2** (1 equiv.) in hydrocarbons led to an immediate colour change of the solution to dark green (Fig. 1; R = 2,4,6-triisopropylphenyl (Tip)). Partial conversion into a new species was proved by the appearance of new ^{29}Si NMR signals at $\delta = 101.99$, 53.89 and -60.54 ppm. The two low-field signals (high parts per million values) are diagnostic for a Si=Si bond unperturbed by coordination of a Lewis base and/or incorporation into a small ring[22]. The ^{13}C signal of the carbenic carbon atom at $\delta = 173.42$ ppm was shifted upfield by $\Delta\delta = 32$ ppm compared to that of free NHC **2**, which indicates involvement in a donor–acceptor interaction. Indeed, the ^{29}Si NMR signal at $\delta = -60.54$ ppm is consistent with an NHC-coordinated silylene moiety, although located at a higher field than those typically observed for such compounds (for example, **II**–**IV**)[15–17]. On the basis of a two-dimensional ^{1}H–^{29}Si correlation experiment, the substitution pattern of the new species was established and thus identified as the NHC adduct of a disilenyl silylene (**3**) (Fig. 2).

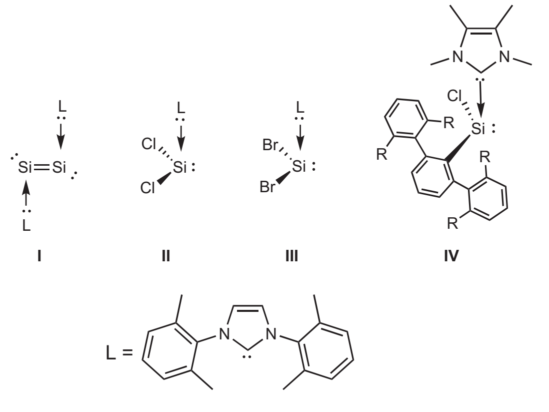

Figure 1 | Selected examples of low-valent silicon species stabilized by *N*-heterocyclic carbenes as reported in the literature. Si_2 species **I** with a formal silicon(0) oxidation state and a Si=Si double bond[14], dichlorosilylene **II**[15], dibromosilylene **III**[16] and aryl(bromo)silylene **IV**[17] (**IV**, R = Me or ^{i}Pr).

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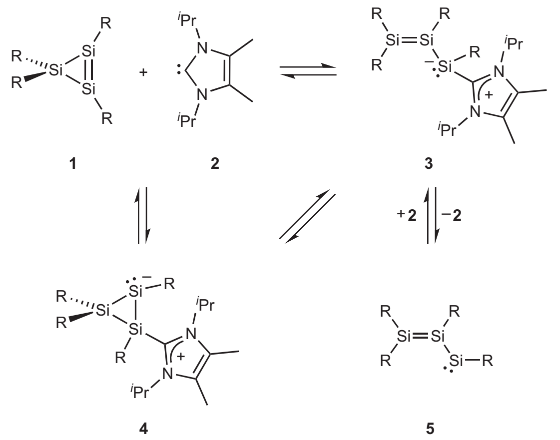

Figure 2 | Equilibrium of cyclotrisilene 1 and *N*-heterocyclic carbene 2 with NHC-coordinated disilenyl silylene 3 and proposed cyclic intermediate 4. The hypothetical dissociation to form free disilenyl silylene **5** (R = Tip) is also shown.

Disilenyl silylene 3 was isolated as dark-green crystals (melting point (T_m) 132 °C with minor decomposition) in 23% yield by crystallization from cyclohexane. The ultraviolet–visible (UV-vis) spectrum recorded in the presence of excess carbene 2 shows an intense band at $\lambda_{max} = 412$ nm as well as a broader absorption centred at 568 nm. Exposure of 3 to air resulted in rapid decomposition in both solid state and solution. The molecular structure of 3, derived from X-ray crystallography, confirms the structural features deduced from NMR spectroscopy (Fig. 3). The open-chained silicon backbone of 3 exhibits typical Si–Si double and single bond lengths (Si1–Si2, 2.1799(6); Si2–Si3, 2.3217(6) Å). The Si=Si double bond displays moderate twisting (twist angle $\tau = 14.2°$) and *trans*-bending (*trans*-bent angle $\theta = 5.4°$ at SiTip$_2$, 17.4° at Si(Tip)Si). The silylene–silicon centre is strongly pyramidalized with a sum of angles of 323.6°, which thus confirms the donor–acceptor interaction of the NHC with the vacant orbital of the silylene moiety. The Si–C(NHC) bond distance is 1.9478(17) Å, slightly longer than that observed in the Si(0) compound **I** (1.9271(15) Å)[14] and an NHC–disilyne adduct (1.9221(16) Å)[23], but shorter than that in a cyclic NHC–cyclotrisilene adduct (1.9843(14) Å)[24].

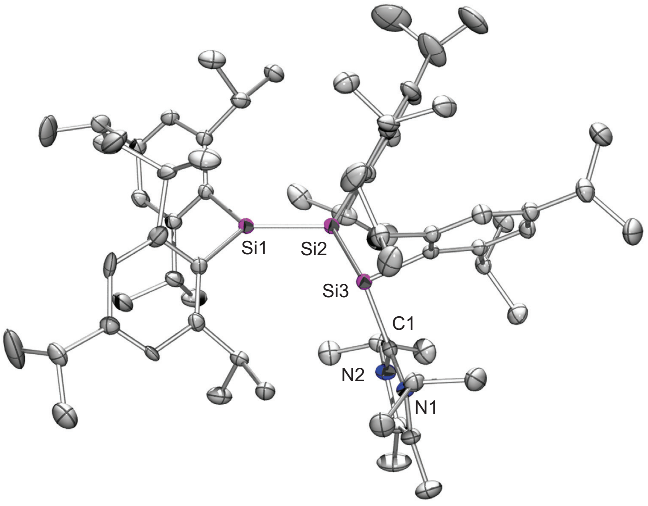

Figure 3 | Molecular structure of 3·C_6H_{12} in the solid state. Hydrogen atoms and co-crystallized cyclohexane are omitted for clarity (thermal ellipsoids at 50%). Selected bond lengths (estimated standard deviation): Si1–Si2 shows a typical double-bond length of 2.1799(6) Å; Si2–Si3 = 2.3217(6) Å indicates a single bond; C1–Si3 = 1.9478(17) Å represents a regular distance for a silylene–NHC complex.

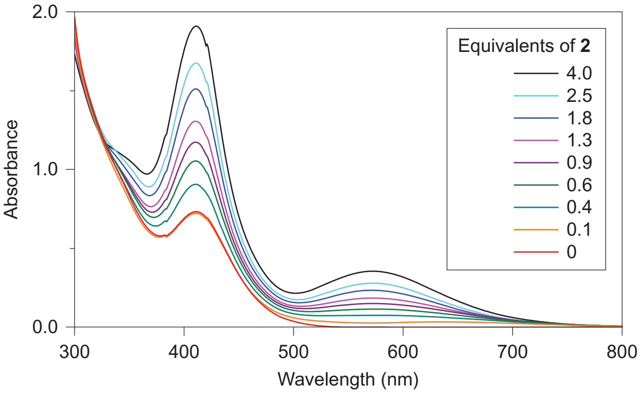

Figure 4 | UV-vis spectra of 1 (red line) in hexane with increasing concentrations of NHC 2 (other lines). As demonstrated by the increasing absorbance at $\lambda_{max} = 568$ nm, the equilibrium is shifted towards NHC-stabilized disilenyl silylene 3.

Remarkably, the formation of 3 from 1 and 2 is fully reversible (Fig. 2). Reversible coordination is a hallmark of transition-metal chemistry, but is increasingly becoming relevant in main-group systems[25]. Dissolving crystalline 3 afforded identical mixtures of 1, 2 and 3 to those obtained by dissolving 1 and 2 in a 1:1 ratio. As solutions were cooled down, the concentration of 3 increased at the expense of 1 and 2 to such an extent that at temperatures below 240 K only minor concentrations of free cyclotrisilene 1 and NHC 2 could be detected by NMR spectroscopy. Using variable-temperature ^{1}H NMR spectroscopy, we determined the Gibbs enthalpy of formation of the NHC-stabilized disilenyl silylene to be $\Delta G_{298} = -2.73 \pm 0.04$ kcal mol^{-1}. UV-vis spectroscopic studies at different concentrations of NHC 2 gave a similar value of $\Delta G_{298} \approx -3.3$ kcal mol^{-1} (Fig. 4 and Supplementary Information).

We recently reported that a Cp*-substituted cyclotrisilene (Cp* = pentamethylcyclopentadienyl) and NHC 2 reversibly form a donor–acceptor complex of type 4 without ring opening to the isomeric disilenyl silylene analogous to 3 (Fig. 2)[24]. We were therefore interested in the potential role of cyclotrisilene–NHC adduct 4 as an intermediate in the conversion of cyclotrisilene 1 into NHC-stabilized disilenyl silylene 3. Indeed, combination of 1 and 2 at 183 K afforded a dark-red solution as opposed to the dark-green colour of 3. The ^{29}Si NMR spectrum at 210 K displays three high-field resonances at $\delta = -45.57$, -95.27 and -126.76 ppm (Supplementary Fig. S8), which are assigned to the cyclic cyclotrisilene–NHC adduct 4 on the basis of their similarity to those reported previously for the Cp*–cyclotrisilene NHC complex[24]. As expected, the cyclic adduct 4 was thermally unstable and slowly rearranged to give the disilenyl silylene adduct 3, even at 210 K (approximately 30% conversion after 2.5 hours at 210 K). On warming solutions of 4 to room temperature, only 3 and free 1 and 2 were observed by NMR spectroscopy. However, shock freezing of such solutions to liquid nitrogen temperatures followed by warming to 210 K resulted in the formation of mixtures of 3 and 4 (Supplementary Fig. S10).

The behaviour we observed is consistent with the role of 4 as an intermediate in the conversion of cyclotrisilene 1 into the disilenyl silylene–NHC adduct 3. At low temperatures the reaction of 1 with carbene 2 initially resulted in the cyclic NHC–adduct 4 as the kinetic product, which slowly converted into the open-chained thermodynamic product 3. Essentially, no uncoordinated cyclotrisilene 1 was observed at these temperatures; entropic effects evidently favour the formation of adducts 3 and 4.

Although at 300 K intermediate 4 could not be observed by NMR spectroscopy, its involvement in the equilibrium is presumed

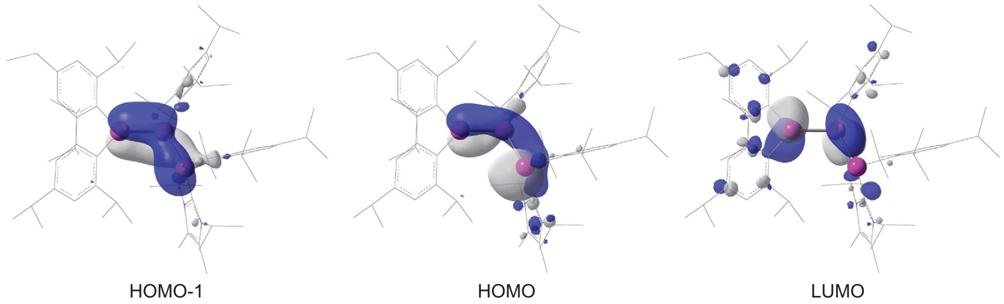

Figure 5 | Frontier molecular orbitals of NHC-coordinated disilenyl silylene 3 at 0.04 atomic units. HOMO-1 is formed by bonding interaction of the Si=Si π bond and the formally vacant *p* orbital at the silylene centre. The HOMO is formed by the corresponding antibonding combination and is thus raised in energy compared to that of a regular Si=Si bond, which accounts for the comparatively small HOMO–LUMO gap. The LUMO mainly consists of the antibonding π^* orbital of the Si=Si moiety.

because of the anticipated high energy of free disilenyl silylene, which would necessarily be formed on initial dissociation of NHC from the open-chained 3. To support further this assertion we carried out density functional theory (DFT) calculations (see Methods). At the B3LYP level of theory, the disilenyl silylene–NHC adduct 3 was 21.4 kcal mol^{-1} higher in free enthalpy (ΔG_{298}) than 1 + 2, in clear discrepancy with the experimental results. More realistic values for the relative stabilities result with dispersion-corrected functionals, which placed adduct 3 with lower ΔG_{298} than 1 + 2 (ωB97XD, −13.3 kcal mol^{-1}; M062X, −10.0 kcal mol^{-1} (see Methods)). Clearly, the stability of 3 is a result not only of donor/acceptor interactions between the NHC ligand and the vacant silylene *p* orbital, but also of stabilizing intramolecular van der Waals interactions between the bulky Tip and isopropyl (^{i}Pr) groups. The stability of alkanes with bulky substituents and unusually long carbon–carbon bonds was attributed recently to similar dispersive forces[26]. The experimental geometry of 3 is well reproduced at both the M062X and ωB97XD levels of theory (for example, Si–Si double bond 2.157 Å (calculated M062X) versus 2.1799(6) Å (observed)). The predicted ^{29}Si chemical shifts ($\delta = 151.5$, 100.0 and −55.5 ppm @ M062X; $\delta = 120.2$, 68.6 and −69.0 ppm @ ωB97XD) suggest that the latter functional best matches the trend observed experimentally ($\delta = 101.99$, 53.89 and −60.54 ppm).

As anticipated, the change in Gibbs energy for the direct dissociation of NHC–adduct 3 into 2 and free disilenyl silylene 5 calculated at the ωB97XD level ($\Delta G_{298} = +13.7$ (2 + 5); −13.3 kcal mol^{-1} (3) (see Methods)) appears to exclude the intermediacy of 5. In comparison to 2 + 5, the cyclic NHC adduct 4 is considerably lower in energy (4, $\Delta G_{298} = -9.6$ kcal mol^{-1}), which corroborates the involvement of 4 (detected at 210 K, *vide supra*) even when its equilibrium concentration at room temperature is too low for NMR spectroscopic detection.

Time-dependent DFT calculations of 3 at the M062X level of theory reproduced well the trends in the experimental UV-vis spectra (Supplementary Fig. S12), although the absorptions are blue shifted by 30–50 nm. The lowest energy band ($\lambda_{max} = 518$ nm (calculated) versus 568 nm (experimental)) results from the transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). A HOMO-1 → LUMO transition is largely responsible for the other significant band in the spectrum ($\lambda_{max} = 379$ nm (calculated) versus 412 nm (experimental)), although a series of weaker transitions from the HOMO and HOMO-1 to orbitals centred on the aryl substituents also contributes.

Inspection of the molecular orbitals revealed the reason for the relatively small HOMO–LUMO gap of 3 and the resulting green colour (Fig. 5). The HOMO and HOMO-1 are obtained formally by linear combination of the Si=Si π bond with the non-bonding electron pair at the silylene centre. The antibonding combination observed in the HOMO increases the energy of this orbital. Conversely, the LUMO shows a bonding interaction between the vacant *p* orbital at the silylene centre and the Si=Si π^* orbital and is therefore stabilized. The comparatively low intensity of the HOMO → LUMO transition in the UV-vis spectrum is explained by less-efficient spatial overlap of the two orbitals involved (see Methods).

Conclusions

According to calculations reported previously on the Si_3H_4 potential energy surface, hydrogen-substituted disilenyl silylene is 6.2 kcal mol^{-1} higher in energy than the cyclotrisilene isomer[10]. Taking advantage of coordination by an NHC, the Tip-substituted version 3 is stabilized relative to cyclotrisilene 1 and hence could be isolated as the first fully characterized example of a heavier vinyl carbene analogue. The full reversibility of the NHC coordination to the silylene functionality suggests the use of strong bases as catalytic components of the deposition of elemental silicon from solution. In addition, the conceptually new approach to vinyl carbenes and heavier analogues hints at novel synthetic strategies towards conjugated systems, both of carbon and heavier group 14 elements.

Methods

Details of experimental procedures, analytical data and X-ray structure determinations are given in the Supplementary Information. Details of the computational procedures are available via the Interactivity Box published on the Figshare.com site at http://dx.doi.org/10.6084/m9.figshare.744825 and the further digital repository links therein. Figshare.com is a dedicated channel for hosting open data as one component of a scientific article, in conjunction with the narrative component, in this case published in the online version of this paper.

Synthesis of disilenyl-silylene 3. 1,3-Diisopropyl-4,5-dimethylimidazol-2-ylidene[27] (2) (220 mg) and 1,1,2,3-tetrakis(2,4,6-triisopropylphenyl)trisilacyclopropene[24] (1) (1 g) were dissolved at 25 °C in cyclohexane (20 ml). The volume of the resulting dark-green solution was reduced *in vacuo* to 10 ml. Storage at room temperature for three days gave dark-green crystals of $3{\cdot}C_6H_{12}$ with a yield of 294 mg, 23%.

Spectroscopic and analytical data for 3. T_m 132 °C; ^{1}H NMR (300.13 MHz, 230 K, d_8-toluene) $\delta = 7.22$ (d, $J_{HH} = 1.4$ Hz, 1 H, Tip CH), 7.19 (d, $J_{HH} = 1.4$ Hz, 1 H, Tip CH), 7.07 (d, $J_{HH} = 1.2$ Hz, 1 H, Tip CH), 7.05 (presumed 1 H, obscured by toluene resonance, Tip CH), 7.00 (d, $J_{HH} = 1.1$ Hz, 1 H, Tip CH), 6.93 (m, 2H, Tip CH), 6.89 (d, $J_{HH} = 1.4$ Hz, 1 H, Tip CH), 6.46 (sept, $^3J_{HH} = 6.9$ Hz, 1 H, NC*H*Me$_2$), 5.43 (sept, $^3J_{HH} = 6.5$ Hz, 1 H, Tip-^{i}Pr-C*H*Me$_2$), 5.32 (sept, $^3J_{HH} = 7.0$ Hz, 1 H, NC*H*Me$_2$), 4.43 (sept, $^3J_{HH} = 6.4$ Hz, 1 H, Tip-^{i}Pr-C*H*Me$_2$), 4.16 (sept, $^3J_{HH} = 6.5$ Hz, 1 H, Tip-^{i}Pr-C*H*Me$_2$), 4.0–3.7 (m, 4 H, Tip-^{i}Pr-C*H*Me$_2$ resonances), 3.51 (sept, $^3J_{HH} = 6.4$ Hz, 1 H, Tip-^{i}Pr-C*H*Me$_2$), 2.87–2.56 (m, 4 H, Tip-^{i}Pr-C*H*Me$_2$ resonances), 1.87 (d, $^3J_{HH} = 6.9$ Hz, 3 H, NCH(C*H*$_3$)$_2$), 1.83 (s, 3 H, C*H*$_3$(N)C=C(N)CH$_3$), 1.62–1.34 (m CH$_3$)*, 1.33–1.0 (m, CH$_3$)*, 0.86 (d, 3 H, $^3J_{HH} = 6.2$ Hz, Tip-^{i}Pr-C*H*$_3$), 0.75 (d, 3 H, $^3J_{HH} = 6.2$ Hz, Tip-^{i}Pr-C*H*$_3$), 0.70–0.51 (m, 12 H, CH$_3$), 0.37 (d, $^3J_{HH} = 6.8$ Hz, 3 H, NCH(C*H*$_3$)$_2$), 0.30 (d, $^3J_{HH} = 6.8$ Hz, 3 H, Tip-^{i}Pr-C*H*$_3$) (*meaningful integration of these signals was not possible because of the presence of cyclohexane signals in this region of the spectrum); ^{29}Si{^{1}H} NMR (59.62 MHz, 230 K, d_8-toluene) $\delta = 100.91$ (Tip$_2$*Si*), 51.53 (Tip$_2$Si=*Si*(Tip)Si(Tip)), −62.91

(Tip$_2$Si=Si(Tip)*Si*(Tip)(NHC)); ^{13}C{^{1}H} NMR (75.46 MHz, 230 K, d_8-toluene) $\delta = 172.35$ (s, NCN), 156.12 (s, Ar-C), 155.37 (s, Ar-C), 154.40 (s, Ar-C), 154.08 (s, Ar-C), 153.51 (s, Ar-C), 153.35 (s, Ar-C), 152.98 (s, Ar-C), 152.78 (s, Ar-C), 148.83 (s, Ar-C), 148.57 (s, Ar-C), 148.47 (s, Ar-C), 147.53 (s, Ar-C), 142.75 (s, Ar-C), 139.02 (s, Ar-C), 138.67 (s, Ar-C), 125.96 (s, -N*C*(CH$_3$)=*C*(CH$_3$)N-), 125.00 (s, -N*C*(CH$_3$)=*C*(CH$_3$)N-), 122.47 (s, br, Ar-*C*H), 122.38 (s, br, Ar-*C*H), 122.24 (s, br, Ar-*C*H), 121.93 (s, br, Ar-*C*H), 121.06 (s, br, Ar-*C*H), 120.93 (s, br, Ar-*C*H), 120.88 (s, br, Ar-*C*H), 120.67 (s, br, Ar-*C*H), 53.89 (s, N*C*HMe$_2$), 50.74 (s, N*C*HMe$_2$), 38.25 (s, br, Tip-^{i}Pr-*C*H), 37.72 (s, br, Tip-^{i}Pr-*C*H), 37.64 (s, br, Tip-^{i}Pr-*C*H), 37.48 (s, br, Tip-^{i}Pr-*C*H), 37.24 (s, br, Tip-^{i}Pr-*C*H), 36.56 (s, br, Tip-^{i}Pr-*C*H), 35.83 (s, br, Tip-^{i}Pr-*C*H), 35.33 (s, br, Tip-^{i}Pr-*C*H), 34.70 (s, Tip-^{i}Pr-*C*H), 34.38 (s, Tip-^{i}Pr-*C*H), 34.26 (s, Tip-^{i}Pr-*C*H), 28.40 (s, Tip-^{i}Pr-*C*H$_3$), 26.64 (s, Tip-^{i}Pr-*C*H$_3$), 26.33 (s, Tip-^{i}Pr-*C*H$_3$), 26.21 (s, Tip-^{i}Pr-*C*H$_3$), 25.79 (s, Tip-^{i}Pr-*C*H$_3$), 25.35 (s, Tip-^{i}Pr-*C*H$_3$), 24.98 (s, NCH(*C*H$_3$)$_2$), 24.86 (s, Tip-^{i}Pr-*C*H$_3$), 24.52 (s, Tip-^{i}Pr-*C*H$_3$), 24.32 (s, Tip-^{i}Pr-*C*H$_3$), 24.17 (s, Tip-^{i}Pr-*C*H$_3$), 24.06 (s, Tip-^{i}Pr-*C*H$_3$), 24.01 (s, Tip-^{i}Pr-*C*H$_3$), 23.93 (s, Tip-^{i}Pr-*C*H$_3$), 23.87 (s, Tip-^{i}Pr-*C*H$_3$), 23.78 (s, Tip-^{i}Pr-*C*H$_3$), 23.53 (s, Tip-^{i}Pr-*C*H$_3$), 22.96 (s, Tip-^{i}Pr-*C*H$_3$), 22.51 (s, Tip-^{i}Pr-*C*H$_3$), 22.14 (s, Tip-^{i}Pr-*C*H$_3$), 21.10 (s, NCH(*C*H$_3$)$_2$), 20.51 (s, Tip-^{i}Pr-*C*H$_3$), 19.60 (s, NCH(*C*H$_3$)$_2$), 10.37 (s, *C*H$_3$(N)C=C(N)*C*H$_3$), 10.03 (*C*H$_3$(N)C=C(N)*C*H$_3$). UV-vis (hexane) λ_{max} 568 nm, 412 nm; analysis (% calculated, % found for $C_{77}H_{124}N_2Si_3$) C (79.58, 79.71), H (10.76, 10.37), N (2.41, 3.58). The value for N is significantly higher than expected. Values for %C and %H are also very variable (for example, for three runs %C = 74.35, 73.29 and 78.79). Together this information suggests that 3 is not amenable to meaningful microanalysis.

Computational details. Details of the computational procedures are available via http://dx.doi.org/10.6084/m9.figshare.744825 and the digital repository links therein.

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Author contributions

M.J.C. conceived and performed experiments, and co-wrote the manuscript. V.H. determined the solid-state structure of 3. H.S.R. performed the theoretical calculations, co-wrote the manuscript and designed the theoretical part of the study. D.S. designed and coordinated the study and co-wrote the manuscript.

Additional information

Supplementary information and chemical compound information are available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to H.S.R. and D.S.

Competing financial interests

The authors declare no competing financial interests.