Supporting Information

The Structure of the Carbene Stabilized Si_2H_2 may be Equally well Described with Coordinate Bonds as with Classical Double Bonds

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Content:

(S1) Syntheses of compounds (Me-cAAC:)$_2$Si$_2$H$_2$ (1) and (Cy-cAAC:)$_2$Si$_2$H$_2$ (2):

All reactions and handling of reagents were performed under an atmosphere of dry nitrogen using standard Schlenk techniques or a glove box where the O_2 and H_2O levels were usually kept below 1 ppm. Me-cAAC: and Cy-cAAC: were prepared according to similar literature methods.[18] Solvents were purified with the M-Braun solvent drying system. Solution NMR spectra were recorded on Bruker Avance 200, Bruker Avance 300, and Bruker Avance 500 MHz NMR spectrometers. Deuterated NMR solvent C_6D_6 was dried by stirring for 2 days over Na/K alloy followed by distillation in vacuum and degassed. ESI-MS spectrum was obtained with maXis (ESI-QTOF-MS) instrument (Bruker) by ESI-MS methods. Elemental analysis was performed by the Analytisches Labor des Instituts fur Anorganische Chemie der Universitat Gottingen. Melting point was measured in sealed glass tubes on a Buchi B-540 melting point apparatus. IR spectrum of the solid sample was measured by Bio-Rad FT 1000 instrument.

(Me-cAAC:)$_2$Si$_2$H$_2$ **(1)** : A mixture of Me-cAAC: (257mg; 0.9 mmol) and KC_8 (368mg; 2.7 mmol) was taken in a 100 mL round bottom flask and 40 mL of THF was added at -78 °C. To this mixture $HSiCl_3$ (0.09mL, 0.9 mmol) was added at -78 °C and the reaction mixture was allowed to warm up to room temperature slowly (30 min) to give a reddish solution. The reaction was then continued for 2 hours to give a dark reddish solution of compound **1**. Then the solvent was removed by high vacuum and the product was extracted by 60 mL of hexane. After filtration of insoluble residue, the solvent was evaporated by high vacuum to get the dark reddish solid of **1** (Yield: 35%). The single crystals were grown at -26 °C from hexane solution of **1**.

Elemental analysis found in % (calcd) for $C_{40}H_{64}N_2Si_2$: C, 76.41(76.37); H, 10.31(10.25); N, 4.39(4.45). Melts at 175 °C, ^{1}H NMR (298 K, C_6D_6, δ ppm, 500.133 MHz): 7.14-7.09 (m, 6H, H_{ar}), 3.59 (s, 2H, Si-*H*), 3.11 (m, 4H, C*H*Me$_2$), 1.77 (s, 12H, NC*Me*$_2$), 1.74 (s, 4H, CH_2), 1.53-1.52 (d, 12H, CH*Me*$_2$), 1.22-1.21 (d, 12H, CH*Me*$_2$) 1.04 (s, 12H, C*Me*$_2$).

^{13}C NMR (298 K, C_6D_6, δ ppm, 126 MHz): 211.84 (C), 148.50, 136.36, 128.49, 125.20, 70.02, 55.36, 49.55, 33.52, 31.90, 29.03, 28.84, 27.75, 24.43, 22.99;

^{29}Si NMR (298 K, C_6D_6, δ ppm, 99.38 MHz): -45.50 [^{1}H-decoupled] and -44.65 to -46.30 (d) [^{1}H-coupled].

ESI-MS: *m/z* (%) 635.5(100) $[M+Li]^+$**.** IR (KBr, cm^{-1}): 2962(m), 2924(m), 2867(w), 2115(w), 1463(m), 1384(m), 1362(m), 1324(w), 1260(s), 1200(w), 1092(s), 1020(s), 931(w), 864(w), 799(s), 752(w), 665(s).

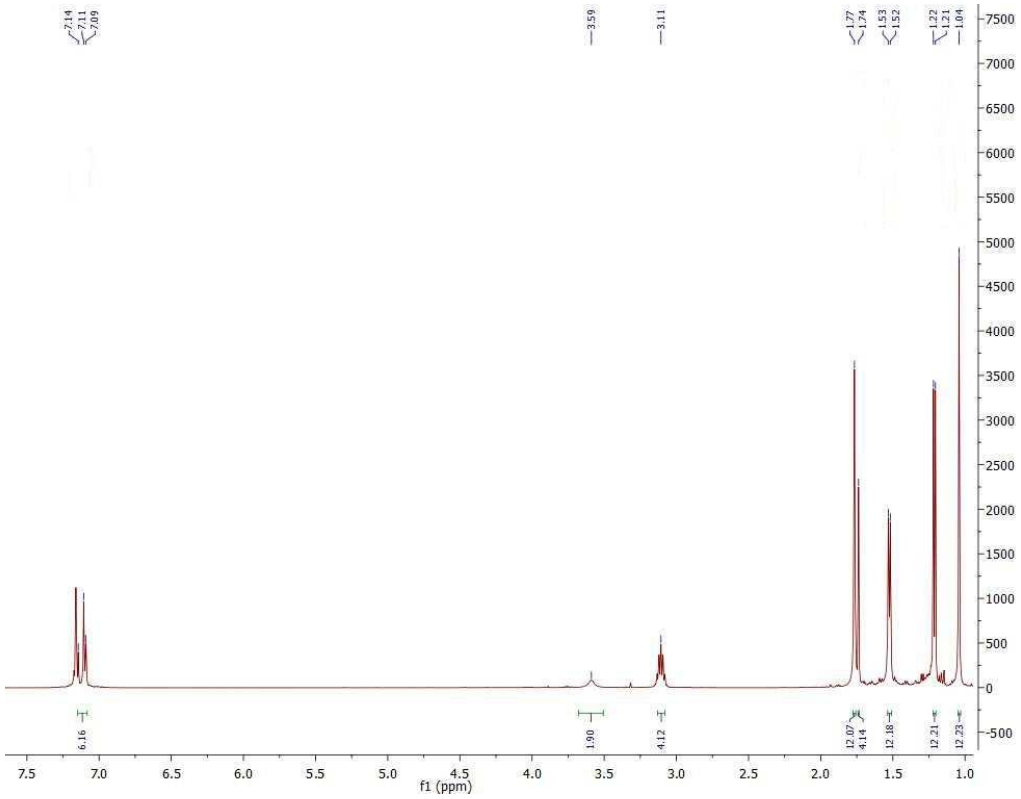
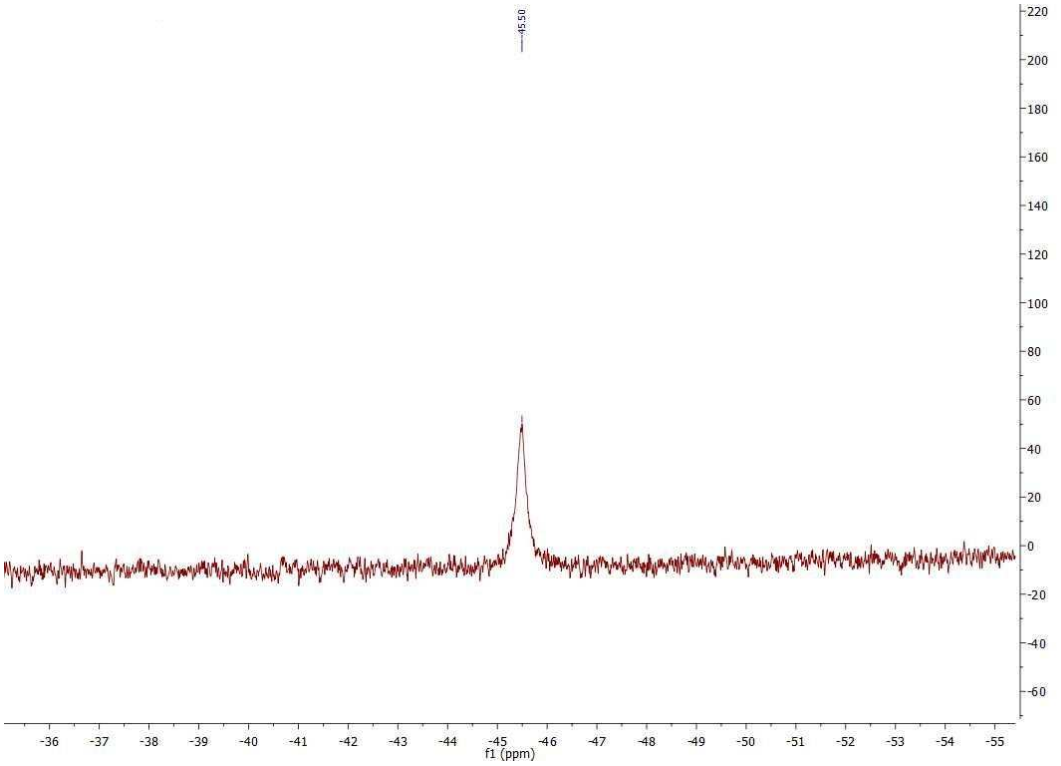


Figure S1. ^{1}H NMR spectrum of **1.**

(a)



(b)

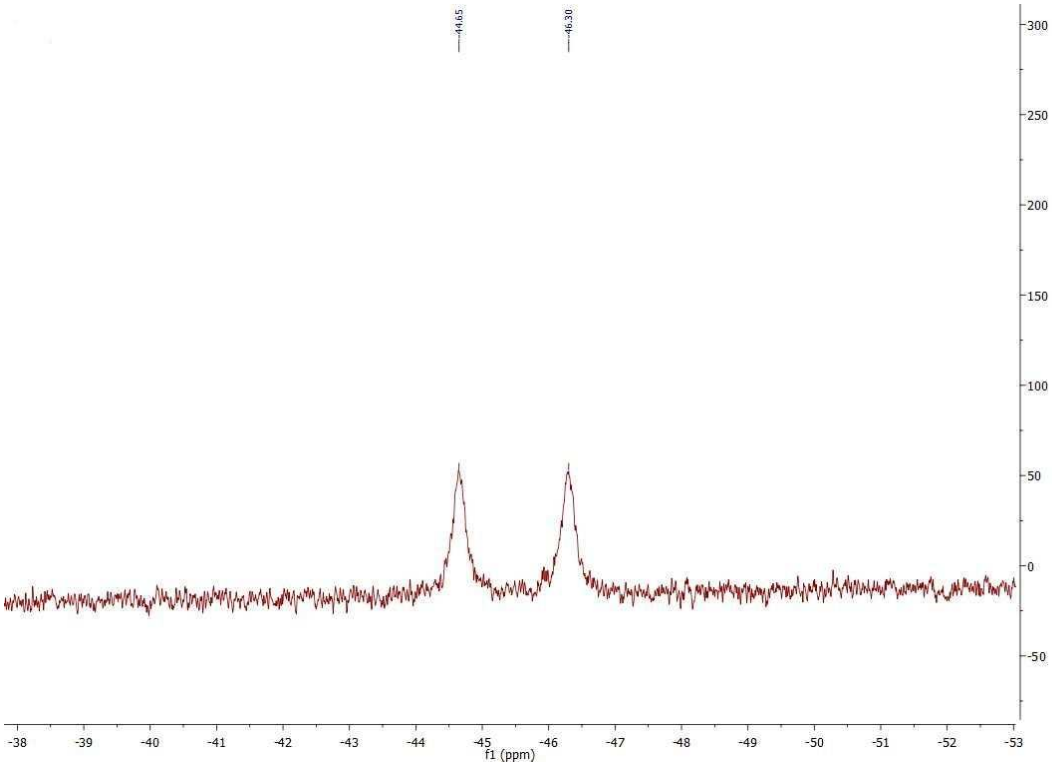


Figure S2. (a) ^{29}Si NMR (^{1}H-decoupled) spectrum of **1,** (b) ^{29}Si NMR (^{1}H-coupled) spectrum of **1.**

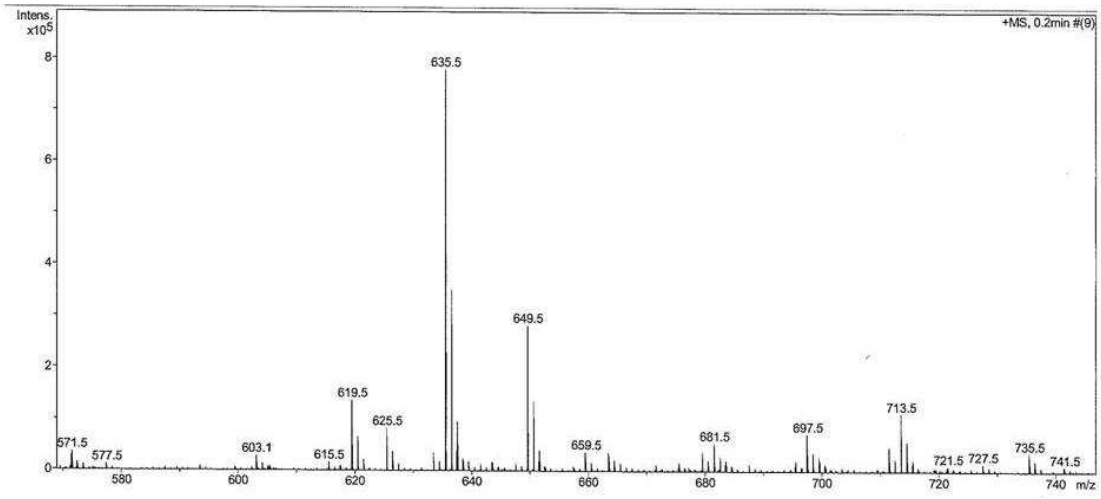


Figure S3. ESI-mass of compound **1**.

(Cy-cAAC:)$_2$Si$_2$H$_2$ **(2)**: A mixture of Cy-cAAC: (292mg; 0.9 mmol) and KC_8 (368mg; 2.7 mmol) was taken in a 100 mL round bottom flask and 40 mL of THF was added at -78 °C. To this mixture $HSiCl_3$ (0.09mL, 0.9 mmol) was added at -78 °C and the reaction mixture was allowed to warm up to room temperature slowly (30 min) to give a reddish solution. The reaction was then continued for 2 hours to give a dark reddish solution of compound **2**. Then the solvent was removed by high vacuum and the product was extracted by 60 mL of hexane. After filtration of insoluble residue, the solvent was evaporated by high vacuum to get the dark reddish solid of **2** (Yield: 31%). The single crystals were grown at -26 °C from hexane solution of **2**. Although the single crystals were very good in morphology they did not give good X-ray diffraction data in several attempts.

Elemental analysis found in % (calcd) for $C_{46}H_{72}N_2Si_2$: C, 78.02(77.90); H, 10.31(10.23); N, 3.87(3.95). Melts at 172 °C, ^{1}H NMR (298 K, C_6D_6, δ ppm, 500.133 MHz): 7.11-7.09 (m,

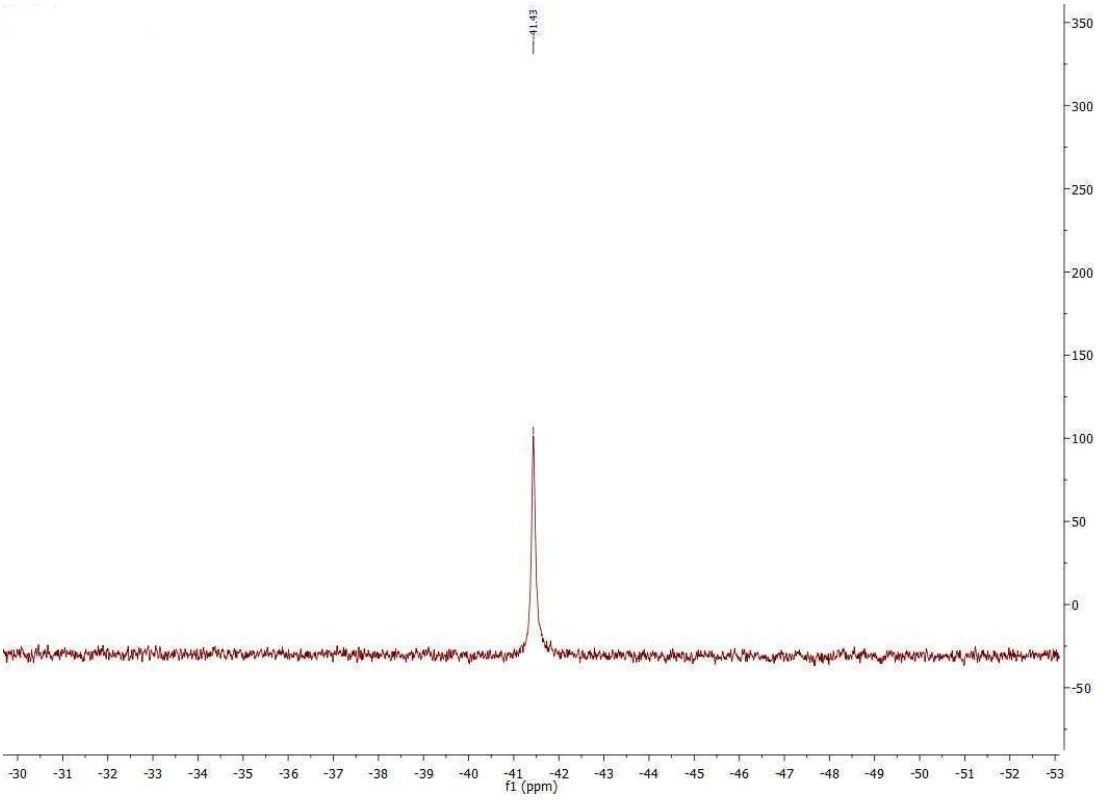
6H, H_{ar}), 3.62 (s, 2H, Si-*H*), 3.15-3.09 (m, 4H, C*H*Me$_2$), 2.73-2.68 (t, 4H, cyclohexane), 1.81 (s, 4H, CH_2), 1.66-1.64 (m, 10H, cyclohexane), 1.56-1.55 (d, 12H, CH*Me*$_2$), 1.30-1.25 (m, 6H, cyclohexane), 1.23-1.22 (d, 12H, CH*Me*$_2$), 1.04 (s, 12H, CN*Me*$_2$)

^{13}C NMR (298 K, C_6D_6, δ ppm, 126 MHz): 210.48 (C), 148.57, 136.38, 128.44, 125.25, 124.27, 70.23, 54.14, 49.14, 40.99, 31.91, 29.45, 28.86, 27.74, 25.81, 24.49, 24.25, 23.00

^{29}Si NMR (298 K, C_6D_6, δ ppm, 99.38 MHz): -41.43 [^{1}H-decoupled] and -40.61 to -42.26 (d) [^{1}H-coupled].

ESI-MS: *m/z* (%) 733.5(100) $[M+Na+2H^+ +2e^-]^+$**.** IR (KBr, cm^{-1}): 2963 (m), 2919(w), 2851(w), 2072(w), 1494(w), 1260(s), 1091(s), 1020(s), 799(s), 665(s).

(a)



(b)

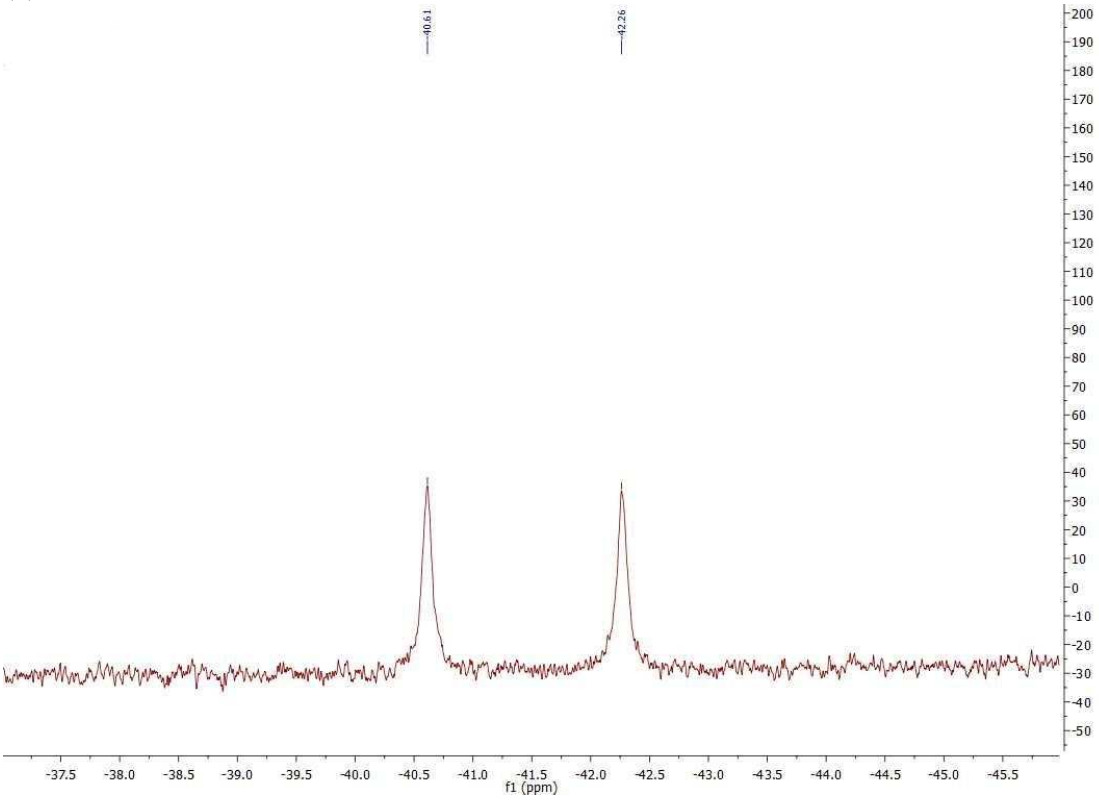


Figure S4. (a) ^{29}Si NMR (^{1}H-decoupled) spectrum of **2,** (b) ^{29}Si NMR (^{1}H-coupled) spectrum of **2.**

(S2) UV-visible spectroscopy of 1 and 2:

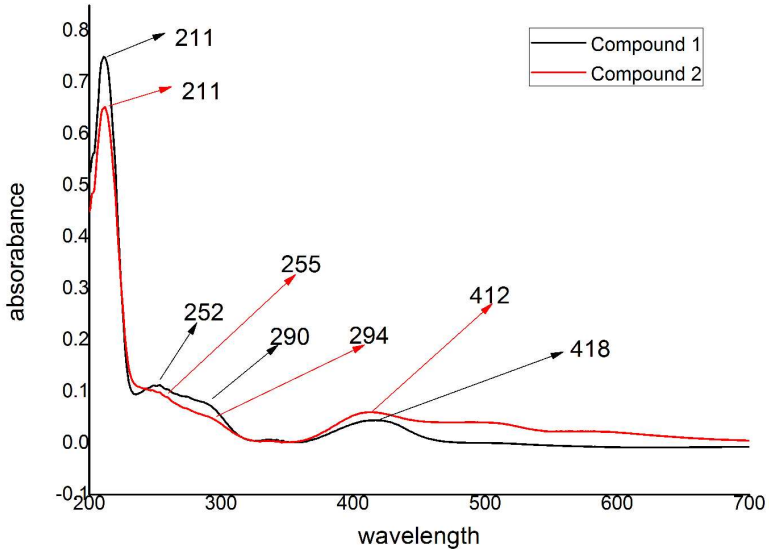


Figure S5. UV-visible spectra of compound **1** and **2** in hexane.

In the UV-visible spectra compound **1** shows absorptions at nearly 211, 252, 290, 418 nm and compound **2** shows absorptions at nearly 211, 255, 294, 412 nm in hexane solution at room temperature.

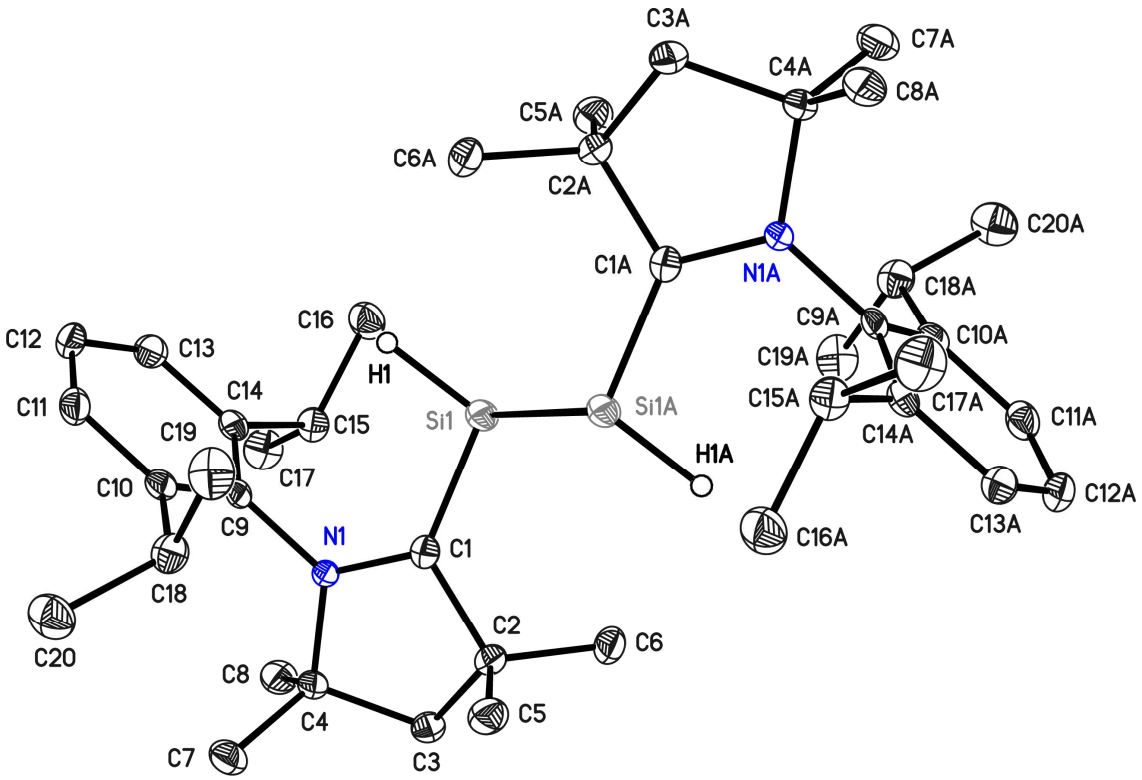
(S3) Crystal data of 1:

Experimental Section

Structural investigations: Single crystals were selected and covered with perfluorinated polyether oil on a microscope slide with the X-Temp2 device.[19] An appropriate crystal was selected using a polarize microscope, mounted on the tip of a MiTeGen©MicroMount, fixed to a goniometer head and shock cooled by the crystal cooling device.

The data of **1** was collected from shock-cooled crystals at 100(2) K on a bruker D8 three circle diffractometer equipped with an incoatec Mo Microsource with mirror optics (MoK_α radiation, λ = 71.073 pm) and smart apex ii detector. The data of **1** was integrated with saint[20] and an semi-empirical absorption correction (sadabs)[21] was applied. The structures were solved by direct methods (shelxt)[22] and refined by full-matrix least-squares methods against F^2 (shelxl).[23] All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms bond to carbon were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to equal to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. The hydrogen atom bond to silicon is freely refined.

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre (1474405). Crystal data, experimental details for the X-ray measurements and copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/ data_request/cif.



1		
Empirical formula	C40 H64 N2 Si2	
Formula weight	629.11	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.229(2) Å	α = 89.69(2)°
	b = 10.253(3) Å	β = 77.64(2)°
	c = 11.671 Å	γ = 64.10(3)°

Volume	965.5(5) $Å^3$
Z	1
Density (calculated)	1.082 Mg/m^3
Absorption coefficient	0.120 mm^{-1}
F(000)	346
Crystal size	0.156 x 0.107 x 0.074 mm^3
Theta range for data collection	2.219 to 25.358°
Index ranges	-11<=h<=11, -12<=k<=12, -14<=l<=14
Reflections collected	20521
Independent reflections	3534 [R(int) = 0.0499]
Completeness to theta = 25.242°	100.0 %
Absorption Correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6957
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	3534 / 0 / 211
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.0775
R indices (all data)	R1 = 0.0557, wR2 = 0.0848
Extinction coefficient	n/a
Largest diff. peak and hole	0.317 and -0.278 $e.Å^{-3}$

(S4) Selected bond distances of 1:

Si1-Si1A	2.3336(13)
Si1-H1	1.437(18)
Si1-C1	1.8173(18)
C1-N1	1.362(2)
C1-Si1-Si1A	111.81(6)
C1-Si1-H1	105.6(7)
Si1A-Si1-H1	110.0(7)
N1-C1-Si1	126.47(12)
C2-C1-Si1	, 125.10(12)
C1-Si1-Si1A-C1A	180.0
H1-Si1-Si1A-H1A	180.0

(S5) Theoretical calculations on 1

Computational Methods:

Geometry optimizations were performed using the Gaussian 09 optimizer[1] together with TurboMole7.0[2] energies and gradients at the M06-2X/def2-TZVPP[3] level of theory. The Hessian matrices were computed to determine the nature of stationary points (one and zero imaginary frequencies for transition states and minima, respectively)[4] and to calculate zero-point energies (ZPEs) as well as thermal corrections and entropy effects using the standard statistical-mechanics relationships for an ideal gas. For the M06-2X calculations the resolution-of-identity method has been applied.[5] The NBO partial charges[6] were computed with GENNBO5.9[7] at the M06-2X/def2-TZVPP level of theory. The bond dissociation

energy values were improved by single point energy calculations at the LCCSD(T)[8]/cc-pVTZ[9] level of theory using M06-2X/def2-TZVPP optimized geometries with the program package MOLPRO 2015.1.[10]

The bonding situation of the donor-acceptor bonds was investigated with the Energy Decomposition Analysis (EDA) method at the BP86-D3(BJ)[11]/TZ2P+[12]//M06-2X/def2-TZVPP level of theory, which was developed by Morokuma[13] and by Ziegler and Rauk.[14] The bonding analysis focuses on the instantaneous interaction energy ΔE_{int} of a bond A-B between two fragments A and B in the particular electronic reference state and in the frozen geometry AB. This energy is divided into three main components (eq 1).

$$\Delta E_{\text{int}} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} + \Delta E_{disp} \qquad (1)$$

The term ΔE_{elstat} corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the prepared atoms (or fragments) and it is usually attractive. The Pauli repulsion ΔE_{Pauli} is the energy change associated with the transformation from the superposition of the unperturbed wave functions of the isolated fragments to the wave function $\Psi_0 = \text{NA}[\Psi_A\Psi_B]$, which properly obeys the Pauli principle through explicit antisymmetrization (A operator) and renormalization (N = constant) of the product wave function. It comprises the destabilizing interactions between electrons of the same spin on either fragment. The orbital interaction ΔE_{orb} accounts for charge transfer and polarization effects.[15] The ΔE_{orb} term can be dissected into contributions from each irreducible representation of the point group of the interacting system. Since the dispersion corrected functional is used, the dispersion correction, ΔE_{disp}, is added to the total interaction energy

ΔE_{int}. Further details on the EDA method[16] and recent applications to the analysis of the chemical bond can be found in the literature.[17]

To obtain the bond dissociation energy (BDE) De the preparation energy ΔE_{prep} which gives the relaxation of the fragments into their electronic and geometrical ground states must be added to ΔE_{int}.

$$\Delta E = -D_e = \Delta E_{\text{int}} + \Delta E_{prep} \qquad (2)$$

To calculate the dissociation energies, we calculated each fragment in its optimized geometry and derived ΔE by eq 2.

Cartesian Coordinates (Å) and Energy (Hartree):

1 (M06-2X/def2-TZVPP)

E(LCCSD(T)/cc-pVTZ)= -2247.28022828

Si	0.988029000000	-0.408739000000	0.471605000000
Si	-0.988488000000	0.412413000000	-0.471236000000
C	2.230324000000	0.918771000000	0.597674000000
C	-2.229370000000	-0.916199000000	-0.599118000000
C	3.364237000000	2.720780000000	1.700826000000
C	1.973652000000	2.304383000000	1.185234000000
N	3.557986000000	0.782442000000	0.412994000000
C	4.398196000000	1.912043000000	0.909821000000
C	0.952998000000	2.315055000000	2.321388000000
C	1.480580000000	3.238370000000	0.067993000000
C	5.533889000000	1.426116000000	1.803569000000
C	5.019758000000	2.693552000000	-0.248883000000
N	-3.557160000000	-0.781664000000	-0.413885000000
C	-4.396144000000	-1.911659000000	-0.911869000000
C	-3.361565000000	-2.717867000000	-1.704585000000
C	-1.971297000000	-2.300693000000	-1.188804000000
C	-0.951016000000	-2.308594000000	-2.325318000000
C	-1.476935000000	-3.235940000000	-0.073168000000
C	-5.532967000000	-1.426037000000	-1.804336000000
C	-5.016009000000	-2.695601000000	0.246107000000
H	-6.215648000000	-0.781167000000	-1.249576000000
H	-5.157503000000	-0.884856000000	-2.670050000000
H	-6.096923000000	-2.288830000000	-2.160877000000

H	-5.641106000000	-3.492898000000	-0.156813000000
H	-4.268838000000	-3.146126000000	0.895011000000
H	-5.649622000000	-2.040919000000	0.844880000000
H	-1.238137000000	-1.608163000000	-3.109156000000
H	0.041452000000	-2.033645000000	-1.969479000000
H	-0.890156000000	-3.311836000000	-2.753195000000
H	-3.439714000000	-2.455978000000	-2.761473000000
H	-3.529226000000	-3.791509000000	-1.613502000000
H	-1.390607000000	-4.253518000000	-0.459540000000
H	-0.497483000000	-2.921055000000	0.287326000000
H	-2.154599000000	-3.251643000000	0.779063000000
H	6.215779000000	0.779268000000	1.250140000000
H	5.157230000000	0.886930000000	2.670010000000
H	6.099060000000	2.288596000000	2.158936000000
H	5.645902000000	3.490391000000	0.153315000000
H	4.273572000000	3.144449000000	-0.898661000000
H	5.652627000000	2.037145000000	-0.846550000000
H	1.239303000000	1.615755000000	3.106534000000
H	-0.039576000000	2.040261000000	1.965699000000
H	0.892771000000	3.319081000000	2.747509000000
H	3.441688000000	2.460534000000	2.758170000000
H	3.533188000000	3.794077000000	1.608056000000
H	1.395073000000	4.256637000000	0.452723000000
H	0.500966000000	2.923778000000	-0.292353000000
H	2.158539000000	3.252056000000	-0.784046000000
C	4.135573000000	-0.323332000000	-0.295458000000
C	4.586718000000	-1.448298000000	0.414351000000
C	4.201949000000	-0.278116000000	-1.700034000000
C	5.209414000000	-2.470837000000	-0.298382000000
C	4.828953000000	-1.327742000000	-2.364551000000
C	5.351138000000	-2.406756000000	-1.672468000000
H	5.571282000000	-3.340725000000	0.234987000000
H	4.893871000000	-1.304931000000	-3.444877000000
H	5.841410000000	-3.209891000000	-2.206958000000
C	-4.136127000000	0.322162000000	0.296468000000
C	-4.589915000000	1.447201000000	-0.411530000000
C	-4.201872000000	0.274775000000	1.701006000000
C	-5.214738000000	2.467272000000	0.302875000000
C	-4.831122000000	1.321954000000	2.367244000000
C	-5.356040000000	2.400761000000	1.676893000000
H	-5.578730000000	3.337123000000	-0.229099000000
H	-4.895707000000	1.297384000000	3.447554000000
H	-5.848115000000	3.201909000000	2.212700000000
C	-4.351788000000	1.652486000000	-1.897604000000
H	-3.841902000000	0.770963000000	-2.286865000000
C	-3.541728000000	-0.813796000000	2.527774000000
H	-3.155720000000	-1.569872000000	1.848735000000
C	3.544744000000	0.810844000000	-2.528638000000
H	3.160774000000	1.569084000000	-1.850876000000
C	4.348028000000	-1.650823000000	1.900714000000
H	3.839500000000	-0.767872000000	2.288498000000
C	-3.424329000000	2.852520000000	-2.127082000000
H	-3.196008000000	2.948943000000	-3.189316000000
H	-3.902878000000	3.777373000000	-1.800010000000
H	-2.487575000000	2.737670000000	-1.584826000000
C	-5.653166000000	1.873304000000	-2.674913000000
H	-6.118825000000	2.814911000000	-2.379966000000
H	-5.446082000000	1.932343000000	-3.744299000000
H	-6.378164000000	1.079448000000	-2.509223000000

C	4.516263000000	1.475897000000	-3.506100000000
H	4.843090000000	0.771184000000	-4.271919000000
H	4.023271000000	2.305076000000	-4.015109000000
H	5.404140000000	1.861018000000	-3.007274000000
C	2.343979000000	0.243580000000	-3.294570000000
H	1.607704000000	-0.179674000000	-2.612758000000
H	1.859176000000	1.033890000000	-3.869619000000
H	2.663926000000	-0.534590000000	-3.990249000000
C	5.649033000000	-1.872387000000	2.678450000000
H	5.441831000000	-1.929274000000	3.747929000000
H	6.113171000000	-2.815249000000	2.385104000000
H	6.375316000000	-1.079980000000	2.511422000000
C	3.418720000000	-2.849052000000	2.132143000000
H	3.190272000000	-2.943392000000	3.194536000000
H	2.482126000000	-2.733624000000	1.589741000000
H	3.895817000000	-3.775188000000	1.806583000000
C	-2.342486000000	-0.244486000000	3.294597000000
H	-1.607801000000	0.182810000000	2.613586000000
H	-2.664721000000	0.530956000000	3.992262000000
H	-1.854939000000	-1.034610000000	3.867574000000
C	-4.511351000000	-1.483084000000	3.504229000000
H	-4.840092000000	-0.780461000000	4.271148000000
H	-5.398170000000	-1.869896000000	3.004839000000
H	-4.016040000000	-2.311684000000	4.011938000000
H	1.585964000000	-1.400873000000	-0.469349000000
H	-1.587619000000	1.402835000000	0.470779000000

Si_2H_2 (M06-2X/def2-TZVPP)

E(LCCSD(T)/cc-pVTZ)= -579.21969357

Si	-0.175912143882	0.144098092340	2.280234777975
Si	0.077286622972	0.106658346881	0.085574173704
H	-0.782698697557	-0.878964114395	1.115105249510
H	1.090131083792	-0.357600405606	1.322600792446

CAAC (M06-2X/def2-TZVPP)

E(LCCSD(T)/cc-pVTZ)= -833.95065920

C	0.054390000000	0.064049000000	-0.013879000000
C	1.528144000000	-0.425463000000	1.881010000000
C	0.069183000000	-0.080751000000	1.499219000000
N	1.300698000000	0.076022000000	-0.392030000000
C	2.383245000000	-0.047119000000	0.665761000000
C	-0.907052000000	-1.174457000000	1.924217000000
C	-0.385839000000	1.262213000000	2.082656000000
C	3.406399000000	-1.118235000000	0.304566000000
C	3.117491000000	1.281325000000	0.839966000000
H	3.919892000000	-0.878446000000	-0.627703000000
H	2.948357000000	-2.100636000000	0.211215000000
H	4.153114000000	-1.171359000000	1.097524000000
H	3.917393000000	1.150217000000	1.568850000000
H	2.459907000000	2.069663000000	1.201353000000
H	3.567719000000	1.602387000000	-0.100440000000
H	-0.648463000000	-2.127755000000	1.459809000000
H	-1.920913000000	-0.916088000000	1.620196000000

H	-0.886671000000	-1.305220000000	3.008402000000
H	1.615952000000	-1.497064000000	2.069691000000
H	1.860785000000	0.094867000000	2.779845000000
H	-0.421176000000	1.203877000000	3.172229000000
H	-1.379058000000	1.515910000000	1.713144000000
H	0.290419000000	2.072914000000	1.807118000000
C	1.673239000000	0.242936000000	-1.774971000000
C	1.849904000000	-0.895133000000	-2.572013000000
C	1.818138000000	1.535459000000	-2.295397000000
C	2.282720000000	-0.715288000000	-3.882918000000
C	2.254062000000	1.664486000000	-3.611800000000
C	2.509400000000	0.551209000000	-4.394059000000
H	2.425139000000	-1.580097000000	-4.517948000000
H	2.373756000000	2.652385000000	-4.036740000000
H	2.852803000000	0.671546000000	-5.412892000000
C	1.378169000000	2.768936000000	-1.531122000000
H	1.261292000000	2.500721000000	-0.484926000000
C	1.462053000000	-2.283799000000	-2.101891000000
H	1.290025000000	-2.247824000000	-1.028404000000
C	2.373883000000	3.923840000000	-1.617457000000
H	2.458691000000	4.304343000000	-2.635893000000
H	2.039451000000	4.750779000000	-0.990189000000
H	3.369113000000	3.625097000000	-1.287065000000
C	-0.005261000000	3.196397000000	-2.033199000000
H	-0.720953000000	2.384660000000	-1.904885000000
H	-0.358593000000	4.066443000000	-1.477631000000
H	0.036154000000	3.460567000000	-3.091509000000
C	2.537021000000	-3.332394000000	-2.383186000000
H	2.249923000000	-4.289691000000	-1.946519000000
H	2.666925000000	-3.489680000000	-3.454469000000
H	3.502008000000	-3.040753000000	-1.968256000000
C	0.129213000000	-2.678357000000	-2.746748000000
H	-0.189518000000	-3.659433000000	-2.391316000000
H	-0.643027000000	-1.949830000000	-2.500949000000
H	0.227531000000	-2.725067000000	-3.832801000000

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