Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

For

Cyclic Alkyl(amino) Carbene Stabilized Biradical of Dimethylsilicon and Dimethylsiliconchloride Radical: Synthesized from Me_2SiCl_2 - an Important Feedstock Material

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Contents:

S1. **Experimental Section**

All manipulations were carried out under a dry argon or nitrogen atmosphere using either Schlenk line or glovebox techniques. Solvents were dried by refluxing with sodium/potassium alloy under dry N_2 prior to use. C_6D_6 was dried by stirring for 12 h over potassium mirror followed by distillation and degassed. NMR spectra were recorded either on a Bruker 300 MHz or Bruker Avance II 500 MHz spectrometer. Melting points of the compounds were recorded in a sealed glass capillary using the Büchi-540 instrument. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. LIFDI spectra were performed on a Joel AccuTOF spectrometer under inert atmosphere. cAAC[1] was prepared according to the literature procedure.

$(cAAC)_2Me_2Si$ (1): A mixture of cAAC (285 mg; 1.0 mmol) and KC_8 (135 mg; 1.0 mmol) were placed in a 100 mL Schlenk flask and 40 mL of Et_2O was added at -78 °C. To this mixture Me_2SiCl_2 [0.06 mL (65 mg), 0.5 mmol] was added at -78 °C and the reaction mixture was allowed to warm slowly to room temperature (4 h) to give a blue coloured solution. The reaction was further continued for 30 min at room temperature. Then the solvent was removed by high vacuum and the product was extracted using 50 mL of hexane. After filtration of the insoluble residue, the solution was evaporated by high vacuum to obtain a dark blue solid of **1** (Yield: 51

%, 160 mg). Single crystals of **1** were grown at -26 °C from hexane solution. Mp: 148 °C (decompose). Anal. Calcd (%) for $C_{42}H_{68}N_2Si$ (Mw = 629.11): C, 80.19; H, 10.90; N, 4.45. Found: C, 79.15; H, 10.49; N, 4.38. MS (LIFDI, THF): *m/z* = 629.6 ($[M+H]^+$). UV λ_{ab} = 575 nm.

(cAAC)Me_2SiCl (2): A mixture of cAAC (285 mg; 1.0 mmol) and KC_8 (135 mg; 1.0 mmol) were placed in a 100 mL Schlenk flask and 30 mL of THF was added at -90 °C. To this mixture Me_2SiCl_2 [0.12 mL (129 mg, 1.0 mmol] was added at -90 °C. Then the temperature of the reaction mixture was allowed to rise slowly to ~ -70 °C (over 30 min). The temperature was then raised to room temperature (over 30 min) and the resulting orange solution was allowed to stir for an additional 15 min. Then the solvent was removed with high vacuum and the product was extracted with 60 mL of hexane. After filtration of the insoluble residue, the volatiles were evaporated by high vacuum to obtain an orange solid of **2** (Yield: 68 %, 257 mg). Single crystals of **2** were grown at -26 °C from hexane solution. Mp: 107 °C. Anal. Calcd (%) for $C_{22}H_{37}ClNSi$ (Mw = 379.08): C, 69.71; H, 9.84; N, 3.69. Found: C, 70.59; H, 9.51; N, 3.81. MS (LIFDI, THF): *m/z* = 378.2 ($[M^+]$). UV λ_{ab} = 435 nm.

Fig S1. UV spectrum of compound **1** in n-hexane

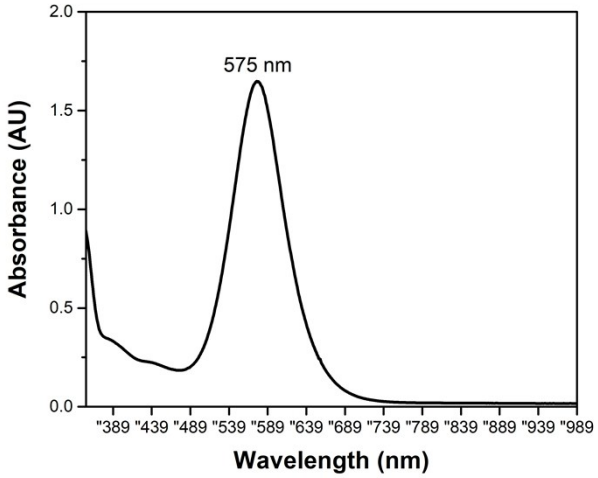
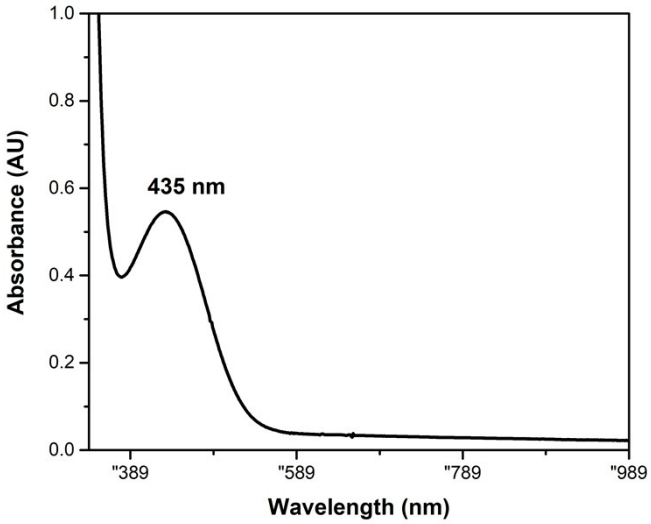


Fig S2. UV spectrum of compound **2** in n-hexane



S2. **Theoretical analysis**:

Theoretical methods. Geometry optimizations without symmetry restrictions were performed with the Gaussian 09[s1] program. The calculations were carried out for all molecules using the BP86 functional[s2,s3] with def2-TZVPP[s4,s5] basis set and dispersion correction by Grimme with Becke-Johnson damping D3(BJ)[s6,s7] (termed as BP86+D3(BJ)/def2-TZVPP). Dispersion corrections are very important to account for the weak and noncovalent interactions. Wiberg bond index P and partial charges q were obtained from a single-point calculation of the molecules at the same level by using NBO 6.0[s8] as implemented with Gaussian 09 program.[s1]

The orbital interactions have been investigated with the help of the EDA-NOCV method[s9] which combines the energy decomposition analysis (EDA)[s10] with the natural orbital for chemical valence (NOCV)[s11,s12] method. The interaction energy between the fragments ΔE_{int} which are calculated with the frozen geometry in the transition state is decomposed into four main components ΔE_{elstat} (electrostatic interactions), ΔE_{Pauli} (Pauli repulsion), ΔE_{disp} (dispersion interactions), and ΔE_{orb} (orbital interactions). The latter term can be separated into contributions which come from pairwise orbital interactions, which makes it possible to identify the dominant orbitals of the interactions in the transition state. For a detailed description of the method[s13-s17], we refer to the literatures. Both fragment orbital analysis and the energy decomposition analysis were conducted at the BP86(D3)/TZ2P [s18] level using the BP86+D3(BJ)/def2-TZVPP optimized geometries. For the open-shell molecules we employed the unrestricted UBP86 method. The EDA-NOCV calculations were carried out with the program package ADF.[s19,s20]

Table S1. EDA-NOCV results of **1** and **2** at the BP86-D3(B)J/TZ2P level of theory using the BP86/def2-TZVP optimized geometries. Energy values are given in kcal/mol.

	1	**2**
fragments	$(CAAC)_2(Q)^{[c]}$ + $SiMe_2(T)^{[c]}$	$(CAAC)(T)^{[c]}$ + $SiClMe_2(D)^{[c]}$
ΔE_{int}	-239.2	-124.7
ΔE_{disp}[a]	-32.5 (4.9 %)	-20.1 (5.6 %)
ΔE_{Pauli}	422.6	232.6
ΔE_{elstat}[a]	-301.8 (45.6 %)	-168.4 (47.1%)
ΔE_{orb}[a]	-327.6 (49.5 %)	-168.8 (47.2%)
$\Delta E_{orb(1)}$ [b]	-143.2 (43.7 %)	-137.8 (81.5 %)
$\Delta E_{orb(2)}$ [b]	-137.7 (42.0 %)	-16.6 (9.8 %)
$\Delta E_{orb(3)}$ [b]	-12.4 (3.8 %)	-4.2 (2.5 %)
$\Delta E_{orb(4)}$ [b]	-11.3 (3.4 %)	
ΔE_{rest}	-23.3 (7.1 %)	-10.4 (6.2 %)

[a]The values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{disp}+\Delta E_{elstat} + \Delta E_{orb}$. [b]The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}. [c]Q = quintet state; T = triplet state; D = doublet state.

Table S2. EDA-NOCV results of Compound **1** at the BP86(D3)/TZ2P//BP86(D3)/def2-TZVPP level using open-shell fragments for electron-sharing bonding and singlet fragments for dative bonding. Energy values are given in kcal/mol.

Fragments	$(CAAC)_2(Q)^{[c]}$ + $SiMe_2(T)^{[c]}$	$(CAAC)_2(S)^{[c]}$ + $SiMe_2(S)^{[c]}$
Bonding	electron-sharing bond	dative bond
ΔE_{int}	-239.18	-144.87
ΔE_{disp}[a]	-32.49 (4.9 %)	-32.49 (3.8 %)
ΔE_{Pauli}	422.64	708.15
ΔE_{elstat}[a]	-301.76 (45.6 %)	-349.54 (41 %)
ΔE_{orb}[a]	-327.57 (49.5 %)	-470.99 (55.2 %)
ΔE_{orb1}[b]	-143.2 (43.7 %)	
ΔE_{orb2}[b]	-137.7 (42 %)	
ΔE_{orb3}[b]	-12.4 (3.8 %)	
ΔE_{orb4}[b]	-11.3 (3.4 %)	
ΔE_{rest}[a]	-23.3 (7.1 %)	

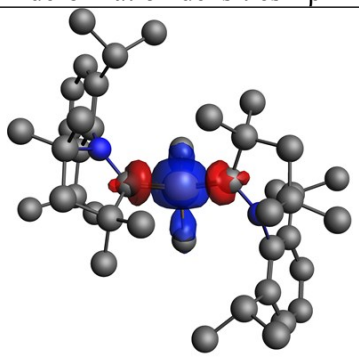
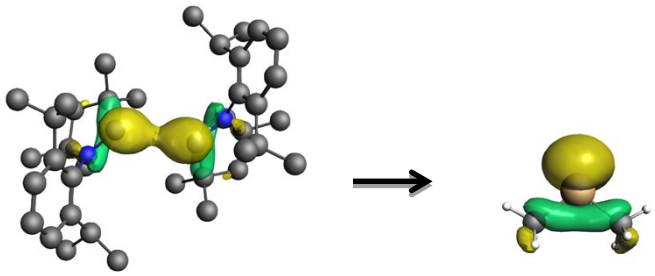
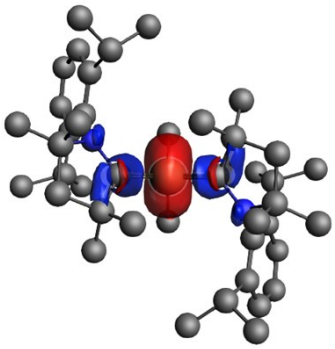
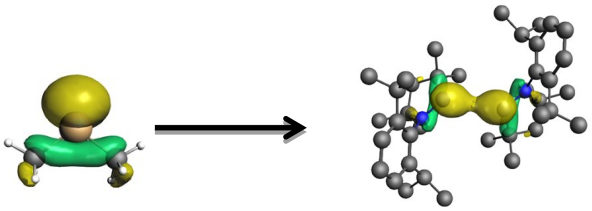
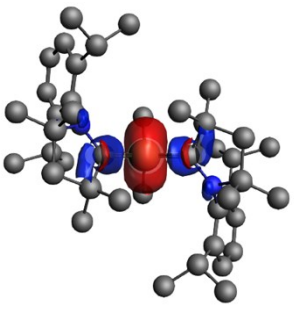
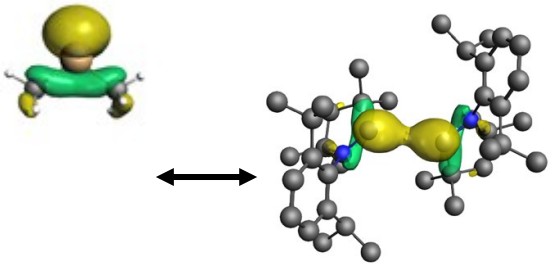
[a]The values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb}+ \Delta E_{disp}$.[b]The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}. . [c]Q = quintet state; T = triplet state; S = singlet state.

Table S3. EDA-NOCV results of Compound **2** at the BP86(D3)/TZ2P//BP86(D3)/def2-TZVPP level using a triplet state of the CAAC ligand for an electron-sharing bond and the singlet state for a dative bond. Energy values are given in kcal/mol.

Fragments	(CAAC) (T) [c] + $SiClMe_2$(D) [c]	(CAAC) (S) [c] + $SiClMe_2$(D) [c]
Bonding	electron-sharing bond	Dative bond[d]
ΔE_{int}	-124.74	-182.75
ΔE_{disp}[a]	-20.06 (5.6 %)	-20.06 (4.8 %)
ΔE_{Pauli}	232.57	234.62
ΔE_{elstat}[a]	-168.44 (47.1%)	-185.47 (44.4 %)
ΔE_{orb}[a]	-168.81 (47.2%)	-211.84 (50.8 %)
ΔE_{orb1}[b]	-137.8 (81.5 %)	
ΔE_{orb2}[b]	-16.6 (9.8 %)	
ΔE_{orb3}[b]	-4.2 (2.5 %)	
ΔE_{rest}[a]	-10.4 (6.2 %)	

[a]The values in parentheses give the percentage contribution to the total attractive interactions ΔE_{elstat} + ΔE_{orb}+ ΔE_{disp}.[b]The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}. .[c]T = triplet state; D = doublet state; S = singlet state. [d]The bonding interactions take place between the CAAC fragment in the singlet state and $SiClMe_2$ in the doublet state, which may also be considered as three electron-sharing bond.

Figure S3. Shape of the most important interacting MOs of fragments, plot of deformation densities Δρ of the pairwise orbital interactions and the associated interaction energies (ΔE_{orb}) between fragments in compound **1**. Eigenvalues of the deformation densities υ. The direction of the charge flow is red to blue.

1	
deformation densities Δρ	interacting MOs
	
$\nu_{\alpha 1} = \pm 0.43$ $\Delta E_{orb(\alpha 1)} = -43.7$ kcal/mol	Frag1-157AA (SOMO) υ = -0.23 ; frag2-16AA (SOMO) υ = 0.436
	
$\nu_{\beta 1} = \pm 0.648$ $\Delta E_{orb(\beta 1)} = -99.5$ kcal/mol	frag2-16AA (SOMO) υ = -0.520 ; Frag1-157AA (SOMO) υ = 0.716
	
$\nu_{\alpha 1+\beta 1} = \pm 1.08$ $\Delta E_{orb(\alpha 1+\beta 1)} = -143.2$ kcal/mol	frag2-16AA (SOMO) υ = -0.146 ; Frag1-157AA (SOMO) υ = 0.487

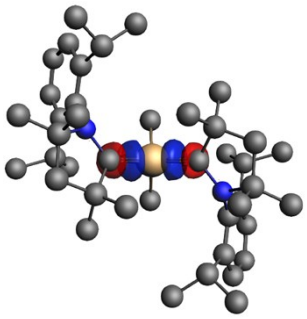
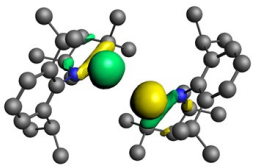
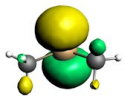
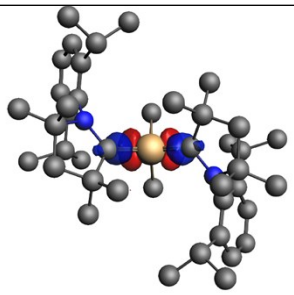
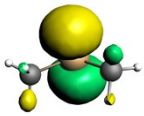
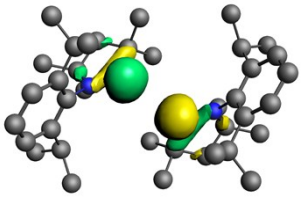
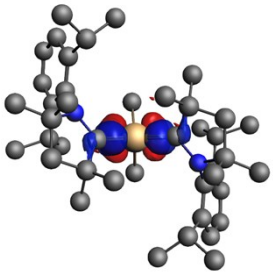
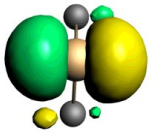
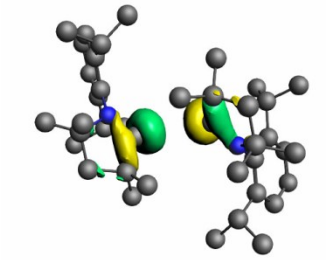
 $\nu_{\alpha 2} = \pm 0.28$ $\Delta E_{orb(\alpha 2)} = -24.3$ kcal/mol	  Frag1-158AA (SOMO) $\nu = -0.259$ Frag2-17AA (SOMO) $\nu = 0.233$
 $\nu_{\beta 2} = \pm 0.63$ $\Delta E_{orb(\beta 2)} = -113.4$ kcal/mol	  Frag2-17AA (SOMO) $\nu = -0.756$ Frag1-158AA (SOMO) $\nu = 0.71$
 $\nu_{\alpha 2+\beta 2} = \pm 0.917$ $\Delta E_{orb(\alpha 2+\beta 2)} = -137.7$ kcal/mol	  Frag2-17AA (SOMO) $\nu = - -0.523$ Frag1-158AA (SOMO) $\nu = 0.451$

Figure S4. Shape of the most important interacting MOs of fragments, plot of deformation densities Δρ of the pairwise orbital interactions and the associated interaction energies (ΔE_{orb}) between fragments in compound **2**. Eigenvalues of the deformation densities υ. The direction of the charge flow is red to blue.

<table>
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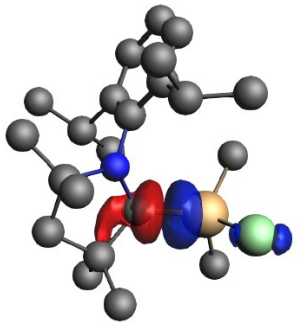
<tr><td>deformation densities Δρ</td><td colspan="2">interacting MOs</td></tr>
<tr><td rowspan="4"> 
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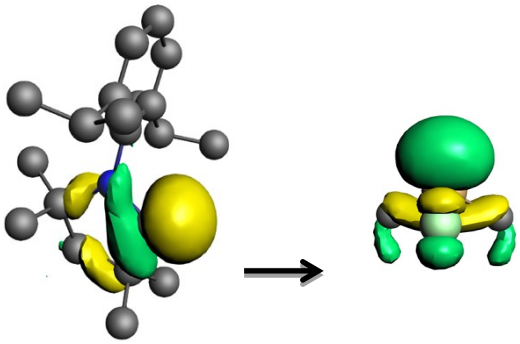
$\Delta E_{orb(\alpha 1)} = -36.6$ kcal/mol</td><td colspan="2">  </td></tr>
<tr><td>Frag1-79AA</td><td>frag2-25AA</td></tr>
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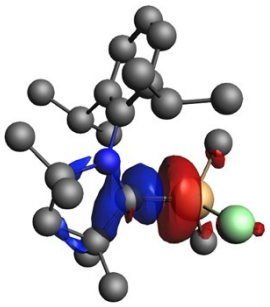
<tr><td>ν = -0.22</td><td>ν = 0.33</td></tr>
<tr><td rowspan="4"> 
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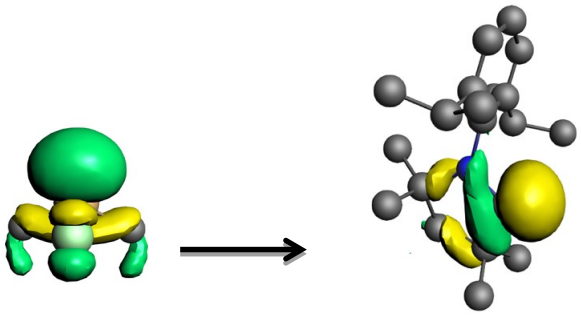
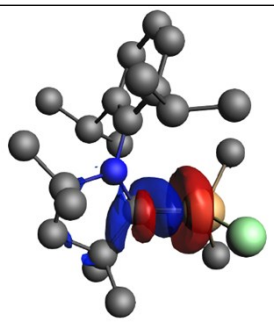
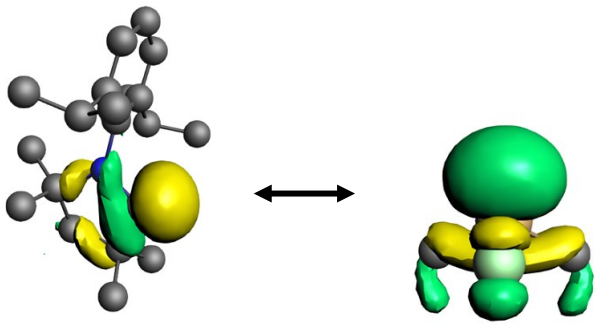
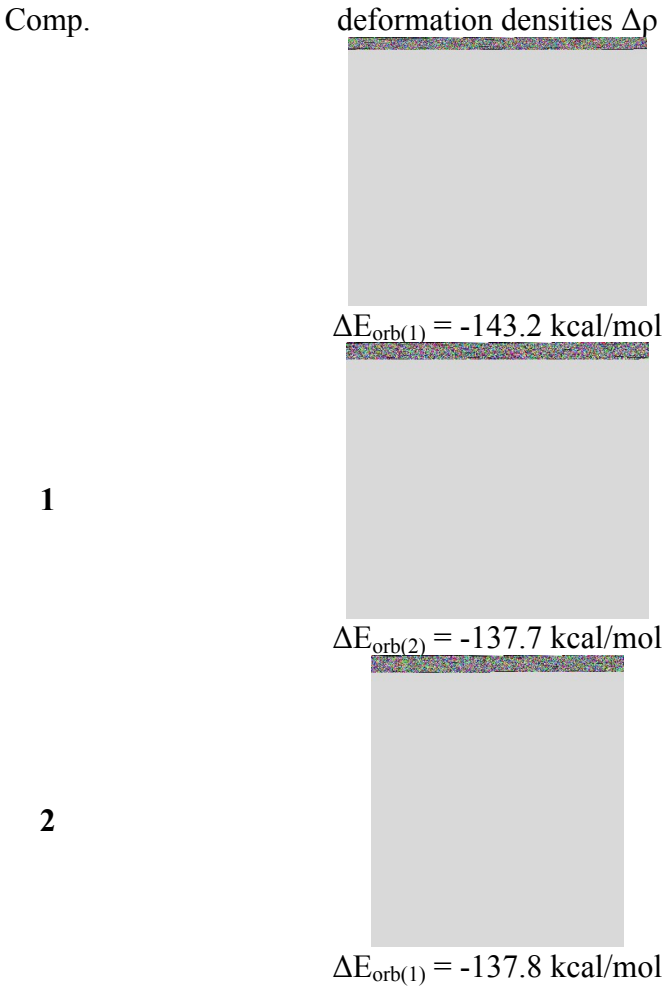
$\Delta E_{orb(\beta 1)} = -101.2$ kcal/mol</td><td colspan="2">  </td></tr>
<tr><td>Frag2-25AA</td><td>Frag1-79AA</td></tr>
<tr><td>(SOMO)</td><td>(SOMO)</td></tr>
<tr><td>ν = -0.604</td><td>ν = 0.653</td></tr>
<tr><td rowspan="3"> 
$\nu_{\alpha 1+\beta 1} = \pm 1.0$
$\Delta E_{orb(\alpha 1+\beta 1)} = -137.8$ kcal/mol</td><td colspan="2">  </td></tr>
<tr><td>Frag1-79AA</td><td>frag2-25AA</td></tr>
</table>

	(SOMO)	(SOMO)
	ν = 0.434	ν = -0.278

Table S4. Coordinates and energies of the calculated molecules at the BP86(D3)/def2-TZVP level.

Figure S5. Plot of deformation densities Δρ of the most important pairwise orbital interactions between the chosen fragments in **1** and **2**. The direction of the charge flow is red→blue.



Compound 1 (diradical) (triplet)

Energy = -2041.2424719

N	-2.62605400	0.52770900	-0.60303400
C	-0.99780800	2.15946500	-1.26711400
C	-1.29306100	0.92460400	-0.40603400

C	-2.38506400	2.50003700	-1.86384400
H	-2.31387600	2.90408900	-2.88419700
H	-2.86886400	3.26406900	-1.23558200
C	-3.22572100	1.21173400	-1.81112100
C	-4.71300800	1.51147600	-1.63589600
H	-5.07341900	2.06550600	-2.51498900
H	-5.30818100	0.59384900	-1.54420000
H	-4.90093100	2.12004200	-0.74286300
C	0.06261000	1.87190900	-2.34920800
H	-0.26333700	1.09190000	-3.04818100
C	-0.49510000	3.37183600	-0.45328500
H	0.48585700	3.17808100	-0.00634500
H	-0.39388200	4.24796500	-1.11477400
H	-1.19327700	3.63612400	0.35247400
C	-3.01583000	0.38411200	-3.09360700
H	-3.22758800	1.01004800	-3.97374600
H	-1.98309500	0.02504300	-3.16992200
H	-3.68417700	-0.48329000	-3.13464900
C	-3.46589200	-0.00840400	0.42367700
H	-4.74921800	0.75407500	3.49855000
C	-3.67277200	0.70716800	1.63763100
C	-2.98344300	2.02606500	1.95359800
H	-2.14769000	2.12526100	1.24810500
C	-2.38427400	2.05313300	3.36890700
H	-1.73433700	1.18644200	3.55030300
H	-1.78244700	2.96444000	3.50643900

H	-3.16535200	2.05735800	4.14436100
C	-3.92377500	3.22726700	1.76142700
H	-3.39757200	4.16799400	1.98735600
H	-4.29927600	3.29185600	0.73134400
H	-4.79478800	3.15642200	2.43143800
H	0.26435400	-1.09268900	-3.04845200
C	1.29304900	-0.92483200	-0.40581600
H	0.28784000	2.78241800	-2.92753700
H	0.99390800	1.52662200	-1.87910800
C	-4.12990300	-1.24816900	0.22034500
C	-4.57617400	0.19668600	2.57587400
C	0.99781700	-2.15987000	-1.26670300
N	2.62596600	-0.52784700	-0.60299300
C	-3.84407400	-2.14887900	-0.97078400
C	-5.03767500	-1.70379600	1.18509100
C	-5.27633600	-0.98821400	2.35349400
C	0.49445500	-3.37193900	-0.45286300
C	-0.06206400	-1.87238500	-2.34936000
C	2.38524700	-2.50079900	-1.86273700
C	3.22573700	-1.21236700	-1.81071100
C	3.46561900	0.00876300	0.42364300
C	-3.35555600	-3.53749600	-0.51995900
C	-5.06502700	-2.31720400	-1.89111800
H	-3.03179300	-1.67975200	-1.54229800
H	-5.55311500	-2.65277000	1.02142700
H	-5.98890800	-1.35654700	3.09370600

H	-0.48707600	-3.17817500	-0.00719200
H	0.39416300	-4.24838800	-1.11408100
H	1.19172600	-3.63573700	0.35384500
H	-0.28723700	-2.78302900	-2.92751000
H	-0.99347800	-1.52678600	-1.87972700
H	2.31441500	-2.90570100	-2.88278300
H	2.86894500	-3.26425900	-1.23368100
C	3.01580000	-0.38526300	-3.09352300
C	4.71306600	-1.51179800	-1.63530900
C	3.67303200	-0.70673100	1.63753600
C	4.12909300	1.24878200	0.22013000
H	-3.00749600	-4.12143500	-1.38536200
H	-2.52709800	-3.46325000	0.19634800
H	-4.16291900	-4.10579500	-0.03378100
H	-4.80969000	-2.93458400	-2.76644900
H	-5.88597000	-2.81873100	-1.35573200
H	-5.45013200	-1.35460300	-2.25369800
H	1.98320000	-0.02576100	-3.16971500
H	3.22706900	-1.01162400	-3.97348100
H	3.68451500	0.48184400	-3.13507100
H	5.07361100	-2.06604400	-2.51421700
H	4.90109800	-2.12001600	-0.74207000
H	5.30804400	-0.59401000	-1.54393100
C	2.98466800	-2.02614200	1.95344600
C	4.57614700	-0.19571000	2.57577100
C	3.84350500	2.14878900	-0.97158300

C	5.03644800	1.70505600	1.18495400
C	3.92612700	-3.22665600	1.76255700
H	2.14954000	-2.12637300	1.24735800
C	2.38457500	-2.05295600	3.36836800
H	4.74965900	-0.75305400	3.49838700
C	5.27542400	0.98971400	2.35344100
H	3.03133200	1.67930900	-1.54296000
C	3.35505900	3.53773800	-0.52181100
C	5.06471700	2.31626300	-1.89172700
H	5.55139900	2.65429000	1.02125800
H	3.40035800	-4.16769000	1.98820800
H	4.30271900	-3.29126200	0.73287300
H	4.79641700	-3.15507100	2.43342700
H	1.78364100	-2.96481900	3.50617400
H	1.73361800	-1.18684200	3.54873000
H	3.16518500	-2.05574400	4.14428600
H	5.98766200	1.35860300	3.09370100
H	3.00721500	4.12114700	-1.38767200
H	2.52642100	3.46402800	0.19433100
H	4.16234400	4.10630900	-0.03584600
H	5.44972100	1.35332800	-2.25352100
H	4.80972300	2.93307400	-2.76755900
H	5.88561900	2.81799000	-1.35645800
C	0.88512600	1.23084500	1.73946000
H	1.42896700	0.70035500	2.53366200
H	1.62534000	1.84713000	1.21626100

H	0.15184600	1.89832200	2.21216700
C	-0.88534700	-1.23080800	1.73956500
H	-1.42853600	-0.70000400	2.53400100
H	-1.62613000	-1.84654000	1.21656600
H	-0.15237600	-1.89884200	2.21193700
Si	-0.00000700	-0.00009200	0.60955000

Compound 2 (monoradical) (doublet).

Energy = -1665.6599343

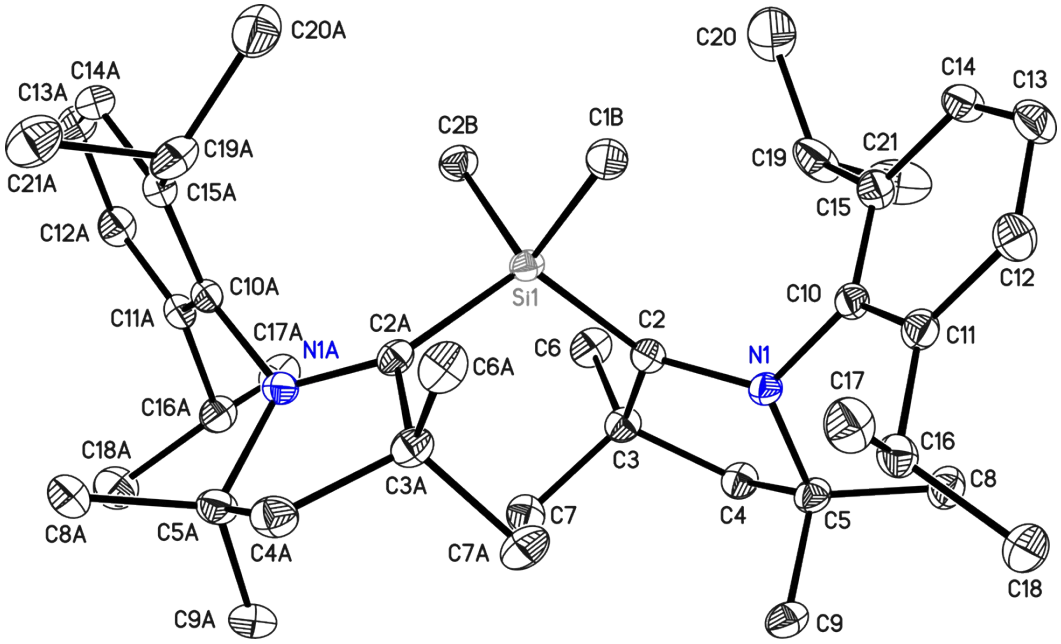
Si	-1.524457000	-0.789727000	-1.415547000
Cl	-1.793400000	-2.837397000	-0.861683000
N	-0.001802000	0.196376000	0.775001000
C	-1.229096000	0.184436000	0.118533000
C	-2.312714000	0.732297000	1.050643000
C	-1.479682000	1.258944000	2.251605000
H	-1.288383000	2.335345000	2.116816000
H	-2.008899000	1.133871000	3.206755000
C	-0.132614000	0.507766000	2.236400000
C	-3.090812000	1.900486000	0.410964000
H	-3.703181000	1.562596000	-0.435186000
H	-3.766745000	2.357348000	1.152441000
C	-3.326790000	-0.348095000	1.485829000
H	-2.835493000	-1.201891000	1.968501000
H	-3.879474000	-0.740258000	0.620539000
H	-4.059577000	0.077437000	2.190229000
C	1.226960000	0.281696000	0.045498000

C	-0.211121000	-0.783527000	3.073220000
H	-0.915806000	-1.500274000	2.632407000
H	-0.550852000	-0.545376000	4.092504000
H	0.768690000	-1.269729000	3.151277000
C	1.025587000	1.370054000	2.735257000
H	0.888961000	1.583654000	3.805144000
H	1.076720000	2.325798000	2.197629000
H	1.988249000	0.853547000	2.611462000
C	1.520279000	1.478926000	-0.656369000
C	2.689552000	1.535710000	-1.422844000
C	3.275409000	-0.709629000	-0.778323000
C	2.103859000	-0.825534000	-0.016468000
C	1.802368000	-2.141382000	0.678686000
H	0.783159000	-2.069582000	1.082159000
C	2.782914000	-2.382192000	1.839964000
H	2.503915000	-3.284362000	2.405539000
H	2.808658000	-1.531556000	2.536750000
C	1.823730000	-3.331789000	-0.294269000
H	2.823229000	-3.480190000	-0.730895000
H	1.103183000	-3.193057000	-1.110390000
H	1.549493000	-4.255745000	0.236421000
C	-3.120629000	-0.305909000	-2.278712000
H	-3.270720000	-0.972430000	-3.141222000
H	-3.071173000	0.728687000	-2.650704000
H	-4.000168000	-0.400318000	-1.628235000
C	-0.142818000	-0.823344000	-2.682907000

H	0.807499000	-1.182014000	-2.270583000
H	0.031640000	0.178437000	-3.100713000
H	-0.440659000	-1.494958000	-3.502590000
H	-2.404179000	2.677322000	0.046029000
C	0.621832000	2.704595000	-0.589768000
C	3.566825000	0.453720000	-1.484609000
H	2.924312000	2.449673000	-1.972446000
H	3.958661000	-1.559223000	-0.835913000
H	3.806662000	-2.525185000	1.460384000
C	1.402370000	3.964606000	-0.179066000
H	-0.136400000	2.514493000	0.181200000
C	-0.124666000	2.936982000	-1.913166000
H	4.477069000	0.519069000	-2.083719000
H	1.967854000	3.803694000	0.750326000
H	0.710428000	4.805804000	-0.021303000
H	2.120155000	4.268313000	-0.955732000
H	-0.752712000	3.838939000	-1.850239000
H	-0.776477000	2.084394000	-2.146407000
H	0.580722000	3.072112000	-2.747576000

S3. X-Ray Crystallographic Analysis

Crystal data for **1** at 100(2) K: $C_{42}H_{68}N_2Si$, $M_r = 629.07$ g/mol, 0.052 x 0.163 x 0.197 mm, monoclinic, *C2/c*, $a = 35.167(3)$ Å, $b = 9.999(2)$ Å, $c = 22.554(3)$ Å, $\beta = 105.62(2)°$, $V = 7638(2)$ Å^3, $Z = 8$, μ (Mo K_α) = 0.092 mm^{-1}, $\theta_{max} = 25.369°$, 90538 reflections measured, 6994 independent ($R_{int} = 0.0308$), $R_1 = 0.0337$ [$I > 2\sigma(I)$], $wR_2 = 0.0863$ (all data), res. density peaks: 0.287 to -0.318 eA^{-3}.



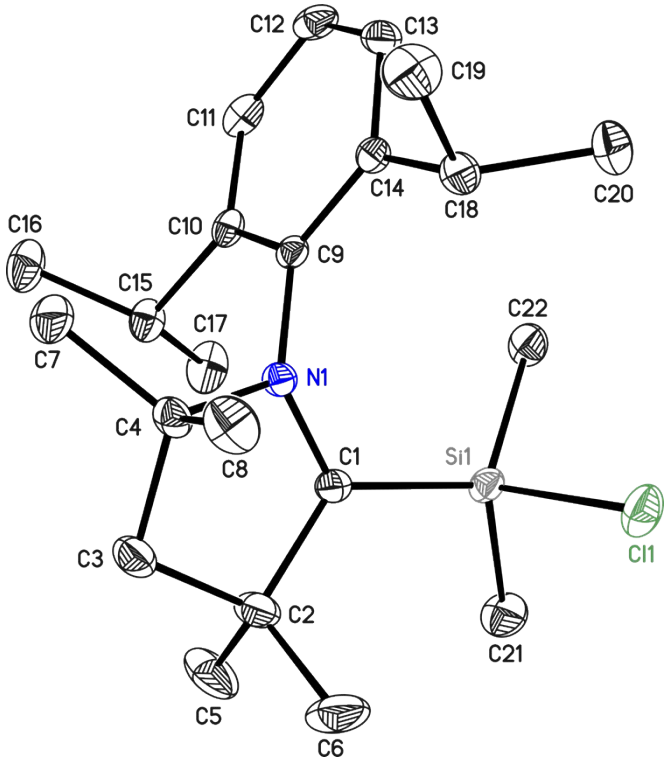
Bond lengths [Å] and angles [°] for 1:

Si(1)-C(2B)	1.8768(13)	N(1)-C(2)-Si(1)	126.77(8)
Si(1)-C(1B)	1.8800(13)	C(3)-C(2)-Si(1)	123.84(9)
Si(1)-C(2)	1.8814(13)	C(5)-C(4)-C(3)	107.07(10)
Si(1)-C(2A)	1.8829(13)	N(1)-C(5)-C(8)	113.16(10)
N(1)-C(2)	1.4059(16)	N(1)-C(5)-C(4)	100.65(9)
N(1)-C(10)	1.4464(15)	C(8)-C(5)-C(4)	111.36(10)
N(1)-C(5)	1.5126(15)	N(1)-C(5)-C(9)	112.05(10)
C(3)-C(7)	1.5352(17)	C(8)-C(5)-C(9)	108.73(11)
C(3)-C(6)	1.5403(17)	C(4)-C(5)-C(9)	110.74(10)
C(3)-C(4)	1.5409(17)	C(11)-C(10)-C(15)	119.73(11)
C(3)-C(2)	1.5430(16)	C(11)-C(10)-N(1)	120.06(11)
C(4)-C(5)	1.5341(17)	C(15)-C(10)-N(1)	120.20(11)
C(5)-C(8)	1.5235(18)	C(12)-C(11)-C(10)	118.85(12)

C(5)-C(9)	1.5373(18)	C(12)-C(11)-C(16)	117.06(11)
C(10)-C(11)	1.4144(17)	C(10)-C(11)-C(16)	124.03(11)
C(10)-C(15)	1.4199(18)	C(13)-C(12)-C(11)	121.52(12)
C(11)-C(12)	1.3951(18)	C(14)-C(13)-C(12)	119.57(12)
C(11)-C(16)	1.5247(18)	C(13)-C(14)-C(15)	121.66(13)
C(12)-C(13)	1.380(2)	C(14)-C(15)-C(10)	118.65(12)
C(13)-C(14)	1.3786(19)	C(14)-C(15)-C(19)	117.36(12)
C(14)-C(15)	1.3945(18)	C(10)-C(15)-C(19)	123.99(11)
C(15)-C(19)	1.5210(18)	C(11)-C(16)-C(18)	112.66(11)
C(16)-C(18)	1.5363(18)	C(11)-C(16)-C(17)	111.48(11)
C(16)-C(17)	1.5397(18)	C(18)-C(16)-C(17)	108.73(11)
C(19)-C(21)	1.530(2)	C(15)-C(19)-C(21)	111.75(12)
C(19)-C(20)	1.532(2)	C(15)-C(19)-C(20)	112.97(12)
N(1A)-C(2A)	1.4109(15)	C(21)-C(19)-C(20)	108.99(12)
N(1A)-C(10A)	1.4475(16)	C(2A)-N(1A)-C(10A)	121.97(10)
N(1A)-C(5A)	1.5137(15)	C(2A)-N(1A)-C(5A)	112.10(10)
C(3A)-C(7A)	1.5366(18)	C(10A)-N(1A)-C(5A)	120.00(10)
C(3A)-C(4A)	1.5385(18)	C(7A)-C(3A)-C(4A)	111.66(11)
C(3A)-C(2A)	1.5389(17)	C(7A)-C(3A)-C(2A)	113.00(10)
C(3A)-C(6A)	1.5444(17)	C(4A)-C(3A)-C(2A)	103.29(10)
C(4A)-C(5A)	1.5328(18)	C(7A)-C(3A)-C(6A)	107.07(10)
C(5A)-C(8A)	1.5271(18)	C(4A)-C(3A)-C(6A)	109.07(10)
C(5A)-C(9A)	1.5367(18)	C(2A)-C(3A)-C(6A)	112.77(10)
C(10A)-C(11A)	1.4143(17)	C(5A)-C(4A)-C(3A)	107.40(10)
C(10A)-C(15A)	1.4159(17)	N(1A)-C(5A)-C(8A)	112.75(10)
C(11A)-C(12A)	1.3947(18)	N(1A)-C(5A)-C(4A)	101.22(10)
C(11A)-C(16A)	1.5228(17)	C(8A)-C(5A)-C(4A)	110.56(11)
C(12A)-C(13A)	1.3791(19)	N(1A)-C(5A)-C(9A)	111.92(10)
C(13A)-C(14A)	1.3824(18)	C(8A)-C(5A)-C(9A)	108.96(11)
C(14A)-C(15A)	1.3931(18)	C(4A)-C(5A)-C(9A)	111.29(11)
C(15A)-C(19A)	1.5219(17)	C(11A)-C(10A)-C(15A)	119.10(11)
C(16A)-C(17A)	1.5329(18)	C(11A)-C(10A)-N(1A)	120.63(11)
C(16A)-C(18A)	1.5378(18)	C(15A)-C(10A)-N(1A)	120.25(10)
C(19A)-C(20A)	1.5320(19)	C(12A)-C(11A)-C(10A)	119.09(11)
C(19A)-C(21A)	1.5368(19)	C(12A)-C(11A)-C(16A)	117.04(11)
C(2B)-Si(1)-C(1B)	106.55(6)	C(10A)-C(11A)-C(16A)	123.87(11)
C(2B)-Si(1)-C(2)	108.33(6)	C(13A)-C(12A)-C(11A)	121.83(12)
C(1B)-Si(1)-C(2)	107.98(6)	C(12A)-C(13A)-C(14A)	118.99(12)
C(2B)-Si(1)-C(2A)	108.40(6)	C(13A)-C(14A)-C(15A)	121.64(12)
C(1B)-Si(1)-C(2A)	108.27(6)	C(14A)-C(15A)-C(10A)	119.23(11)
C(2)-Si(1)-C(2A)	116.86(5)	C(14A)-C(15A)-C(19A)	116.71(11)
C(2)-N(1)-C(10)	122.58(10)	C(10A)-C(15A)-C(19A)	124.05(11)
C(2)-N(1)-C(5)	112.18(9)	C(11A)-C(16A)-C(17A)	111.76(11)
C(10)-N(1)-C(5)	120.19(9)	C(11A)-C(16A)-C(18A)	111.60(11)

C(7)-C(3)-C(6)	107.49(10)	C(17A)-C(16A)-C(18A)	108.83(11)
C(7)-C(3)-C(4)	112.21(10)	C(15A)-C(19A)-C(20A)	111.31(11)
C(6)-C(3)-C(4)	108.57(10)	C(15A)-C(19A)-C(21A)	111.92(11)
C(7)-C(3)-C(2)	112.43(10)	C(20A)-C(19A)-C(21A)	109.26(11)
C(6)-C(3)-C(2)	113.09(10)	N(1A)-C(2A)-C(3A)	108.39(10)
C(4)-C(3)-C(2)	103.04(10)	N(1A)-C(2A)-Si(1)	126.97(9)
N(1)-C(2)-C(3)	108.17(10)	C(3A)-C(2A)-Si(1)	122.75(9)

Crystal data for **2** at 100(2) K: $C_{22}H_{37}ClNSi$, M_r = 379.06 g/mol, 0.086 x 0.137 x 0.211 mm, orthorhombic, *Pbca*, a = 16.345(2) Å, b = 16.183(2) Å, c = 17.291(3) Å, V = 4573.7(11) Å^3, Z = 8, μ (Mo K_α) = 0.225 mm^{-1}, θ_{max} = 26.364°, 105432 reflections measured, 4676 independent (R_{int} = 0.0359), R_1 = 0.0281 [$I > 2\sigma(I)$], wR_2 = 0.0791 (all data), res. density peaks: 0.327 to -0.240 eA^{-3}.



Bond lengths [Å] and angles [°] for 2:

Si(1)-C(1)	1.8323(12)	N(1)-C(1)-C(2)	109.13(10)

Si(1)-C(22)	1.8633(13)	N(1)-C(1)-Si(1)	124.39(8)
Si(1)-C(21)	1.8645(13)	C(2)-C(1)-Si(1)	124.49(8)
Si(1)-Cl(1)	2.1228(5)	C(1)-C(2)-C(6)	112.93(11)
N(1)-C(1)	1.3917(15)	C(1)-C(2)-C(5)	112.14(11)
N(1)-C(9)	1.4359(14)	C(6)-C(2)-C(5)	108.79(12)
N(1)-C(4)	1.5009(14)	C(1)-C(2)-C(3)	102.41(9)
C(1)-C(2)	1.5352(16)	C(6)-C(2)-C(3)	111.36(11)
C(2)-C(6)	1.538(2)	C(5)-C(2)-C(3)	109.06(11)
C(2)-C(5)	1.5406(19)	C(4)-C(3)-C(2)	107.54(10)
C(2)-C(3)	1.5482(17)	N(1)-C(4)-C(7)	112.65(9)
C(3)-C(4)	1.5294(16)	N(1)-C(4)-C(3)	101.23(9)
C(4)-C(7)	1.5237(17)	C(7)-C(4)-C(3)	111.95(10)
C(4)-C(8)	1.5351(16)	N(1)-C(4)-C(8)	110.68(9)
C(9)-C(14)	1.4076(15)	C(7)-C(4)-C(8)	109.06(10)
C(9)-C(10)	1.4161(15)	C(3)-C(4)-C(8)	111.13(10)
C(10)-C(11)	1.3921(17)	C(14)-C(9)-C(10)	120.53(10)
C(10)-C(15)	1.5225(16)	C(14)-C(9)-N(1)	120.75(10)
C(11)-C(12)	1.3838(18)	C(10)-C(9)-N(1)	118.70(10)
C(12)-C(13)	1.3806(18)	C(11)-C(10)-C(9)	118.43(10)
C(13)-C(14)	1.3970(16)	C(11)-C(10)-C(15)	118.73(10)
C(14)-C(18)	1.5222(16)	C(9)-C(10)-C(15)	122.84(10)
C(15)-C(17)	1.5359(17)	C(12)-C(11)-C(10)	121.34(11)
C(15)-C(16)	1.5384(17)	C(13)-C(12)-C(11)	119.89(11)
C(18)-C(19)	1.5339(17)	C(12)-C(13)-C(14)	121.20(11)
C(18)-C(20)	1.5373(17)	C(13)-C(14)-C(9)	118.60(10)
C(1)-Si(1)-C(22)	117.67(6)	C(13)-C(14)-C(18)	118.12(10)
C(1)-Si(1)-C(21)	113.16(6)	C(9)-C(14)-C(18)	123.27(10)
C(22)-Si(1)-C(21)	108.22(6)	C(10)-C(15)-C(17)	111.68(10)
C(1)-Si(1)-Cl(1)	108.56(4)	C(10)-C(15)-C(16)	111.48(10)
C(22)-Si(1)-Cl(1)	104.05(4)	C(17)-C(15)-C(16)	109.84(10)
C(21)-Si(1)-Cl(1)	103.91(5)	C(14)-C(18)-C(19)	110.75(10)
C(1)-N(1)-C(9)	122.01(9)	C(14)-C(18)-C(20)	111.89(10)
C(1)-N(1)-C(4)	112.66(9)	C(19)-C(18)-C(20)	109.44(10)
C(9)-N(1)-C(4)	123.04(9)		

S4. References

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