Supporting Information

Synthesis, Structure, and Bonding of Stable Dialkylsilaketenimines

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1. Experimental Details

Synthesis of *N*-(2,6-diisopropylphenyl)-1,1-[1,1,4,4-tetrakis(trimethylsilyl)butane-1,4-diyl]silaketenimine (2a)

To a hexane solution (15 ml) of silylene **3** (350 mg, 0.940 mmol) in a Schlenk flask, 2,6-diisopropylphenylisonitrile (DipNC, 176 mg, 0.940 mmol) was added at –30 °C. After the mixture was stirred for 10 minutes at the same temperature, concentration of the resulting solution and recrystallization from hexane at –30 °C gave pure silaketenimine **2a** as air- and moisture sensitive blue crystals (470 mg, 0.840 mmol, 89.4% yield). Similarly, C^{13}-labelled **2a** was synthesized by the reaction of **3** with ^{13}C-enriched DipN^{13}C, which was prepared by the reaction of 99% ^{13}C-encriched chloroform and 2,6-diisopropylaniline with potassium *tert*-butoxide. The $J(^{29}\text{Si-}^{13}\text{C})$ value was measured using the C^{13}-labelled **2a.**

2a: blue crystals; mp < 0 °C (decomp.); ^{1}H NMR (toluene-d_8, 233K, δ) 0.25 (s, 36H, $SiMe_3$), 1.10-1.13 (m, 14H, *i*-Pr), 1.85 (s, 4H, CH_2), 3.65 (sept, 2 H, CH), 6.80-6.90 (m, 3H, aryl); ^{13}C NMR (toluene-d_8, 233K, δ) 2.7, 23.9, 29.4, 34.7, 36.6, 122.6, 124.1, 130.2, 143.5, 214.6; ^{29}Si NMR (toluene-d_8, 233K, δ) 3.6 ($SiMe_3$), 15.9 (<u>Si</u>=C=N, $J(^{29}\text{Si-}^{13}\text{C})$ = 65.0 Hz); UV-vis (hexane, 233 K) λ_{max}/nm (ε) 647 (156), 374 (6.57×10^3), 273 (9.83×10^3).

Synthesis of *N*-(1-adamantyl)-1,1-[1,1,4,4-tetrakis(trimethylsilyl)butane-1,4-diyl]silaketenimine (2b)

In a Schlenk flask equipped with a stirring bar, silylene **3** (530 mg, 1.42 mmol) and 1-adamantylisonitrile (1-AdNC, 250 mg, 1.55 mmol) were placed. Into the mixture, dry hexane was transferred through vacuum line. Stirring the resulting solution at –30 °C for 10 min under argon atmosphere gave red solution. Removal of the solvent and recrystallization from hexane at –30 °C gave silaketenimine **2b** (645 mg, 1.21 mmol) in 85% yield.

2b: red crystals; mp < 0 °C (decomp.); ^{1}H NMR (toluene-d_8, 233 K, δ) 0.29 (s, 36 H, $SiMe_3$), 1.50-2.10 (m, 19 H, Ad+CH_2); ^{13}C NMR (toluene-d_8, 233 K, δ) 3.1, 14.4, 23.1, 30.3, 36.5, 42.6, 221.3 (Si=<u>C</u>=N); ^{29}Si NMR (toluene-d_8, 233 K, δ) 4.5, 23.9 (<u>Si</u>=C=N); UV-vis (hexane, 233 K) λ_{max}/nm (ε) 465 (109), 346 (5.65×10^3).

2. Uv-vis Spectra of Silaketenimines 2a and 2b

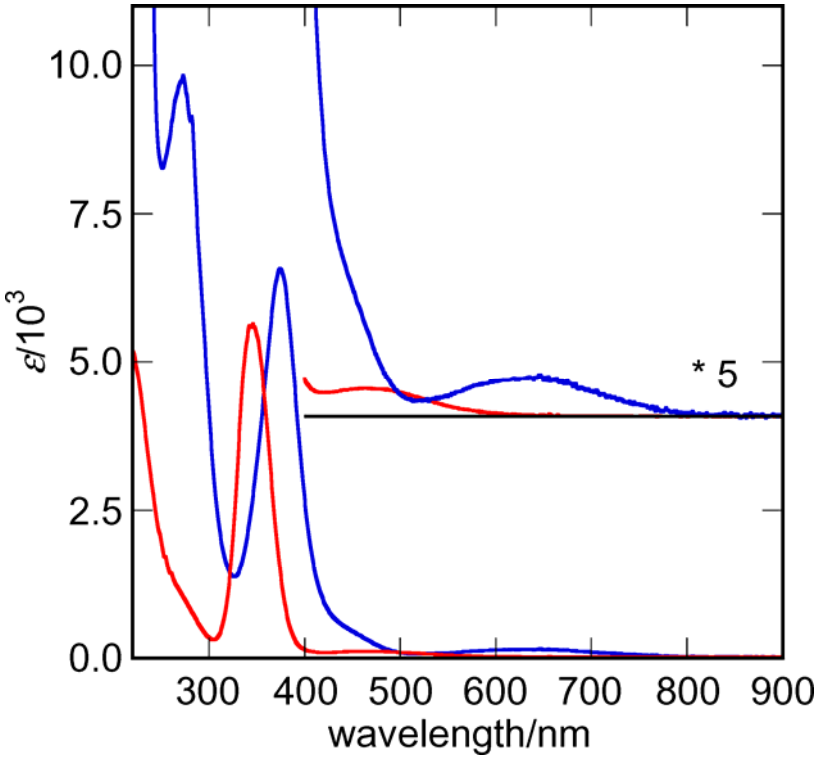
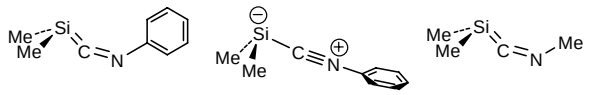


Figure S1. UV-vis spectra of silaketenimines **2a** (blue) and **2b** (red) in hexane at 233 K.

3. Details of Theoretical Calculations

All DFT calculations were carried out using a Gaussian 98 program.[S1] Basis sets were 6-31+G(d,p) for H, C, N, and Si atoms. Geometry optimization was carried out at the B3LYP level. Selected structural parameters optimized at the B3LYP/6-31+G(d,p) level, excitation energy and oscillator strength at the TD-B3LYP/6-311++G(d,p) and chemical shift calculated at the GIAO/B3LYP/6-311++G(2df,p) level are summarized in Table 1. Optimized structure and atomic coordinates of optimized structure of **5a'**, **5a"**, and **5b** at the B3LYP/6-31+G(d,p) level are shown in Figures S2-S4 and Tables S2-S4. Kohn-Sham orbitals of **5a'**, **5a"**, and **5b** at the B3LYP/6-311++G(d,p)//B3LYP/6-31+G(d,p) level are shown in Figure S5. Details for UV-vis absorption calculated at the TD-B3LYP/6-311++G(d,p)//B3LYP/6-31+G(d,p) are shown in Table S5.

Table S1. Calculated structural parameters, absorption data, and chemical shifts of **5a'**, **5a"**, and **5b**.



5a' **5a"** **5b** .

	Distance/Å [WBI][a,b]		Angles/deg[a]		λ_{max} /nm(f)[c]		Chemical Shift[d]		ΔE
	Si-C	C-N	Si-C-N	C-N-C	Band I	Band II	δ_{Si}	δ_{C}	(kcal·mol^{-1})
5a'	1.808 [1.316]	1.214 [2.079]	164.5	135.3	566 (0.001)	337 (0.316)	+3.1	+233.6	0.0
5a"	1.877 [1.064]	1.184 [2.221]	162.0	178.2	486 (0.004)	427 (0.539)	-26.8	+186.4	+0.7
5b	1.809 [1.326]	1.210 [2.160]	162.6	131.4	418 (0.004)	334 (0.255)	+6.4	+230.2	-

a. Geometry was optimized at B3LYP/6-31+G(d,p) level. b. Values in the parentheses are Wiberg bond index.[S2] c. Excitation energy and oscillator strength were calculated at the TD-B3LYP/6-311++(d,p)//B3LYP/6-31+G(d,p) level. d. δ_{Si} and δ_{C} values were calculated at the GIAO/B3LYP/6-311+G(2df,p)//B3LYP/6-31+G(d,p) level.

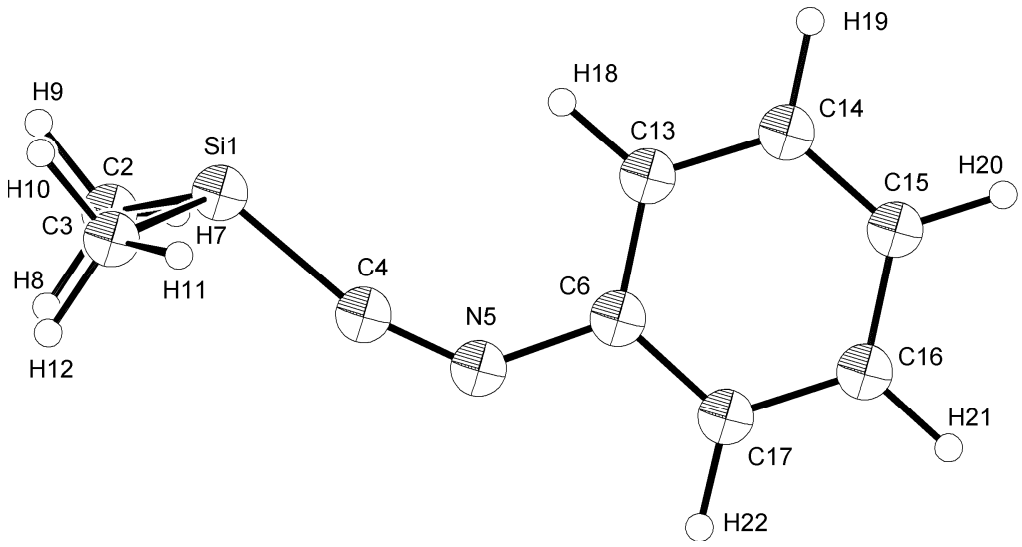


Figure S2. Optimized structure of $Me_2SiCNMe$ **5a'** (*Cs* symmetry) at the B3LYP/6-31+G(d,p) level.

Table S2. Atomic Coordinates of $Me_2SiCNMe$ **5a'** (*Cs* symmetry) at the B3LYP/6-31+G(d,p) level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	-0.089677	-2.617957	0.000000
2	6	0	-0.686327	-3.531600	1.568853
3	6	0	-0.686327	-3.531600	-1.568853
4	6	0	-0.829136	-0.967807	0.000000
5	7	0	-1.010625	0.232624	0.000000
6	6	0	-0.176740	1.376099	0.000000
7	1	0	-0.584432	-2.894891	2.453215
8	1	0	-1.730122	-3.854473	1.488369
9	1	0	-0.067105	-4.420889	1.730037
10	1	0	-0.067105	-4.420889	-1.730037
11	1	0	-0.584432	-2.894891	-2.453215
12	1	0	-1.730122	-3.854473	-1.488369
13	6	0	1.220387	1.261752	0.000000
14	6	0	1.999914	2.416761	0.000000
15	6	0	1.393699	3.679138	0.000000
16	6	0	0.000000	3.784882	0.000000
17	6	0	-0.789595	2.633592	0.000000
18	1	0	1.673931	0.274328	0.000000
19	1	0	3.082987	2.333560	0.000000
20	1	0	2.006861	4.575453	0.000000
21	1	0	-0.472887	4.762310	0.000000
22	1	0	-1.873259	2.690650	0.000000

(energy with zero point energy: -693.634804 hartree)

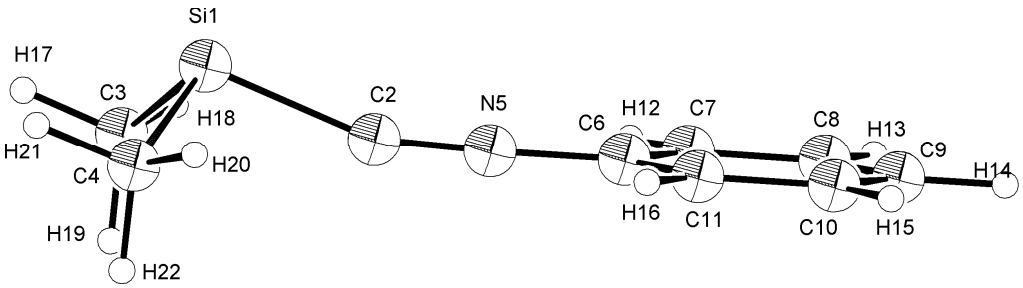


Figure S3. Optimized structure of $Me_2SiCNMe$ **5a"** (*Cs* symmetry) at the B3LYP/6-31+G(d,p) level.

Table S3. Atomic Coordinates of $Me_2SiCNMe$ **5a"** (*Cs* symmetry) at the B3LYP/6-31+G(d,p) level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	0.000000	3.016564	-0.000000
2	6	0	0.259029	1.157236	0.000000
3	6	0	1.034520	3.541555	1.542380
4	6	0	1.034520	3.541555	-1.542380
5	7	0	0.051585	-0.007957	0.000000
6	6	0	-0.231645	-1.346829	-0.000000
7	6	0	-0.374312	-2.030953	1.222016
8	6	0	-0.659141	-3.394232	1.209654
9	6	0	-0.802623	-4.082577	-0.000000
10	6	0	-0.659141	-3.394232	-1.209654
11	6	0	-0.374312	-2.030953	-1.222016
12	1	0	-0.261558	-1.488860	2.154610
13	1	0	-0.770242	-3.921254	2.152461
14	1	0	-1.024295	-5.144989	-0.000000
15	1	0	-0.770242	-3.921254	-2.152461
16	1	0	-0.261558	-1.488860	-2.154610
17	1	0	0.891794	4.617435	1.697589
18	1	0	0.681875	3.038774	2.449446
19	1	0	2.109018	3.356530	1.432527
20	1	0	0.681875	3.038774	-2.449446
21	1	0	0.891794	4.617435	-1.697589
22	1	0	2.109018	3.356530	-1.432527

(energy with zero point energy: -693.633676 hartree)

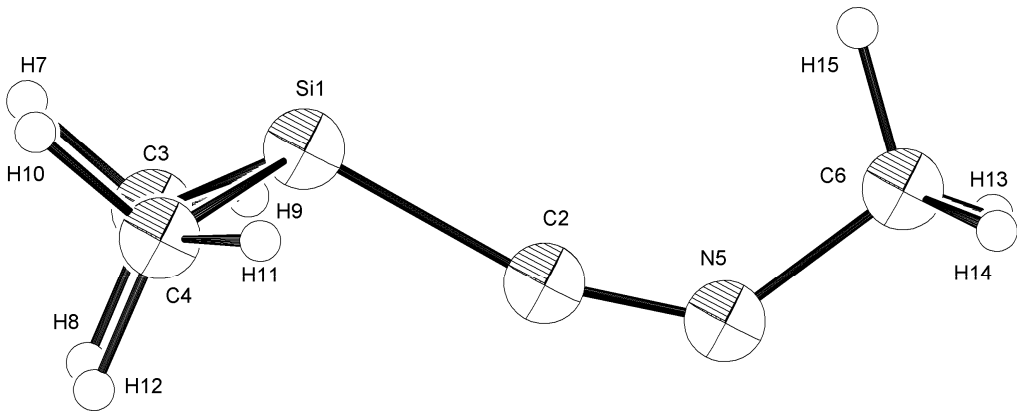


Figure S4. Optimized structure of $Me_2SiCNMe$ **5b** (*Cs* symmetry) at the B3LYP/6-31+G(d,p) level.

Table S4. Atomic Coordinates of $Me_2SiCNMe$ **5b** (*Cs* symmetry) at the B3LYP/6-31+G(d,p) level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	0.000000	0.971521	0.000000
2	6	0	-0.047808	-0.836975	0.000000
3	6	0	-0.890568	1.597679	-1.568785
4	6	0	-0.890568	1.597679	1.568785
5	7	0	0.284210	-2.000791	0.000000
6	6	0	1.598622	-2.626981	0.000000
7	1	0	-0.646793	2.653408	-1.730788
8	1	0	-1.979825	1.509765	-1.490117
9	1	0	-0.558365	1.044274	-2.452745
10	1	0	-0.646793	2.653408	1.730788
11	1	0	-0.558365	1.044274	2.452745
12	1	0	-1.979825	1.509765	1.490117
13	1	0	1.684049	-3.264111	-0.884288
14	1	0	1.684049	-3.264111	0.884288
15	1	0	2.394293	-1.870716	0.000000

(energy with zero point energy: -501.935310 hartree)

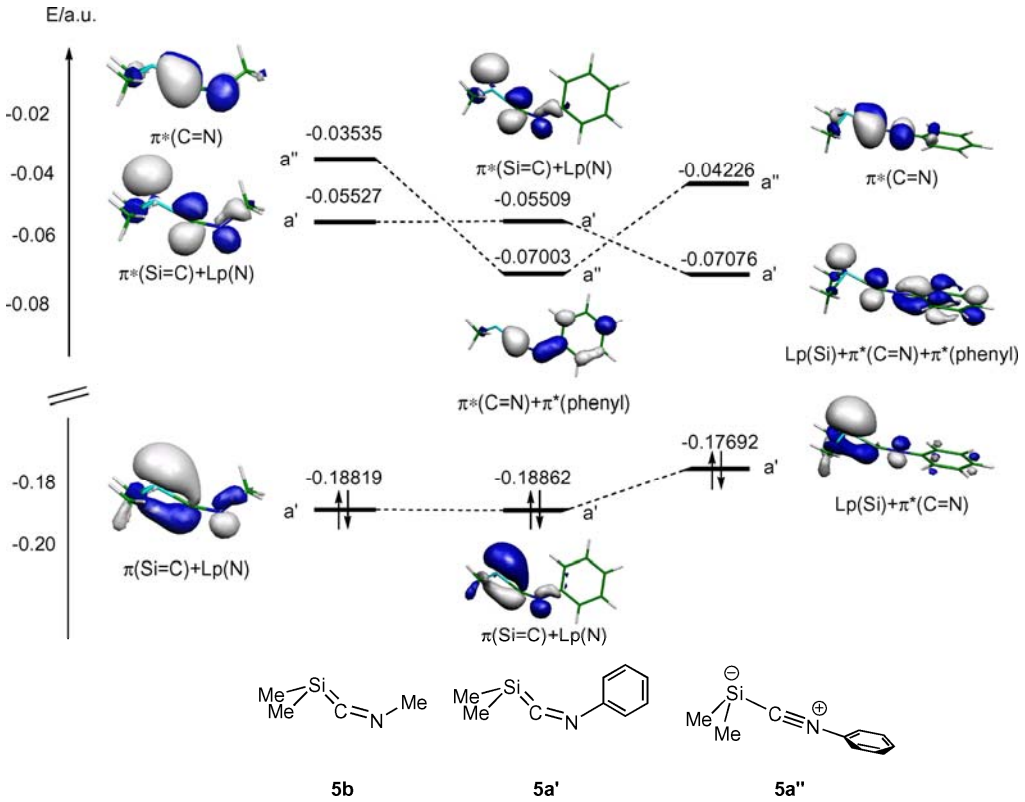


Figure S5. Kohn-Sham orbitals of **5a'**, **5a"**, and **5b** at the B3LYP/6-311++G(d,p)//B3LYP/6-31+G(d,p) level.

Table S5. Ultraviolet-visible Absorption Maxima Calculated for **5a'**, **5a"**, and **5b** (TDB3LYP/6-311++G(d,p) //B3LYP/6-31+G(d,p)).

Compound	λ_{max}/nm	oscillator strength[a]	Major contribution (coefficient)[b,c]
5a'[d]	566	0.001	π(Si=C)+Lp(N)→π*(C=N)+π*(phenyl) (0.685)
	337	0.316	π(Si=C)+Lp(N)→π*(Si=C)+Lp(N) (0.557)
5a"[d]	486	0.004	Lp(Si)+π*(C=N)→π*(C=N) (0.682)
	427	0.539	Lp(Si)+π*(C=N)→Lp(Si)+π*(C=N)+π*(Ph) (0.588)
5b[d]	418	0.004	π(Si=C)+Lp(N)→π*(C=N) (0.681)
	334	0.255	π(Si=C)+Lp(N)→π*(Si=C)+Lp(N) (0.555)

a. Transitions with oscillator strengths <0.001 are omitted. b. Transitions with absolute values of coefficients <0.5 are omitted. c. Orbitals and relative energy levels are shown in Fig. S5. d. Atomic coordinates are shown in Fig. S2-S4.

4. References

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(S2) NBO version 3.1, Glendening, E. A.; Reed, A. E.; Carpenter, J. E.; Weinhold, F.