Supporting Information

Formation of a Donor-Stabilized Tetrasilacyclobutadiene Dication by a Lewis-Acid Assisted Reaction of an N-Heterocyclic Chloro Silylene

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Experimental Section

General Procedures.

All experiments and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or in an MBraun inert atmosphere dry box containing an atmosphere of purified nitrogen. All solvents were dried by standard methods and freshly distilled prior to use. Pentamethylcyclopentadienyl zirconium trichloride Cl_3ZrCp^* (Cp* = pentamethylcyclopentadienyl) (Aldrich) was used as received. The starting material, chloro silylene [LSiCl][1] was prepared according to the literature. The ^1H, ^{13}C, and ^{29}Si, NMR spectra were recorded on Bruker ARX200 and AV 400 Spectrometers.

Single-Crystal X-ray Structure Determinations: Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data of Compound **2** was collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K (Mo-$K_\alpha$radiation, λ = 0.71073 Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97 software package.[2] The positions of the H atoms were calculated and considered isotropically according to a riding model.

Preparation of 2 $[(LSiCl)_2L_2Si_4]^+ \cdot 2[Zr_2Cl_7Cp^*_2]^-$: Toluene (20 mL) was added to a mixture of chloro silylene [LSiCl] (676 mg, 2.29 mmol) and pentamethylcyclopentadienyl zirconium trichloride (501 mg, 1.55 mmol) at ambient temperature. The solution slowly turned to a yellow color and was stirred for 8 days. The solvent was removed and the residue was washed with hexane (30 mL). The residue was recrystallized from toluene at –30 °C, yielding **2** as yellow crystals (597 mg, 0.22 mmol, 29%). M.p. 121-122 °C. ^1H NMR (400.13 MHz, CD_2Cl_2, 298K) δ = 1.17 (s, 36 H, *t*Bu), 1.31 (s, 36 H, *t*Bu), 2.06 (s, br, 60 H, $C_5(Me_3)_5$), 7.12-7.73 (m, 20 H, Ph). ^{13}C NMR (100.61 MHz, CD_2Cl_2, 298K): δ = 13.3 ($C_5(Me_3)_5$), 31.4, 31.7 ($NCMe_3$) 56.8, 56,6 ($NCMe_3$), 128.1 ($C_5(Me_3)_5$), 128.5, 128.7, 128.9, 129.3, 129.9, 130.6, 130.8, 132.7 (Ph), 172.7, 179.8 (NCN). ^{29}Si NMR (79.49 MHz, CD_2Cl_2, 298K): δ = −128.7 (s, $LSi_2Si_2(LSiCl)_2$), 7.7 (s, $LSi_2Si_2(LSiCl)_2$), 53.4 (s, $LSi_2Si_2(LSiCl)_2$).

Crystallographic data for compound 2:

Empirical formula	C112 H164 Cl16 N8 Si6 Zr4	
Formula weight	2723.13	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 12.4280(5) Å	α= 90°.
	b = 16.2309(6) Å	β= 98.835(4)°.
	c = 32.2578(14) Å	γ = 90°.
Volume	6429.8(4) $Å^3$	
Z	2	
Density (calculated)	1.407 Mg/m^3	
Absorption coefficient	0.751 mm^{-1}	
F(000)	2816	
Crystal size	0.43 x 0.32 x 0.11 mm^3	
Theta range for data collection	3.32 to 25.00°.	
Index ranges	-9<=h<=14, -16<=k<=19, -38<=l<=32	
Reflections collected	24733	
Independent reflections	11303 [R(int) = 0.0786]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9220 and 0.7384	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11303 / 374 / 778	
Goodness-of-fit on F^2	0.826	
Final R indices [I>2sigma(I)]	R1 = 0.0542, wR2 = 0.0817	
R indices (all data)	R1 = 0.1184, wR2 = 0.0922	
Largest diff. peak and hole	0.555 and -0.548 e.$Å^{-3}$	

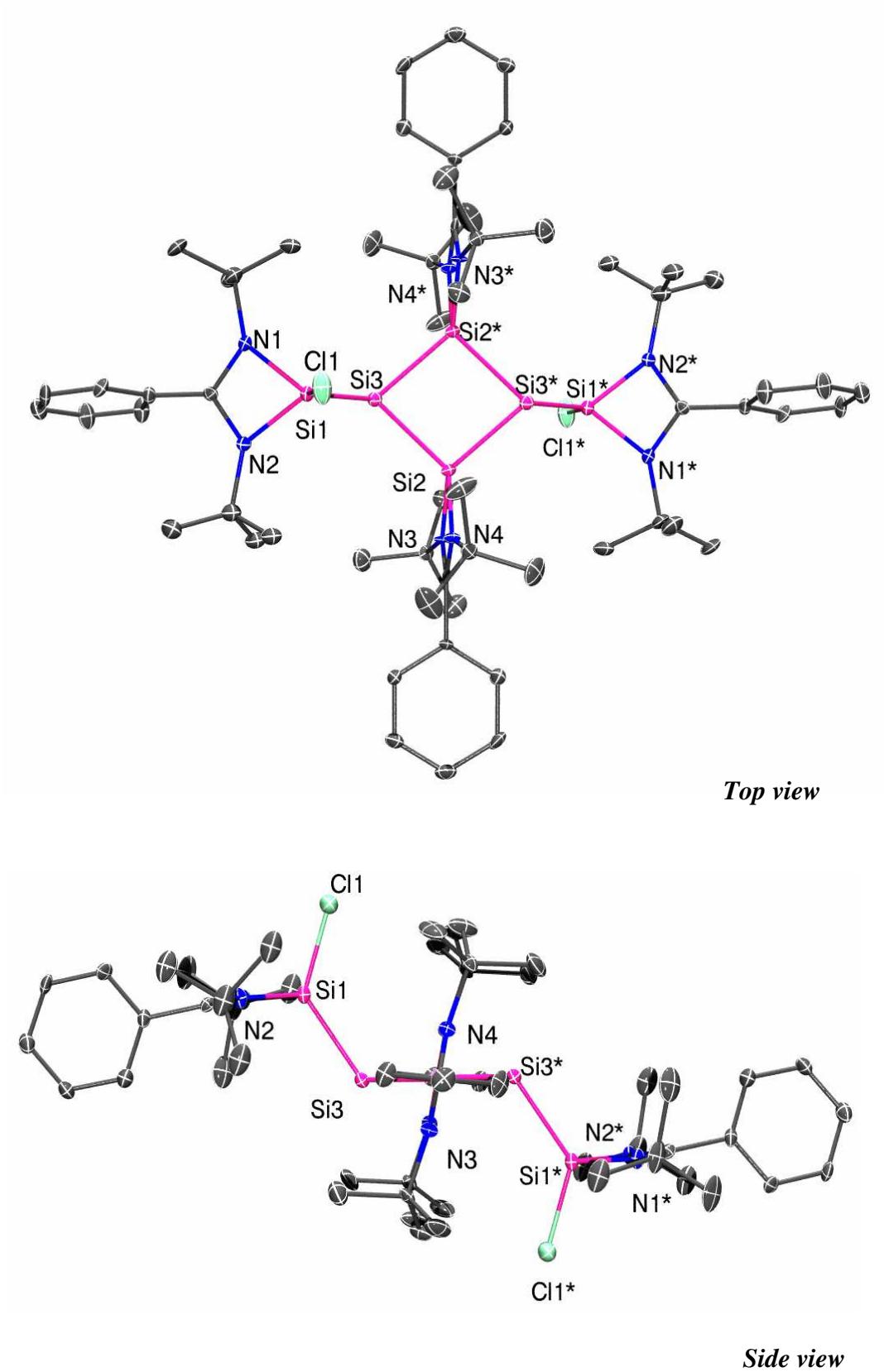

Figure 1. Molecular structure of compound **2** (top view and side view)**.** Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms and two counter anions [$Zr_2Cl_7Cp^*_2$] are omitted for clarity.

Table 1. Selected bond lengths and angles of compound **2**

Interatomic distances (Å)		Angles(°)	
Si(1)-N(2)	1.800(4)	N(2)-Si(1)-N(1)	73.1(2)
Si(1)-N(1)	1.804(4)	N(2)-Si(1)-Cl(1)	106.08(16)
Si(1)-Cl(1)	2.061(2)	N(1)-Si(1)-Cl(1)	105.78(16)
Si(1)-Si(3)	2.3044(19)	N(2)-Si(1)-Si(3)	115.19(16)
Si(2)-N(3)	1.830(4)	N(1)-Si(1)-Si(3)	115.26(15)
Si(2)-N(4)	1.834(4)	Cl(1)-Si(1)-Si(3)	127.99(9)
Si(2)-Si(3)	2.321(2)	N(3)-Si(2)-N(4)	71.71(19)
Si(2)-Si(3)#1	2.331(2)	N(3)-Si(2)-Si(3)	116.39(16)
Si(3)-Si(2)#1	2.331(2)	N(4)-Si(2)-Si(3)	128.17(14)
N(1)-C(1)	1.343(6)	N(3)-Si(2)-Si(3)#1	128.35(14)
N(1)-C(8)	1.480(7)	N(4)-Si(2)-Si(3)#1	115.18(15)
N(2)-C(1)	1.341(6)	Si(3)-Si(2)-Si(3)#1	98.85(7)
N(2)-C(12)	1.500(7)	Si(1)-Si(3)-Si(2)	115.35(8)
N(3)-C(16)	1.339(6)	Si(1)-Si(3)-Si(2)#1	115.53(8)
N(3)-C(23)	1.493(6)	Si(2)-Si(3)-Si(2)#1	81.15(7)
N(4)-C(16)	1.353(6)	C(16)-N(3)-Si(2)	91.6(3)
N(4)-C(27)	1.492(6)	C(23)-N(3)-Si(2)	136.6(4)
		C(16)-N(4)-C(27)	131.4(4)
		C(16)-N(4)-Si(2)	91.0(3)
		C(27)-N(4)-Si(2)	136.3(3)

Computational Methods

DFT calculations of the dicationic compound **2** was performed at the B3LYP level using 6-31G(d) basis set with the GAUSSIAN-03 program package.[3] The structure obtained by X-ray analysis was used as the input for these calculation of compound **2.** Optimized structures of **2** are shown in Figure 2. Cartesian coordinates of optimized structures are shown in Table 2. The NBO approach was used to calculate the orbital populations, Wiberg Bond Indices (WBI), and Natural Population Analysis (NPA). The GIAO calculations was performed at B3LYP level using 6-311(d) basis set for H, C, N, and Cl atoms; 6-311G(3d) basis set for Si atom.

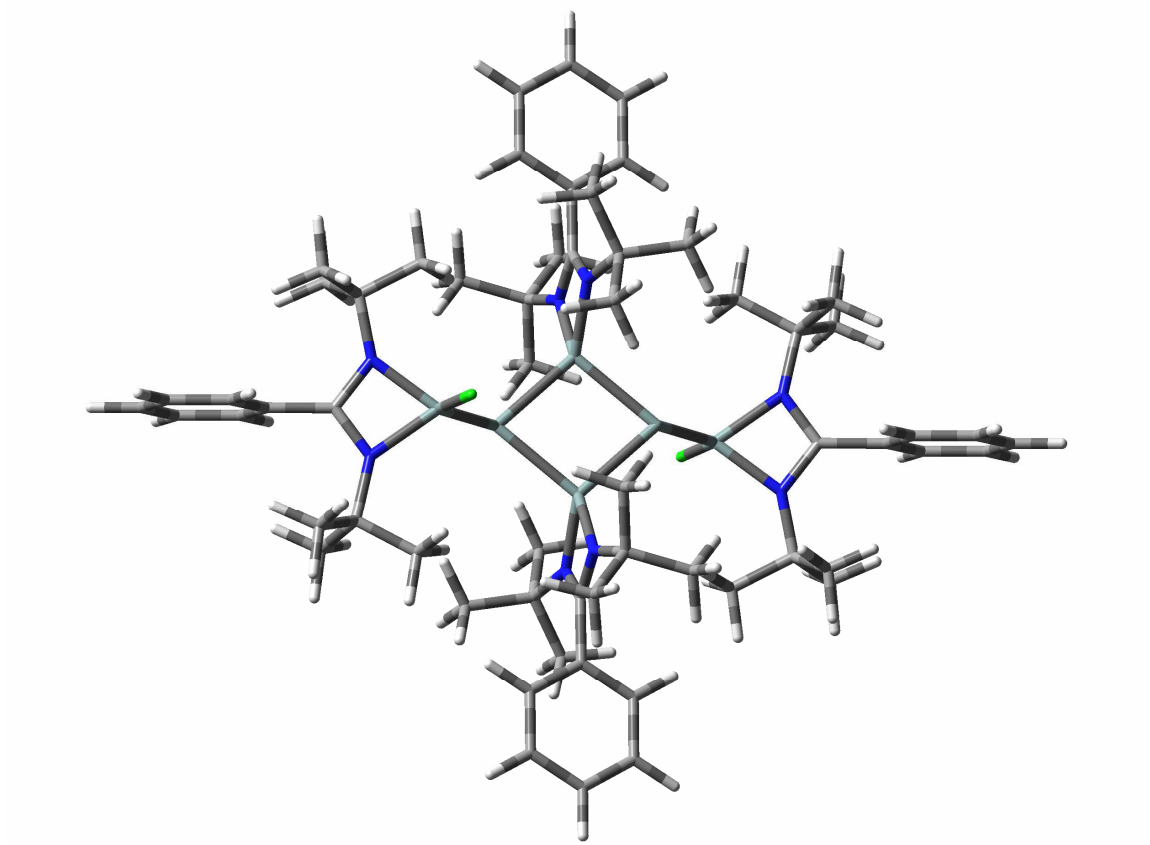

Figure 2. Optimized structure of compound **2**.

Table 2. Cartesian coordinates (x, y, z) for the optimized structure of **2**.

Si	1.715054	0.053725	0.461063	N	-0.14929	3.072429	1.062764
Si	-0.04582	1.552571	-0.008824	C	-0.136185	5.362506	-0.027404
Si	3.578024	0.103419	-0.966377	C	-0.106398	3.872179	-0.022514
C	3.560219	0.194547	-3.060562	N	-0.030978	3.062889	-1.09815
N	4.972051	-0.98848	-0.496674	N	4.967159	1.169968	-0.422714
C	7.068734	0.064037	0.47152	C	5.713873	0.082667	-0.143144
C	-0.245452	3.355329	-2.550485	C	0.077842	3.379465	2.509562

C	1.061804	6.091189	-0.029749
C	1.032287	7.485752	-0.021074
C	7.192884	-0.032278	1.865817
C	8.217026	0.13943	-0.330289
C	1.573852	3.658258	2.750575
C	9.602335	0.023757	1.650743
C	-1.384017	7.4398	-0.017285
C	-1.361045	6.045164	-0.019029
C	6.429654	3.026109	-1.203823
C	-0.189179	8.161973	-0.016356
C	5.294846	-2.446552	-0.531656
C	8.459359	-0.050352	2.450027
C	9.479793	0.117834	0.263154
C	0.092826	2.068151	-3.318137
C	5.580261	-2.98428	0.881464
C	-0.770073	4.570604	2.990519
C	4.048654	-3.139519	-1.102814
C	-1.720999	3.720645	-2.80021
C	5.540743	3.011434	1.170921
C	-0.342934	2.128078	3.295479
C	5.25346	2.630003	-0.291667
C	0.679129	4.482879	-3.043576
C	3.984551	3.351211	-0.771871
C	6.48718	-2.708489	-1.470709
Si	-1.714859	-0.053606	-0.461069
Si	0.045922	-1.552444	0.009168
Si	-3.578124	-0.103405	0.965987
C	-3.560741	-0.194636	3.06017
N	-4.972137	0.988414	0.496044
C	-7.068536	-0.064216	-0.472636
C	0.245388	-3.354658	2.551234
N	0.149332	-3.072547	-1.062076
C	0.136049	-5.362378	0.028603
C	0.106355	-3.872052	0.023379
N	0.030961	-3.062518	1.098833
N	-4.967072	-1.170031	0.422008
C	-5.713803	-0.082773	0.142311
C	-0.077733	-3.379887	-2.508817
C	-1.061988	-6.090983	0.03109
C	-1.032561	-7.48555	0.022725
C	-7.192403	0.032116	-1.866957
C	-8.216992	-0.139682	0.328935
C	-1.573773	-3.658474	-2.749888
C	-9.601895	-0.024055	-1.652384
C	1.383747	-7.439755	0.018961
C	1.360865	-6.045117	0.020397
C	-6.42953	-3.026363	1.202759
C	0.188861	-8.16185	0.018173
C	-5.295079	2.446452	0.531053
C	-8.458758	0.050127	-2.45143
C	-9.479636	-0.118144	-0.26477
C	-0.092536	-2.067208	3.318585
C	-5.580361	2.984225	-0.882077
C	0.770014	-4.571289	-2.989418
C	-4.04904	3.13952	1.102419
C	1.72084	-3.720312	2.801027
C	-5.540223	-3.011446	-1.171837
C	0.343329	-2.12876	-3.294997
C	-5.253222	-2.630085	0.290826
C	-0.679492	-4.481843	3.0446
C	-3.984325	-3.351205	0.771196
C	-6.487572	2.708207	1.469954
H	2.013333	5.569547	-0.046998
H	1.963976	8.043413	-0.021613
H	6.30433	-0.090514	2.487773
H	8.125387	0.210643	-1.409935
H	2.18246	2.80232	2.43879
H	1.754294	3.832238	3.816759
H	1.905483	4.54851	2.207333
H	10.58664	0.008159	2.108647
H	-2.336104	7.961853	-0.01251
H	-2.292547	5.488276	-0.003598
H	6.243549	2.719752	-2.238343
H	7.369344	2.582295	-0.868025
H	6.553459	4.113935	-1.187218
H	-0.209822	9.247477	-0.012058
H	8.551607	-0.12296	3.529394
H	10.366215	0.174599	-0.361068
H	1.128188	1.760305	-3.147088
H	-0.034228	2.24127	-4.391129
H	-0.571564	1.246263	-3.032508
H	6.48932	-2.5529	1.305876
H	5.718915	-4.069716	0.836726
H	4.74536	-2.773977	1.558426
H	-0.438609	5.521083	2.570093
H	-0.685746	4.642533	4.079687
H	-1.827214	4.428323	2.744769
H	3.170686	-2.97128	-0.468955
H	4.224395	-4.218153	-1.158073
H	3.826688	-2.788114	-2.116122
H	-2.380998	2.916382	-2.456712
H	-1.891841	3.862865	-3.872601
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H	6.46422	2.557046	1.536003
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H	0.243895	1.252635	2.999527
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H	-6.303722	0.090412	-2.488727
H	-8.125572	-0.210899	1.408599
H	-2.182259	-2.802371	-2.438317
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H	-1.905595	-4.548563	-2.206495
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H	2.3358	-7.96187	0.014313
H	2.292404	-5.488292	0.004855
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H	-7.369194	-2.582549	0.866885
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H	-1.127842	-1.759171	3.147539
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H	0.438347	-5.52161	-2.568794
H	0.685769	-4.643462	-4.078577
H	1.827159	-4.429135	-2.743611
H	-3.170971	2.971414	0.468668
H	-4.224908	4.218132	1.157718
H	-3.827173	2.78808	2.115736
H	2.381049	-2.916281	2.45739
H	1.891642	-3.862387	3.873443
H	1.996995	-4.649672	2.295013
H	-5.652731	-4.098017	-1.248475
H	-6.463639	-2.557054	-1.537068
H	-4.717845	-2.706577	-1.827693
H	1.403946	-1.904782	-3.149426
H	0.176344	-2.295118	-4.363571
H	-0.243365	-1.253142	-2.999296
H	-0.426553	-5.451118	2.612245
H	-0.584833	-4.567824	4.13191
H	-1.726686	-4.258541	2.815484
H	-3.756255	-3.105595	1.813845
H	-4.136812	-4.433133	0.711798
H	-3.120447	-3.095885	0.146882
H	-6.30015	2.293363	2.465717
H	-6.638993	3.787633	1.574247
H	-7.413511	2.281486	1.07854

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