Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for Synthesis, Structures, and Computations

Abnormal Carbene-Silicon Halide Complexes

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SUPPORTING INFORMATIONS of SYNTHESES

Materials and Methods

General.

The syntheses of air-sensitive compounds were performed under purified argon using Schlenk techniques and an inert atmosphere drybox (M-Braun LabMaster SP). Chemicals were purchased from Aldrich and Strem and used as received. The solvents were dried and distilled under argon from Na/benzophenone prior to use. ^{1}H NMR, ^{13}C{^{1}H} NMR and ^{29}Si NMR spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer or on a Varian Unity Inova 500 MHz spectrometer. The chemical shifts were referenced to an external TMS standard for ^{29}Si NMR spectra. X-ray intensity data for **7·THF**, **8·THF**, **9·CH_2Cl_2** were collected on a Bruker SMART APEX II X-ray diffractometer system with graphite-monochromated Mo K radiation (λ = 0.71073 Å), using the ω-scan technique.

Compound **7**: $SiCl_4$ (0.22 g, 1.29 mmol) in 20 mL of hexane was added to a Schlenk flask containing compound **1** (0.50 g, 1.27 mmol) in 50 mL of hexane at -78 °C. The mixture was allowed to gradually warm to room temperature overnight and stirred at room temperature for 4 h. After filtration, the volatile materials were removed from the filtrate in vacuo, giving compound **7** as yellow powder (0.510 g, 77.0% yield). Mp: decomposed and melt (> 146°C). X-ray quality colorless crystals of **7** were obtained by recrystallization of **7** in THF. ^{1}H NMR (400 MHz, C_6D_6): δ 1.09 [d, 6H, CH(CH_3)$_2$], 1.21 [d, 6H, CH(CH_3)$_2$], 1.29 [d, 6H, CH(CH_3)$_2$], 1.34 [d, 6H, CH(CH_3)$_2$], 2.84 [m, 4H, C*H*(CH$_3$)$_2$], 7.13 (d, 2H, Ar-*H*), 7.17 (d, 2H, Ar-*H*), 7.27 (t, 1H, Ar-*H*), 7.28 (t, 1H, Ar-*H*), 7.35 (s, 1H, NC*H*). ^{1}H NMR (400 MHz, THF-d_8): δ 1.17 [d, 6H, CH(CH_3)$_2$], 1.18 [d, 6H, CH(CH_3)$_2$], 1.21 [d, 6H, CH(CH_3)$_2$], 1.32 [d, 6H, CH(CH_3)$_2$], 2.65 [m, 2H, C*H*(CH$_3$)$_2$], 2.75 [m, 2H, C*H*(CH$_3$)$_2$], 7.29 (d, 2H, Ar-*H*), 7.31 (d, 2H, Ar-*H*), 7.41 (t, 1H, Ar-*H*), 7.43 (t, 1H, Ar-*H*), 8.08 (s, 1H, NC*H*). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ 22.2 [CH(*C*H$_3$)$_2$], 24.1 [CH(*C*H$_3$)$_2$], 24.9 [CH(*C*H$_3$)$_2$], 26.6 [CH(*C*H$_3$)$_2$], 29.5 [*C*H(CH$_3$)$_2$], 30.0 [*C*H(CH$_3$)$_2$], 124.1, 124.4 (N*C*H), 125.5, 130.1, 130.6, 137.7, 137.8, 138.4, 146.7, 147.3 (Ar-*C*), 227.8 (N*C*N). ^{29}Si NMR (THF-d_8, 99.30 MHz): δ -13.47. Crystal data for **7·THF**: $C_{31}H_{43}N_2OSiCl_3$, fw = 594.11, monoclinic, *P*2/n, a = 17.5567(10) Å, b = 11.8858(7) Å, c = 32.4529(18) Å, β = 96.6710(10)°, V = 6726.3(7) Å^3, Z = 8, R1 = 0.0618 for 6604 data ($I > 2\sigma(I)$), wR_2 = 0.1888 (all data).

Compound **8**: 50 mL of THF was added to a Schlenk flask containing both **7** (3.18 g, 6.09 mmol) and HCl·NEt_3 (0.84 g, 6.10 mmol), which was then sonicated for 45 min and stirred over 1 h at room temperature. After filtration, the volatile materials were removed from the filtrate in vacuo, giving compound **8** as pale yellow powder (3.26 g, 95.9% yield). Mp: gradually decomposed (> 211°C) and melt (> 260°C). X-ray quality crystals of **8** were obtained by recrystallization of **8** in hexane/THF mixed solvent. ^{1}H NMR (400 MHz, THF-d_8): δ 1.09 [d, 6H, CH(CH_3)$_2$], 1.23 [d, 6H, CH(CH_3)$_2$], 1.28 [d, 6H, CH(CH_3)$_2$], 1.41 [d, 6H, CH(CH_3)$_2$], 2.58 [m, 2H, C*H*(CH$_3$)$_2$], 3.04 [m, 2H, C*H*(CH$_3$)$_2$], 7.39 (d, 2H, Ar-*H*), 7.45 (d, 2H, Ar-*H*), 7.55 (t, 1H, Ar-*H*), 7.61 (t, 1H, Ar-*H*), 8.10 (s, 1H, NC*H*), 9.37 (s, 1H, NC(*H*)N). ^{13}C{^{1}H} NMR (100.62 MHz, THF-d_8): δ 22.6, 24.4,

24.6, 27.0 [CH(CH$_3$)$_2$], 29.93, 29.96 [CH(CH$_3$)$_2$], 125.0, 125.5 (NCH), 128.0, 131.8, 132.54, 132.57, 132.62, 138.2, 146.6, 147.6 (Ar-C), 148.9 (NCN). ^{29}Si NMR (THF-d$_8$, 99.30 MHz): δ -103.60. Crystal data for **8·THF**: $C_{31}H_{44}N_2OSiCl_4$, fw = 630.57, monoclinic, $P2_1/c$, a = 11.770(2) Å, b = 18.000(3) Å, c = 17.322(3) Å, β = 109.493(2)°, V = 3459.5(10) Å^3, Z = 4, R1 = 0.0654 for 3124 data ($I > 2\sigma(I)$), wR_2 = 0.1938 (all data).

Compound **9**: Compound **7** (1.00 g, 1.92 mmol) was added to a Schlenk tube containing CH_2Cl_2 (7.00 g, 82.4 mmol) in 20 mL of hexane, which was then heated to 70 °C for 10 days. The colorless crystals of **9** were gradually formed on the inside walls of the Schlenk tube and isolated by filtration (0.34 g, 75.6% yield, in terms of the fact that half amount of **7** is involved in the formation of **9**).[1] Mp: gradually decomposed (> 117°C) and melt (> 276°C). X-ray quality colorless crystals of **9** were obtained by recrystallization of **9** in the CH_2Cl_2/hexane mixed solvent. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.11 [d, 12H, CH(CH_3)$_2$], 1.21 [d, 12H, CH(CH_3)$_2$], 1.27 [d, 12H, CH(CH_3)$_2$], 1.34 [d, 12H, CH(CH_3)$_2$], 2.36 [m, 4H, CH(CH$_3$)$_2$], 2.82 [m, 4H, CH(CH$_3$)$_2$], 6.18 (s, 2H, NCH), 7.29-7.38 (m, 10H, Ar-H), 7.61 (t, 2H, Ar-H), 9.87 (s, 2H, NC(H)N). ^{13}C{^{1}H} NMR (125.68 MHz, CD_2Cl_2): δ 22.2, 24.2, 25.2, 27.1 [CH(CH$_3$)$_2$], 29.3, 29.8 [CH(CH$_3$)$_2$], 124.9, 125.1 (NCH), 125.9, 130.3, 131.7, 132.27, 132.32, 138.4, 145.6, 147.7 (Ar-C), 146.8 (NCN). ^{29}Si NMR (THF-d$_8$, 99.30 MHz): δ -102.55. Crystal data for **9·CH_2Cl_2**: $C_{55}H_{74}N_4SiCl_6$, fw = 1031.97, orthorhombic, $Pna2_1$, a = 22.491(2) Å, b = 24.236(2) Å, c = 10.5002(10) Å, V = 5723.7(10) Å^3, Z = 4, R1 = 0.0499 for 9269 data ($I > 2\sigma(I)$), wR_2 = 0.1365 (all data).

SUPPORTING INFORMATIONS of COMPUTATIONS

All computations employed the Gaussian 94 and Gaussian09 programs:
For Gaussian 94: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andes, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94*,* Revision B.3; Gaussian Inc.: Pittsburgh, PA, 1995.
For Gaussian 09: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09*, revision D.01; Gaussian, Inc., Wallingford CT, 2013.

Table S1. Coordinates of the B3LYP/6-311+G** geometry of **a** isomer of **[9-Ph]**$^+$ optimized in C_2 symmetry

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	0.000000	0.000000	-0.323676
2	17	0	1.730498	0.428844	-1.512636
3	17	0	0.000000	0.000000	1.851373
4	17	0	-1.730498	-0.428844	-1.512636
5	7	0	-0.414470	4.164347	-0.391410
6	7	0	-1.655251	2.506117	0.275724
7	7	0	1.655251	-2.506117	0.275724
8	7	0	0.414470	-4.164347	-0.391410
9	6	0	-1.578392	3.838204	0.173740
10	1	0	-2.348454	4.529107	0.471880
11	6	0	0.268853	2.987823	-0.664631
12	1	0	1.246776	3.010437	-1.107856
13	6	0	-0.485151	1.920335	-0.255761
14	6	0	1.578392	-3.838204	0.173740
15	1	0	2.348454	-4.529107	0.471880
16	6	0	0.485151	-1.920335	-0.255761
17	6	0	-0.268853	-2.987823	-0.664631
18	1	0	-1.246776	-3.010437	-1.107856
19	6	0	0.037052	5.501058	-0.675761
20	6	0	0.505686	5.800034	-1.953338
21	6	0	0.000000	6.466723	0.327850
22	6	0	0.942941	7.093437	-2.226109
23	1	0	0.512709	5.039143	-2.724567
24	6	0	0.428210	7.760025	0.037827
25	1	0	-0.337073	6.208206	1.324841
26	6	0	0.901226	8.073247	-1.235101
27	1	0	1.306308	7.336188	-3.217289
28	1	0	0.404209	8.517134	0.812180
29	1	0	1.239154	9.078904	-1.454149
30	6	0	-2.847982	1.894754	0.840619
31	6	0	-2.918563	1.678062	2.213557
32	6	0	-3.930795	1.628522	0.006963
33	6	0	-4.095734	1.168718	2.757439
34	1	0	-2.065399	1.896878	2.841650
35	6	0	-5.102515	1.120212	0.561673
36	1	0	-3.853846	1.808706	-1.057556
37	6	0	-5.184593	0.888579	1.933900
38	1	0	-4.159958	0.995562	3.824930
39	1	0	-5.949759	0.908646	-0.079428
40	1	0	-6.099019	0.494880	2.361824
41	6	0	2.847982	-1.894754	0.840619
42	6	0	2.918563	-1.678062	2.213557
43	6	0	3.930795	-1.628522	0.006963
44	6	0	4.095734	-1.168718	2.757439
45	1	0	2.065399	-1.896878	2.841650
46	6	0	5.102515	-1.120212	0.561673
47	1	0	3.853846	-1.808706	-1.057556

48	6	0	5.184593	-0.888579	1.933900
49	1	0	4.159958	-0.995562	3.824930
50	1	0	5.949759	-0.908646	-0.079428
51	1	0	6.099019	-0.494880	2.361824
52	6	0	-0.037052	-5.501058	-0.675761
53	6	0	-0.505686	-5.800034	-1.953338
54	6	0	0.000000	-6.466723	0.327850
55	6	0	-0.942941	-7.093437	-2.226109
56	1	0	-0.512709	-5.039143	-2.724567
57	6	0	-0.428210	-7.760025	0.037827
58	1	0	0.337073	-6.208206	1.324841
59	6	0	-0.901226	-8.073247	-1.235101
60	1	0	-1.306308	-7.336188	-3.217289
61	1	0	-0.404209	-8.517134	0.812180
62	1	0	-1.239154	-9.078904	-1.454149

Table S2. Coordinates of the B3LYP/6-311+G** geometry of **b** isomer of **[9-Ph]**$^+$ optimized in C_1 symmetry

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	0.333770	0.885056	0.462811
2	17	0	0.284024	-0.146126	2.468603
3	17	0	0.283714	1.307601	-1.780433
4	17	0	0.876959	2.782487	1.112379
5	7	0	-3.555602	-0.399071	0.183312
6	7	0	-2.546085	1.510402	-0.087266
7	7	0	2.138276	-1.384474	-0.256057
8	7	0	4.136248	-0.555729	-0.051983
9	6	0	-3.722994	0.881631	-0.164509
10	1	0	-4.662668	1.349319	-0.404507
11	6	0	-2.224231	-0.578360	0.521245
12	1	0	-1.853378	-1.537117	0.837002
13	6	0	-1.564004	0.607708	0.349805
14	6	0	3.447887	-1.658842	-0.354909
15	1	0	3.869346	-2.614020	-0.616768
16	6	0	1.967643	-0.055265	0.128321
17	6	0	3.230646	0.451892	0.251228
18	1	0	3.559008	1.443396	0.507609
19	6	0	-2.444884	2.944655	-0.298916
20	6	0	-2.451021	3.783943	0.811249
21	6	0	-2.403596	3.444596	-1.595993
22	6	0	-2.413300	5.161236	0.612393
23	1	0	-2.479175	3.367237	1.810802
24	6	0	-2.369848	4.824703	-1.781195
25	1	0	-2.372833	2.767702	-2.439564
26	6	0	-2.373362	5.680188	-0.680852
27	1	0	-2.415487	5.825756	1.467827
28	1	0	-2.331678	5.228066	-2.785758
29	1	0	-2.343833	6.752899	-0.830962
30	6	0	-4.595296	-1.393871	0.237887
31	6	0	-4.762101	-2.135028	1.405817
32	6	0	-5.413772	-1.590815	-0.872060
33	6	0	-5.772444	-3.091862	1.457309
34	1	0	-4.127789	-1.951768	2.264974
35	6	0	-6.428040	-2.543171	-0.802546
36	1	0	-5.250679	-1.022866	-1.780592
37	6	0	-6.606236	-3.294045	0.358070
38	1	0	-5.915472	-3.669030	2.362781
39	1	0	-7.071085	-2.702774	-1.659547
40	1	0	-7.395016	-4.035028	0.406726
41	6	0	5.572839	-0.442490	-0.035628
42	6	0	6.197495	0.055550	1.105576
43	6	0	6.303565	-0.827031	-1.157406
44	6	0	7.585316	0.166539	1.118623
45	1	0	5.610698	0.335708	1.972252
46	6	0	7.692151	-0.722135	-1.125807
47	1	0	5.796345	-1.179505	-2.047862
48	6	0	8.331994	-0.224746	0.008036
49	1	0	8.081876	0.550205	2.001525

50	1	0	8.270212	-1.016079	-1.993442
51	1	0	9.411767	-0.139081	0.025278
52	6	0	1.104824	-2.365600	-0.509699
53	6	0	0.791095	-3.288350	0.485854
54	6	0	0.473757	-2.383401	-1.751230
55	6	0	-0.171512	-4.260914	0.222536
56	1	0	1.283293	-3.234531	1.448958
57	6	0	-0.488778	-3.360269	-1.999953
58	1	0	0.727035	-1.642119	-2.498635
59	6	0	-0.807906	-4.297964	-1.018427
60	1	0	-0.418699	-4.989711	0.985175
61	1	0	-0.979980	-3.392032	-2.965135
62	1	0	-1.549618	-5.061551	-1.221779

SUPPORTING INFORMATIONS of X-RAY

Compound 7·THF

Table S3. Crystal data and structure refinement for **7·THF**

Identification code	**7·THF**
Empirical formula	$C_{31}H_{43}Cl_3N_2OSi$
Formula weight	594.11
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 2/n
Unit cell dimensions	a = 17.5567(10) Å alpha = 90 deg. b = 11.8858(7) Å beta = 96.6710(10) deg. c = 32.4529(18) Å gamma = 90 deg.
Volume	6726.3(7) A^3
Z, Calculated density	8, 1.173 Mg/m^3
Absorption coefficient	0.333 mm^-1
F(000)	2528
Crystal size	0.500 x 0.200 x 0.130 mm
Theta range for data collection	2.074 to 26.022 deg.
Limiting indices	-21<=h<=21, -14<=k<=14, -40<=l<=40
Reflections collected / unique	77815 / 13266 [R(int) = 0.0854]
Completeness to theta = 25.242	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.6376
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13266 / 8 / 685
Goodness-of-fit on F^2	1.015
Final R indices [I>2sigma(I)]	R1 = 0.0618, wR2 = 0.1509
R indices (all data)	R1 = 0.1380, wR2 = 0.1888
Extinction coefficient	n/a
Largest diff. peak and hole	0.409 and -0.299 e.A^-3

Table S4. Bond lengths [Å] and angles [deg] for **7·THF**

Si(1)-C(3)	1.819(3)
Si(1)-Cl(2)	2.0017(15)
Si(1)-Cl(1)	2.0109(15)
Si(1)-Cl(3)	2.0107(16)
Si(2)-C(30)	1.812(4)
Si(2)-Cl(4)	2.0045(18)
Si(2)-Cl(5)	2.0148(14)
Si(2)-Cl(6)	2.0115(15)
N(1)-C(1)	1.373(4)
N(1)-C(2)	1.369(4)
N(1)-C(16)	1.444(4)
N(2)-C(1)	1.355(4)
N(2)-C(3)	1.412(4)
N(2)-C(4)	1.449(4)
N(3)-C(29)	1.359(4)
N(3)-C(28)	1.379(4)
N(3)-C(43)	1.455(4)
N(4)-C(28)	1.360(4)
N(4)-C(30)	1.410(4)
N(4)-C(31)	1.452(4)
C(2)-C(3)	1.347(4)
C(4)-C(9)	1.395(5)
C(4)-C(5)	1.397(5)
C(5)-C(6)	1.392(5)
C(5)-C(13)	1.506(5)
C(6)-C(7)	1.355(6)
C(7)-C(8)	1.368(6)
C(8)-C(9)	1.389(5)
C(9)-C(10)	1.521(5)
C(10)-C(12)	1.539(6)
C(10)-C(11)	1.528(6)
C(13)-C(15)	1.529(5)
C(13)-C(14)	1.534(6)
C(16)-C(17)	1.393(5)
C(16)-C(21)	1.392(5)
C(17)-C(18)	1.390(5)
C(17)-C(25)	1.525(5)
C(18)-C(19)	1.375(5)
C(19)-C(20)	1.365(6)
C(20)-C(21)	1.390(5)
C(21)-C(22)	1.515(5)
C(22)-C(23)	1.476(6)
C(22)-C(24)	1.521(6)
C(25)-C(26)	1.524(6)
C(25)-C(27)	1.506(6)
C(29)-C(30)	1.361(5)
C(31)-C(32)	1.394(4)
C(31)-C(36)	1.401(4)
C(32)-C(33)	1.384(5)
C(32)-C(40)	1.517(5)
C(33)-C(34)	1.371(5)

C(34)-C(35)	1.363(5)
C(35)-C(36)	1.387(5)
C(36)-C(37)	1.513(5)
C(37)-C(38)	1.531(5)
C(37)-C(39)	1.525(5)
C(40)-C(42)	1.517(5)
C(40)-C(41)	1.520(5)
C(43)-C(48)	1.392(6)
C(43)-C(44)	1.399(5)
C(44)-C(45)	1.394(5)
C(44)-C(52)	1.506(5)
C(45)-C(46)	1.360(6)
C(46)-C(47)	1.371(6)
C(47)-C(48)	1.385(6)
C(48)-C(49)	1.512(6)
C(49)-C(50)	1.508(8)
C(49)-C(51)	1.523(10)
C(52)-C(54)	1.494(6)
C(52)-C(53)	1.541(6)
O(1)-C(55)	1.322(9)
O(1)-C(58)	1.365(8)
C(55)-C(56)	1.338(8)
C(56)-C(57)	1.439(10)
C(57)-C(58)	1.395(8)
O(2)-C(62)	1.389(15)
O(2)-C(59)	1.539(12)
C(59)-C(60)	1.385(12)
C(60)-C(61)	1.45(2)
C(61)-C(62)	1.443(13)

C(3)-Si(1)-Cl(2)	113.61(12)
C(3)-Si(1)-Cl(1)	108.06(11)
Cl(2)-Si(1)-Cl(1)	107.84(8)
C(3)-Si(1)-Cl(3)	113.28(12)
Cl(2)-Si(1)-Cl(3)	106.79(8)
Cl(1)-Si(1)-Cl(3)	106.94(8)
C(30)-Si(2)-Cl(4)	113.84(12)
C(30)-Si(2)-Cl(5)	107.61(12)
Cl(4)-Si(2)-Cl(5)	107.33(8)
C(30)-Si(2)-Cl(6)	113.25(12)
Cl(4)-Si(2)-Cl(6)	107.24(8)
Cl(5)-Si(2)-Cl(6)	107.23(7)
C(1)-N(1)-C(2)	112.4(3)
C(1)-N(1)-C(16)	122.6(3)
C(2)-N(1)-C(16)	124.9(3)
C(1)-N(2)-C(3)	113.5(2)
C(1)-N(2)-C(4)	121.9(3)
C(3)-N(2)-C(4)	124.5(3)
C(29)-N(3)-C(28)	113.3(3)
C(29)-N(3)-C(43)	122.5(3)
C(28)-N(3)-C(43)	124.3(3)
C(28)-N(4)-C(30)	114.4(3)
C(28)-N(4)-C(31)	122.5(3)
C(30)-N(4)-C(31)	123.1(3)
N(2)-C(1)-N(1)	101.9(3)
C(3)-C(2)-N(1)	108.2(3)
C(2)-C(3)-N(2)	104.0(3)

C(2)-C(3)-Si(1)	126.1(2)
N(2)-C(3)-Si(1)	129.9(2)
C(9)-C(4)-C(5)	123.5(3)
C(9)-C(4)-N(2)	118.7(3)
C(5)-C(4)-N(2)	117.8(3)
C(4)-C(5)-C(6)	116.1(3)
C(4)-C(5)-C(13)	123.1(3)
C(6)-C(5)-C(13)	120.7(3)
C(7)-C(6)-C(5)	121.8(4)
C(6)-C(7)-C(8)	120.8(4)
C(9)-C(8)-C(7)	121.1(4)
C(8)-C(9)-C(4)	116.7(4)
C(8)-C(9)-C(10)	120.9(3)
C(4)-C(9)-C(10)	122.3(3)
C(9)-C(10)-C(12)	113.3(3)
C(9)-C(10)-C(11)	110.4(3)
C(12)-C(10)-C(11)	110.3(3)
C(5)-C(13)-C(15)	113.7(3)
C(5)-C(13)-C(14)	109.5(3)
C(15)-C(13)-C(14)	110.6(4)
C(17)-C(16)-C(21)	122.8(3)
C(17)-C(16)-N(1)	118.6(3)
C(21)-C(16)-N(1)	118.5(3)
C(16)-C(17)-C(18)	117.3(3)
C(16)-C(17)-C(25)	122.9(3)
C(18)-C(17)-C(25)	119.8(3)
C(17)-C(18)-C(19)	120.8(4)
C(20)-C(19)-C(18)	120.7(4)
C(19)-C(20)-C(21)	121.2(4)
C(20)-C(21)-C(16)	117.2(4)
C(20)-C(21)-C(22)	120.3(4)
C(16)-C(21)-C(22)	122.5(3)
C(23)-C(22)-C(21)	114.0(4)
C(23)-C(22)-C(24)	112.7(5)
C(21)-C(22)-C(24)	109.5(4)
C(26)-C(25)-C(17)	111.6(3)
C(26)-C(25)-C(27)	111.1(4)
C(17)-C(25)-C(27)	111.3(3)
N(4)-C(28)-N(3)	100.9(3)
N(3)-C(29)-C(30)	108.2(3)
C(29)-C(30)-N(4)	103.3(3)
C(29)-C(30)-Si(2)	126.5(3)
N(4)-C(30)-Si(2)	130.2(2)
C(32)-C(31)-C(36)	123.1(3)
C(32)-C(31)-N(4)	118.5(3)
C(36)-C(31)-N(4)	118.3(3)
C(31)-C(32)-C(33)	116.8(3)
C(31)-C(32)-C(40)	122.5(3)
C(33)-C(32)-C(40)	120.6(3)
C(34)-C(33)-C(32)	121.6(4)
C(35)-C(34)-C(33)	120.2(3)
C(34)-C(35)-C(36)	121.8(3)
C(31)-C(36)-C(35)	116.5(3)
C(31)-C(36)-C(37)	122.4(3)
C(35)-C(36)-C(37)	121.0(3)
C(36)-C(37)-C(38)	109.5(3)
C(36)-C(37)-C(39)	113.5(3)

C(38)-C(37)-C(39)	109.8(3)
C(32)-C(40)-C(42)	114.3(3)
C(32)-C(40)-C(41)	109.1(3)
C(42)-C(40)-C(41)	110.4(3)
C(48)-C(43)-C(44)	122.9(3)
C(48)-C(43)-N(3)	118.5(3)
C(44)-C(43)-N(3)	118.5(3)
C(45)-C(44)-C(43)	116.5(4)
C(45)-C(44)-C(52)	120.6(4)
C(43)-C(44)-C(52)	122.7(3)
C(46)-C(45)-C(44)	121.3(4)
C(45)-C(46)-C(47)	121.1(4)
C(48)-C(47)-C(46)	120.7(5)
C(43)-C(48)-C(47)	117.4(4)
C(43)-C(48)-C(49)	122.6(4)
C(47)-C(48)-C(49)	119.9(4)
C(48)-C(49)-C(50)	112.6(5)
C(48)-C(49)-C(51)	110.8(6)
C(50)-C(49)-C(51)	109.3(7)
C(44)-C(52)-C(54)	110.0(4)
C(44)-C(52)-C(53)	113.4(4)
C(54)-C(52)-C(53)	108.9(5)
C(55)-O(1)-C(58)	111.6(7)
C(56)-C(55)-O(1)	107.8(8)
C(55)-C(56)-C(57)	107.3(8)
C(58)-C(57)-C(56)	106.0(7)
C(57)-C(58)-O(1)	104.9(6)
C(62)-O(2)-C(59)	90.9(13)
C(60)-C(59)-O(2)	118.1(15)
C(59)-C(60)-C(61)	92.9(15)
C(62)-C(61)-C(60)	108.2(16)
C(61)-C(62)-O(2)	101.2(13)

Symmetry transformations used to generate equivalent atoms:

Compound 8·THF

Table S5. Sample and crystal data for **8·THF**

Identification code	**8·THF**	
Chemical formula	$C_{31}H_{44}Cl_4N_2OSi$	
Formula weight	630.57 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.050 x 0.160 x 0.450 mm	
Crystal system	monoclinic	
Space group	$P2_1/c$ (No. 14)	
Unit cell dimensions	a = 11.770(2) Å	α = 90°
	b = 18.000(3) Å	β = 109.493(2)°
	c = 17.322(3) Å	γ = 90°
Volume	3459.5(10) $Å^3$	
Z	4	
Density (calculated)	1.211 g/cm^3	
Absorption coefficient	0.402 mm^{-1}	
F(000)	1336	

Table S6. Data collection and structure refinement for **8·THF**

Theta range for data collection	1.84 to 25.25°	
Index ranges	-14<=h<=14, -21<=k<=21, -20<=l<=20	
Reflections collected	37742	
Independent reflections	6249 [R(int) = 0.1171]	
Coverage of independent reflections	100.0%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7454 and 0.5747	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	6249 / 5 / 356	
Goodness-of-fit on F^2	1.011	
Final R indices	3124 data; $I>2\sigma(I)$	R1 = 0.0654, wR2 = 0.1499
	all data	R1 = 0.1458, wR2 = 0.1938
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0765P)^2+2.7213P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.363 and -0.356 eÅ^{-3}	
R.M.S. deviation from mean	0.053 eÅ^{-3}	

Table S7. Bond lengths (Å) for **8·THF**

Si1-C3	1.885(4)	Si1-Cl2	2.0552(19)
Si1-Cl3	2.064(2)	Si1-Cl1	2.191(2)
Si1-Cl4	2.201(2)	N1-C1	1.319(5)
N1-C2	1.383(5)	N1-C16	1.459(5)
N2-C1	1.330(5)	N2-C3	1.408(5)
N2-C4	1.459(5)	C1-H1	0.94(5)
C2-C3	1.352(5)	C4-C9	1.387(6)
C4-C5	1.394(6)	C5-C6	1.391(6)
C5-C13	1.523(7)	C6-C7	1.367(7)
C7-C8	1.369(8)	C8-C9	1.395(7)
C9-C10	1.527(7)	C10-C11	1.543(7)
C10-C12	1.544(7)	C13-C15	1.521(7)
C13-C14	1.521(7)	C16-C21	1.380(7)
C16-C17	1.399(7)	C17-C18	1.397(6)
C17-C25	1.510(7)	C18-C19	1.351(8)
C19-C20	1.386(9)	C20-C21	1.410(7)
C21-C22	1.514(8)	C22-C24	1.527(9)
C22-C23	1.517(9)	C25-C26	1.530(7)
C25-C27	1.539(8)	O1-C31	1.329(10)
O1-C28	1.398(9)	C28-C29	1.465(10)
C29-C30	1.470(11)	C30-C31	1.491(12)

Table S8. Bond angles (°) for **8·THF**

C3-Si1-Cl2	123.18(15)	C3-Si1-Cl3	114.70(15)
Cl2-Si1-Cl3	122.11(8)	C3-Si1-Cl1	90.52(14)
Cl2-Si1-Cl1	89.92(8)	Cl3-Si1-Cl1	90.18(9)
C3-Si1-Cl4	88.85(14)	Cl2-Si1-Cl4	90.56(10)
Cl3-Si1-Cl4	89.93(10)	Cl1-Si1-Cl4	179.35(9)
C1-N1-C2	108.1(3)	C1-N1-C16	125.5(3)
C2-N1-C16	126.3(4)	C1-N2-C3	108.8(3)
C1-N2-C4	123.9(3)	C3-N2-C4	127.1(3)
H1-C1-N1	127.(3)	H1-C1-N2	124.(3)
N1-C1-N2	109.4(4)	C3-C2-N1	108.8(4)
C2-C3-N2	105.0(3)	C2-C3-Si1	125.4(3)
N2-C3-Si1	129.6(3)	C9-C4-C5	124.3(4)
C9-C4-N2	118.2(4)	C5-C4-N2	117.5(4)
C4-C5-C6	116.5(5)	C4-C5-C13	123.1(4)
C6-C5-C13	120.3(5)	C7-C6-C5	121.1(5)
C6-C7-C8	120.6(5)	C7-C8-C9	121.7(5)
C4-C9-C8	115.8(5)	C4-C9-C10	123.3(4)
C8-C9-C10	120.8(5)	C9-C10-C11	109.5(4)
C9-C10-C12	113.2(4)	C11-C10-C12	109.5(5)
C5-C13-C15	108.6(4)	C5-C13-C14	112.7(4)
C15-C13-C14	109.8(5)	C21-C16-C17	125.5(4)
C21-C16-N1	116.7(4)	C17-C16-N1	117.8(4)
C18-C17-C16	115.1(5)	C18-C17-C25	121.3(5)
C16-C17-C25	123.5(4)	C19-C18-C17	122.0(6)
C18-C19-C20	121.3(5)	C21-C20-C19	120.2(6)
C16-C21-C20	115.8(5)	C16-C21-C22	123.9(4)
C20-C21-C22	120.3(5)	C21-C22-C24	111.6(6)
C21-C22-C23	112.1(6)	C24-C22-C23	110.5(6)
C17-C25-C26	110.7(5)	C17-C25-C27	113.3(5)
C26-C25-C27	109.6(5)	C31-O1-C28	110.6(6)
C29-C28-O1	106.8(7)	C28-C29-C30	102.3(7)
C29-C30-C31	102.2(8)	O1-C31-C30	103.7(8)

Compound $9\cdot CH_2Cl_2$

Table S9. Crystal data and structure refinement for $9\cdot CH_2Cl_2$

Identification code	$9\cdot CH_2Cl_2$
Empirical formula	$C_{55}H_{74}Cl_6N_4Si$
Formula weight	1031.97
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P n a 21
Unit cell dimensions	a = 22.491(2) Å alpha = 90 deg. b = 24.236(2) Å beta = 90 deg. c = 10.5002(10) Å gamma = 90 deg.
Volume	5723.7(10) A^3
Z, Calculated density	4, 1.198 Mg/m^3
Absorption coefficient	0.359 mm^-1
F(000)	2192
Crystal size	0.290 x 0.140 x 0.130 mm
Theta range for data collection	1.811 to 26.021 deg.
Limiting indices	-27<=h<=27, -29<=k<=29, -12<=l<=12
Reflections collected / unique	65600 / 11266 [R(int) = 0.0849]
Completeness to theta = 25.242	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.6261
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11266 / 3 / 603
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0499, wR2 = 0.1245
R indices (all data)	R1 = 0.0659, wR2 = 0.1365
Absolute structure parameter	0.03(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.598 and -0.577 e.A^-3

Table S10. Bond lengths [Å] and angles [deg] for **9·CH_2Cl_2**

Si(1)-C(29)	1.893(5)
Si(1)-C(3)	1.896(5)
Si(1)-Cl(3)	2.0529(18)
Si(1)-Cl(1)	2.2209(19)
Si(1)-Cl(2)	2.2475(19)
N(1)-C(1)	1.334(6)
N(1)-C(2)	1.395(6)
N(1)-C(16)	1.446(6)
N(2)-C(1)	1.336(6)
N(2)-C(3)	1.409(6)
N(2)-C(4)	1.445(6)
N(3)-C(28)	1.347(6)
N(3)-C(29)	1.401(6)
N(3)-C(43)	1.451(6)
N(4)-C(28)	1.321(6)
N(4)-C(30)	1.381(6)
N(4)-C(31)	1.451(6)
C(1)-H(1)	0.96(3)
C(2)-C(3)	1.368(6)
C(4)-C(9)	1.396(7)
C(4)-C(5)	1.411(7)
C(5)-C(6)	1.402(7)
C(5)-C(13)	1.503(8)
C(6)-C(7)	1.389(9)
C(7)-C(8)	1.373(9)
C(8)-C(9)	1.400(7)
C(9)-C(10)	1.518(8)
C(10)-C(12)	1.526(8)
C(10)-C(11)	1.543(8)
C(13)-C(15)	1.527(8)
C(13)-C(14)	1.550(7)
C(16)-C(21)	1.382(7)
C(16)-C(17)	1.397(7)
C(17)-C(18)	1.399(7)
C(17)-C(25)	1.503(8)
C(18)-C(19)	1.365(9)
C(19)-C(20)	1.382(9)
C(20)-C(21)	1.397(7)
C(21)-C(22)	1.512(8)
C(22)-C(23)	1.526(9)
C(22)-C(24)	1.525(8)
C(25)-C(27)	1.516(9)
C(25)-C(26)	1.550(9)
C(28)-H(28)	0.96(3)
C(29)-C(30)	1.362(7)
C(31)-C(36)	1.391(8)
C(31)-C(32)	1.401(8)
C(32)-C(33)	1.383(8)
C(32)-C(40)	1.510(9)
C(33)-C(34)	1.386(10)
C(34)-C(35)	1.374(10)
C(35)-C(36)	1.398(8)

C(36)-C(37)	1.531(9)
C(37)-C(39)	1.514(9)
C(37)-C(38)	1.519(9)
C(40)-C(41)	1.522(10)
C(40)-C(42)	1.531(9)
C(43)-C(48)	1.396(7)
C(43)-C(44)	1.400(7)
C(44)-C(45)	1.403(7)
C(44)-C(52)	1.508(8)
C(45)-C(46)	1.362(8)
C(46)-C(47)	1.382(8)
C(47)-C(48)	1.387(7)
C(48)-C(49)	1.523(7)
C(49)-C(50)	1.524(8)
C(49)-C(51)	1.537(8)
C(52)-C(54)	1.526(9)
C(52)-C(53)	1.531(8)
C(55)-Cl(5)	1.768(7)
C(55)-Cl(6)	1.774(7)

C(29)-Si(1)-C(3)	131.8(2)
C(29)-Si(1)-Cl(3)	108.89(16)
C(3)-Si(1)-Cl(3)	119.26(15)
C(29)-Si(1)-Cl(1)	90.15(16)
C(3)-Si(1)-Cl(1)	89.19(16)
Cl(3)-Si(1)-Cl(1)	93.77(8)
C(29)-Si(1)-Cl(2)	87.28(16)
C(3)-Si(1)-Cl(2)	87.23(16)
Cl(3)-Si(1)-Cl(2)	93.79(8)
Cl(1)-Si(1)-Cl(2)	172.44(8)
C(1)-N(1)-C(2)	108.8(4)
C(1)-N(1)-C(16)	125.5(4)
C(2)-N(1)-C(16)	125.7(4)
C(1)-N(2)-C(3)	109.4(4)
C(1)-N(2)-C(4)	124.0(4)
C(3)-N(2)-C(4)	126.5(4)
C(28)-N(3)-C(29)	109.4(4)
C(28)-N(3)-C(43)	123.2(4)
C(29)-N(3)-C(43)	127.0(4)
C(28)-N(4)-C(30)	109.4(4)
C(28)-N(4)-C(31)	124.9(4)
C(30)-N(4)-C(31)	125.2(4)
H(1)-C(1)-N(1)	127(4)
H(1)-C(1)-N(2)	124(4)
N(1)-C(1)-N(2)	108.6(4)
C(3)-C(2)-N(1)	107.7(4)
C(2)-C(3)-N(2)	105.5(4)
C(2)-C(3)-Si(1)	128.6(3)
N(2)-C(3)-Si(1)	125.9(3)
C(9)-C(4)-C(5)	124.1(5)
C(9)-C(4)-N(2)	117.6(4)
C(5)-C(4)-N(2)	118.3(4)
C(6)-C(5)-C(4)	116.0(5)
C(6)-C(5)-C(13)	120.6(5)
C(4)-C(5)-C(13)	123.4(4)
C(7)-C(6)-C(5)	121.4(5)
C(8)-C(7)-C(6)	120.3(5)

C(7)-C(8)-C(9)	121.7(5)
C(4)-C(9)-C(8)	116.5(5)
C(4)-C(9)-C(10)	123.1(5)
C(8)-C(9)-C(10)	120.2(5)
C(9)-C(10)-C(12)	113.2(5)
C(9)-C(10)-C(11)	109.4(5)
C(12)-C(10)-C(11)	111.2(5)
C(5)-C(13)-C(15)	113.1(5)
C(5)-C(13)-C(14)	109.6(5)
C(15)-C(13)-C(14)	109.7(5)
C(21)-C(16)-C(17)	123.7(5)
C(21)-C(16)-N(1)	118.7(4)
C(17)-C(16)-N(1)	117.5(4)
C(18)-C(17)-C(16)	116.5(5)
C(18)-C(17)-C(25)	120.2(5)
C(16)-C(17)-C(25)	123.2(5)
C(19)-C(18)-C(17)	121.2(5)
C(18)-C(19)-C(20)	120.6(5)
C(19)-C(20)-C(21)	120.7(5)
C(16)-C(21)-C(20)	117.1(5)
C(16)-C(21)-C(22)	122.5(4)
C(20)-C(21)-C(22)	120.3(5)
C(21)-C(22)-C(23)	108.4(5)
C(21)-C(22)-C(24)	112.4(5)
C(23)-C(22)-C(24)	111.7(5)
C(17)-C(25)-C(27)	112.4(5)
C(17)-C(25)-C(26)	110.1(6)
C(27)-C(25)-C(26)	110.9(5)
H(28)-C(28)-N(4)	132(3)
H(28)-C(28)-N(3)	120(3)
N(4)-C(28)-N(3)	108.0(4)
C(30)-C(29)-N(3)	105.2(4)
C(30)-C(29)-Si(1)	124.6(4)
N(3)-C(29)-Si(1)	130.2(4)
C(29)-C(30)-N(4)	108.0(4)
C(36)-C(31)-C(32)	124.3(5)
C(36)-C(31)-N(4)	119.0(5)
C(32)-C(31)-N(4)	116.7(5)
C(33)-C(32)-C(31)	116.5(6)
C(33)-C(32)-C(40)	121.5(5)
C(31)-C(32)-C(40)	121.9(5)
C(32)-C(33)-C(34)	120.9(6)
C(35)-C(34)-C(33)	121.0(5)
C(34)-C(35)-C(36)	120.8(6)
C(31)-C(36)-C(35)	116.5(6)
C(31)-C(36)-C(37)	122.0(5)
C(35)-C(36)-C(37)	121.5(5)
C(39)-C(37)-C(38)	109.4(6)
C(39)-C(37)-C(36)	114.6(5)
C(38)-C(37)-C(36)	110.1(6)
C(32)-C(40)-C(41)	112.5(5)
C(32)-C(40)-C(42)	110.1(6)
C(41)-C(40)-C(42)	111.8(6)
C(48)-C(43)-C(44)	124.0(4)
C(48)-C(43)-N(3)	118.8(4)
C(44)-C(43)-N(3)	117.3(4)
C(43)-C(44)-C(45)	115.9(5)

C(43)-C(44)-C(52)	122.9(4)
C(45)-C(44)-C(52)	120.7(5)
C(46)-C(45)-C(44)	121.5(5)
C(45)-C(46)-C(47)	120.8(5)
C(46)-C(47)-C(48)	121.0(5)
C(47)-C(48)-C(43)	116.7(5)
C(47)-C(48)-C(49)	120.7(5)
C(43)-C(48)-C(49)	122.2(4)
C(48)-C(49)-C(50)	112.9(5)
C(48)-C(49)-C(51)	108.8(4)
C(50)-C(49)-C(51)	110.5(5)
C(44)-C(52)-C(54)	109.2(5)
C(44)-C(52)-C(53)	112.4(5)
C(54)-C(52)-C(53)	110.6(5)
Cl(5)-C(55)-Cl(6)	109.6(3)

Symmetry transformations used to generate equivalent atoms:

Table S11. Hydrogen bonds for **9·CH_2Cl_2** [Å and deg.]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(1)-H(1)...Cl(4)	0.96(3)	2.32(3)	3.269(5)	171(5)
C(28)-H(28)...Cl(4)#1	0.96(3)	2.32(3)	3.264(5)	165(5)

Symmetry transformations used to generate equivalent atoms:
#1 -x+3/2,y+1/2,z+1/2

Reference

1 A. J. Arduengo, F. Davidson, H. V. R. Dias, J. R. Goerlich, D. Khasnis, W. J. Marshall and T. K. Prakasha, *J. Am. Chem. Soc.*, 1997, **119**, 12742-12749.