Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information – Complementary bonding analysis of the N–Si interaction in pentacoordinated silicon compounds using quantum crystallography

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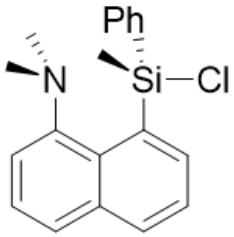
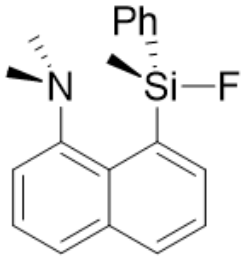
1 Characterization of the compounds

8-(Chloro(methyl)(phenyl)silyl)-N,N-dimethylnaphthalen-1-amine, 3



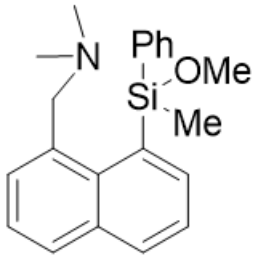
White crystals; melting point = 149 - 150°C; 1H NMR (401 MHz, $CDCl_3$) δ 8.73 (dd, J = 7.0, 1.1 Hz, 1H), 7.97 (dd, J = 8.1, 1.0 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.69 (dd, J = 8.1, 7.0 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.37 (m, 2H), 7.40-7.33 (m, 3H), 7.22 (dd, J = 7.4, 0.8 Hz, 1H), 2.57 (s, 3H, NMe_2), 1.69 (s, 3H, NMe_2), 1.08 (s, 3H, SiMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 140.1, 139.6, 134.7, 134.0, 131.3, 130.5, 129.0, 128.2, 128.0, 126.7, 126.2, 126.0, 116.5, 48.3 (NMe_2), 47.9 (NMe_2), 3.2 (SiMe); ^{29}Si{^{1}H} NMR (80 MHz, $CDCl_3$) δ -14.4; HRMS (EI) calculated for $C_{19}H_{20}ClNSi$ $[M]^+$: 325.10481, found: 325.10531.

8-(Fluoro(methyl)(phenyl)silyl)-N,N-dimethylnaphthalen-1-amine, 1



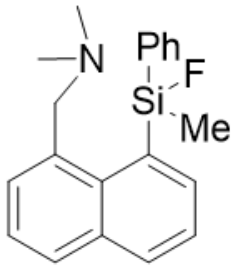
White crystals; mp = 84 - 85°C; ^{1}H NMR (401 MHz, $CDCl_3$) δ 8.34 (dd, J = 6.8, 0.7 Hz, 1H), 7.96 (d, J = 8.1 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.64 (dd, J = 7.7, 7.3 Hz, 1H), 7.48-7.38 (m, 3H), 7.34-7.22 (m, 4H), 2.54 (s, 3H, NMe_2), 1.67 (s, 3H, NMe_2), 0.77 (d, 3JHF = 8.4 Hz, 3H, SiMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 138.2 (d, $^{2}J_{FC}$ = 23.0 Hz), 137.3 (d, $^{3}J_{FC}$ = 9.0 Hz), 135.1 (d, J_{FC} = 2.6 Hz), 134.3 (d, J_{FC} = 1.4 Hz), 132.4 (d, J_{FC} = 1.0 Hz), 130.4 (d, J_{FC} = 0.9 Hz), 129.6 (d, $^{2}J_{FC}$ = 18.3 Hz), 129.2 (d, J_{FC} = 1.1 Hz), 127.8, 126.5, 126.2, 125.9, 117.2, 48.3 (NMe_2), 47.8 (NMe_2), -2.1 (d, $^{2}J_{FC}$ = 22.8 Hz, SiMe); ^{19}F NMR (377 MHz, $CDCl_3$) δ -134.5 (bs); ^{29}Si{^{1}H} NMR (80 MHz, $CDCl_3$) δ -11.7 (d, $^{1}J_{SiF}$ = 264.4 Hz); HRMS (EI) calculated for $C_{19}H_{20}FNSi$ $[M]^{+}$: 309.13490, found: 309.13389.

1-(8-(Methoxy(methyl)(phenyl)silyl)naphthalen-1-yl)-N,N-dimethylmethanamine, 4



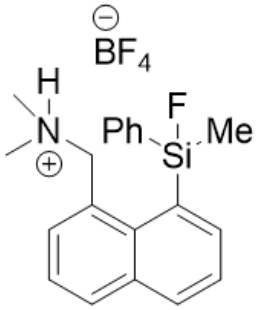
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, J = 6.9, 1.3 Hz, 1H), 7.95 (dd, J = 8.1, 1.3 Hz, 1H), 7.77 (dd, J = 10.3, 7.7 Hz, 2H), 7.57–7.44 (m, 4H), 7.41–7.29 (m, 3H), 3.76 (d-AB, J = 14.0 Hz, 1H, CH_2), 3.72 (d-AB, J = 14.0 Hz, 1H, CH_2), 3.40 (d, J = 3.4 Hz, 3H, SiOMe), 1.88 (s, 6H, NMe_2), 0.80 (s, 3H, SiMe); ^{29}Si{^{1}H} NMR (80 MHz, CD_2Cl_2) δ -2.50.

1-(8-(Fluoro(methyl)(phenyl)silyl)naphthalen-1-yl)-N,N-dimethylmethanamine, 2



White crystals; mp = 79-80°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 7.1 Hz, 1H), 7.98 (dd, J = 8.1, 1.3 Hz, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.58 (dd, J = 7.7, 7.5 Hz, 1H), 7.55-7.50 (m, 2H), 7.45-7.26 (m, 5H), 3.86 (d-AB, ^{2}J = 14.6 Hz, 1H, CH_2), 3.82 (d-AB, ^{2}J = 14.6 Hz, 1H, CH_2), 1.85 (s, 6H, NMe_2), 0.84 (d, $^{3}J_{HF}$ = 9.5 Hz, 3H, SiMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0 (d, J_{FC} = 12.0 Hz), 135.7, 134.4, 133.9, 132.6, 132.0, 129.7, 128.9, 127.7, 127.7, 125.2, 124.9, 64.8 (CH_2), 45.5 (NMe_2), -0.5 (d, J_{FC} = 28.3 Hz, SiMe); ^{19}F NMR (377 MHz, $CDCl_3$) δ -112.5 (bs); ^{29}Si{^{1}H} NMR (80 MHz, $CDCl_3$) δ -26.5 (d, J = 262.7 Hz); HRMS (EI) calculated for $C_{20}H_{22}FNSi$ $[M]^{+}$: 323.15001, found: 323.14977.

1-(8-(Fluoro(methyl)(phenyl)silyl)naphthalen-1-yl)-N,N-dimethyl ammonium tetrafluoroborate, 5



White crystals; mp = 119-120°C; ^{1}H NMR (401 MHz, CD_2Cl_2) δ 11.23 (bs, 1H, NH), 8.16 (ddd, J = 9.6, 7.6, 1.4 Hz, 2H), 8.09 (dd, J = 8.1, 1.4 Hz, 1H), 7.79 (dd, J = 7.2, 1.4 Hz, 1H), 7.71-7.62 (m, 2H), 7.57-7.48 (m, 3H), 7.43 (tm, J = 7.3 Hz, 2H), 4.81 (dd-ABX, J = 13.7, 6.3 Hz, 1H, CH_2), 4.41 (ddd-ABX, J = 13.7, 6.1, 1.5 Hz, 1H, CH_2), 2.44 (d, J = 4.6 Hz, 3H, NMe_2), 2.43 (d, J = 4.7 Hz, 3H, NMe_2), 0.88 (d, $^{3}J_{HF}$ = 7.9 Hz, 3H, SiMe); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 140.1 (d, J_{FC} = 5.0 Hz), 136.5, 135.6, 135.4 (d, J_{FC} = 16.2 Hz), 134.5, 134.0 (d, J_{FC} = 1.7 Hz), 133.7, 132.3, 132.0, 129.4, 128.3 (d, J_{FC} = 15.4 Hz), 126.9, 126.9, 125.8, 60.9 (d, J_{FC} = 8.6 Hz, CH_2), 43.6 (NMe_2), 43.1 (d, J_{FC} = 2.5 Hz, NMe_2), 0.7 (d, J_{FC} = 17.7 Hz, SiMe); ^{19}F NMR (377 MHz, CD_2Cl_2) δ -151.63 (4F, BF_4), -153.15 (q, $^{3}J_{FH}$ = 7.8 Hz, 1F, SiF); ^{29}Si{^{1}H} NMR (80 MHz, CD_2Cl_2) δ 12.1 (d, J_{SiF} = 282.5 Hz); HR ESI-TOF MS (Positive mode) calculated for $C_{20}H_{23}FNSi$: 324.1584, found: 324.1581.

2 Crystallographic details

2.1 Fractal dimension plots

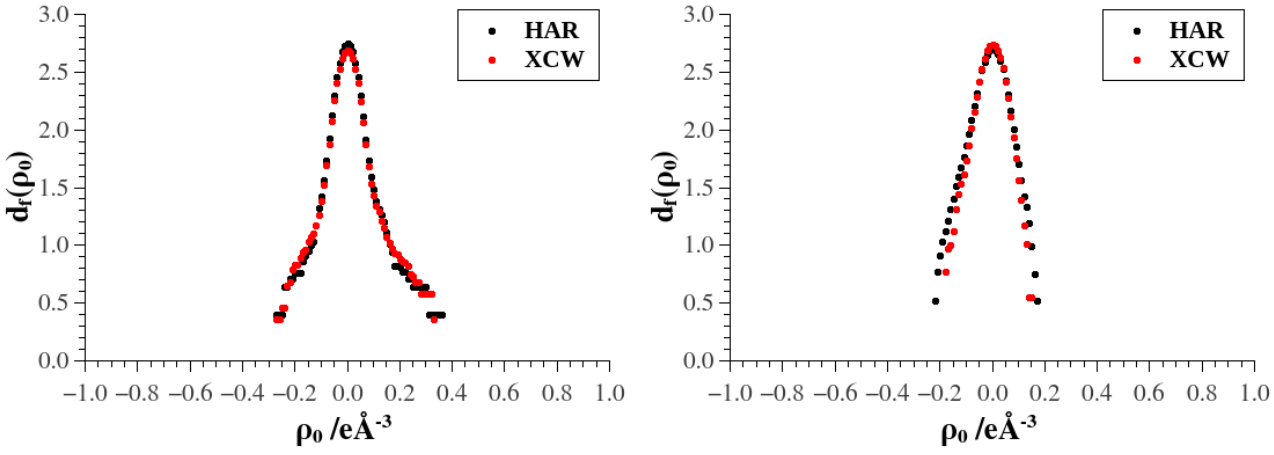


Figure S1. Fractal dimension plot of the HAR and XCW of the Me_2N substituted compound **1** from the synchrotron measurement (left) and of the Me_2NCH_2 substituted compound **2** from the home measurement (right).

2.2 Residual and deformation density plots

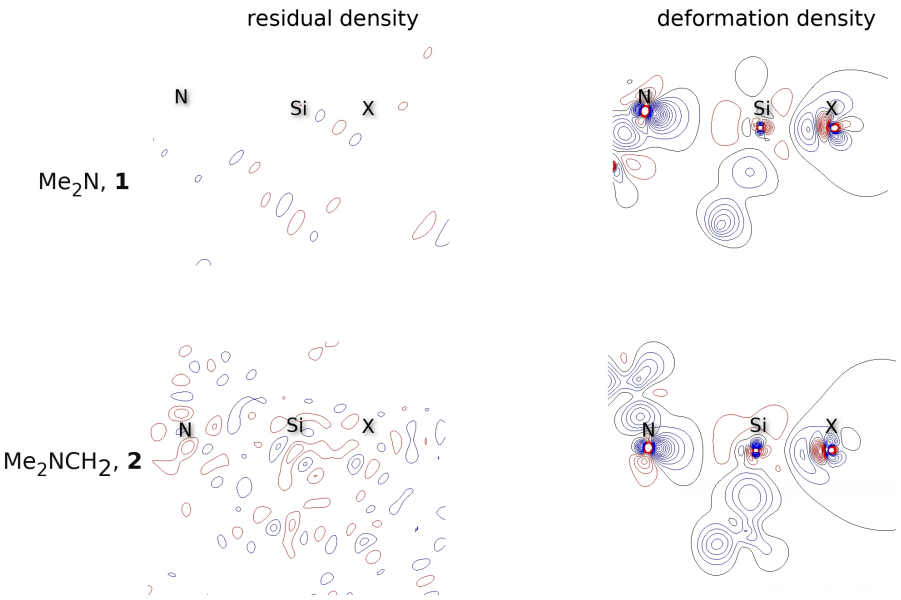


Figure S2. Residual and deformation density contour plots of the N – Si – X plane of both compounds after XWR. Blue and red lines refer to positive and negative contour lines, respectively. The line separation is 0.05 e·Å^{-3} in the residual density maps and 0.1 e·Å^{-3} for the deformation density maps.

3 Coordinates of the optimized structures

Table S1. Coordinates of the isolated molecule optimization of compound **1**.

		x /Å	y /Å	z /Å
1	Si	10.098775	3.595633	2.791147
2	F	10.382040	3.108906	4.329202
3	N	9.843913	4.672309	0.269702
4	C	13.322215	6.031645	3.664503
5	C	9.468911	1.146900	1.478516
6	C	11.764999	5.410620	-1.083508
7	C	11.430271	4.911171	2.603378
8	C	11.739902	1.864554	1.216049
9	C	12.001469	0.754852	0.421709
10	C	11.194904	5.128783	0.134470
11	C	11.910231	5.369093	1.339748
12	C	10.991728	-0.162008	0.151714
13	C	13.040285	6.003840	-1.159896
14	C	13.837777	6.389592	2.448968
15	C	12.144927	5.260049	3.733571
16	C	9.723840	0.033597	0.686797
17	C	10.467405	2.086851	1.752638
18	C	13.707850	6.350435	-0.016584
19	C	13.161886	6.049986	1.253802
20	C	8.939270	5.824334	0.382049
21	C	9.387928	3.752732	-0.767525
22	C	8.276695	4.006657	2.898081
23	H	7.736076	3.810486	1.974439
24	H	8.438927	3.316034	-0.455730
25	H	12.535724	2.572614	1.409513
26	H	9.230652	4.248504	-1.734586
27	H	8.934569	-0.680163	0.486041
28	H	14.774804	6.929157	2.382111
29	H	8.472422	1.285064	1.881522
30	H	14.668180	6.848513	-0.066889
31	H	11.221150	5.209166	-1.996001
32	H	11.821529	4.894700	4.698564
33	H	9.244142	6.452804	1.216601
34	H	7.923248	5.476355	0.557788
35	H	8.120134	5.051435	3.169467
36	H	13.840940	6.295996	4.577194
37	H	13.470046	6.216655	-2.130160
38	H	11.192705	-1.025802	-0.469269
39	H	12.992679	0.606131	0.011952
40	H	10.109292	2.949206	-0.889333
41	H	8.950695	6.429367	-0.534028
42	H	7.838583	3.393660	3.687947

Table S2. Coordinates of the isolated molecule optimization of compound **2**.

		x /Å	y /Å	z /Å
1	Si	4.967131	7.457496	2.479674
2	F	6.272435	6.725492	1.782263
3	N	2.864939	8.652628	3.558314
4	C	5.405173	10.347988	3.347530
5	C	6.443882	9.435931	1.359713
6	C	5.590902	9.248023	2.435851
7	C	4.462311	10.385792	4.424787
8	C	5.014795	6.580475	4.130734
9	C	6.204155	11.530096	3.155440
10	C	4.389564	4.711718	5.552013
11	C	4.281624	5.412014	4.355890
12	C	5.885080	7.010134	5.138367
13	C	5.996628	6.317093	6.337345
14	C	7.161800	10.622439	1.137053
15	C	3.456614	9.305473	4.725057
16	C	5.244030	5.167342	6.548850
17	C	7.067208	11.637852	2.041714
18	C	4.416979	11.477916	5.264135
19	C	6.131715	12.613104	4.061131
20	C	5.265473	12.584397	5.115258
21	C	2.261905	9.614964	2.636277
22	C	1.848481	7.711681	4.021418
23	C	3.693275	6.907843	1.220158
24	H	6.605536	8.619707	0.669895
25	H	3.810270	3.809628	5.704627
26	H	2.661129	9.756551	5.336552
27	H	3.017137	10.290019	2.243507
28	H	6.480752	7.902813	4.987936
29	H	3.613049	5.039040	3.588919
30	H	5.329445	4.625022	7.481883
31	H	7.642497	12.547876	1.922053
32	H	1.481157	10.211326	3.130225
33	H	3.683738	11.486564	6.061438
34	H	2.289885	7.005005	4.719821
35	H	3.910632	8.523351	5.333515
36	H	6.672433	6.671929	7.105339
37	H	3.927646	5.883106	0.925752
38	H	6.769569	13.471218	3.888675
39	H	1.809266	9.080067	1.802764
40	H	7.808066	10.705738	0.272831
41	H	1.434559	7.158045	3.180009
42	H	1.023417	8.235008	4.526577
43	H	5.202943	13.412753	5.808599
44	H	2.656106	6.948561	1.534875
45	H	3.798619	7.527182	0.326163

Table S3. Coordinates of compound **1** with an implicit water solvation.

		x /Å	y /Å	z /Å
1	F	5.529848	9.535195	1.294919
2	Si	4.388115	8.905336	2.318801
3	N	2.681655	7.598786	3.914336
4	C	4.330569	11.733271	5.362906
5	C	6.40902	4.705543	2.767303
6	C	5.140816	4.292448	4.850786
7	C	6.677606	5.504613	1.687979
8	C	3.560752	6.545539	4.329395
9	C	2.099277	8.384354	5.002227
10	C	5.203114	11.20916	6.31079
11	C	4.640222	6.248102	3.454455
12	C	4.728646	9.825265	3.910181
13	C	4.098793	11.046015	4.176517
14	C	3.350356	5.790811	5.458036
15	C	5.84638	10.001145	6.061053
16	C	5.400108	5.064354	3.692527
17	C	4.161713	4.670298	5.73107
18	C	5.996708	6.729049	1.525916
19	C	5.6114	9.320493	4.871678
20	C	1.620798	7.041937	3.055629
21	C	4.992225	7.126282	2.387817
22	C	2.840235	9.451992	1.426844
23	H	7.446496	5.223976	0.979524
24	H	5.73613	3.406394	5.032616
25	H	5.380714	11.738574	7.238233
26	H	3.977919	4.089627	6.625646
27	H	2.537166	6.028707	6.129268
28	H	6.303996	7.38752	0.725025
29	H	2.88483	8.716492	5.675603
30	H	1.349502	7.822296	5.570767
31	H	3.827555	12.673673	5.55027
32	H	1.613132	9.261945	4.577332
33	H	6.969166	3.793457	2.933442
34	H	6.527724	9.588198	6.794367
35	H	0.979066	7.845236	2.701697
36	H	1.008231	6.319797	3.607943
37	H	3.405909	11.465227	3.456617
38	H	2.013613	9.671323	2.098911
39	H	2.064901	6.541093	2.197757
40	H	6.113074	8.376543	4.698705
41	H	3.072677	10.35974	0.866791
42	H	2.508064	8.697552	0.712649

Table S4. Coordinates of compound **2** with implicit water solvation.

		x /Å	y /Å	z /Å
1	Si	4.811973	7.522685	2.536691
2	F	6.140688	6.737808	1.845386
3	N	2.91668	8.644157	3.527252
4	C	5.392283	10.372182	3.362829
5	C	6.406056	9.435932	1.377415
6	C	5.548157	9.269856	2.451994
7	C	4.450379	10.412839	4.437131
8	C	4.949989	6.600658	4.168105
9	C	6.210384	11.539979	3.174816
10	C	4.457743	4.666853	5.557779
11	C	4.271222	5.397936	4.388941
12	C	5.844451	7.034114	5.153745
13	C	6.035203	6.31037	6.325457
14	C	7.153395	10.607041	1.159586
15	C	3.444979	9.328911	4.716408
16	C	5.338044	5.124468	6.532172
17	C	7.078875	11.62818	2.062578
18	C	4.410936	11.500413	5.281924
19	C	6.146632	12.621845	4.083874
20	C	5.273418	12.598499	5.134724
21	C	2.308714	9.608524	2.595902
22	C	1.881207	7.70058	3.97354
23	C	3.626081	6.92024	1.213004
24	H	6.539844	8.621134	0.680224
25	H	3.916299	3.741112	5.707375
26	H	2.612494	9.774686	5.273944
27	H	3.065176	10.272462	2.188942
28	H	6.397216	7.955295	5.009919
29	H	3.580938	5.021272	3.643586
30	H	5.483056	4.559256	7.443973
31	H	7.673084	12.525494	1.940239
32	H	1.544934	10.207614	3.104205
33	H	3.676472	11.513983	6.077892
34	H	2.295065	7.024415	4.715829
35	H	3.878849	8.564864	5.36056
36	H	6.727566	6.67054	7.076108
37	H	3.70451	5.832219	1.156478
38	H	6.7943	13.473848	3.91839
39	H	1.837688	9.073085	1.775826
40	H	7.801662	10.677891	0.295623
41	H	1.516382	7.118135	3.130758
42	H	1.036443	8.239108	4.418181
43	H	5.21733	13.426278	5.829264
44	H	2.578769	7.180132	1.317002
45	H	3.978381	7.311504	0.255356