Electronic Supplementary Information for Dalton Transactions

Ligand dependence of π-complex character in disilene-palladium complexes

Takeaki Iwamoto, Yumiko Sekiguchi, Naoki Yoshida, Chizuko Kabuto and Mitsuo Kira*

Department of Chemistry, Graduate School of Science, Tohoku University

Aoba-ku, Sendai, 980-8578, Japan

Contents

Supplementary Information

1. DFT calculations of model compounds 2', 8', 8", 9' and 9"

All DFT calculations were carried out using a Gaussian 98 program.[S1] Basis sets were 6-31G(d) for H, C, Si, and Lanl2dz for Pd atoms. Geometry optimization was carried out at the B3LYP level. Selected structural parameters are summarized in Table S1. Atomic coordinates of **2-9"** are shown in Tables S2-S6. Structural parameters of **2-9"** are drawn in Figures S1-S5.

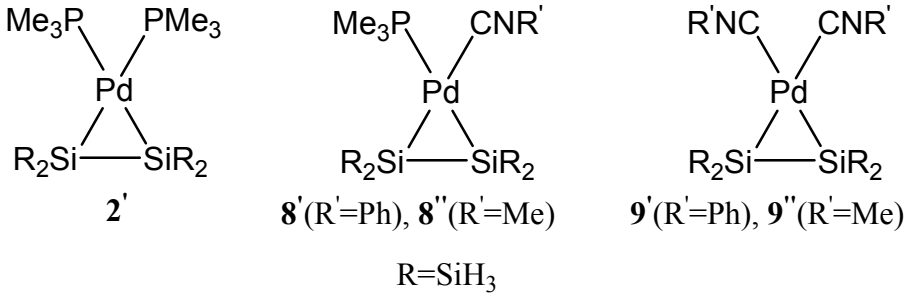
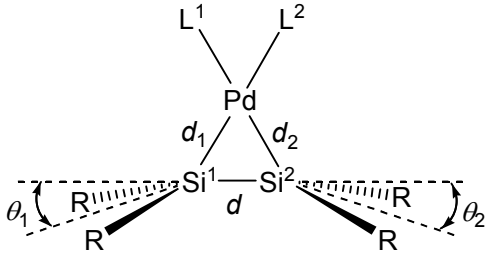


Table S1. Comparison of structural parameters of various disilene palladium complexes



Compound	L^1	L^2	d/Å	Δd/Å (%$\Delta d/d_0$)[a]	θ_1/°	θ_2/°	$\theta_{av.}$/°[b]	d_1/Å	d_2/Å	φ/°[c]
2'	PMe_3	PMe_3	2.2666	0.094 (4.3)	27.6	28.2	27.9	2.4561	2.4523	4.41
8'	PhNC	PMe_3	2.2685	0.096 (4.4)	19.6	31.0	25.3	2.4625	2.4595	2.45
8"	MeNC	PMe_3	2.2685	0.096 (4.4)	20.0	31.1	25.5	2.4605	2.4565	0.28
9'	PhNC	PhNC	2.2625	0.090 (4.1)	21.9	21.9	21.9	2.4665	2.4665	1.82
9"	MeNC	MeNC	2.2635	0.091 (4.2)	22.5	22.5	22.5	2.4615	2.4615	0.16

[a] d_0 is the Si=Si distance in $(H_3Si)_2Si=Si(SiH_3)_2$ (2.173 Å) optimized at the B3LYP / 6-31G(d) level. $\Delta d = d - d_0 = d - 2.173$. [b] $\theta_{av.} = (\theta_1 + \theta_2)/2$ [c] dihedral angle between plane (L^1-Pd-L^2) and plane (Si-Pd-Si)

Table S2. Atomic coordinates of $(Me_3P)_2Pd((H_3Si)_2Si=Si(SiH_3)_2)$ **2'**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	-0.423468	-0.002076	-0.032686
2	14	0	1.780374	1.081966	-0.056538
3	14	0	1.724520	-1.179706	0.082573
4	15	0	-1.852670	1.947358	-0.003938
5	15	0	-1.974199	-1.854038	-0.042709
6	14	0	2.341748	2.343126	1.835161
7	14	0	2.466216	2.065149	-2.069830
8	14	0	2.361984	-2.445957	-1.782253
9	14	0	2.241385	-2.191418	2.131407
10	6	0	-2.338062	2.443906	1.715503
11	6	0	-3.508131	1.881345	-0.847537
12	6	0	-1.206287	3.547721	-0.674261
13	6	0	-1.346849	-3.574835	0.226563
14	6	0	-2.899816	-2.061840	-1.637357
15	6	0	-3.361023	-1.804505	1.192529
16	1	0	2.074218	1.583856	3.088891
17	1	0	3.771904	2.769893	1.853836
18	1	0	1.530789	3.599332	1.910294
19	1	0	2.139073	1.189956	-3.230321
20	1	0	1.791339	3.377904	-2.306291
21	1	0	3.933692	2.336347	-2.102842
22	1	0	2.173226	-1.674980	-3.042982
23	1	0	3.786278	-2.888727	-1.724858
24	1	0	1.542454	-3.691450	-1.908794
25	1	0	1.960046	-1.269222	3.267279
26	1	0	1.430098	-3.426442	2.362630
27	1	0	3.671783	-2.607988	2.224896
28	1	0	-2.983069	3.330671	1.713858
29	1	0	-1.436510	2.660275	2.296521
30	1	0	-2.865250	1.619363	2.205544
31	1	0	-4.069219	2.813929	-0.713628
32	1	0	-4.102774	1.054078	-0.447196
33	1	0	-3.363939	1.708759	-1.919276
34	1	0	-1.941062	4.354500	-0.565307
35	1	0	-0.956310	3.430898	-1.733015
36	1	0	-0.290948	3.821792	-0.142486
37	1	0	-2.159100	-4.310250	0.180078
38	1	0	-0.858580	-3.639807	1.203352
39	1	0	-0.600582	-3.815223	-0.536215
40	1	0	-3.593611	-2.909959	-1.595731
41	1	0	-2.185266	-2.227271	-2.449789
42	1	0	-3.462626	-1.151180	-1.863761
43	1	0	-4.028911	-2.667837	1.087590
44	1	0	-3.946712	-0.888454	1.066150
45	1	0	-2.944020	-1.802070	2.204902

Framework Group: C1. E (+ZPVE) = -2793.2093906 hartree (no imaginary number frequencies).

Table S3. Atomic coordinates of $(Me_3P)(PhNC)Pd((H_3Si)_2Si{=}Si(SiH_3)_2)$ **8'**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.524473	3.231384	1.219496
2	15	0	-1.320328	2.711810	-0.087256
3	6	0	-0.063795	4.073266	0.015497
4	6	0	-2.216546	3.159846	-1.644209
5	46	0	-0.478981	0.443779	0.036547
6	6	0	1.541429	0.559447	0.075729
7	7	0	2.718712	0.520408	0.067198
8	6	0	4.093448	0.374887	0.017499
9	14	0	-2.564204	-0.858518	-0.024852
10	14	0	-3.955469	-0.822223	1.859714
11	14	0	-0.617163	-2.013371	0.108061
12	14	0	0.302363	-3.035501	-1.786428
13	14	0	-3.748265	-0.912939	-2.045287
14	14	0	0.082588	-2.942653	2.140223
15	1	0	-2.829548	-1.107962	-3.201643
16	1	0	-4.772554	-1.997622	-2.083974
17	1	0	-4.484129	0.367676	-2.281489
18	1	0	-0.216291	-2.416760	-3.037956
19	1	0	1.791580	-2.891125	-1.807108
20	1	0	0.023632	-4.500673	-1.851257
21	1	0	-3.161966	-0.927201	3.116018
22	1	0	-4.734801	0.451838	1.936999
23	1	0	-4.958210	-1.927471	1.855456
24	1	0	-0.553042	-2.242547	3.290868
25	1	0	-0.252004	-4.393671	2.248093
26	1	0	1.562849	-2.831403	2.305665
27	1	0	-2.063119	3.119201	2.205941
28	1	0	-2.837443	4.274113	1.088294
29	1	0	-3.405050	2.583708	1.185549
30	1	0	0.664792	3.957230	-0.793324
31	1	0	-0.525397	5.065195	-0.059046
32	1	0	0.472704	4.001236	0.967150
33	1	0	-3.087255	2.509291	-1.766602
34	1	0	-2.546250	4.205583	-1.632831
35	1	0	-1.556183	3.003710	-2.503248
36	6	0	4.913959	1.284704	0.698445
37	6	0	6.297045	1.127895	0.641719
38	6	0	6.858973	0.077799	-0.088811
39	6	0	6.032715	-0.823624	-0.765360
40	6	0	4.647760	-0.683836	-0.716837
41	1	0	4.461746	2.094636	1.261393
42	1	0	6.936609	1.829022	1.169817
43	1	0	7.938000	-0.038580	-0.129865
44	1	0	6.466534	-1.641973	-1.332396
45	1	0	3.990888	-1.377026	-1.232230

Framework Group: C1. E (+ZPVE) = -2656.254220 hartree (no imaginary number frequencies).

Table S4. Atomic coordinates of $(Me_3P)(MeNC)Pd((H_3Si)_2Si{=}Si(SiH_3)_2)$ **8"**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.538371	0.098802	-1.443741
2	15	0	2.638808	0.834396	-0.002158
3	6	0	3.541157	0.096232	1.436346
4	46	0	0.228336	0.595732	-0.002221
5	14	0	-0.028041	-1.847304	0.005371
6	14	0	0.525104	-3.003474	1.966163
7	14	0	-1.921984	-0.599906	-0.003196
8	14	0	-3.152407	-0.312230	-1.973904
9	14	0	-3.163209	-0.298186	1.958576
10	6	0	-0.540149	2.479969	-0.003033
11	7	0	-1.069478	3.526734	0.000514
12	6	0	-1.794537	4.747045	0.008005
13	1	0	-2.735926	4.614749	0.549861
14	14	0	0.533320	-3.019141	-1.943735
15	6	0	3.310398	2.564606	-0.001123
16	1	0	0.010841	-2.294942	3.171526
17	1	0	-0.014508	-4.394819	1.986488
18	1	0	2.006864	-3.126336	2.128924
19	1	0	-2.318333	-0.517702	3.165519
20	1	0	-3.709186	1.091147	2.043741
21	1	0	-4.335087	-1.218850	2.049417
22	1	0	0.022343	-2.321603	-3.156870
23	1	0	2.015841	-3.141165	-2.100278
24	1	0	-0.004155	-4.411420	-1.954179
25	1	0	-2.300931	-0.543067	-3.174100
26	1	0	-4.324350	-1.232988	-2.063148
27	1	0	-3.696467	1.076664	-2.073569
28	1	0	3.171050	0.549125	-2.371512
29	1	0	4.620118	0.263167	-1.371072
30	1	0	3.339607	-0.975669	-1.490387
31	1	0	2.948093	3.094476	0.885818
32	1	0	4.406901	2.580515	-0.002591
33	1	0	2.945588	3.096602	-0.885752
34	1	0	3.342090	-0.978223	1.481801
35	1	0	4.622800	0.260374	1.361689
36	1	0	3.175922	0.545212	2.365595
37	1	0	-1.205625	5.529910	0.495302
38	1	0	-2.013143	5.051566	-1.019874

Framework Group: C1. E (+ZPVE) = -2464.569448 hartree (no imaginary number frequencies).

Table S5. Atomic coordinates of $(PhNC)_2Pd\{(H_3Si)_2Si{=}Si(SiH_3)_2\}$ **9'**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.684563	-0.979739	-0.047392
2	46	0	0.000000	0.172751	0.000000
3	6	0	-1.684568	-0.979729	0.047394
4	7	0	-2.702907	-1.568668	0.058250
5	6	0	-3.933388	-2.200500	0.045831
6	7	0	2.702896	-1.568688	-0.058250
7	6	0	3.933375	-2.200526	-0.045842
8	14	0	1.129618	2.363566	-0.060270
9	14	0	2.407556	2.828336	1.845128
10	14	0	-1.129606	2.363571	0.060285
11	14	0	-2.407537	2.828355	-1.845114
12	14	0	2.195163	2.844810	-2.088949
13	14	0	-2.195150	2.844807	2.088967
14	1	0	1.295883	2.559929	-3.241055
15	1	0	2.620011	4.272833	-2.181175
16	1	0	3.426992	2.018063	-2.259855
17	1	0	-1.632257	2.566716	-3.089153
18	1	0	-3.629303	1.966791	-1.891408
19	1	0	-2.885697	4.241591	-1.889943
20	1	0	1.632285	2.566678	3.089168
21	1	0	3.629327	1.966780	1.891404
22	1	0	2.885707	4.241575	1.889970
23	1	0	-1.295870	2.559915	3.241070
24	1	0	-2.619991	4.272831	2.181201
25	1	0	-3.426983	2.018065	2.259868
26	6	0	4.089171	-3.428670	-0.702950
27	6	0	5.333122	-4.055488	-0.685369
28	6	0	6.410452	-3.467586	-0.017501
29	6	0	6.244503	-2.243513	0.635942
30	6	0	5.008547	-1.601302	0.625974
31	1	0	3.241811	-3.871116	-1.216265
32	1	0	5.459796	-5.006241	-1.194769
33	1	0	7.377487	-3.961842	-0.006873
34	1	0	7.080489	-1.783899	1.154848
35	1	0	4.861899	-0.649180	1.125376
36	6	0	-4.089257	-3.428528	0.703140
37	6	0	-5.333211	-4.055340	0.685546
38	6	0	-6.410471	-3.467549	0.017469
39	6	0	-6.244449	-2.243591	-0.636173
40	6	0	-5.008489	-1.601386	-0.626195
41	1	0	-3.241950	-3.870889	1.216616
42	1	0	-5.459941	-5.006002	1.195102
43	1	0	-7.377508	-3.961800	0.006832
44	1	0	-7.080381	-1.784062	-1.155241
45	1	0	-4.861787	-0.649352	-1.125747

Framework Group: C1. E (+ZPVE) = -2519.629898 hartree (no imaginary number frequencies).

Table S6. Atomic coordinates of $(MeNC)_2Pd\{(H_3Si)_2Si{=}Si(SiH_3)_2\}$ **9"**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-2.679469	2.645842	0.000817
2	6	0	-1.678156	2.037348	-0.000555
3	6	0	-3.925619	3.324816	0.004026
4	46	0	0.000000	0.856375	0.000000
5	14	0	-1.131574	-1.329348	-0.002739
6	14	0	-2.297489	-1.813320	-1.974262
7	14	0	1.131526	-1.329378	0.002740
8	14	0	2.297440	-1.813356	1.974261
9	14	0	2.307670	-1.813963	-1.962536
10	6	0	1.678220	2.037289	0.000548
11	7	0	2.679552	2.645752	-0.000870
12	6	0	3.925716	3.324702	-0.004002
13	1	0	4.732996	2.617746	-0.218110
14	14	0	-2.307721	-1.813931	1.962535
15	1	0	-4.096737	3.786222	-0.973072
16	1	0	-1.459076	-1.533541	-3.172951
17	1	0	-2.738055	-3.237825	-2.046838
18	1	0	-3.532820	-0.979708	-2.087330
19	1	0	1.476464	-1.532768	-3.165895
20	1	0	3.544434	-0.981356	-2.068280
21	1	0	2.747612	-3.238738	-2.033410
22	1	0	-1.476513	-1.532740	3.165893
23	1	0	-3.544482	-0.981320	2.068279
24	1	0	-2.747665	-3.238705	2.033406
25	1	0	1.459008	-1.533628	3.172948
26	1	0	2.738048	-3.237850	2.046811
27	1	0	3.532746	-0.979710	2.087358
28	1	0	-4.733386	2.617023	0.213482
29	1	0	-3.921725	4.104304	0.771697
30	1	0	3.920210	4.107353	-0.768438
31	1	0	4.098965	3.782057	0.974625

Framework Group: C1. E (+ZEP) = -2136.260727 hartree (no imaginary number frequencies).

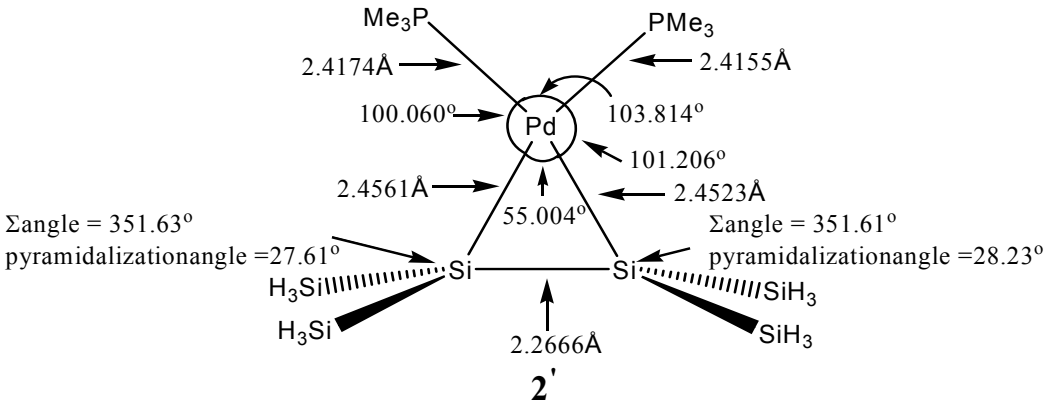


Figure S1. Selected structural parameters of **2'**.

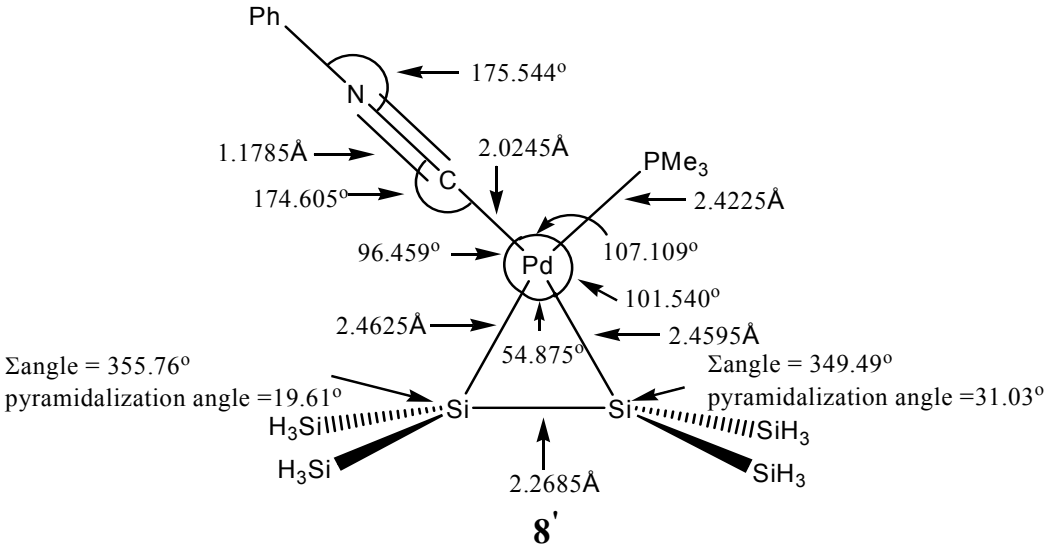
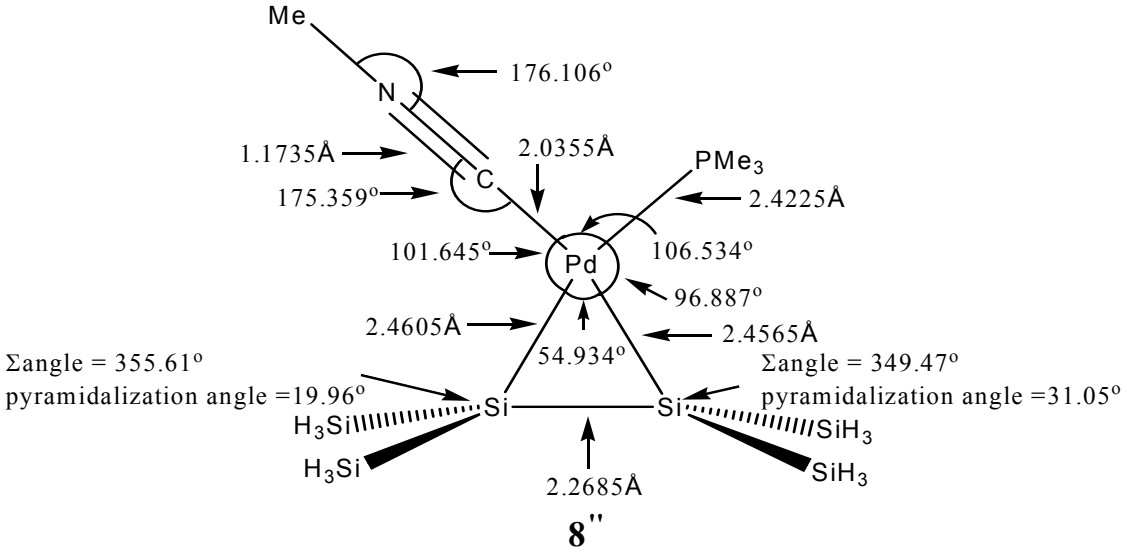
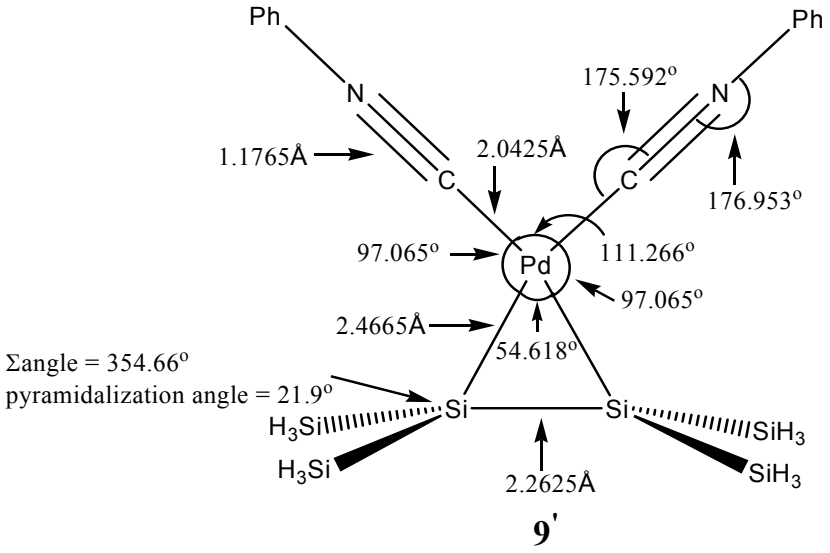


Figure S2. Selected structural parameters of **8'**.



8''

Figure 3. Selected structural parameters of **8"**.



9'

Figure 4. Selected structural parameters of **9'**.

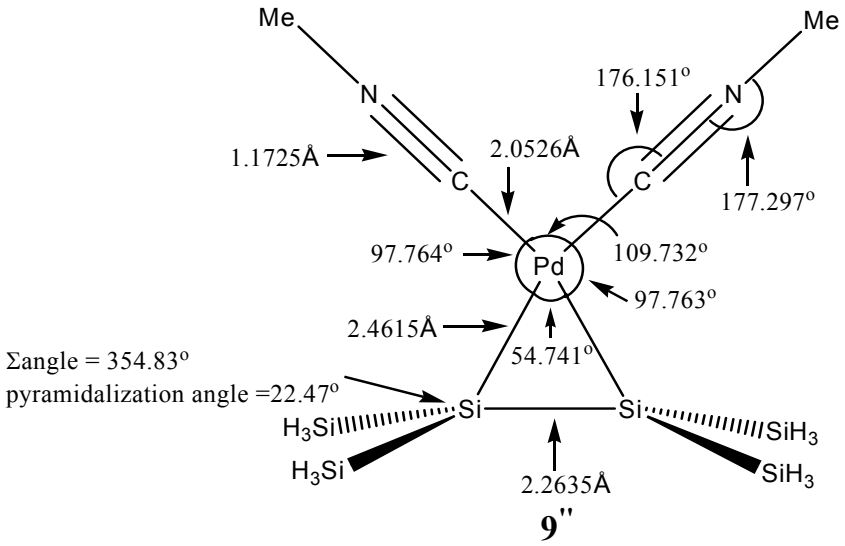


Figure 5. Selected structural parameters of **9"**.

2. References

S1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, revision A.11.4; Gaussian, Inc.: Pittsburgh, PA, 2001.