Supplementary Material (ESI) for Chemical Communications

Supersilyl radicals from the dissociation of superdisilane observed by gas electron diffraction

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Electronic Supplementary Information

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GED experimental details

Data were collected for the vapour product of hexa-tert-butyldisilane using the Edinburgh gas-phase electron diffraction apparatus.[S1] An accelerating voltage of around 40 kV was used, representing an electron wavelength of approximately 6.0 pm. Scattering intensities were recorded on Kodak Electron Image films at nozzle-to-film distances of 261 mm (sample and nozzle temperatures held at 421 K and 444 K respectively) and 98 mm (sample and nozzle temperatures held at 443 K and 464 K respectively). The weighting points for the off-diagonal weight matrices, correlation parameters and scale factors for both camera distances are given in Table S1. Also included are the electron wavelengths as determined from the scattering patterns for benzene, which were recorded immediately after the patterns for the sample compounds. The scattering intensities were measured using an Epson Expression 1600 Pro Flatbed Scanner and converted to mean optical densities as a function of the scattering variable, *s*, using an established program.[S2] The data reduction and the least-squares refinement processes were carried out using the ed@ed program[S3] employing the scattering factors of Ross *et al.*.[S4]

S1. C. M. Huntley, G. S. Laurenson and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1980, 954.

S2. H. Fleischer, D. A. Wann, S. L. Hinchley, K. B. Borisenko, J. R. Lewis, R. J. Mawhorter, H. E. Robertson and D. W. H. Rankin, *Dalton Trans.*, 2005, 3221.

S3. S. L. Hinchley, H. E. Robertson, K. B. Borisenko, A. R. Turner, B. F. Johnston, D. W. H. Rankin, M. Ahmadian, J. N. Jones and A. H. Cowley, *Dalton Trans.*, 2004, 2469.

S4. A. W. Ross, M. Fink and R. Hilderbrandt, *International Tables for Crystallography*, Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, Boston and London, 1992; Vol. C, p. 245.

S5. HF and MP2 calculations were performed using the resources of the National Service for Computational Chemistry Software (http://www.nsccs.ac.uk). DFT calculations were performed using the resources of the EaStCHEM Research Computing Facility (http://www.eastchem.ac.uk/rcf). Calculations were performed using the the Gaussian 03 suite of programs. HF and MP2 calculations were performed using Gaussian 03, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R.

Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004. DFT calculations were performed using Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, 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, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

Table S1 Nozzle-to-film distances (mm), weighting functions (nm^{-1}), correlation parameters, scale factors and electron wavelengths (pm) used in the electron-diffraction study

Nozzle-film distance[a]	261.0	97.8
Δs	1	2
s_{min}	20	60
sw_1	40	80
sw_2	120	276
s_{max}	140	320
Correlation Parameter	0.4957	0.2648
Scale Factor[b]	0.634(3)	0.670(8)
Electron Wavelength	6.13	6.13

[a] Determined by reference to the scattering pattern of benzene vapour

[b] Values in parentheses are the estimated standard deviations

Table S2 Geometries from the *ab initio* molecular orbital calculations performed for $Si_2Bu^t_6$ (**1**), $^{\cdot}SiBu^t_3$ (**2**), $HSiBu^t_2CMe_2{}^{\cdot}CH_2$ (**3**), $MeSiBu^t_2{}^{\cdot}CMe_2$ (**4**), $MeSiBu^t_2CHMe^{\cdot}CH_2$ (**5**) and $HSiBu^t_3$ (**6**) at the MP2/6-31G* level

Atom	*x*	*y*	*z*
$Si_2Bu^t_6$ (1)			
Si(1)	0.0177	1.3605	0.0000
C(2)	-1.0918	2.1148	-1.4809
C(3)	-0.8680	1.4204	-2.8312
H(4)	-1.1096	0.3610	-2.7996
H(5)	0.1551	1.5226	-3.1946
H(6)	-1.5258	1.8872	-3.5782
C(7)	-2.5953	1.9926	-1.1840
H(8)	-2.9067	0.9609	-1.0188
H(9)	-2.9069	2.5888	-0.3252
H(10)	-3.1564	2.3640	-2.0531
C(11)	-0.8202	3.6100	-1.7431
H(12)	-1.5471	3.9604	-2.4897
H(13)	-0.9349	4.2389	-0.8613
H(14)	0.1718	3.7835	-2.1637
C(15)	1.8693	2.0760	-0.2288
C(16)	2.3612	1.9281	-1.6779
H(17)	2.3533	0.8925	-2.0188
H(18)	3.4016	2.2783	-1.7333
H(19)	1.7850	2.5281	-2.3836
C(20)	1.9900	3.5731	0.1210
H(21)	3.0067	3.9008	-0.1388
H(22)	1.2961	4.2097	-0.4264
H(23)	1.8615	3.7610	1.1883
C(24)	2.9131	1.3707	0.6480
H(25)	2.7184	1.4887	1.7144
H(26)	2.9855	0.3072	0.4349

H(27)	3.8979	1.8159	0.4466
C(28)	-0.6952	2.1098	1.7097
C(29)	-1.9900	1.4352	2.1833
H(30)	-2.8139	1.5614	1.4802
H(31)	-1.8625	0.3710	2.3647
H(32)	-2.2989	1.8975	3.1317
C(33)	-1.0286	3.6128	1.6224
H(34)	-1.8850	3.8106	0.9754
H(35)	-1.3051	3.9575	2.6290
H(36)	-0.1952	4.2293	1.2880
C(37)	0.3110	1.9549	2.8617
H(38)	0.5896	0.9154	3.0371
H(39)	-0.1538	2.3250	3.7864
H(40)	1.2220	2.5351	2.7087
Si(41)	-0.0177	-1.3605	0.0000
C(42)	1.0918	-2.1148	-1.4809
C(43)	0.8680	-1.4204	-2.8312
H(44)	1.1096	-0.3610	-2.7996
H(45)	-0.1551	-1.5226	-3.1946
H(46)	1.5258	-1.8872	-3.5782
C(47)	2.5953	-1.9926	-1.1840
H(48)	2.9067	-0.9609	-1.0188
H(49)	2.9069	-2.5888	-0.3252
H(50)	3.1564	-2.3640	-2.0531
C(51)	0.8202	-3.6100	-1.7431
H(52)	1.5471	-3.9604	-2.4897
H(53)	0.9349	-4.2389	-0.8613
H(54)	-0.1718	-3.7835	-2.1637
C(55)	-1.8693	-2.0760	-0.2288
C(56)	-2.3612	-1.9281	-1.6779
H(57)	-2.3533	-0.8925	-2.0188

H(58)	-3.4016	-2.2783	-1.7333
H(59)	-1.7850	-2.5281	-2.3836
C(60)	-1.9900	-3.5731	0.1210
H(61)	-3.0067	-3.9008	-0.1388
H(62)	-1.2961	-4.2097	-0.4264
H(63)	-1.8615	-3.7610	1.1883
C(64)	-2.9131	-1.3707	0.6480
H(65)	-2.7184	-1.4887	1.7144
H(66)	-2.9855	-0.3072	0.4349
H(67)	-3.8979	-1.8159	0.4466
C(68)	0.6952	-2.1098	1.7097
C(69)	1.9900	-1.4352	2.1833
H(70)	2.8139	-1.5614	1.4802
H(71)	1.8625	-0.3710	2.3647
H(72)	2.2989	-1.8975	3.1317
C(73)	1.0286	-3.6128	1.6224
H(74)	1.8850	-3.8106	0.9754
H(75)	1.3051	-3.9575	2.6290
H(76)	0.1952	-4.2293	1.2880
C(77)	-0.3110	-1.9549	2.8617
H(78)	-0.5896	-0.9154	3.0371
H(79)	0.1538	-2.3250	3.7864
H(80)	-1.2220	-2.5351	2.7087

$^{\bullet}SiBu^{t}_{3}$	*x*	*y*	*z*
Si(1)	-0.0001	0.0000	-0.5324
C(2)	-1.8763	-0.1756	-0.0300
C(3)	-2.7462	0.7176	-0.9316
H(4)	-2.6224	0.4575	-1.9881
H(5)	-2.5282	1.7798	-0.8173
H(6)	-3.8036	0.5678	-0.6725
C(7)	-2.3743	-1.6128	-0.2431
H(8)	-2.2227	-1.9488	-1.2740
H(9)	-1.8946	-2.3286	0.4282
H(10)	-3.4535	-1.6491	-0.0399
C(11)	-2.1280	0.2010	1.4389
H(12)	-3.1917	0.0560	1.6760
H(13)	-1.5491	-0.4218	2.1279
H(14)	-1.8889	1.2474	1.6458
C(15)	0.7860	1.7127	-0.0301
C(16)	-0.2094	2.8627	-0.2439
H(17)	-0.5756	2.8993	-1.2750
H(18)	0.2989	3.8154	-0.0407
H(19)	-1.0694	2.8054	0.4270
C(20)	1.2375	1.7427	1.4389
H(21)	1.6438	2.7364	1.6759
H(22)	0.4084	1.5531	2.1276
H(23)	2.0240	1.0124	1.6463
C(24)	1.9950	2.0190	-0.9314
H(25)	2.8056	1.2989	-0.8166
H(26)	1.7082	2.0416	-1.9880
H(27)	2.3941	3.0096	-0.6724
C(28)	1.0902	-1.5371	-0.0303
C(29)	0.7515	-2.7370	-0.9321
H(30)	-0.2774	-3.0793	-0.8176

H(31)	0.9146	-2.4995	-1.9886
H(32)	1.4099	-3.5778	-0.6732
C(33)	0.8901	-1.9435	1.4386
H(34)	-0.1356	-2.2597	1.6456
H(35)	1.5477	-2.7923	1.6754
H(36)	1.1402	-1.1309	2.1276
C(37)	2.5839	-1.2497	-0.2437
H(38)	2.7989	-0.9504	-1.2746
H(39)	3.1549	-2.1662	-0.0407
H(40)	2.9640	-0.4764	0.4277

$HSiBu^t_2CMe_2{}^{\cdot}CH_2$ (3)	***x***	***y***	***z***
Si(1)	-0.0039	0.0126	-0.5189
H(2)	-0.0231	0.0020	-2.0192
C(3)	-0.0478	1.9000	-0.0339
C(4)	0.2859	2.1569	1.4434
C(5)	0.9471	2.5765	-0.9146
C(6)	-1.4318	2.5088	-0.3366
H(7)	-0.4106	1.6447	2.1134
H(8)	1.2987	1.8345	1.6986
H(9)	0.2201	3.2325	1.6515
H(10)	0.7384	2.7125	-1.9703
H(11)	1.9174	2.8886	-0.5491
H(12)	-1.3850	3.5943	-0.1861
H(13)	-1.7377	2.3304	-1.3726
H(14)	-2.2056	2.1136	0.3265
C(15)	-1.5898	-0.9712	0.0066
C(16)	-1.9871	-0.7305	1.4695
C(17)	-2.7654	-0.5702	-0.9018
C(18)	-1.3889	-2.4812	-0.1950
H(19)	-1.1864	-1.0020	2.1649
H(20)	-2.2576	0.3128	1.6553
H(21)	-2.8636	-1.3445	1.7193
H(22)	-2.5341	-0.7486	-1.9574
H(23)	-3.6428	-1.1801	-0.6459
H(24)	-3.0517	0.4763	-0.7909
H(25)	-2.3374	-2.9988	0.0052
H(26)	-1.0969	-2.7207	-1.2231
H(27)	-0.6415	-2.9003	0.4827
C(28)	1.6588	-0.8371	-0.0119
C(29)	2.8462	0.1094	-0.2477
C(30)	1.6859	-1.2800	1.4582

C(31)	1.9014	-2.0648	-0.9080
H(32)	2.8756	0.4812	-1.2769
H(33)	2.8344	0.9705	0.4238
H(34)	3.7804	-0.4389	-0.0634
H(35)	0.9278	-2.0370	1.6773
H(36)	2.6650	-1.7215	1.6904
H(37)	1.5333	-0.4410	2.1444
H(38)	2.8798	-2.5009	-0.6638
H(39)	1.1527	-2.8463	-0.7725
H(40)	1.9168	-1.7887	-1.9677

MeSiBu$^t_2$·CMe$_2$ (4)	***x***	***y***	***z***
Si(1)	-0.0180	0.1010	0.4088
C(2)	-0.0635	1.8868	-0.1650
C(3)	0.1143	2.3002	-1.5992
C(4)	-0.2190	3.0481	0.7744
H(5)	0.2209	1.4597	-2.2876
H(6)	-0.7412	2.9016	-1.9412
H(7)	1.0029	2.9397	-1.7120
H(8)	-0.3350	2.7491	1.8179
H(9)	0.6534	3.7164	0.7140
C(10)	1.6487	-0.7124	-0.1306
C(11)	1.6761	-1.1776	-1.5920
C(12)	2.7616	0.3291	0.0657
C(13)	1.9670	-1.9206	0.7641
H(14)	0.9582	-1.9816	-1.7797
H(15)	1.4656	-0.3629	-2.2917
H(16)	2.6748	-1.5669	-1.8354
H(17)	2.7804	0.7204	1.0894
H(18)	3.7405	-0.1310	-0.1292
H(19)	2.6481	1.1777	-0.6157
H(20)	2.9229	-2.3652	0.4540
H(21)	2.0645	-1.6335	1.8154
H(22)	1.2036	-2.7013	0.6955
C(23)	-1.6071	-0.8040	-0.1976
C(24)	-2.7925	-0.2169	0.5853
C(25)	-1.8736	-0.5748	-1.6910
C(26)	-1.5512	-2.3130	0.0722
H(27)	-2.7348	-0.4525	1.6524
H(28)	-2.8481	0.8730	0.4792
H(29)	-3.7339	-0.6364	0.2040
H(30)	-1.0618	-0.9468	-2.3231

H(31)	-2.7908	-1.1032	-1.9868
H(32)	-2.0200	0.4867	-1.9125
H(33)	-2.5209	-2.7700	-0.1705
H(34)	-0.7930	-2.8114	-0.5394
H(35)	-1.3395	-2.5347	1.1243
H(36)	-1.0922	3.6591	0.5005
C(37)	-0.0469	0.0935	2.3043
H(38)	-0.1469	-0.9238	2.6953
H(39)	0.8742	0.5158	2.7192
H(40)	-0.8828	0.6786	2.6973

MeSiBu$^t_2$CHMe˙CH$_2$ (5)	***x***	***y***	***z***
Si(1)	-0.0050	0.1149	0.4403
C(2)	-0.4849	1.9494	0.0462
C(3)	-0.2619	2.3347	-1.3724
C(4)	-1.9017	2.3375	0.5039
H(5)	0.7001	2.6791	-1.7301
H(6)	-1.0614	2.2494	-2.0987
H(7)	-2.1076	2.0212	1.5308
H(8)	-2.0284	3.4244	0.4560
C(9)	1.8265	-0.1557	-0.1054
C(10)	1.9841	-0.3904	-1.6139
C(11)	2.6428	1.0917	0.2737
C(12)	2.4455	-1.3468	0.6440
H(13)	1.5192	-1.3273	-1.9340
H(14)	1.5478	0.4226	-2.2014
H(15)	3.0517	-0.4522	-1.8680
H(16)	2.5533	1.3365	1.3384
H(17)	3.7065	0.9072	0.0702
H(18)	2.3466	1.9715	-0.3036
H(19)	3.4941	-1.4644	0.3375
H(20)	2.4364	-1.1936	1.7278
H(21)	1.9341	-2.2885	0.4304
C(22)	-1.2662	-1.1493	-0.2866
C(23)	-2.5384	-1.1547	0.5782
C(24)	-1.6626	-0.8055	-1.7285
C(25)	-0.7014	-2.5776	-0.2610
H(26)	-2.3324	-1.4900	1.5994
H(27)	-3.0127	-0.1717	0.6340
H(28)	-3.2697	-1.8502	0.1436
H(29)	-0.7983	-0.7618	-2.3978
H(30)	-2.3470	-1.5734	-2.1159

H(31)	-2.1808	0.1559	-1.7861
H(32)	-1.4826	-3.2837	-0.5757
H(33)	0.1449	-2.7028	-0.9414
H(34)	-0.3798	-2.8740	0.7437
H(35)	-2.6612	1.8931	-0.1455
C(36)	-0.0450	-0.0494	2.3317
H(37)	0.1015	-1.0869	2.6493
H(38)	0.7449	0.5511	2.7950
H(39)	-0.9990	0.2883	2.7463
H(40)	0.2282	2.5075	0.6724

$HSiBu^t_3$ (6)	***x***	***y***	***z***
Si(1)	0.0000	0.0000	0.5132
H(2)	0.0000	0.0000	2.0157
C(3)	1.2842	-1.3625	0.0081
C(4)	2.7234	-0.8736	0.2351
C(5)	1.1099	-2.5977	0.9100
C(6)	1.1567	-1.7943	-1.4600
H(7)	3.0028	-0.0607	-0.4389
H(8)	2.8844	-0.5403	1.2659
H(9)	3.4169	-1.7049	0.0473
H(10)	0.1470	-3.0915	0.7780
H(11)	1.8911	-3.3317	0.6686
H(12)	1.2158	-2.3375	1.9686
H(13)	1.9315	-2.5379	-1.6929
H(14)	0.1888	-2.2559	-1.6734
H(15)	1.2899	-0.9545	-2.1494
C(16)	0.5378	1.7934	0.0081
C(17)	1.6947	2.2601	0.9100
C(18)	0.9755	1.8988	-1.4600
C(19)	-0.6051	2.7954	0.2351
H(20)	1.4164	2.2217	1.9686
H(21)	2.6038	1.6731	0.7780
H(22)	1.9398	3.3036	0.6686
H(23)	0.1817	1.5943	-2.1494
H(24)	1.2321	2.9417	-1.6929
H(25)	1.8593	1.2915	-1.6734
H(26)	-0.2320	3.8116	0.0473
H(27)	-1.4488	2.6308	-0.4389
H(28)	-0.9743	2.7681	1.2659
C(29)	-1.8220	-0.4309	0.0081
C(30)	-2.8047	0.3376	0.9100

C(31)	-2.1322	-0.1046	-1.4600
C(32)	-2.1183	-1.9217	0.2351
H(33)	-2.6323	0.1158	1.9686
H(34)	-2.7508	1.4185	0.7780
H(35)	-3.8309	0.0281	0.6686
H(36)	-1.4715	-0.6398	-2.1494
H(37)	-3.1636	-0.4038	-1.6929
H(38)	-2.0481	0.9644	-1.6734
H(39)	-3.1849	-2.1067	0.0473
H(40)	-1.5540	-2.5701	-0.4389
H(41)	-1.9101	-2.2278	1.2659