Supporting Information for

Kinetics and Mechanism of the Addition of Aliphatic Amines to Transient Silenes

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Figure 1. Plots of (k_{decay}-k_0) *vs.* [amine], for quenching of 1,1-bis(4-trifluoromethylphenyl)silene (**1b**) by *n*-butyl amine (*n*-$BuNH_2$; ○), *tert*-butyl amine (*t*-$BuNH_2$; □), and *N,N*-diethyl amine (Et_2NH; ◇) in (a) hexane and (b) acetonitrile solution at 23 °C.

Table 1. Absolute rate constants for reaction of **1a,b** with *n*-$BuNH_2$ in hexane solution.

Table 2. Absolute rate constants for reaction of **1a,b** with *n*-$BuNH_2$ in MeCN solution.

Table 3. Absolute rate constants for reaction of **1a,b** with *n*-$BuNH_2$ in THF solution.

Table 4. Absolute rate constants for reaction of **1a,b** with *t*-$BuNH_2$ in MeCN solution.

Table 5. Absolute rate constants for reaction of **1a,b** with Et_2NH in MeCN solution.

Table 6. Spectroscopic data for aminosilanes **5a, 6a,** and **5b-7b**.

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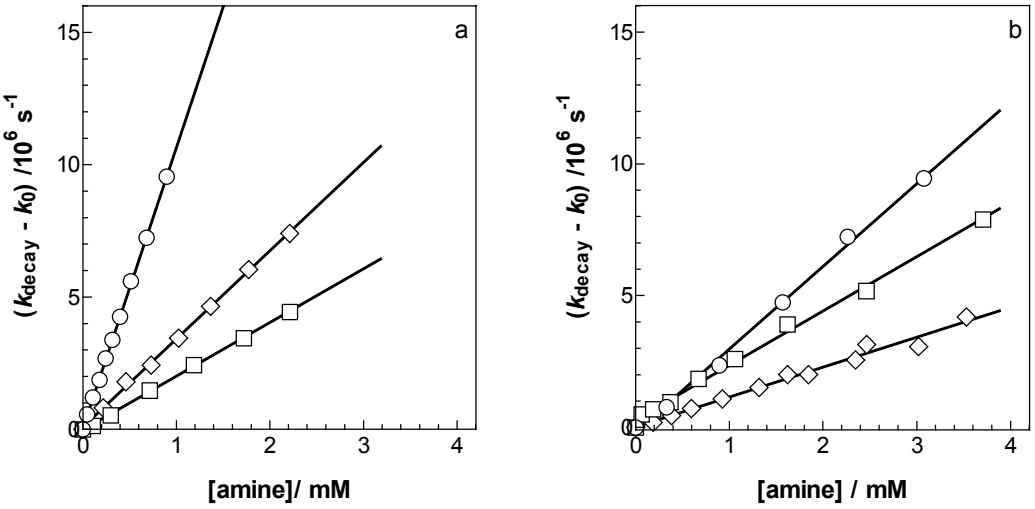

Table 1. Absolute rate constants for reaction of **1a,b** with *n*-$BuNH_2$ in hexane solution.

1a			**1b**		
T (^{o}C)	k_{nBuNH2} / 10^9 $M^{-1}s^{-1}$	σ	T (^{o}C)	k_{nBuNH2} / 10^9 $M^{-1}s^{-1}$	σ
2	5.32	0.10	3	7.25	0.16
13	5.82	0.07	12	8.83	0.35
23	6.49	0.06	23	10.61	0.07
40	5.59	0.07	40	11.95	0.26
58	4.10	0.03	60	11.06	0.24

Table 2. Absolute rate constants for reaction of **1a,b** with *n*-$BuNH_2$ in MeCN solution.

1a			**1b**		
T (^{o}C)	k_{nBuNH2} / 10^9 $M^{-1}s^{-1}$	σ	T (^{o}C)	k_{nBuNH2} / 10^9 $M^{-1}s^{-1}$	σ
2	1.83	0.03	2	1.76	0.03
10	2.12	0.04	12	2.39	0.03
23	2.81	0.03	23	3.28	0.03
32	3.12	0.03	41	4.02	0.04
43	3.17	0.04	57	4.62	0.02
54	3.38	0.06			

Table 3. Absolute rate constants for reaction of **1a,b** with *n*-$BuNH_2$ in THF solution.

1a			**1b**		
T (^{o}C)	k_{nBuNH2} / 10^8 $M^{-1}s^{-1}$	σ	T (^{o}C)	k_{nBuNH2} / 10^8 $M^{-1}s^{-1}$	σ
0	1.29	0.04	3	0.61	0.02
12	2.27	0.04	13	0.66	0.01
23	3.20	0.20	24	0.94	0.01
34	5.92	0.16	39	1.61	0.08
44	9.07	0.24	54	2.4	0.06
55	11.41	0.45			

Table 4. Absolute rate constants for reaction of **1a,b** with *t*-$BuNH_2$ in MeCN solution.

1a			**1b**		
T (^{o}C)	$k_{t\text{-}BuNH2}$ / 10^9 $M^{-1}s^{-1}$	σ	T (^{o}C)	$k_{t\text{-}BuNH2}$ / 10^9 $M^{-1}s^{-1}$	σ
2	1.25	0.02	1	1.16	0.02
12	1.35	0.02	12	1.53	0.03
23	1.60	0.04	24	2.06	0.05
39	1.88	0.03	40	2.21	0.02
57	1.83	0.01	59	2.61	0.02

Table 5. Absolute rate constants for reaction of **1a,b** with Et_2NH in MeCN solution.

1a			**1b**		
T (^{o}C)	k_{Et2NH} / 10^9 $M^{-1}s^{-1}$	σ	T (^{o}C)	k_{Et2NH} / 10^9 $M^{-1}s^{-1}$	σ
1	1.18	0.02	2	0.75	0.01
13	1.31	0.03	13	0.95	0.02
23	1.48	0.01	23	1.46	0.01
40	1.67	0.01	40	1.80	0.02
59	1.64	0.01	58	2.07	0.04

Table 6. Spectroscopic data for aminosilanes **5a, 6a,** and **5b-7b**.

Diphenyl(n-butylamino)methylsilane (**5a**).

^{1}H NMR ($CDCl_3$), δ = 7.60 (m, 4H), 7.41 (m, 6H), 2.78 (dt, 2H), 1.60 (br m, 1H), 1.39 (m, 4H), 0.90 (t, 3H) 0.59 (s, 3H); ^{13}C NMR ($CDCl_3$), δ = 134.8, 134.5, 129.2, 127.7, 41.9, 36.8, 19.9, 13.9, -2.7; IR (neat), 3404 (w), 2958 (s), 2928 (s), 2861 (m), 1428 (m), 1252 (m), 1115 (s), 835 (m), 788 (m); EIMS, *m/z* (I) = 269 (9), 254 (14), 227 (44), 226 (94), 198 (100), 195 (32), 165 (20), 155 (16), 121 (33), 119 (19), 106 (17), 105 (16); HRMS (EI), *m/z* calcd. for $C_{17}H_{23}NSi$ (M^+) 269.1600; found, 269.1599.

Table 6, continued.

Bis-(4-trifluoromethylphenyl)(n-butylamino)methylsilane (**5b**). ^{1}H NMR ($CDCl_3$), δ = 7.68 (d, 4H), 7.61 (d, 4H), 2.80 (dt, 2H), 1.34 (m, 4H), 0.96 (br s, 1H), 0.88 (t, 3H), 0.63 (s, 3H); ^{13}C NMR ($CDCl_3$), δ = 142.1, 134.7, 134.2, 124.4, 41.9, 36.7, 19.9, 13.9, -3.0; IR (neat), 3036 (w), 2962 (m), 2932 (m), 2874 (m), 1392 (m), 1326 (s), 1269 (m), 1166 (s), 1128 (s), 1062 (s), 1017(s), 830 (m), 798 (m), 771 (m); EIMS, *m/z* (I) = 390 (5), 363 (21), 362 (90), 334 (24), 333 (100), 319 (5), 271 (5), 232 (5), 201 (5), 183 (8), 127 (9); HRMS (EI), calcd. for $C_{18}H_{18}NF_6Si$ (M^+-CH_3), 390.1113; found, 390.1098.
Diphenyl(tert-butylamino)methylsilane (**6a**). ^{1}H NMR ($CDCl_3$), δ (ppm) = 7.63 (m, 4H), 7.35 (m, 6H), 1.16 (s, 9H), 0.69 (s, 3H); ^{13}C NMR ($CDCl_3$), δ (ppm) = 140.0, 134.8, 134.5, 129.0, 127.5, 50.0, 33.8, 0.1; IR (neat), 3385 (w), 2963 (s), 1429 (m), 1377 (m), 1362 (m), 1251 (m), 1225 (m), 1112 (s), 1017 (m), 789 (m), 724 (m), 700 (s) ; EIMS, *m/z* (I) = 269 (3), 255 (22), 254 (100), 198 (19), 197 (89), 181 (10), 165 (9), 119 (7), and 105 (18); HRMS (EI), *m/z* calcd. for $C_{17}H_{23}NSi$ (M^+), 269.1600; found, 269.1588.
Bis-(4-trifluoromethylphenyl)(tert-butylamino)methylsilane (**6b**). ^{1}H NMR ($CDCl_3$), δ = 7.70 (d, 2H), 7.60 (d, 2H), 1.17 (s, 9H), 0.73 (s, 3H); ^{13}C NMR ($CDCl_3$), δ = 143.5, 134.7, 124.4, 50.1, 33.7, -0.2; IR (neat), 3251 (w), 2965 (m), 1393 (s), 1327 (s), 1269 (m), 1167 (s), 1127 (s), 1129 (s) 1062 (s), 1017 (s), 830 (m), 799 (s); EIMS, *m/z* (I), 391 (25), 390 (100), 334 (13), 333 (53); HRMS (EI), Calcd. for $C_{18}H_{18}NF_6Si$ (M^+-CH_3), 390.1113; found, 390.1097.
Bis-(4-trifluoromethylphenyl)(N,N-diethylamino)methylsilane (**7b**). ^{1}H NMR ($CDCl_3$), δ = 7.65 (dd, 4H), 2.93 (q, 4H), 1.01 (t, 6H), 0.64 (s, 3H); ^{13}C NMR ($CDCl_3$), δ = 142.2, 135.0, 134.1, 124.4, 40.2, 15.4, -2.5; IR (neat), 2970 (m), 1393 (m), 1326 (s), 1269 (m), 1167 (s), 1129 (s), 1061 (s), 1019 (m), 830 (m), 797 (m); EIMS**,** *m/z* (I) = 405 (6), 391 (22), 390 (91), 334 (21), 333 (100), 189 (9), 127 (8); HRMS (EI), Calcd. for $C_{19}H_{21}NF_6Si$ (M^+) 405.1347; found, 405.1330.