In particular the pattern observed in the Zr complex, strongly reminiscent of that found in classical metallocenes,[29] witnesses a more parallel array of the two rings. The trend of He I versus He II relative intensity changes observed on passing from the Ti to the Zr complex (and incidentally we note the present complexes represent the first case of a group IVB divalent complex studied by PE spectroscopy) provides direct evidence of greater 4d cross section under the higher frequency ionizing radiation, as observed indirectly in earlier studies.[22]

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Registry No. $Ti(Cp)_2(CO)_2$, 12129-51-0; $Zr(Cp)_2(CO)_2$, 59487-85-3.

Hydrolysis of Cyclodisilazanes

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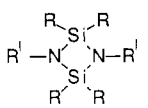
The relatively unhindered *N,N'*-diphenyltetramethylcyclodisilazane, $(Me_2SiNPh)_2$, readily undergoes hydrolysis in the presence of catalytic amounts of acid or base. Under basic conditions, an intermediate diaminodisiloxane, $[Me_2Si(NHPh)]_2O$, can be isolated. Under acidic conditions, hydrolysis rates are proportional to the strength of the acid used with the exception of tetrafluoroboric acid which exhibits an accelerated hydrolysis rate. The more sterically congested hexaphenylcyclodisilazane, $(Ph_2SiNPh)_2$, is resistant to acid hydrolysis, but it is readily hydrolyzed in the presence of base. Hydrolysis of the hexaphenyl derivative in the presence of fluoride ion gives rise to several fluorine-containing products such as $(Ph_2SiF)_2NPh$.

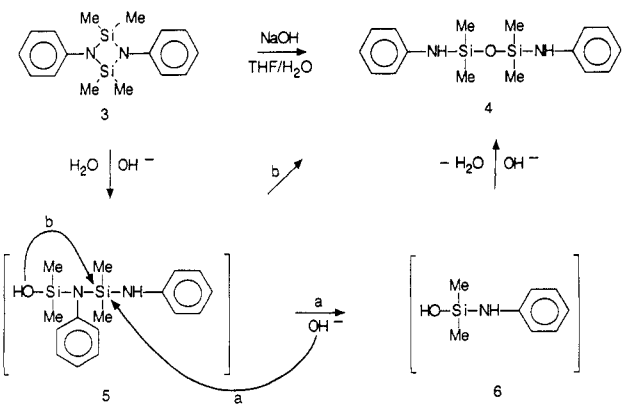
The thermally stable[1] cyclodisilazane ring **1** is a potentially useful structure in small-ring chemistry. These planar, relatively unstrained systems[2] were incorporated into the backbone of linear polymer chains to enhance their thermal stability[3] and into silazane polymer networks to increase yields of silicon nitride and silicon carbide ceramics.[4] Despite their attractive thermal characteristics, only a handful of examples are cited that use these cyclic units in polymeric materials. This is in part because of the hydrolytic instability of the silicon–nitrogen bond.

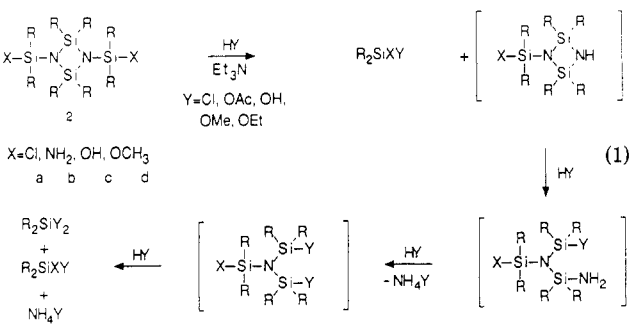


1

Several studies were published on the hydrolysis of silylamines, linear silazanes,[5] and *N*-silyl-substituted cyclodisilazanes **2**. In the latter, when R = methyl, reactions of **2** with alcohols,[6] water,[7] acetic acid,[8] and hydrogen chloride[9] initially resulted in cleavage of the exocyclic Si–N bond (eq 1). Further reaction with the cyclodisilazane ring then occurred to give the products shown. The amount of protic reagent (stoichiometric or excess) and the presence or absence of a proton acceptor (Et_3N) dictated the

Scheme I





(1) (a) Breed, L. W.; Elliott, R. L.; Ferris, A. F. *J. Org. Chem.* **1962**, *27*, 1114. (b) Fink, W. *Helv. Chim. Acta* **1969**, *52*, 1841.

(2) (a) Parkanyi, L.; Bihatsi, L.; Hencsei, P.; Szollosy, A. *J. Organomet. Chem.* **1987**, *321*, 7. (b) Szollosy, A.; Parkanyi, L.; Bihatsi, L.; Hencsei, P. *Ibid.* **1983**, *251*, 159. (c) Gergo, E.; Schultz, G.; Hargittai, I. *Ibid.* **1985**, *292*, 343. (d) Parkanyi, L.; Argay, G.; Hencsei, P.; Nagy, J. *Ibid.* **1976**, *116*, 299. (e) Parkanyi, L.; Szollosy, A.; Bihatsi, L.; Hencsei, P.; Nagy, J. *Ibid.* **1983**, *256*, 235. (f) Bihatsi, L.; Hencsei, P.; Parkanyi, L. *Ibid.* **1981**, *219*, 145. (g) Parkanyi, L.; Dunaj-Jurco, D.; Bihatsi, L.; Hencsei, P. *Cryst. Struct. Commun.* **1980**, *9*, 1049.

(3) Fink, W. *J. Paint Technol.* **1970**, *42*, 220 and references therein.

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(5) Bazant, V.; Chvalovsky, V.; Rathousky, J. *Organosilicon Compounds*; Academic: New York, 1965; Vol. I, pp 76–88 and references therein.

(6) Varezhkin, Y. M.; Morgunova, M. M.; Zhinkin, D. Y. *Zh. Obshch. Khim.* **1980**, *50*, 2009 (Engl. Transl.).

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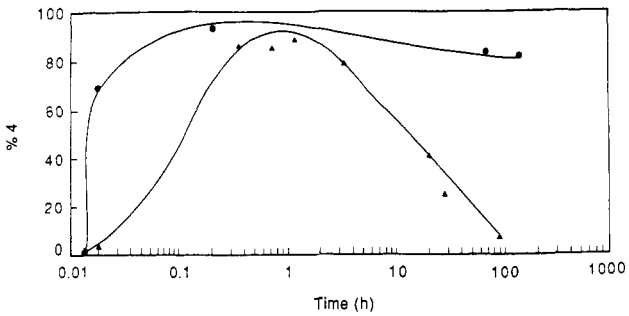


Figure 1. Base hydrolysis of **3**: ●, 2% NaOH/11 equiv of H_2O; ▲, 20% NaOH/11 equiv of H_2O.

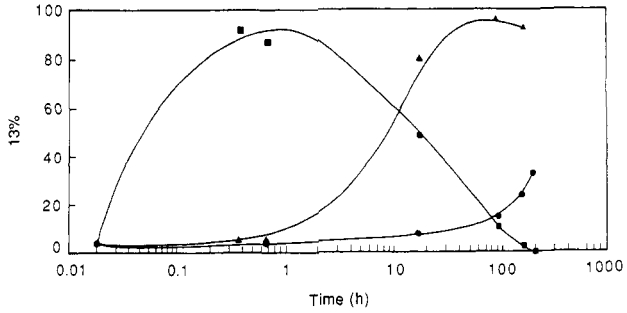


Figure 2. Base hydrolysis of **12**: ●, 2% NaOH/11 equiv of H_2O; ▲, 2% NaOH/55 equiv of H_2O; ■, 20% NaOH/11 equiv of H_2O.

extent to which hydrolysis occurred and therefore which products were isolated.

As expected, bulky groups such as phenyl rings greatly decreased the reactivity of the substrate. When R = phenyl in compound **2**, hydrolysis under acidic or basic conditions still left the ring intact.[10]

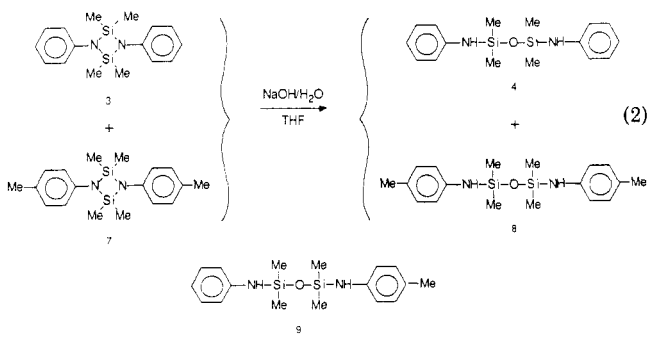
Pursuant to work in this laboratory, we wished to determine the hydrolytic stability of simple cyclodisilazanes under acidic and basic conditions. The results of this investigation follow.

Base Hydrolysis

A 0.01-M solution of **3** in tetrahydrofuran (THF) at room temperature was treated with 2 mol % hydroxide ion (based on 100 mol % or 1 equiv of starting cyclodisilazane) in 11 equiv of water. As observed by gas chromatography (GC), the starting cyclic material disappeared rapidly (<30 min), and a new compound emerged, which was isolated and identified as **4**. This result was unexpected considering the reported activity of Si–N bonds toward hydrolysis.[5] While not stable indefinitely, **4** can be isolated from the reaction mixture before further hydrolysis occurs. Two possible routes for the formation of this product are outlined in Scheme I.

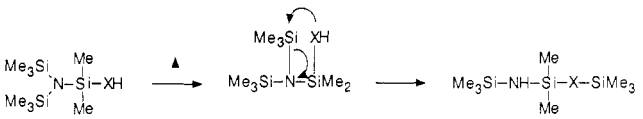
Hydroxide attack at silicon results in ring opening to give intermediate **5**. Compound **5** can be further hydrolyzed by hydroxide ion to give 2 equiv of the aminosilanol **6**, which can self-condense to produce the observed product (path a).

If path a correctly represents the formation mode of **4**, then the hydrolysis of a mixture of two cyclodisilazanes with the same reactivity should form at least some cross-coupled products. To this end, an equimolar mixture of **3** and the methyl-substituted derivative **7** were treated with aqueous hydroxide (eq 2). Analysis of the reaction products showed only clean formation of **4** and **8**. No cross-coupled product **9** was observed.



(2)

Path b of Scheme I illustrates a route that is consistent with the data. After initial ring opening of the cyclodisilazane occurs, deprotonation of the silanol **5** is followed by intramolecular attack of the anion on the distant silicon atom. Rearrangement followed by reprotonation then gives the product. This is similar to a mechanism proposed for the thermal rearrangement of (aminodimethylsilyl)-bis(trimethylsilyl)amine (**10**) and the analogous silanol **11** (eq 3).[11] Cross-coupling experiments with these compounds indicated that silyl migration occurs exclusively in an intramolecular fashion, which is contrary to results reported earlier.[12]

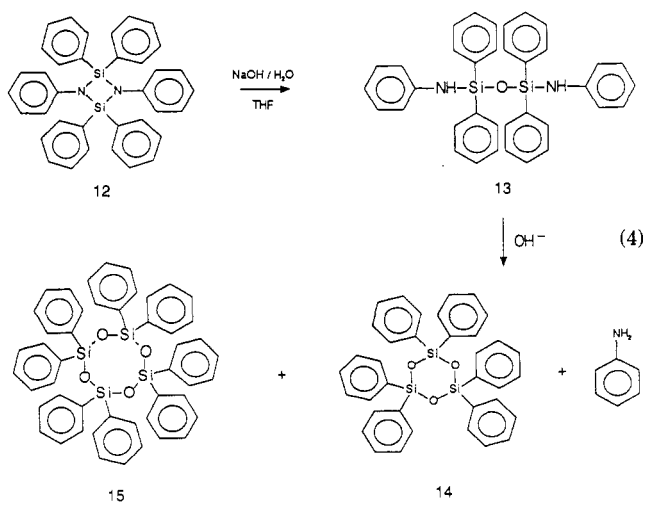


(3)

10 X=NH
11 X=O

The rate of hydrolysis of **3** was relatively insensitive to the concentration of hydroxide ion present. With 2 or 20% hydroxide, loss of starting material was complete within 1 h (Figure 1). However, the rate of decomposition of **4** to form aniline and dimethylsiloxane differed greatly. Figure 1 shows that 80% of **4** is still retained after 1 week in the presence of 2% hydroxide. In contrast, less than 5% of **4** was observed after the same period of time with 20% hydroxide.

To determine if hydrolysis can be retarded by bulky phenyl groups, the hydrolysis of hexaphenylcyclodisilazane **12** was examined (eq 4). With 20% hydroxide, **12** was



(4)

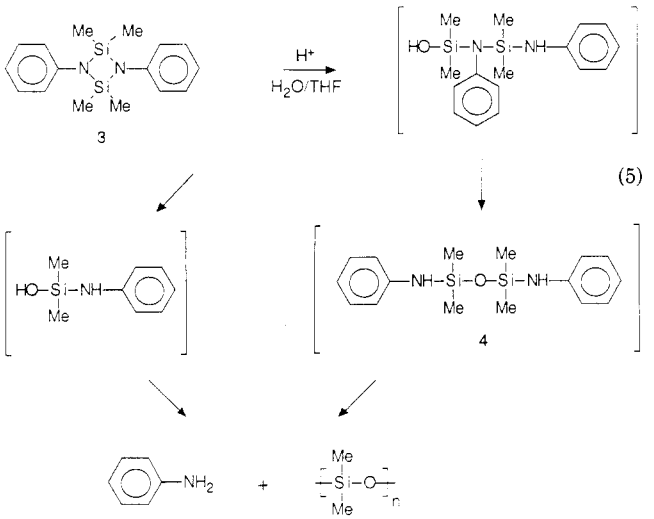
(10) (a) Varezhkin, Y. M.; Zhinkin, D. Y.; Morgunova, M. M.; Anosov, V. P. *Zh. Obshch. Khim.* **1977**, *47*, 1907 (Engl. Transl.). (b) Voronkov, N. G.; Varezhkin, Y. M.; Zhinkin, D. Y.; Morgunova, M. M.; Gurgova, S. N.; Gusev, A. I.; Alekseev, N. V. *Dokl. Akad. Nauk SSSR* **1977**, *237*, 629 (Engl. Transl.).

(11) Bush, R. P.; Lloyd, N. C. *J. Chem. Soc. A* **1969**, 257.

(12) Wannagat, U.; Niederprum, H. *Z. Anorg. Allg. Chem.* **1961**, *308*, 337.

hydrolyzed to **13** at the same rate as **3** was to **4** (Figure 2). The presence of the phenyl groups apparently had little effect on the initial hydrolysis and rearrangement, unlike that reported for basic solutions of **2** when R = phenyl.[10]

In addition, both intermediate hydrolysis products decomposed at the same rate to aniline and their respective siloxane derivatives. The diphenylsiloxane products were the cyclic trimer **14** and tetramer **15** (eq 5), which can be



detected by gas chromatography. The dimethyl derivatives were likely hydroxy-terminated linear oligomers, which were not seen by GC but were observed by ^{1}H NMR.

With 2% hydroxide ion, the hydrolysis of **12** to **13** was much slower. After 4 days, less than 20% of **13** was formed. The hydrolysis can be accelerated if a fivefold increase in water is present at the beginning of the reaction (55 equiv versus 11 equiv). In this case, a maximum of 90% of **13** was formed after 4 days, which then slowly decomposed to aniline and the cyclic trimer and tetramer.

Acid Hydrolysis

Exposure of **3** to aqueous tetrafluoroboric acid (HBF_4) in THF also resulted in very rapid (<1 min) hydrolysis of the starting material. In this acidic medium, aniline and a dimethylsiloxy compound were formed. No intermediate diaminodisiloxane was detected. Once the initial ring opening occurs, the product(s) formed rapidly undergoes further hydrolysis to give the observed products (eq 5). This reaction may produce **4** as an intermediate, but it is too reactive under these conditions to be seen, as was confirmed by the independent hydrolysis of **4** under acidic conditions.

Figure 3 shows that total hydrolysis of **3** occurred within 1 min in the presence of 20% HBF_4 and 11 equiv of water. Even with 6% acid, hydrolysis to aniline was complete in less than 1 h. With 4% acid, complete hydrolysis was slow and with 2% HBF_4 and hydrolysis stopped after slightly less than 50% completion, although it can be induced to continue if an extra 2% catalyst is added. A fivefold increase in water present at the beginning of the reaction (55 equiv versus 11 equiv) was sufficient to promote complete hydrolysis of **3** by 2% HBF_4.

While protonation of cyclodisilazanes has been reportedly difficult,[13] Corriu has reported that Si–N bond cleavage can be accelerated by the presence of fluoride ion.[14] Fluoride could be present in the solution in the form

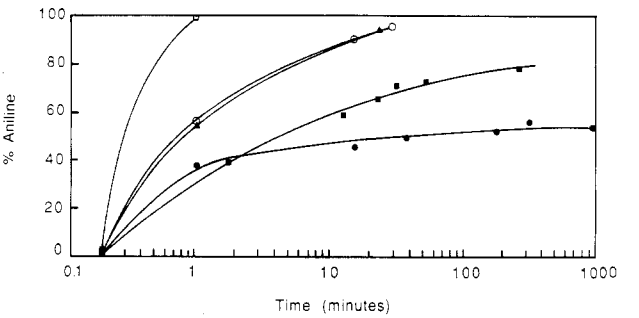


Figure 3. HBF_4 acid hydrolysis of **3**: ●, 2% HBF_4/11 equiv of H_2O; ■, 4% HBF_4/11 equiv of H_2O; ▲, 6% HBF_4/11 equiv of H_2O; □, 20% HBF_4/11 equiv of H_2O; ○, 2% HBF_4/55 equiv of H_2O.

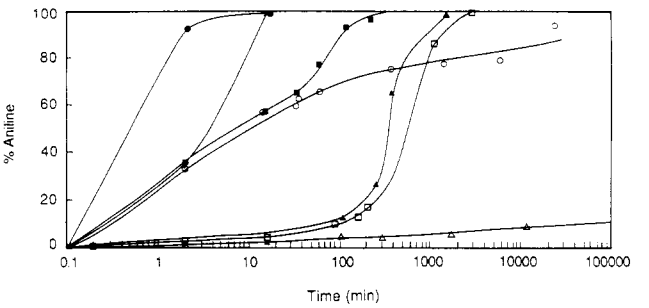


Figure 4. Acid hydrolysis of **3**: ●, 4% HCl/11 equiv of H_2O; ×, 4% Cl_3CCOOH/11 equiv of H_2O; ■, 4% H_2SO_4/11 equiv of H_2O; ▲, 4% $Cl_2CHCOOH$/11 equiv of H_2O; ○, 4% HBF_4/11 equiv of H_2O; □, 4% $ClCH_2COOH$/11 equiv of H_2O; △, 4% H_3CCOOH/11 equiv of H_2O.

of HF which arises through the equilibrium of $HBF_4 \rightleftharpoons BF_3 + HF$.[15] To determine if any rate enhancement occurred during the hydrolysis of **3**, a number of other acid catalysts were examined. Figure 4 summarizes the results.

Hydrolysis occurred most rapidly with the strongest acids, and the rates decreased in the same order as the acid dissociation constants with the single exception of HBF_4. Hydrolyses catalyzed by hydrochloric ($pK < 0$)[17] and trifluoroacetic ($pK = 0.70$)[17] acids were complete in less than 15 min while that catalyzed by sulfuric acid ($pK_1 < 0$, $pK_2 = 1.9$)[17] was a bit slower. With pK values of 2.85[17] and 2.77,[16] respectively, one would expect that chloroacetic acid and HBF_4 would have similar hydrolysis rates if fluoride was not involved. Figure 4 shows that hydrolysis of **3** in the presence of chloroacetic acid is slow while there is very rapid hydrolysis, to about 60% completion, with HBF_4. The rate then slows appreciably which is likely due to the covalent attachment of fluoride to silicon and thus rendering it incapable of accelerating further hydrolysis. The initial rate of hydrolysis of **3** with HBF_4 is also much faster than that with the stronger dichloroacetic acid ($pK = 1.5$).[17] However, after several hours hydrolysis is complete in the presence of dichloroacetic acid and is not with HBF_4.

When **12** was treated with 20% HBF_4, the phenyl-substituted dimer was hydrolyzed much more slowly, as expected, but very little aniline was detected by gas chromatography. Rather, several other products were formed, some of which contained fluorine.

As seen in the hydrolysis of **3**, HBF_4 drastically altered the hydrolysis rate and the same occurred with **12**. Not

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(16) Sudakova, T. N.; Ageev, A. A.; Denisov, D. A.; Krasnoshekov, V. V.; Frolov, Y. G. *Russ. J. Phys. Chem. (Engl. Transl.)* **1978**, *52*, 469.
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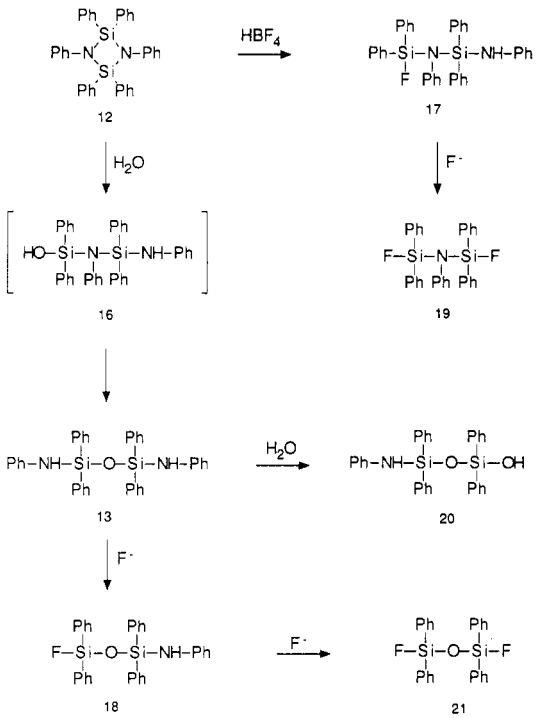
Scheme II



only did the hydrolysis occur more rapidly than in the absence of HBF_4 or fluoride (described later), but there was competition between water and fluoride ion as the nucleophile. This competition was not seen in the HBF_4 hydrolysis of **3** because this much less sterically encumbered dimer allowed rapid attack of water which was present in a concentration at least 50 times greater than that of fluoride. When fluoride ions were deliberately added to **12** in the form of 20% HF, the same products were formed, although more rapidly than with HBF_4.

Scheme II illustrates a plausible pathway for the formation of the identified products. Initially, ring opening by fluoride occurs to produce **17**. This intermediate is then subject to further attack by fluoride-giving compound **19**. Also likely is slow attack by water to give a reactive intermediate **16**, which rapidly rearranges to give **13**. The reaction manifold allows for the formation of compounds **18**, **20**, and **21** by additional reaction with water or fluoride ion. Implied in this scheme are pathways that also lead to cyclic trimer **14**, tetramer **15**, and aniline. With time, levels of **17** and **18** decrease and **19** and **21** increase, indicating **17** and **18** are intermediates in the reaction scheme. There was no evidence for any silicon–phenyl group bond cleavage in these reactions, although such cleavage has been reported in the presence of trifluoromethanesulfonic acid[18] and hydrochloric acid.[19]

All fluorine-containing products can be eliminated if sulfuric, hydrochloric, or trichloroacetic acid is employed as the proton source. In the presence of 20% H_2SO_4 and 55 equiv of water, silazane **12** hydrolyzed very slowly to aniline and the cyclic trimer and tetramer. After 2 weeks, 80% of the starting material was still intact. The bulky phenyl rings effectively retarded attack by water.

Under neutral conditions (no deliberately added acid or base), hydrolysis of **3** with 55 equiv of water proceeded very slowly. After 1 week, greater than 60% of the dimer was intact. Surprisingly, phenyl dimer **12** appeared to hydrolyze a little faster than **3** but still showed approximately the same behavior toward water (Figure 5).

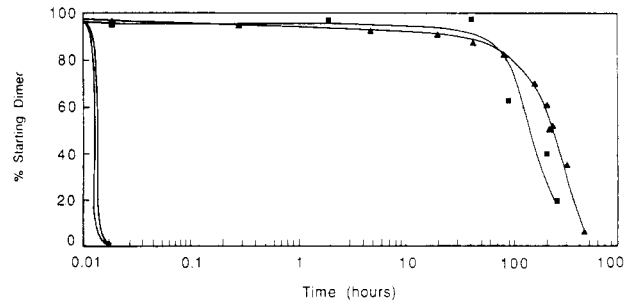


Figure 5. Neutral hydrolyses of **3** and **12**: ▲, 3:55 equiv of H_2O; ■, 12:55 equiv of H_2O; ●, **3**, 20% KF, 55 equiv of H_2O; ×, **12**, 20% KF, 55 equiv of H_2O.

When 20% KF was present under neutral conditions, both **3** and **12** rapidly underwent hydrolysis with 55 equiv of water to give the ring-opened products **4** and **13**, respectively, in less than 1 min (Figure 5). It is interesting to note that about 20% of these ring-opened products also hydrolyzed quickly to aniline and the siloxane derivatives. Further hydrolysis of **4** and **13** was then very slow; comparable to the rate with just water present. This suggests that fluoride activated the silazane rings toward hydrolysis and then competed with water as a nucleophile in further reactions of **4** and **13** to produce aniline. Once the fluoride was consumed, hydrolyses were slow.

Conclusions

These experiments show that the relatively unhindered cyclodisilazane **3** readily undergoes acid- and base-catalyzed hydrolysis in the presence of excess water. Under basic conditions, a diaminodisiloxane intermediate can be isolated from an intramolecular rearrangement. This intermediate slowly hydrolyzes to aniline. In an acidic environment, the dimer hydrolyzes to aniline, with no intermediate detected, at a rate proportional to the strength of the acid. The exception is HBF_4 in which the fluoride ions present accelerate the hydrolysis. Hydrolysis is extremely slow with no catalyst present.

In basic THF solutions, the more sterically congested, phenylated cyclodimer **12** ring opened at rates similar to that of **3** with 20% NaOH and at slower rates with less catalyst. The subsequent reaction to form aniline and cyclic trimer and tetramer was also similar to that of **3**. Acidic solutions of **12** that contained fluoride gave products resulting from both fluoride and water attack. Omission of any fluoride source showed that hydrolysis was extremely slow.

Experimental Section

General Procedures. All reactions were carried out at room temperature (23 ± 1 °C) under a nitrogen atmosphere in prewashed and oven-dried, screw-topped glass vials equipped with a Teflon stirring bar and a Teflon-coated septum. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl. Sodium hydroxide (reagent grade, Eastman Kodak Co.), sulfuric acid (concentrated, reagent grade, J. T. Baker Chemical Co.), tetrafluoroboric acid (49% in water, Kodak), trichloroacetic acid (Kodak), dichloroacetic acid (Kodak), chloroacetic acid (Kodak), glacial acetic acid (Fisher Scientific), and hydrofluoric acid (50% in water, Kodak) were used as received and diluted to the appropriate concentrations. Aniline (Kodak) was distilled before use, and *p*-toluidine (Kodak) and dichlorodimethylsilane (Kodak) were used as received. Reactions were monitored on an HP 5890 gas chromatograph using a 15 m, 0.1-μm DB-5 column (0.32-mm i.d.) and a flame-ionization detector. Helium flow rate through the column was 3.9 mL/min. The GC parameters employed for analysis were as follows: injection port, 250 °C; detector, 300 °C;

(18) Matyjaszewski, K.; Chen, Y. L. *J. Organomet. Chem.* **1988**, *340*, 7.

(19) Eaborn, C. *J. Organomet. Chem.* **1975**, *100*, 43.

temperature ramp from (hold 1 min) to 300 °C (hold 2 min) at 20 °C/min. For the hexaphenylcyclodisilazane, a second ramp of 20 °C/min to 325 °C (hold for 4 min) was employed. Gas chromatography–mass spectroscopy data were obtained on an HP 5987A system using a 15 m, 0.25-μm DB-5 column programmed from 50 to 325 °C at 20 °C/min, holding for 10 min at 325 °C. Electron-impact data were obtained at 70 eV with only the most important ions reported. Molecular ions were confirmed by CI–MS using isobutane as the reagent gas. Proton NMR spectra were recorded on a Nicolet Instrument Corp. QE 300 (300 MHz) spectrometer using chloroform as an internal standard. Infrared spectra were recorded on a Nicolet 60SX spectrometer as KBr pellets or neat films.

Preparation of Starting Materials. *N,N'*-Diphenyltetramethylcyclodisilazane (**3**) was prepared by a literature procedure.[20] The product was recrystallized from toluene as white crystals (32%): mp 250–251 °C (lit. mp 252.5 °C); ^{1}H NMR ($CDCl_3$) δ 0.66 (s, 12, CH_3), 6.66 (d, J = 8.2 Hz, 4, ortho H), 6.82 (t, J = 7.3 Hz, 2, para H), 7.22 (app t, J = 7.5 Hz, 4, meta H); IR (KBr) 3030, 2960, 1595, 1485, 1308, 1260, 960, 900, 800, 755 cm^{-1}; mass spectroscopy, m/z (relative intensity) 298 (70), 284 (26), 283 (100), 267 (5), 210 (6), 149 (14), 134 (9), 73 (9), 43 (10).

N,N'-Di-*p*-tolyltetramethylcyclodisilazane (**7**) was prepared as previously reported.[2b] Recrystallization from hexane gave **7** as white crystals (17%): mp 198–199 °C (lit. mp 196–197 °C); ^{1}H NMR ($CDCl_3$) δ 0.64 (s, 12, CH_3), 2.30 (s, 6, $ArCH_3$), 6.59 (d, J = 8.2 Hz, 4, ortho H), 7.04 (d, J = 8.2 Hz, 4, meta H); IR (KBr) 3020, 2960, 2920, 1615, 1510, 1290, 1255, 960, 900, 815, 790 cm^{-1}.

Hexaphenylcyclodisilazane (**12**) was made by an established procedure[20] and recrystallized from bromobenzene (79%): mp 352–354 °C (lit. mp 355.5 °C); ^{1}H NMR ($CDCl_3$) δ 6.72 (m, 6, ortho and para H on aniline ring), 7.00 (t, J = 7.8 Hz, 4, meta H on aniline ring), 7.45 (t, J = 7.2 Hz, 8, meta H), 7.54 (t, J = 6.1 Hz, 4, para H), 7.90 (d, J = 6.7 Hz, 8, ortho H); IR (KBr) 1600, 1495, 1430, 1300, 1120, 950, 890, 700, 505 cm^{-1}; mass spectroscopy, m/z (relative intensity) 546 (61), 469 (24), 391 (10), 376 (20), 272 (24), 255 (18), 196 (43), 195 (100), 186 (41), 181 (34), 105 (37).

Hydrolysis Reactions. To a dry vial was added the appropriate amount of cyclodisilazane, which was then diluted to 0.01 M with THF. When a homogeneous solution had formed, the prescribed amount of aqueous acid or base was added by microliter syringe with efficient mixing. Aliquots were removed at timed intervals for GC analysis. Retention times (min) of various compounds are as follows: **3** (8.1), **4** (8.3), **7** (8.9), **8** (9.1), **12** (15.0), **13** (15.4), **14** (14.5), **15** (18.8), **17** (14.7), **18** (13.0), **19** (12.6), **20** (13.5), **21** (10.7).

Analytical data on isolated hydrolysis products are as follows.

4: ^{1}H NMR ($CDCl_3$) δ 0.37 (s, 12, CH_3), 3.81 (s, 2, NH), 6.79 (d, J = 7.7 hz, 4, ortho H), 6.84 (t, J = 7.3 Hz, 2, para H), 7.22 (app t, J = 7.8 Hz, 4, meta H); IR (neat) 3380, 3040, 2960, 1605, 1500, 1480, 1385, 1295, 1260, 1050, 905, 835, 805, 755, 695 cm^{-1}; mass spectroscopy, m/z (relative intensity) 316 (6), 224 (25), 223 (100), 208 (54), 150 (5), 148 (4), 134 (5), 132 (4), 120 (3), 91 (4), 73 (4).

8: ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 12, CH_3), 2.33 (s, 6, $ArCH_3$), 3.71 (s, 2, NH), 6.70 (d, J = 8.1 Hz, 4, ortho H), 7.03 (d, J = 8.1 Hz, 4, meta H); IR (neat) 3380, 3040, 3015, 2960, 2880, 1615, 1520, 1440, 1365, 1285, 1260, 1050, 905, 840, 810 cm^{-1}; mass spectroscopy, m/z (relative intensity) 344 (4), 238 (27), 237 (100), 222 31), 164 (4), 148 (4), 132 (4), 107 (5), 106 (5), 77 (3), 73 (7).

13: ^{1}H NMR ($CDCl_3$) δ 4.17 (s, 2, NH), 6.62 (d, J = 7.7 Hz, 4, ortho H), 6.69 (t, J = 7.7 hz, 2, para H), 6.95 (app t, J = 7.7 Hz, 4, meta H), 7.32 (app t, J = 7.5 Hz, 8, meta H), 7.43 (t, J = 7.3 Hz, 4, para H), 7.63 (d, J = 7.2 Hz, 8, ortho H); mass spectroscopy, m/z (relative intensity) 564 (2), 472 (44), 471 (100), 394 (20), 379 (15), 272 (31), 257 (20), 204 (15), 196 (24), 181 (14), 105 (9), 93 (7).

Mass spectral data on other hydrolysis products are as follows.

14: m/z (relative intensity) 594 (6), 516 (9), 440 (44), 439 (100), 362 (21), 317 (13), 219 (31), 197 (20), 181 (26), 154 (19), 77 (14).

15: m/z (relative intensity) 792 (0.5), 714 (2), 637 (12), 559 (33), 439 (10), 318 (7), 280 (83), 241 (100), 180 (9), 154 (8), 77 (7).

17: m/z (relative intensity) 566 (15), 489 (4), 472 (2), 396 (32), 318 (23), 273 (100), 201 (28), 199 (26), 196 (46), 181 (21), 105 (16).

18: m/z (relative intensity) 491 (57), 413 (6), 399 (7), 336 (19), 321 (100), 257 (17), 199 (62), 167 (28), 152 (11), 92 (5), 77 (9).

19: m/z (relative intensity) 493 (31), 416 (4), 338 (13), 273 (100), 259 (31), 210 (17), 199 (15), 181 (12), 168 (12), 47 (8).

20: m/z (relative intensity) 489 (16), 411 (5), 334 (14), 319 (100), 257 (35), 197 (74), 167 (34), 93 (57), 77 (22).

21: m/z (relative intensity) 418 (24), 340 (19), 263 (100), 199 (39), 186 (36), 170 (17), 154 (78), 143 (15), 77 (10), 51 (4).

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