New Skeletally Stabilized Silazanes and Siloxazanes

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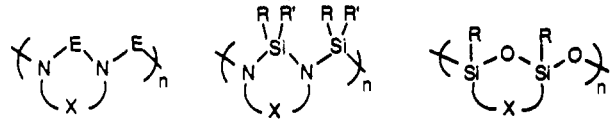
Siladiazoles $C_6H_4(NH)_2SiPh_2$ (**7**) and $C_6H_4(NH)_2SiPhMe$ (**8**) and cyclic siloxazanes $C_6H_4(NHSiPh_2)_2O$ (**9**) and $C_6H_4(NHSiPhMe)_2O$ (**10A/10B**) are obtained from reactions of 1,2-$(NH_2)_2C_6H_4$ with Ph_2SiCl_2, $PhMeSiCl_2$, $(Ph_2SiCl)_2O$, and $(PhMeSiCl)_2O$, respectively. The **8**/$PhMeSiCl_2$/Et_3N reaction produces skeletally stabilized chlorodisilazane diastereomers $C_6H_4(NH)SiPhMe(N)Si(Cl)PhMe$ (**11A/11B**); the latter are quantitatively aminated by *i*-$PrNH_2$ to $C_6H_4(NH)SiPhMe(N)Si(i\text{-}PrNH)PhMe$ diastereomers **13A/13B**. **10A/10B**, **11A/11B**, and **13A/13B** are all formed as 1:1 diastereomer mixtures; there is no evidence for diastereoselectivity in their formation. $PhMeSiCl_2$/$PhMeSi(i\text{-}PrNH)_2$ (**14**)/Et_3N reactions yield the redistribution product $PhMeSi(i\text{-}PrNH)Cl$ (**15**) and no acyclic or cyclic disilazanes. **7–11** and **13–15** were characterized by spectral data (MS, IR, and ^1H and ^{29}Si NMR). **9** was further characterized by X-ray crystallography: orthorhombic, *Fdd*2, a = 18.211 (6) Å, b = 28.344 (11) Å, c = 9.752 (3) Å, V = 5033 (3) Å^3, Z = 8, R = 0.0325, R_w = 0.0416. The absence of diastereoselective silazane and siloxazane formation and the contrast that exists with the formation of structurally analogous phosph(III)azanes are discussed.

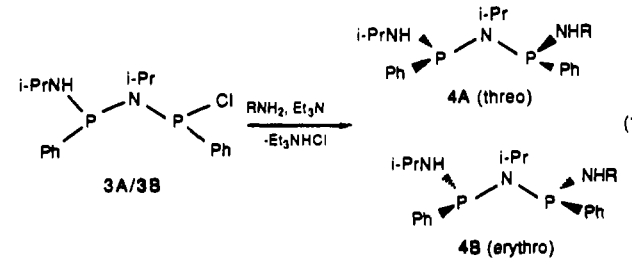
Introduction

New oligomeric and polymeric main-group element azanes (**1**), e.g. phosphazanes (**1A**)[2-4] and borazanes (**1B**),[5] can be stabilized by the introduction of bridging groups (X) between

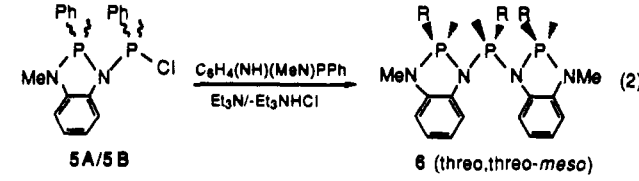


1A, E = PR(lone pair) 1B, E = BR — 2A — 2B

adjacent nitrogen atoms in the azane skeleton. Similar stabilization of silazanes (**2A**) and siloxanes (**2B**) might also be possible, although so far only fragmentary reports of such compounds have appeared.[6,7] An especially interesting feature of phosphazanes (**1A**), silazanes (**2A**; R ≠ R'), and siloxanes (**2B**) is that in each case they could exhibit stereoisomerism and potentially give rise to stereoregular acyclic oligomers/polymers.[8] However, only for the recently reported P(III) diphosphazanes **4** (R = Me, Et, *i*-Pr, *t*-Bu, Ph)[9,10] and triphosphazane **6**,[11] obtained from amination of



3A/3B — 4A (threo) — 4B (erythro) (1)



5A/5B — 6 (threo,threo-*meso*) (2)

chlorodiphosphazanes **3A/3B** and **5A/5B**, respectively, has the diaselective formation of products been shown.

Stereoselection of *erythro* (*meso* if R = *i*-Pr) **4B** occurs; in contrast, **6** forms with opposite (*threo*) stereoselectivity.

Although the synthesis of acyclic and cyclic silazanes[6,8,12-15] and siloxanes[6,8,15-17] has received considerable study, skeletally stabilized analogs have not. Because of the potential for observing

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more general diastereoselectivity and our interest in new classes of silazanes and siloxazanes, we undertook the studies described below.

Experimental Section

Apparatus and Materials. All operations were carried out in N_2-flushed glovebags and standard vacuum-line equipment.[18] ^1H (300 MHz) and ^{29}Si (59.6 MHz) NMR spectra were recorded on Varian Associates Gemini 300 and VXR 300S spectrometers. ^1H and ^{29}Si NMR chemical shifts (+δ = downfield) were measured relative to internal Me_4Si. ^{29}Si NMR experiments were usually performed with gated ^1H decoupling using a 30° pulse width and a 2-s delay.[19] When appropriate, a DEPT pulse sequence was also employed.[20] Infrared and mass spectra were obtained using Mattson FTIR (Polaris) and VG Analytical 7070 EQ-HF spectrometers, respectively. X-ray crystallographic data were collected at room temperature using a Nicolet Analytical Instruments P3/F automated diffractometer (Mo Kα radiation, graphite monochromator). Elemental analyses were performed by Huffman Labs, Golden, CO.

All solvents were freshly distilled and stored over N_2. Et_3N (Baker), i-$PrNH_2$ (Aldrich), and CH_2Cl_2 (Mallinckrodt) were dried over CaH_2 before use. Toluene (Mallinckrodt) was distilled from Na/benzophenone. 1,2-$(NH_2)_2C_6H_4$ (Aldrich) was recrystallized from toluene and then sublimed prior to use. CD_2Cl_2 and benzene-d_6 (Aldrich) and $MePhSiCl_2$, Ph_2SiCl_2, $(MePhSiCl)_2O$, and $(Ph_2SiCl)_2O$ (Petrarch Systems) were used as obtained.

Reactions of 1,2-$(NH_2)_2C_6H_4$. (A) With Ph_2SiCl_2 To Form $C_6H_4(NH)_2SiPh_2$ (7). Ph_2SiCl_2 (3.52 g, 13.9 mmol) was added to a stirred 1,2-$(NH_2)_2C_6H_4$ (1.50 g, 13.9 mmol)/Et_3N (3.03 g, 30 mmol)/CH_2Cl_2 (50 mL) solution at room temperature. After 12 h, the solution was filtered to remove Et_3NHCl. CH_2Cl_2 was removed *in vacuo*. Extraction of the resulting solid with toluene followed by recrystallization from CH_2Cl_2 yielded **7** (yield 70%). Anal. Calcd for $C_{18}H_{16}N_2Si$: mol wt 288.1083. Found: mol wt (EI$^+$, exact mass) 288.1097. MS (EI$^+$): M^+ *m/e*: 288 ($C_{18}H_{16}N_2Si^+$). ^1H NMR (CD_2Cl_2): δ 4.24 (s, area 2; NH), 6.62 (d of m, area 4; phenylene CH), 7.42 (m, area 6; phenyl CH), 7.68 (m, area 4; phenyl CH). ^{29}Si NMR (CD_2Cl_2): δ 11.8. **7** showed significant decomposition (ca. 10%) in toluene solution during 8 h at 25 °C.

Separations of products from the initial 1,2-$(NH_2)_2C_6H_4$/Ph_2SiCl_2 reaction solutions were attempted using flash chromatography.[21] Only $C_6H_4(NHSiPh_2)_2O$ (**9**) (yield 10%) was isolated (see also below).

(B) With $MePhSiCl_2$ To Form $C_6H_4(NH)_2SiMePh$ (8). $MePhSiCl_2$ (1.53 g, 8.0 mmol) in CH_2Cl_2 (5 mL) was added to a stirred 1,2-$(NH_2)_2C_6H_4$ (8.53 g, 7.9 mmol)/Et_3N (2.62 g, 25.9 mmol)/CH_2Cl_2 (45 mL) solution. After 12 h, the gold-colored solution was filtered to remove Et_3NHCl. The CH_2Cl_2 was removed *in vacuo*. Recrystallization from toluene yielded pure **8** (mp 124–131 °C; yield 83%). Anal. Calcd for $C_{13}H_{14}N_2Si$: mol wt 226.0926. Found: mol wt (EI$^+$, exact mass) 226.0931. MS (EI$^+$): M^+ *m/e* 226 ($C_{13}H_{14}N_2{}^{28}Si^+$). ^1H NMR (CD_2Cl_2): δ 0.71 (s, area 3; $SiCH_3$), 3.96 (s, area 2; NH), 6.56 (m, area 4; C_6H_4), 7.4 (m, area 3; phenyl CH), 7.62 (m, area 2; phenyl CH). ^{29}Si NMR (CD_2Cl_2): δ –0.72. IR (KBr, cm^{-1}): 3386 (s), 3364 (s), 1592 (m), 1501 (m), 1429 (m), 1280 (m), 1262 (m), 1124 (s), 1034 (s), 1017 (vs), 996 (s), 874 (w), 789 (s), 748 (s), 732 (s), 699 (m), 484 (w). **8** showed significant decomposition (ca. 10–15%) in toluene solution during 8 h at 25 °C.

(C) With $(Ph_2SiCl)_2O$ To Form $C_6H_4(NHSiPh_2)_2O$ (9). $(Ph_2SiCl)_2O$ (5.59 g, 12.4 mmol) was added to a stirred 1,2-$(NH_2)_2C_6H_4$ (1.24 g, 11.5 mmol)/Et_3N (3.19 g, 31.6 mmol)/CH_2Cl_2 (40 mL) solution. After 6 h, Et_3NHCl was filtered out, CH_2Cl_2 was removed *in vacuo*, and the resulting solid was extracted with toluene. Recrystallization from CH_2Cl_2 yielded yellow crystalline **9** (mp 230–231 °C; yield 45%). Anal. Calcd for $C_{30}H_{26}N_2OSi_2$: C, 74.03; H, 5.38; N, 5.75; mol wt 486.1584. Found: C, 73.70; H, 5.75; N, 5.81; mol wt (EI$^+$, exact mass) 486.1595. MS (EI$^+$): M^+ *m/e*: 486 ($C_{30}H_{26}N_2O^{28}Si_2^+$). MS (CI$^-$) *m/e* (rel int) 485 (51) ($C_{30}H_{25}N_2OSi_2^+$). ^1H NMR (CD_2Cl_2): δ 4.02 (s, area 2; NH), 6.70 (s, area 4; C_6H_4), 7.39 (m, area 12; phenyl CH), 7.71 (m, area 8; phenyl CH). ^{29}Si NMR (CD_2Cl_2): δ –26.2. IR (KBr, cm^{-1}): 3379 (m), 3071 (w), 3052 (w), 3024 (w), 1593 (m), 1496 (s), 1430 (vs), 1378 (vs), 1296 (s), 1223 (w), 1126 (vs), 1111 (vs), 963 (vs), 889 (s), 785 (m), 756 (m), 741 (vs), 719 (s), 696 (vs), 541 (m), 519 (vs).

(D) With $(MePhSiCl)_2O$ To Form $C_6H_4(NHSiMePh)_2O$ (10A/10B). $(MePhSiCl)_2O$ (3.99 g, 12.2 mmol) in CH_2Cl_2 (6 mL) was added to a stirred 1,2-$(NH_2)_2C_6H_4$ (1.27 g, 11.8 mmol)/Et_3N (3.11 g, 30.8 mmol)/CH_2Cl_2 (50 mL) solution at 25 °C. After 12 h, the solution was filtered and CH_2Cl_2 was removed *in vacuo*. The resulting solid was extracted with toluene. Removal of toluene *in vacuo* yields a 1:1 mixture of *meso*- and *d,l*-$C_6H_4(NHSiMePh)_2O$ (**10A/10B**). Repeated recrystallization from toluene yielded crystalline **10A** (mp 121–124 °C; yield 34%). Anal. Calcd for $C_{20}H_{22}N_2OSi_2$: C, 66.25; H, 6.12; N, 7.73; mol wt 362.1271. Found: C, 66.36; H, 6.25; N, 7.71; mol wt (EI$^+$, exact mass) 362.1266. MS (EI$^+$): *m/e* for highest-mass ion 362 ($C_{20}H_{22}N_2OSi_2^+$). ^1H NMR (CD_2Cl_2): δ 0.50 (s, area 6; $SiCH_3$), 3.81 (s, area 2; NH), 6.63 (s, area 4; C_6H_4), 7.39 (m, area 6; phenyl CH), 7.68 (m, area 4; phenyl CH). ^{29}Si NMR (CD_2Cl_2): δ –14.71. IR (KBr, cm^{-1}): 3370 (s), 3060 (m), 3050 (m), 3000 (w), 2995 (w), 2960 (w), 1588 (m), 1393 (s), 1304 (s), 1252 (s), 1119 (s), 978 (s), 915 (s), 826 (s), 781 (s), 741 (s), 719 (s), 704 (s). **10B** could not be obtained pure; however, NMR data were obtained from a **10A/10B** mixture. ^1H NMR (CD_2Cl_2): δ 0.53 (s, area 6; $SiCH_3$), 3.82 (s, area 2; NH), 6.63 (s, area 4; C_6H_4), 7.39 (m, area 6; phenyl CH), 7.68 (m, area 4; phenyl CH). ^{29}Si NMR (CD_2Cl_2): δ –14.66.

Reaction of 8 with $MePhSiCl_2$ To Form $C_6H_4(NH)SiMePhNSi(Cl)MePh$ (11A/11B). $MePhSiCl_2$ (3.51 g, 18.4 mmol) in CH_2Cl_2 (6 mL) was added to **8** (4.18 g, 18.5 mmol) and Et_3N (4.72 g, 46.7 mmol) in CH_2Cl_2 (43 mL). After 48 h, ^1H NMR spectral analysis showed the reaction was complete. The solution was filtered, and CH_2Cl_2 was removed *in vacuo*. The solid was extracted with toluene. Evaporation of toluene yielded a gum, a 1:1 mixture of $C_6H_4(NH)SiMePhNSi(Cl)MePh$ diastereomers (**11A/11B**; 90% yield). Attempts to obtain pure **11A** or **11B** by crystallization, chromatography (thin layer or column flash), or sublimation resulted in decomposition. Anal. Calcd for $C_{20}H_{21}N_2Si_2Cl$: mol wt 380.0932. Found: mol wt (EI$^+$, exact mass) 380.0927. MS (EI$^+$): M^+ *m/e* 382 ($C_{20}H_{21}N_2{}^{28}Si_2{}^{37}Cl$). MS (CI$^+$): *m/e*; 381 ($C_{20}H_{22}N_2{}^{28}Si_2{}^{35}Cl$). ^1H NMR (CD_2Cl_2): δ 0.67 (s, area 3; N_2SiCH_3), 0.69 (s, area 3; N_2SiCH_3), 0.74 (s, area 3; $ClSiCH_3$), 0.75 (s, area 3; $ClSiCH_3$), 3.97 (s, area 2; NH), 6.39–6.72 (s, area 8; C_6H_4), 7.31–7.62 (s, area 20; SiC_6H_5). ^{29}Si NMR (CD_2Cl_2): δ 4.98 (s, area 1; NSiCl), 4.94 (s, area 1; NSiCl), –0.036 (s, area 1; N_2Si), –0.18 (s, area 1; N_2Si). IR (CCl_4, cm^{-1}): 3435 (m), 3070 (m), 3050 (m), 3025 (m), 2962 (w), 2920 (w), 1591 (s), 1489 (vs), 1461 (s), 1429 (s), 1405 (w), 1364 (vs), 886 (vs), 859 (vs), 826 (m), 792 (vs, CCl_4), 732 (vs), 697 (vs), 636 (m), 520 (vs).

Mass spectral data showed minor amounts (<10% of spectral area) of the trisilazane, $C_6H_4[NSi(Cl)MePh]_2SiMePh$ (**12**). Anal. Calcd for $C_{27}H_{28}N_2Si_3Cl_2$: mol wt 534.0937. Found: mol wt (EI$^+$, exact mass) 534.0936. MS (EI$^+$): M^+ *m/e* (rel int) 538 (2.7) ($C_{27}H_{28}N_2Si_3{}^{37}Cl_2$): (CI$^+$): M^+, *m/e* (rel int); 534 (9.2) ($C_{27}H_{29}N_2Si_3{}^{35}Cl_2$).

Reactions of 11A/11B. (A) With i-$PrNH_2$/Et_3N To Form $C_6H_4(NH)SiMePhNSi(i\text{-}PrNH)MePh$ (13A/13B). Excess i-$PrNH_2$ (0.69 g, 11.7 mmol) and Et_3N (0.73 g, 7.2 mmol) were added to a toluene solution (10 mL) of **11A/11B** (1.33 g, 2.48 mmol). After 48 h, Et_3NHCl was filtered out. Removal of toluene *in vacuo* yielded a 1:1 mixture of diastereomers **13A/13B**. Anal. Calcd for $C_{23}H_{29}N_3Si_2$: mol wt 403.1900. Found (EI$^+$, exact mass): mol wt 403.1893. MS (EI$^+$): M^+ *m/e* 404 ($C_{23}H_{30}N_3{}^{28}Si_2^+$). ^1H NMR (CD_2Cl_2): δ 0.40 (s, area 3; $SiCH_3$), 0.44 (s, area 3; $SiCH_3$), 0.74 (s, area 3; $SiCH_3$), 0.79 (s, area 3; $SiCH_3$), 0.83 [d, $^3J_{HH}$ = 5.86, area 3; $CH(CH_3)_2$], 0.88 [d, $^3J_{HH}$ = 6.19, area 3; $CH(CH_3)_2$], 0.98 [d, $^3J_{HH}$ = 6.26, area 3; $CH(CH_3)_2$], 0.99 [d, $^3J_{HH}$ = 6.22, area 3; $CH(CH_3)_2$], 1.26 (s, area 2; *i*-PrN*H*), 2.95 [m, area 2; $CH(CH_3)_2$], 3.93 (s, area 2; NHC_6H_4), 6.3–6.7 (m, area 8; C_6H_4), 7.28–7.41 (m, area 12; C_6H_5), 7.42–7.66 (m, area 8; C_6H_5). ^{29}Si NMR (CD_2Cl_2): δ 2.94 (s, area 1; N_2Si), 2.82 (s, area 1; N_2Si), –16.37 [s, area 1; NSi(*i*-PrNH)], –17.17 [s, area 1; NSi(*i*-PrNH)].

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Table 1. Crystallographic Data for $C_6H_4(NHSiPh_2)_2O$ (**9**)

formula	$C_{30}H_{26}N_2OSi_2$	d_{calcd}, g/cm^3	1.152
fw	486.7	Z	8
space group	*Fdd*2	T, °C	−80
a, Å	18.211(6)	λ(Mo Kα), Å	0.710 73
b, Å	28.344(11)	μ(Mo Kα), cm^{-1}	1.61
c, Å	9.752(3)	R^b	0.033
V, Å^3	5033(3)	R_w	0.042

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] Based on observed data.

(B) With Et_3N. Excess Et_3N was added to a toluene solution of **11A/11B**. No reaction was evident (by ^{29}Si NMR spectroscopy) after 48 h at 25 °C and 72 h at 110 °C.

Reaction of $MePhSiCl_2$ with H_2O To Form $(MePhSiCl)_2O$. H_2O (5.6 μmol) was added to a CD_2Cl_2 solution of $MePhSiCl_2$ (0.124 mmol). The solution was examined by ^{1}H NMR specifically for $(MePhSiCl)_2O$. After 1 h, the ^{1}H NMR spectrum showed two new CH_3 resonances at δ 0.81 and 0.78 (*meso*: *d,l* = 1:1), in agreement with those observed in commercially obtained (Petrarch Systems) $(MePhSiCl)_2O$.

Preparation of $MePhSi(i\text{-}PrNH)_2$ (14). *i*-$PrNH_2$ (8.02 g, 136 mmol) and Et_3N (17.2 g, 170 mmol) in toluene (20 mL) were added to a stirred $MePhSiCl_2$ (11.8 g, 61.7 mmol)/toluene (110 mL) solution at 0 °C. After 6 h, Et_3NHCl was filtered out and toluene was removed *in vacuo*. The resulting oil was distilled (37 °C/0.04 mm) to give pure **14**. Anal. Calcd for $C_{13}H_{24}N_2Si$: C, 66.04; H, 10.23; N, 11.85; mol wt 236.1709. Found: C, 65.55; H, 10.02; N, 10.42, mol wt (EI$^+$, exact mass) 236.1719. MS (EI$^+$): M$^+$ *m/e*: 236 ($C_{13}H_{24}N_2{}^{28}Si^+$). ^{1}H NMR ($C_6D_6$): δ 0.25 (s, area 3; $SiCH_3$), 0.56 (d, J = 10.5 Hz, area 2; NH), 1.00 [d, J = 6.35 Hz, area 6; $CH(CH_3)_2$], 1.04 [d, J = 6.35 Hz, area 6; $CH(CH_3)_2$], 3.13 (d of septets, area 2, J = 10.5 Hz, J = 6.35; CH), 7.23 (m, area 3; phenyl CH), 7.62 (m, area 2; phenyl CH). ^{29}Si NMR (C_6D_6): δ −19.82. IR (neat, cm^{-1}): 3398 (m), 3067 (m), 3050 (m), 2957 (vs), 2927 (s), 2867 (s), 1462, (s), 1428 (s), 1398 (vs), 1378 (vs), 1361 (vs), 1296 (s), 1251 (vs), 1167 (vs), 1126 (vs), 1018 (vs), 883 (vs), 863 (s), 820 (s), 779 (vs), 735 (vs), 702 (vs), 670 (m).

Reaction of $MePhSi(i\text{-}PrNH)_2$ (14) with $MePhSiCl_2$ To Form $MePhSi(i\text{-}PrNH)Cl$ (15). $MePhSiCl_2$ (11.2 g, 58.6 mmol) in toluene (10 mL) was added to a toluene solution (90 mL) of $MePhSi(i\text{-}PrNH)_2$ (13.9 g, 58.8 mmol) and Et_3N (6.0 g, 59 mmol) at 0 °C. The solution was warmed to room temperature. After 15 h, small quantities of Et_3NHCl formed. After 90% of the volatile materials were removed, the ^{1}H NMR spectrum showed resonances due to **14** and $MePhSiCl_2$ (area ratio 1:1) and one at δ 0.45 which was growing in. After 21 h, the ^{29}Si NMR showed three resonances at δ 19.4 ($MePhSiCl_2$), −0.99 (**15**), and −19.9 [$MePhSi(i\text{-}PrNH)_2$] (**14**). After 29 h, the ^{1}H NMR showed complete conversion to $MePhSi(i\text{-}PrNH)Cl$ (**15**). Toluene was removed *in vacuo*. Distillation (43 °C/0.13 mm) yielded clear liquid **15** (yield 86%). Anal. Calcd for $C_{10}H_{16}NSiCl$: C, 56.18; H, 7.54; N, 6.55; mol wt 213.0741. Found: C, 55.82; H, 7.60; N, 6.24, mol wt (EI$^+$, exact mass) 213.0751. MS (EI$^+$): M$^+$ *m/e*, 213 ($C_{10}H_{16}NSi^{35}Cl^+$). MS (CI$^+$): *m/e* 214 ($C_{10}H_{17}NSi^{35}Cl^+$). ^{1}H NMR (CD_2Cl_2): δ 0.59 (s, area 3; $SiCH_3$), 1.08 [d, $^3J_{HH}$ = 6.35 Hz, area 3; $CH(CH_3)_2$], 1.11 [d, $^3J_{HH}$ = 6.35 Hz, area 3; $CH(CH_3)_2$], 1.36 (d, $^3J_{HH}$ = 10.8, area 1; *i*-PrN*H*), 3.14 (d of septets, $^3J_{HH}$ = 10.7 Hz, $^3J_{HH}$ = 6.35 Hz, area 1; $CH(CH_3)_2$], 7.34–7.44 (m, area 3; aryl CH), 7.70–7.74 (m, area 2; aryl CH). ^{29}Si NMR (C_6D_6): δ −0.99. IR (neat, cm^{-1}): 3382 (s), 3072 (s), 3052 (s), 2961 (vs), 2929 (s), 2871 (s), 1591 (m), 1487 (m), 1464 (s), 1429 (vs), 1402 (vs), 1381 (s), 1364 (s), 1299 (s), 1258 (vs), 1167 (vs), 1125 (vs), 1022 (vs), 998 (s), 885 (vs), 822 (s), 788 (vs), 738 (vs), 698 (vs), 678 (vs).

X-ray Structure Analysis of $C_6H_4(NHSiPh_2)_2O$ (9). Crystals of **9** suitable for X-ray analysis were obtained from toluene. Crystals were mounted on a glass fiber and coated with epoxy resin. Crystal data and details of the data collection and structure refinement are summarized in Table 1. Cell parameters were determined on the diffractometer and refined by a least-squares fit to 25 centered reflections in the range 27.2° ≤ 2θ ≤ 35.4°. The structure was solved by direct methods[22] and refined anisotropically, except for the hydrogen atoms, which were included in idealized positions with isotropic thermal parameters. Amine hydrogens were refined into positions corresponding to nitrogen sp^2 hybridization and therefore were included in idealized positions. Final positional parameters for **9** are given in Table 2. Thermal parameters are included in the supplementary material.

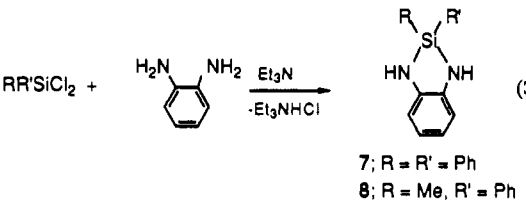
Table 2. Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $C_6H_4(NHSiPh_2)_2O$ (**9**)

	x	y	z	U_{eq}[a]
O(1)	0	0	1058	297 (5)
Si(1)	234(1)	483(1)	238(2)	244(1)
N(1)	−223(1)	492(1)	−1322(3)	297(4)
C(1)	−120(1)	999(1)	1199(3)	271(4)
C(2)	−844(1)	1009(1)	1656(3)	402(6)
C(3)	−1138(1)	1409(1)	2265(4)	477(7)
C(4)	−705(1)	1806(1)	2455(3)	405(6)
C(5)	14(1)	1803(1)	2027(3)	404(6)
C(6)	305(1)	1401(1)	1406(3)	359(6)
C(7)	1245(1)	512(1)	2(3)	278(5)
C(8)	1546(1)	623(1)	−1273(3)	371(5)
C(9)	2301(1)	656(1)	−1460(4)	453(7)
C(10)	2771(1)	583(1)	−366(4)	447(7)
C(11)	2486(1)	472(1)	908(3)	444(7)
C(12)	1732(1)	437(1)	1094(3)	381(6)
C(13)	−118(1)	239(1)	−2549(3)	272(5)
C(14)	−252(1)	456(1)	−3811(3)	350(6)
C(15)	−133(1)	229(1)	−5048(3)	418(7)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results and Discussion

Reactions which form stabilized silazanes that have the potential to form disilazanes diastereoselectively, analogous to those in eqs 1 and 2, have been examined. For these reactions, the siladiazoles **7** and **8** were synthesized from reactions of 1,2-$(NH_2)_2C_6H_4$ with equimolar Ph_2SiCl_2 or $MePhSiCl_2$ in the presence of Et_3N (eq 3). Apparently, only the dimethyl analog,



(3)

7; R = R' = Ph
8; R = Me, R' = Ph

$C_6H_4(NH)_2SiMe_2$, had been reported earlier.[23] **7** and **8** show characteristic ^{1}H NMR resonances for NH, Ph (and Me for **8**), and C_6H_4 protons, mass spectral parent ions at *m/e* 288 and 226, and ^{29}Si resonances[19] at δ 11.8 and −0.72, respectively. **7** and **8** form in 70–85% yields and are best isolated by crystallization. Attempts to separate **7** from its reaction mixture by flash chromatography on silica gel led to isolation of only the cyclic disiloxazane $C_6H_4(NHSiPh_2O)_2O$ (**9**) in low yield (10%) (see below). Both **7** and **8** are somewhat thermally unstable in solution. During 8 h in toluene at 25 °C, both undergo 10–15% decomposition to so-far uncharacterized products.

Reaction of **8** with $MePhSiCl_2$ to form disilazane **11** and the subsequent amination of **11** to **13** (Scheme 1) provide a test of diasteroselectivity, first in a reaction involving condensation formation of the chlorodisilazane (**11A/11B**) (eq 4) and then in one involving amination of the chlorosilyl group of **11A/11B** to form **13A/13B** (eq 5). Reaction of **8** with $MePhSiCl_2$ occurs smoothly to form a 1:1 *erythro/threo* **11A/11B** diastereomer mixture (>90% yield). Under no conditions was there evidence for preferential selection of either isomer. Attempts to separate the **11A/11B** mixture by fractional crystallization or chromatography failed; the latter technique results in complete sample decomposition. Thus **11A/11B** were characterized as a mixture. **11A/11B** show a parent mass spectral ion at *m/e* 380. The ^{29}Si NMR spectrum shows resonances at δ −0.04 and −0.18 for siladiazole silicon atoms and at δ 4.98 and 4.94 for the terminal

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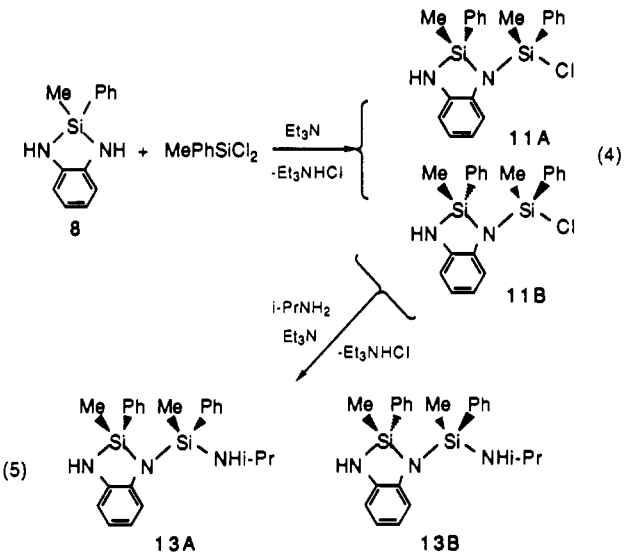
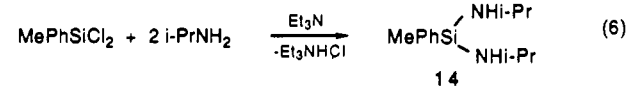
Scheme 1



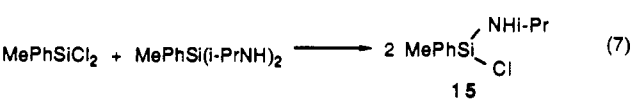
Ph(Me)SiCl groups.[19] Characteristic ^{1}H NMR spectral resonances are observed at δ 0.74 and 0.75 for methyls on the terminal Ph(Me)SiCl groups and and at δ 0.67 and 0.69 for those on the siladiazole rings. Mass spectral analysis of $MePhSiCl_2$/**8** reaction mixtures also showed weak peaks (estimated <10 mol %) which were tentatively assigned to the trisilazane $C_6H_4[NSi(Cl)MePh]_2$-SiMePh (**12**), the product of reaction of **8** with 2 equiv of $MePhSiCl_2$.

Reaction of the **11A/11B** chlorodisilazane diastereomer mixture with *i*-$PrNH_2$ is of interest to compare with those of chlorodiphosphazanes **3A/3B** (eq 1)[9,10] and **5A/5B** (eq 2).[11] In contrast to what occurs with the phosphazanes, no significant diastereoselectivity is seen. Initially, immediately after first addition of *i*-$PrNH_2$, the reaction mixture shows one set of ^{1}H NMR spectral resonances due to either **13A** or **13B**. However, by the time reaction is complete (48 h), essentially quantitative formation of a 1:1 *erythro/threo* diastereomer mixture (**13A/13B**) occurs. Two sets of ^{29}Si NMR resonances are seen at δ 2.94 and 2.82, due to siladiazole silicon atoms, and at δ −16.37 and −17.17, due to Ph(Me)Si(*i*-PrNH)-type silicons. In addition, the two diastereomers show four CH_3–Si groups and two sets of $(CH_3)_2CH$–N resonances in the ^{1}H NMR spectrum.

The $MePhSiCl_2$/*i*-$PrNH_2$and $MePhSiCl_2$/$MePhSi(i\text{-}PrNH)_2$ (**14**) reactions were examined as potential routes to new disilazanes, since it was demonstrated earlier that the analogous $PhPCl_2$/*i*-$PrNH_2$ and $PhP(i\text{-}PrNH)_2/PhPCl_2$ reactions produced **3A/3B** and **4A/4B** in high yields.[9,10] However, neither reaction produced the desired compounds. Reaction of $MePhSiCl_2$ with *i*-$PrNH_2$ in the presence of excess Et_3N ($MePhSiCl_2$:*i*-$PrNH_2$ = 1:2) yields **14** (95%). Similarly, $MePhSiCl_2$/**14** reactions lead

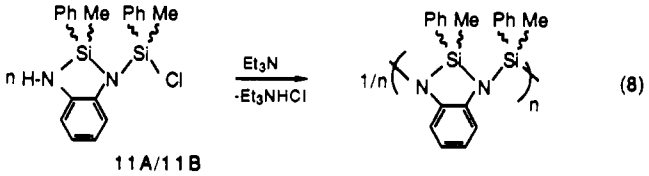


only to redistribution of Cl and *i*-PrNH groups. **15** is the only observed product. Even after 24 h ar 25 °C, no significant



condensation occurs to acyclic[12] or cyclic[7,12] disilazanes. This contrasts with earlier reports on chloro(alkylamino)dialkylsilanes which were found to condense to higher silazanes under mild heating.[24] Although both **14** and **15** apparently are new, analog compounds have been reported.[25,26] Isomeric $MePhSi(n\text{-}PrNH)_2$[25,27] is known and the transaminative redistribution reaction is known to be an excellent route to $R_2Si(R'NH)Cl$ products.[25]

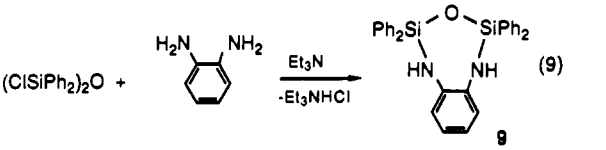
The low tendency of chlorosilazanes to undergo chain extension, compared to that of analogous phosphazanes, is shown further in thermolysis reactions of **11A/11B**. It is known that under ambient-temperature conditions, the chlorodiphosphazanes C_6H_4-(NH)PR(N)PRCl in the presence of Et_3N form oligomers/polymers, including the cyclodimer $[C_6H_4N_2(PR)_2]_2$ (R = Me, Et, Ph)[3] and cyclotrimer $[C_6H_4N_2(PR)_2]_3$ (R = Me).[28] In contrast, **11A/11B** when heated in the presence of excess Et_3N showed no tendency to chain-extend to higher acyclic silazanes, e.g. as in eq 8; even after 72 h at 110 °C, no reaction had occurred.



Clearly, if skeletally stabilized chlorodisilazanes are to be used as precursors in silazane chain extension reactions, either stronger bases for removal of HCl and/or catalytic reaction conditions must be found.

Siloxanes (**2B**) could also show diastereoselected formation, even though it appears that such behavior in simple acyclic systems has not been observed. Interestingly, during chromatographic separation studies of $1,2\text{-}(NH_2)_2C_6H_4/Ph_2SiCl_2$ reaction products, we serendipitously obtained the novel disiloxazane **9**. **9** apparently results from hydrolysis of **7** by the incompletely dried silica column. This product, in which the siloxane skeleton is stabilized by 1,2-$(NH)_2C_6H_4$ units, is prototypical of a system in which diastereoselectivity can be examined.

Siloxazane **9** also forms quantitatively from reaction of $(ClSiPh_2)_2O$ with $1,2\text{-}(NH_2)_2C_6H_4$ (eq 9) and is readily isolated by crystallization. It exhibits the expected MS and NMR spectral



parameters, a M^+ ion at *m/e* 486, a single ^{29}Si resonance at δ −26.2, and characteristic C_6H_4, C_6H_5, and NH ^{1}H NMR spectral resonances. However, unambiguous characterization was obtained by X-ray analysis. The structure of **9** is shown in Figure 1. The structure consists of a seven-membered ring of silicon, oxygen, carbon, and nitrogen atoms; the Si–N, Si–O, and C–N bond lengths around the ring are as expected.[29,30] The six *o*-phenylene ring carbon atoms [C(13)/C(14)/C(15)/C(13A)/C(14A)/C(15A)], the two nitrogen atoms, and the oxygen atom are very close to coplanar; a C_2 rotation axis passes through the O atom and bisects the *o*-phenylene plane. The $C_2N_2Si_2O$ ring

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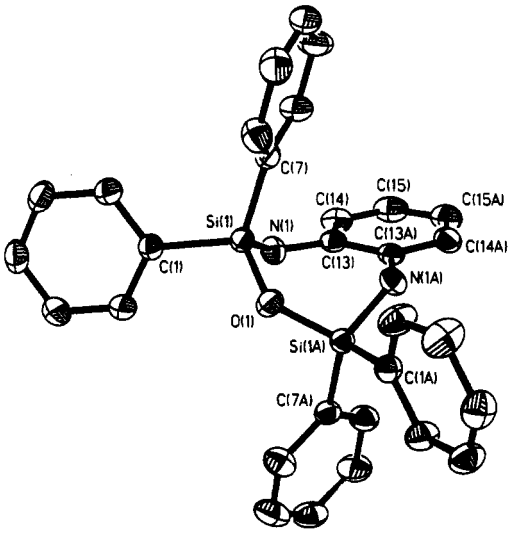


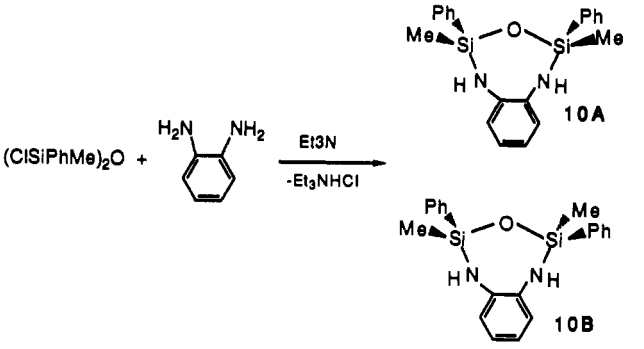
Figure 1. Structure and numbering scheme for $C_6H_4(NHSiPh_2)_2O$ (**9**). Thermal ellipsoids are shown at the 50% probability level.

Table 3. Selected Structural Parameters for $C_6H_4(NHSiPh_2)_2O$ (**9**)

(a) Bond Distances (Å)			
O(1)–Si(1)	1.640(1)	O(1)–Si(1A)	1.641(1)
Si(1)–N(1)	1.734(3)	Si(1)–C(1)	1.853(2)
Si(1)–C(7)	1.858(2)	N(1)–C(13)	1.408(4)
C(13)–C(14)	1.396(4)	C(13)–C(13A)	1.424(4)
C(14)–C(15)	1.384(4)	C(15)–C(15A)	1.385(5)
(b) Bond Angles (deg)			
Si(1)–O(1)–Si(1A)	121.7(1)	O(1)–Si(1)–N(1)	108.4(1)
O(1)–Si(1)–C(1)	108.8(1)	N(1)–Si(1)–C(1)	105.4(1)
O(1)–Si(1)–C(7)	110.8(1)	N(1)–Si(1)–C(7)	111.5(1)
C(1)–Si(1)–C(7)	111.8(1)	Si(1)–N(1)–C(13)	132.3(1)
Si(1)–C(1)–C(2)	120.5(1)	Si(1)–C(1)–C(6)	121.8(2)
Si(1)–C(7)–C(8)	120.7(2)	Si(1)–C(7)–C(12)	121.8(2)
N(1)–C(13)–C(14)	120.2(2)	N(1)–C(13)–C(13A)	121.7(1)
C(14)–C(13)–C(13A)	118.1(1)	C(13)–C(14)–C(15)	122.5(2)
C(14)–C(15)–C(15A)	119.3(1)		

is severely twisted, as shown by the fact that the two silicon atoms are oppositely displaced above and below the C_6N_2O plane and the dihedral angle between the [C(13)/C(13A)/N(1)/N(1A)/O] and [O(1)/Si(1)/N(1)] planes is 53.6°. A significant distortion of each Si atom from one of its attached phenyl rings is seen; Si(1) deviates from the [C(1)/C(2)/C(3)/C(4)/C(5)/C(6)] plane by 0.16 Å.

Compound **9** likely forms from 1,2-$(NH_2)_2C_6H_4$ and $(ClSiPh_2)_2O$ in two steps, with the second condensation step resulting in ring closure. Hence, if the chlorodisilane reactant has two different R groups ($R \neq R'$), a product in two diasteromeric forms is possible and diaselection could occur in the final ring-closure step. However, suprisingly, this type of reaction shows no stereoselection. Reaction of $(ClSiPhMe)_2O$ with 1,2-$(NH_2)_2C_6H_4$ occurs cleanly to form diastereomers **10A** and **10B**



in a 1:1 ratio. **10A/10B** show two sets of methyl resonances (δ 0.50 and 0.53) in the ^1H NMR and two singlet resonances at δ −14.71 and −14.66 in the ^{29}Si NMR spectra. No excess of either diastereomer is evident even at the stage of reaction when product is first seen in the ^1H NMR spectrum.

Why diaselection occurs in phosphazane systems (**4A/4B** and **6**) and not in the analogous silazanes (**13A/13B**) or the new siloxazanes (**10A/10B**) remains unclear. Although isomer equilibration through chain opening and closing could account for this in acyclic systems, this should be inhibited in the skeletally stabilized systems. With the siloxazane **10A/10B**, it may be that intragroup interactions along the skeleton, between the silicon R groups and the electron pairs on oxygen atoms, are not sufficiently important to cause preferential formation of either isomer.

However, the silazanes are structurally more closely akin to the phosphazanes. Typical Si–N bond distances of 1.73[29] are closely similar to the phosphazane P–N distances of 1.68–1.72 Å. In both systems, the skeletal N atoms are likely planar with the lone-pair electrons in an unhybridized p orbital. It is possible that the skeletal nitrogen lone-pair electrons in silazanes are more involved in π_{p-d} bonding with Si in silazanes than they are with P in phosphazanes and as a result are less localized and sterically demanding. Consequently, intragroup interactions along the silazane skeleton are both less and different from those in the phosphazanes. Studies of the factors that influence stereocontrol in azane systems in general are in progress and will be reported later.

Acknowledgment. Support of this work by grants from the National Science Foundation (CHE 8714951) and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Supplementary Material Available: Tables of crystal data and refinement details, anisotropic thermal parameters, hydrogen atom positions, nonessential bond distances and angles, and least-squares planes for **9** (8 pages). Ordering information is given on any current masthead page.