osmium cluster contains a ligand arising from activation of, like in **2**, the vinylic $C_\alpha$–H bond of MAD.[60]

## Conclusions

It has been shown that $Ru_3(CO)_{12}$ reacts thermally with $R^1,R^2$-MAD in a complicated reaction sequence, involving breakdown of the trinuclear cluster and formation of the dinuclear complexes $Ru_2(CO)_6[R^1CH_2CC(H)NR^2]$ (**2**) and $Ru_2(CO)_6[R^1C{=}C(H)CH_2NR^2]$ (**3**; $R^2 \neq$ *t*-Bu), containing a four- and five-membered azaruthenacycle, respectively. Subsequent conversion of these species into the linear tetranuclear cluster $Ru_4(CO)_{10}[R^1C{=}C(H)C(H){=}NR^2]_2$ (**5**) takes place via the air-sensitive intermediate $HRu_2(CO)_5[R^1C{=}C(H)C(H){=}NR^2]$ (**4**), which could be isolated for $R^1$, $R^2$ = $C_6H_5$, *i*-Pr. In the presence of a hydrogen acceptor (MAD, crotonaldehyde), however, thermolysis of **3** ($R^1$ = $CH_3$) results in dehydrogenation of the enyl–amido ligand and $Ru_2(CO)_6[CH_2CC(H)C(H){=}NR^2]$ (**6**) is obtained instead of **5**. For crotonaldehyde this conversion is accompanied by the chemoselective hydrogenation of its olefin moiety. The observed interconversions provide insights into isomerization, dimerization, and hydrogen-transfer reactions of unsaturated substrates taking place on (small) clusters and metal surfaces.

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**Supplementary Material Available:** Tables of complete crystal structure data, all bond lengths and angles, anisotropic thermal parameters of the non-H atoms, and calculated fractional coordinates and the isotropic thermal parameters of the H atoms (5 pages); a listing of structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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# New Azasilatranes: Thermal Conversion of Unusual Azasilatranium Pseudohalides to Neutral 1-(Pseudohalogeno)azasilatranes

J. Woning and J. G. Verkade*

*Department of Chemistry, Iowa State University, Ames, Iowa 50011*

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The azasilatranes $Z\text{–}\overline{Si(NHCH_2CH_2)_3N}$ (**5a**, Z = H; **5b**, Z = Me) react with the weakly electrophilic $Me_3SiN_3$ or $Me_3SiNCS$ to give (among other products) salts, containing equatorially protonated cations of the type $[Z\text{–}\overline{Si(NH_2CH_2CH_2)(NRCH_2CH_2)_2N}]^+$ (**6**, Z = R = H; **10**, Z = H, R = $SiMe_3$; **11**, Z = Me, R = H). The constitution of the crystalline salts is apparently dependent on subtle differences in the crystal-packing forces among the cations, the counterions, and the parent neutral azasilatrane molecules. Thus, cocrystallization of **5a** with cation **6** occurs with $N_3^-$ but not with $SCN^-$ as the counterion, whereas the reverse is true for cocrystallization of **5b** with cation **11**. In the crystal structures of cations **6**[8] and **10**, the $Si\text{–}N_{eq}{}^+H_2$ bond is 10% longer than the other two $Si\text{–}N_{eq}H$ bonds. Furthermore, cation **10** (but not **6**) features a shorter $Si\text{–}N_{ax}$ bond than that in the parent azasilatrane **5a** present in **7**. Also in cation **10**, the $N_{ax}SiH$ fragment is bent significantly away from linearity. When they are heated, **6**($N_3$) in **7** and **10**(NCS) easily undergo elimination of $H_2$ (along with disproportionation in the case of **10**), leading to the new azasilatranes $Z\text{–}\overline{Si(NHCH_2CH_2)_3N}$ (**8**, Z = $N_3$; **13** X = NCS–; **14**, X = –NCS). The IR and $^{13}C$ and $^{29}Si$ NMR spectra are consistent with the presence of five-coordinate silicon in these compounds. The $^{29}Si$ NMR chemical shift values of **8** and, in particular, of **13** appear to be anomalously low, relative to that of 1-chloroazasilatrane, indicating that the electronegativity of the axial substituent X alone cannot solely account for the observed trend in the $\delta(^{29}Si)$ values of these compounds. Compound **8** represents the firt example of a species in which a silicon atom is coordinated by five nitrogen ligands. Compound **10** belongs to the noncentric space group $P2_1$ with $a$ = 9.804 (1) Å, $b$ = 8.2600 (7) Å, $c$ = 13.230 (2) Å, $\beta$ = 99.379 (5)°, and $Z$ = 2.

## Introduction

In comparison with the substitution chemistry of silatranes of type **1a**,[1] that of the isoelectronic azasilatranes **1b** is of much wider scope, owing to the presence in the latter of three $N_{eq}H$ functional groups as well as the Z group. This has resulted in the synthesis of a variety of new azasilatranes,[2] including **2a–d**, in which the strength of the $Si\text{–}N_{ax}$ bond is varied systematically by fine tuning the steric repulsions among the substituents on the silicon and $N_{eq}$ atoms.[3] The weakness of the $Si\text{–}N_{ax}$ bond in **2b** has been reported[3] to render the $N_{ax}$ atom of this com-

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[1] (a) Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Curr. Chem.* **1986**, *131*, 99. (b) Voronkov, M. G.; Dyakov, V. M.; Kirpichenko, S. V. *J. Organomet. Chem.* **1982**, *233*, 1.

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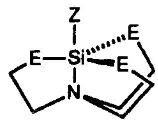
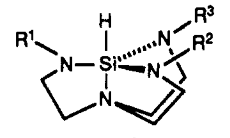
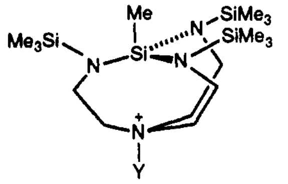


**1a**: E = O
**b**: E = NH



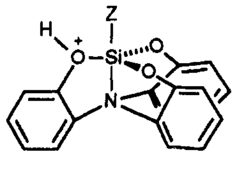
**2a**: $R^1 = R^2 = R^3 = H$
**b**: $R^1 = SiMe_3$, $R^2 = R^3 = H$
**c**: $R^1 = R^2 = SiMe_3$, $R^3 = H$
**d**: $R^1 = R^2 = R^3 = SiMe_3$



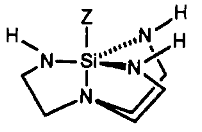
**3a**: Y = $BH_3^-$
**b**: Y = Me

pound sufficiently basic for bonding to $BH_3$ or $CH_3^+$, giving **3a**[4] and **3b**,[3] respectively.

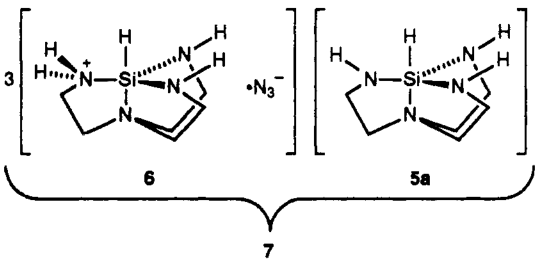
In silatranes and azasilatranes possessing a Si–$N_{ax}$ bond, the quaternary $N_{ax}$ atom should bear some degree of positive charge and hence the $N_{eq}$ atoms should be more basic than $N_{ax}$. Regioselective quaternization of an equatorial ligand should therefore be possible for these compounds. Owing to the low intrinsic basicity of $O_{eq}$ atoms, no electrophile strong enough to accomplish this reaction with silatrane **1a** has been found to give isolable compounds,[1b,5] although an unstable equatorially protonated silatrane species **4** has been postulated to form in a rapid equilibrium with its unprotonated parent, prior to the rate-determining cleavage of the Si–$O_{eq}$ bond in an acid-catalyzed hydrolysis reaction.[6]



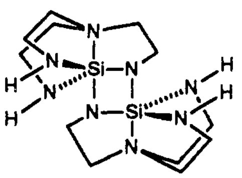
**4**: Z = $C_6H_5$, o-tolyl, p-tolyl



**5a**: Z = H
**5b**: Z = Me
**8**: Z = $N_3$
**13**: Z = –SCN
**14**: Z = –NCS



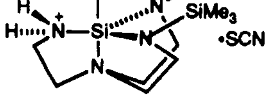
**7**



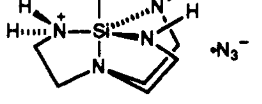
**9**

In view of the greater basicity of the $N_{eq}$ atom relative to that of $O_{eq}$, and the greater Si–$N_{ax}$ bond strength in azasilatranes compared with that of silatranes,[7] attempts were made to quaternize an $N_{eq}$ atom in **5a** with $CF_3SO_3H$ and $CF_3SO_3Me$.[8] However, these attempts resulted in destruction of the atrane cage,[8] presumably because of attack by the $CF_3SO_3^-$ anion on an initially formed equatorially quaternized azasilatrane species. The reaction of **5** with the weakly electrophilic $Me_3SiN_3$, however, afforded the equatorially protonated azasilatrane cation **6**, which was recently isolated and structured by X-ray means in our laboratories as compound **7**, in which **6** and **5a** are cocrystallized.[8] In cation **6** of **7**, the site of protonation is signaled by one Si–$N_{eq}$ bond that is significantly longer (189 pm), compared with the other two Si–$N_{eq}$ bond lengths (169 pm, average) and the Si–$N_{eq}$ bond lengths in the cocrystallized molecule **5a** (173 pm, average). The Si–$N_{ax}$ bond lengths in cation **6** of **7** and in the neutral molecule **5a** of **7** are equal within experimental error. In addition to an $M^+$ peak for cation **6**, the CI mass spectrum of **7**[8] displays weak M + 1 peaks corresponding to the molecular formulas of 1-azidoazasilatrane (**8**, m/e 213) and the dimeric compound **9** (m/e 340), suggesting that one or both of these compounds featuring a silicon atom coordinated by five nitrogen ligands might be prepared by pyrolysis of **7**.

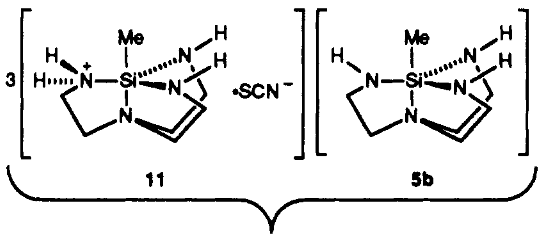
Here we report that the reactions of **5a,b** with the weakly electrophilic $Me_3SiN_3$ and $Me_3SiNCS$ give the new compounds **10–12**. Like **7**, **12** is a cocrystallized mixture of the parent compound and its protonated form. Interestingly, thermolysis of **7** and **10** affords the novel azasilatranes **8** and isomeric **13** and **14**, respectively. Compound **8** is the first reported example of a compound in which silicon is coordinated by five nitrogens. The crystal structure parameters of **7** and **10** are compared, and the FT-IR and $^{13}C$ and $^{29}Si$ MAS NMR spectroscopic data of **7**, **8**, and **10–14** are discussed.



**10**



**11**



**12**

## Experimental Section

All reactions and IR and NMR sample preparations were carried out with strict exclusion of moisture. Solvents were dried by standard methods and distilled under $N_2$ prior to use. $Me_3SiN_3$ and $Me_3SiNCS$ were purchased from Aldrich Chemical Co. and purified by distillation. The starting materials **5a,b** were prepared according to published procedures[2b,9] and purified three times

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**Table I. Assignments of IR Spectra Bands ($cm^{-1}$) of Azasilatranes[a]**

| | 5a | 5b | 7 (6, 5a) | 8 | 10 | 11 | 12 (11, 5b) | 13 |
|---|---|---|---|---|---|---|---|---|
| NH str | 3413 s | 3369 s | 3376 s | 3447 s | 3385 s | 3383 s, 3355 s | 3368 s | 3428 s |
| NH···H str | 3376 m | | 3321 s | 3431 s | 3366 s, 3332 s | 3308 s, 3296 s | 3327 s | |
| $CH_3$ str | 2960 s, 2876 s | 2953 s | 2972 s, 2870 s | | 2963 br | 2961 br | 2949 s | 2972 m, 2903 m |
| $CH_2$ str | 2910 s, 2866 s, 2833 s | 2935 s, 2853 s | 2942 s, 2924 s, 2854 s | 2974 m, 2934 m, 2887 s, 2845 s | 2856 br | 2926 br, 2854 sh, 2802 sh | not resolved | 2935 w, 2839 m |
| overtones | 2779 s to 1733 w (12 peaks) | 2797 s to 1728 w (17 peaks) | 2689 s to 1730 w (12 peaks) | 2780 m, 2680 w, 2037 w | 2700 m to 1800 w (9 peaks) | 2698 s to 1600 w (13 peaks) | 2706 s to 2100 w (7 peaks) | 2781 w, 2691 w, 1734 w |
| N≡N str | | | 2037 vs | 2104 vs | | 2037 vs | | |
| N≡C str | | | | | 2071 vs | | 2062 s | 2104 vs[b] |
| SiH str | 1967 vs | | 2023 vs | | 2010 s | | | |
| NH, $NH_2$ bend | 1600 w (br) | 1580 w | 1601 m | 1600 br | 1603 m | 1603 m, 1568 m | 1612 s | |
| $CH_2$ scissor | 1483 m, 1448 s | 1479 m, 1450 s | 1501 m, 1477 m, 1454 s | 1489 m, 1456 s | 1499 w, 1487 m, 1475 s, 1452 s | 1480 w, 1471 sh, 1450 s | 1488 m, 1470 sh, 1452 s, 1440 sh | 1489 w, 1452 m |
| – | 1398 s | 1414 s[c] | 1404 m, 1375 m | 1398 s | 1406 m | 1422 s, 1379 m[c] | 1408 s, 1373 s[c] | 1402 m |
| $CH_2$ wag | 1355 s, 1302 s | 1358 s, 1313 s, 1300 s | 1352 m, 1312 s | 1354 m, 1298 s | 1366 m, 1354 s, 1327 s, 1302 s | 1370 s, 1360 s, 1317 s | 1360 s, 1355 s, 1313 s (br) | 1354 m, 1304 s |
| $CH_2$ twist | 1256 s, 1204 s | 1265 s, 1231 s, 1207 s | 1259 m, 1245 m, 1313 s | 1252 m, 1199 s | 1283 m, 1260 s,[d] 1213 s, 1205 s | 1250 m, 1244 s, 1221 s | 1250 s, 1215 m, 1182 m | 1254 m, 1204 s |
| $\nu_{10}$(E) | 1148 s | 1153 s | 1147 m | 1144 m | 1148 m, 1134 s | 1151 m, 1134 s | 1151 m | 1142 m |
| $\nu_1(A_1)$ | 1107 s | 1113 s | 1128 m, 1115 s | 1107 s | 1107 s | 1117 s | 1124 s, 1110 s | 1121 m, 1103 s |
| – | 1076 s | 1076 s[d] | 1094 s | 1080 m | 1068 m | 1080 s,[e] 1064 s[e] | 1090 s,[e] 1069 s[e] | 1078 s |
| $\nu_{12}$(E) | 1036 s | 1043 s | 1055 m | 1030 s | 1040 br | 1031 s | 1030 m | 1028 m |
| – | 1011 s | 1009 s | 1028 s, 1015 s | 1015 s | 1010 br | 1016 s | 1013 s, 995 m | 1016 s |
| $\nu_2(A_1)$ | 951 s | 930 s | 974 s | | 976 br | 941 s | 959 br | |
| $\nu_3(A_1)$ | 923 sh | 922 s | 941 s, 922 sh | 930 s | 940 br | 922 s | 925 br | 926 s |
| $CH_2$ rock | 862 s | 887 m, 825 br | 874 s, 860 s, 847 s | 887 w, 812 s (br) | 839 br, 805 m | 897 s, 872 s, 827 m, 809 s | 895 m, 860–810 br | 874, 824 s (br) |
| $\nu_{13}$(E) | 746 s | 779 sh | 787 w, 765 w | | 754 s | 777 sh | 777 m | 781 sh |
| *f* | 685 s | 682 s, 649 s[g] | 713 m, 667 s | 704 m, 679 s | 713 m, 686 m | 713 m, 683 s, 655 sh[g] | 750 m, 681 s, 650 s[g] | 704 m |
| $\nu_4(A_1)$ | 622 s | 621 m | 627 s | 632 m | 625 s | 627 sh, 604 m | 606 m | 623 w |

[a] The spectra (0.1–0.5% of the compound in KBr) were assigned by following the vibrational analysis of analogous compounds in ref 14. [b] The corresponding value for 14 is 2071 $cm^{-1}$ from a comparison of the spectra of 13 and a 2:1 mixture of 13 and 14. [c] $CH_3$ def. [d] Coincident with $(CH_3)_3Si$ def. [e] $CH_3$ rock. [f] The absorptions between 665 and 690 $cm^{-1}$ are probably Si–C str vibrations. [g] Assigned to Si(1)–$CH_3$ str.

by vacuum sublimation at 60 °C and $10^{-3}$–$10^{-4}$ Torr. Solution NMR spectra were recorded on Nicolet NT-300 ($^1H$, $^{13}C$) or Bruker WM-200 ($^{13}C$) instruments, with TMS as the internal standard. Gated decoupling was used to obtain the coupled spectra of **5b** and **13**. For the measurement of solid-state NMR spectra, the spinner was charged with a powdered, polycrystalline sample (50–300 mg), which was then sealed with a threaded Teflon plunger. Spectra were obtained on a Bruker MSL 300 spectrometer under proton decoupling using the CP-MAS technique. A 90° pulse was employed with mixing times for polarization transfer of 1–3 ms for $^{13}C$ and 0.5–3 ms for $^{29}Si$. Spinning rates were 3–4 kHz. Chemical shifts were referenced to external TMS. Mass spectra were recorded on Kratos MS-50 (70 eV EI, high resolution) and Finnigan 4000 (70 eV EI, CI) instruments. Microanalyses were carried out by Schwarzkopf Microanalytical laboratories.

**Compound 7.** The preparation of **7** in $CH_3CN$ as well as the $^1H$ NMR and mass spectroscopic data were reported previously.[8] Anal. (averaged of three C, H, N analyses). Calcd (found, $3\sigma$): C, 35.22 (35.44 ± 0.17); H, 8.25 (8.56 ± 0.24); N, 42.79 (42.79 ± 0.44). Anal. (single Si analysis). Calcd (found): Si, 13.73 (13.44). Compound **7** was also prepared in $CH_2Cl_2$. Anal. (average of three, C, H, N analyses) Calcd (found, $3\sigma$): C, 35.22 (35.05 ± 0.50); H, 8.25 (8.60 ± 0.07); N, 41.79 (41.81 ± 0.26). Anal. (single Si analysis). Calcd (found): Si, 13.73 (13.46). See Tables I and II for IR and NMR data, respectively. Reversal of the order in which the reactants were mixed (i.e., adding the solution of **5b** in $CH_3CN$ to a solution of $Me_3SiN_3$ in $CH_3CN$) did not influence the stoichiometry or properties of the product **7**.

**1-Azidoazasilatrane (8).** Freshly prepared **7** (0.72 g, 0.88 mmol) was molten at ca. 180 °C under $N_2$. Heating was continued (ca. 15 min) until gas evolution ceased. The solid residue was sublimed under vacuum at 60–140 °C and $10^{-3}$ Torr, affording 0.15 g (7.0 mmol, 80%) of crude **8**, contaminated with ca. 5% of $(H_2NCH_2CH_2)_3N$ (tren) as shown by $^1H$ NMR spectroscopy. A second vacuum sublimation at 110–135 °C and $10^{-3}$ Torr afforded 80 mg of pure **8**, mp >275 °C. Anal. Calcd (found): C, 33.78 (33.40); H, 7.09 (7.01); N, 45.96 (44.57); Si, 13.17 (13.41). MS (EI, 70 eV): *m/e* 213.1160 (calcd for $M^+$, 213.11583), 183.0818 (calcd for ($M^+ - H_2C{=}NH_2$), 183.0816), 171.1066 (calcd for ($M^+ - N_3$), 171.1066). $^1H$ NMR ($CDCl_3$): $\delta$ 3.10 t (6 H, $^3J_{HH}$ = 5.92 Hz, $H_2CN_{ax}$), 2.81 t (6 H, $H_2CN_{eq}$), 1.24 (3 H, N$H$). The IR and additional NMR spectra are given in Tables I and II, respectively.

**Compound 10.** $Me_3SiNCS$ (0.7 mL, 4.54 mmol) was added to a solution of 0.71 g (4.12 mmol) of **5a** in 15 mL of $CH_3CN$ at room temperature. The resulting precipitate of crude **10** was dissolved in the mother liquor by heating the latter to the boiling point (82 °C). The hot solution was filtered and cooled slowly to 0 °C, affording pure **10** (as indicated by $^{29}Si$ MAS NMR spectroscopy) as large colorless crystals suitable for X-ray diffraction studies. The crystals were filtered, rinsed with benzene (2 × 3 mL), and dried under vacuum (yield 0.44 g, 29%). The filtrate was refrigerated overnight at ca. −20 °C, affording a second crop (0.15 g, 10%) of **10**, mp 116 °C dec. $^1H$ NMR ($CDCl_3$): $\delta$ 4.42 s (1 H,

**Table II. $^{29}$Si and $^{13}$C NMR Chemical Shifts of Compounds 5a,b, 7, 8, and 10–14[a]**

| | $\delta_{Si}$ (MAS) | | C(3), C(7), C(10) | | C(4), C(6), C(11) | | | |
|---|---|---|---|---|---|---|---|---|
| compd | Si(1) cation | Si(1) neutral | $\delta_C$ (MAS) | $\delta_C$ ($CDCl_3$) | $\delta_C$ (MAS) | $\delta_C$ ($CDCl_3$) | $\delta_C$ $H_3CSi(1)$ | $\delta_C$ (MAS) SCN |
| **5a** | | −84.7 | | 36.08 | | 50.89 | | |
| **5b** | | −69.9 | | 36.23[c] | | 49.79[e] | 2.12[g] | |
| **7 (6, 5a)** | −86.3 | −83.0 | 35.3 | | 47.9,[i] 51.4 | | | |
| **8** | | −92.4 | 35.3 | 36.74 | 47.9,[i] 51.4 | 50.90 | | |
| **10**[b] | −84.7 | | 36.9 | | 50.9 | | | 130.1 |
| **11** | −64.6 | | 35.9 | | 48.1,[i] 52.2 | | 4.28[h] | |
| **12 (11, 5b)** | −66.7 | −66.0 | 35.9 | | 51.4 | | 5.39,[i] 11.6[i] | 129.5 |
| **13** | | −97.0 | 36.8 | 36.52*d* | 50.5 | 51.09[f] | | 129.5 |
| **14** | | −85.6 | | 36.10 | | 50.94 | | 129.4 |

[a] Referenced to TMS. [b] $\delta_{Si}(SiMe_3)$ = 7.67 and 8.11 ppm in intensity ratio 1:1 ($^{29}$Si MAS NMR). [c] $^1J_{CH}$ = 134.6 Hz. [d] $^1J_{CH}$ = 135.2 Hz. [e] $^1J_{CH}$ = 138 Hz. [f] $^1J_{CH}$ = 139 Hz. [g] In $CDCl_3$. [h] In the solid state. [i] Solid-state spectrum with an intensity ratio of 3:1 corresponding to values for the cation and the neutral molecule. [j] Shoulder on major peak.

Si*H*), 2.98 t (broad, 4 H, $^3J_{HH}$ = 5.9 Hz, $H_2C(6)$, $H_2C(11)$), 2.93 t ($H_2C(3)$), 2.89 t (broad, 4 H, $H_2C(4)$, $H_2C(7)$), 2.82 t (broad, 2 H, $^3J_{HH}$ = 5.7, $H_2C(3)$), 0.12 s (18 H, $Si(CH_3)_3$). MS (CI–$NH_3$): *m/e* 317 ($M^+$ (of cation), 30%), 315 ($M^+ - 2$, 6%), 245 ($M^+ - 72$ ($Me_3SiCH_2$), 16%), 173 ($M^+ - 144$, 100%. MS (EI, 70 eV): *m/e* 315 ($M^+$ (of cation) − 2, 25%), 243 ($M^+ - 72$, 13%), 171 ($M^+ - 144$, 100%). See Tables I and II for IR and additional NMR spectra, respectively.

**Compound 11.** Crystalline **11** was prepared from **5b** (900 mg, 4.83 mmol) and $Me_3SiN_3$ (0.7 mL, 5 mmol) in $CH_3CN$ (18 mL) according to the procedure described for **7**:[8] yield 60%; mp 165–170 °C dec. Anal. Calcd (found): C, 36.66 (37.64); H, 8.35 (8.41); N, 42.75 (40.95); Si, 12.24 (12.83). MS (CI–$NH_3$): *m/e* 187 ($M^+$ (of cation), 100%). MS (EI, 70 eV): *m/e* 186 ($M^+$ (of cation) − 1, 2.6%), 171 ($M^+$ − 16 ($CH_4$), 100%). 156 (5.4%), 128 (12%), 101 (11%), 59 (27%), 58 (11%). $^1$H NMR ($CDCl_3$): δ 3.00 t (6 H, $^3J_{HH}$ = 5.9 Hz, $H_2CN_{ax}$), 2.72 t (6 H, $H_2CN_{eq}$), 2.25 s (broad, 4 H, N*H*, N$H_2$). 0.25 s (3 H, $H_3CSi$). See Tables I and II for IR and NMR data, respectively.

**Compound 12.** Crystalline **12** was prepared in 55% yield from 0.57 g (3.1 mmol) of **5b** and 0.52 mL (3.4 mmol) of $Me_3SiNCS$ in 12 mL of $CH_3CN$ according to the procedure described for **10**; mp 113–116 °C dec. MS (CI–$NH_3$): *m/e* 187 ($M^+ + 1$ (neutral) or $M^+$ (cation), 100%). MS (EI, 70 eV): *m/e* 186 ($M^+$ (neutral) or $M^+ - 1$ (cation), 2.9%), 171 ($M^+$ (neutral) − 15 ($CH_3$) or $M^+$ (cation) − 16 ($CH_4$), 100%), 156 (5.5%), 128 (12%), 101 (11%), 59 (35%), 58 (12%). $^1$H NMR ($CDCl_3$): δ 3.00 t (6 H, $^3J_{HH}$ = 5.9 Hz, $H_2CN_{ax}$), 2.70 t (6 H, $H_2CN_{eq}$), 2.5 s (broad, 4 H, N*H*, N$H_2$), 0.30 s (3 H, $H_3CSi$). See Tables I and II for IR and additional NMR data, respectively.

**1-(Thiocyanato)azasilatrane (13).** A freshly prepared sample of **10** (0.57 g, 1.5 mmol) was heated at 140 °C for 15 min. The resulting residue was freed from volatile liquids by vacuum distillation of the liquids into a cold trap and then sublimed under vacuum ($10^{-3}$ Torr) at 110–150 °C to give pure **13**: yield 33%; mp >200 °C. MS (EI, 70 eV): *m/e* 229.0818 (calcd for $M^+$, 229.08175), 199.0473 (calcd for $M^+ - H_2C{=}NH_2$, 199.04736), 187.0467 (calcd for $M^+ - CH_3CNH$, 187.0474), 171.1053 (calcd for $M^+$ − SCN, 171.1066). $^1$H NMR ($CDCl_3$): δ 3.08 t (6 H, $^3J_{HH}$ = 5.92 Hz, $H_2CN_{ax}$), 2.81 t (6 H, $H_2CN_{eq}$), 1.31 s (3 H, N*H*). See Tables I and II for IR and additional NMR data, respectively. The volatile liquid collected in the cold trap consisted of essentially pure $Me_3SiNCS$ (δ(H) 0.31 ppm (lit.[10] 0.33 ppm)).

**Compound 14.** When the preparation of **13** was attempted with an older, partially decomposed sample of **10** (50% as judged by $^1$H NMR spectroscopy), a 2:1 mixture of **13** and **14** was isolated in poor (5–10%) yield. The high-resolution mass spectrum of the mixture is identical, within the experimental error, with that of **13**. For the $M^+$ peak of **13** (**14**) in the mixture, *m/e* 229.0820 (calcd 229.08175) was found. By comparison of the $^1$H NMR spectrum of the mixture with that of pure **13**, the following peaks could be assigned to **14**: δ 3.03 t (6 H, $^3J_{HH}$ = 5.95 Hz, $H_2CN_{ax}$), 2.78 t (6 H, $H_2CN_{eq}$); IR (KBr, $cm^{-1}$) 2073 s (C≡N stretch of NCS). See Table II for $^{13}$C and $^{29}$Si NMR data.

**Table III. Crystal Data for $HSi(H_2NCH_2CH_2)(Me_3SiNCH_2CH_2)_2N \bullet SCN$ (10)**

| | |
|---|---|
| formula | $[C_{12}H_{33}N_4Si_3][NCS]$ |
| fw | 375.76 |
| space group | $P2_1$ |
| *a*, Å | 9.804 (1) |
| *b*, Å | 8.2600 (7) |
| *c*, Å | 13.230 (2) |
| β, deg | 99.379 (5) |
| *V*, Å$^3$ | 1057.0 (2) |
| *Z* | 2 |
| $d_{calcd}$, g/cm$^3$ | 1.181 |
| cryst size, mm | 0.27 × 0.38 × 0.70 |
| μ(Mo Kα), cm$^{-1}$ | 3.174 |
| data collecn instrument | Enraf-Nonius CAD4 |
| radiation (monochromated in incident beam) | Mo Kα (λ = 0.71073 Å) |
| orientation rflns: no.; range (2θ), deg | 25; 21.4–32.3 |
| temp, °C | −20 |
| scan method | θ–2θ |
| data collecn range, 2θ, deg | 4–55 |
| no. of data collected | 5249 |
| unique data: total no.; no. with $F_o^2 > 3\sigma F_o^2$ | 2588; 2390 |
| no. of parameters refined | 211 |
| $R^a$ | 0.024 |
| $R_w^b$ | 0.033 |
| quality-of-fit indicator[c] | 1.12 |
| largest shift/esd, final cycle | 0.01 |
| largest peak, e/Å$^3$ | 0.20 (4) |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit = $[\sum w(|F_o| - |F_c|^2/(N_{observns} - N_{params})]^{1/2}$.

**Crystal Structure Determination of 10.** A block-shaped colorless crystal of the title compound was cleaved from a larger crystal and mounted on the end of a glass fiber with its long axis approximately parallel to the ψ axis of the diffractometer. The crystal was then moved to the diffractometer and slowly cooled to −20 °C. The cell constants were determined from a list of reflections found by an automated searh routine. Pertinent data collection and reduction information is given in Table III. The intensities of three standards varied only within the errors of the measurements. Azimuthal scans of several reflections having χ near 90° indicated that no absorption correction was necessary.

Absences indicated that the space group was either $P2_1/m$ or its noncentric counterpart $P2_1$. Intensity statistics favored the noncentric group, as did the expected formula and value of *Z*. Successful solution and refinement confirmed the choice of $P2_1$. Direct methods produced peaks corresponding to all 22 non-hydrogen atoms.[11a] Following anisotropic least-squares refinement of all of the non-hydrogen atoms, a difference map was calculated with only those reflections for which (sin θ)/λ < 0.50. Peaks

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(10) Pouchert, C. J. *The Aldrich Library of NMR Spectra*, 2nd ed.; Aldrich: Milwaukee, WI, Vol. 2, p 1003C.

(11) (a) Sheldrick, G. M. SHELXS-86; Institut für Anorganische Chemie der Universität, Göttingen, FRG, 1986. (b) Neutral-atom scattering factors and anomalous scattering corrections were taken from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV. (c) Enraf-Nonius Structure Determination Package; Enraf-Nonius: Delft, Holland.

**Table IV. Positional Parameters and Their Estimated Standard Deviations for $\overline{\mathrm{HSi(H_2NCH_2CH_2)(Me_3SiNCH_2CH_2)_2N}}\bullet\mathrm{SCN}$ (10)**

| atom | $x$ | $y$ | $z$ | $B$,[a,b] Å$^2$ |
|---|---|---|---|---|
| Si(1) | −0.77112 (5) | 0.58285 (7) | 0.24486 (3) | 1.960 (8) |
| Si(2) | −1.06294 (5) | 0.52001 (8) | 0.30179 (4) | 2.611 (9) |
| Si(3) | −0.75136 (5) | 0.48174 (8) | 0.02825 (4) | 2.58 (1) |
| N(1) | −0.6978 (2) | 0.8117 (2) | 0.2854 (1) | 2.22 (3) |
| N(2) | −0.9202 (2) | 0.6416 (2) | 0.2889 (1) | 2.34 (3) |
| N(3) | −0.7218 (2) | 0.6245 (2) | 0.1278 (1) | 2.44 (3) |
| N(4) | −0.6294 (2) | 0.5207 (2) | 0.3546 (1) | 2.58 (3) |
| C(1) | −0.9292 (2) | 0.8089 (3) | 0.3258 (2) | 3.28 (4) |
| C(2) | −0.8246 (2) | 0.9115 (3) | 0.2829 (2) | 3.04 (4) |
| C(3) | −0.6797 (2) | 0.7893 (3) | 0.1063 (2) | 3.03 (4) |
| C(4) | −0.6143 (2) | 0.8635 (3) | 0.2074 (2) | 2.78 (4) |
| C(5) | −0.5310 (2) | 0.6507 (3) | 0.3953 (2) | 2.99 (4) |
| C(6) | −0.6146 (2) | 0.8050 (3) | 0.3893 (2) | 2.72 (4) |
| C(7) | −1.2115 (2) | 0.5687 (5) | 0.1994 (2) | 4.66 (6) |
| C(8) | −1.0221 (3) | 0.3002 (4) | 0.2983 (2) | 4.96 (6) |
| C(9) | −1.1175 (2) | 0.5646 (4) | 0.4274 (2) | 4.23 (5) |
| C(10) | −0.9395 (3) | 0.4418 (4) | −0.0103 (2) | 4.52 (6) |
| C(11) | −0.6860 (3) | 0.5631 (5) | −0.0857 (2) | 5.93 (7) |
| C(12) | −0.6633 (3) | 0.2873 (4) | 0.0675 (2) | 5.73 (7) |
| S | −0.28022 (5) | 0.000 | 0.40853 (4) | 3.47 (1) |
| N(5) | −0.4497 (2) | 0.2503 (3) | 0.3341 (2) | 4.53 (5) |
| C(13) | −0.3753 (2) | 0.1478 (3) | 0.3643 (2) | 2.88 (4) |
| H(1) | −0.815 (2) | 0.425 (4) | 0.226 (2) | 1.2 (5)* |
| H(2) | −0.584 (3) | 0.438 (5) | 0.332 (2) | 3.0 (7)* |
| H(3) | −0.675 (3) | 0.493 (4) | 0.399 (2) | 2.2 (6)* |

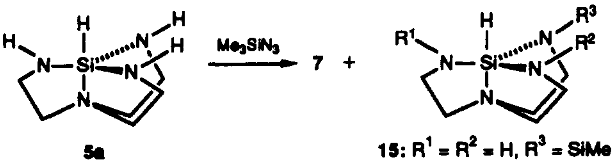
[a] Starred values denote atoms refined isotropically. [b] Anisotropically refined atoms are given the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

corresponding to all of the expected hydrogen atoms were located in the map; however, parameters were added to the least-squares calculations for only the hydrogen atom bound to the central Si atom and the two hydrogen atoms bound to atom N(4). All other hydrogen atoms were placed in idealized positions and used for the calculation of structure factors with C–H distances fixed at 0.95 Å and isotropic $B$ values set equal to 130% of that for the corresponding carbon atom. Refinement of the enantiomorph resulted in no change in the agreement factors and no significant structural changes; therefore, the absolute configuration was not determined.

Refinement calculations were performed on a Digital Equipment Corp. MicroVAX II computer using the CAD4-SDP programs.[11b,c] The positional parameters appear in Table IV, and pertinent bond distances and angles are collected in Table V.

## Discussion

**Formation, Thermolysis, and Structures of 7 and 10.** As was described earlier,[8] 7 is formed by a pathway in which trimethylsilylation of equatorial nitrogens of **5a** (resulting in **15–17**) liberates $HN_3$, which then protonates **5a**, giving **7** (reaction 1). Compound **10** is formed in a similar reaction, except that the crystalline product is a single species representing the protonation of **5b** as well as its bis(trimethylsilyl)ation.

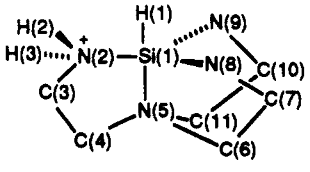


(1)

**5a**

**15**: $R^1 = R^2 = H$, $R^3 = SiMe_3$
**16**: $R^1 = H$, $R^2 = R^3 = SiMe_3$
**17**: $R^1 = R^2 = R^3 = SiMe_3$

Selected structural data for 7 and 10 are presented in Table V, and the ORTEP drawing for 10 is shown in Figure 1. For the numbering of the atoms in these compounds, see the generalized structure



N(2), N(8), N(9) = $N_{eq}$
C(4), C(6), C(11) = $C(N_{ax})$
N(5) = $N_{ax}$

Owing to the simplicity of the unit cell of 10 relative to that of 7, the hydrogen atoms at the protonation site N(2) and at the Si(1) atom of 10 could be located. In agreement with the structural assignment proposed[8] for cation 6, for which the hydrogens could not be located, the Si(1)–N(2)

**Table V. Selected Structural Data for 10, 6 (in 7), and 5a (in 7)**

| | 10[a] | 6 (in 7)[b] | 5a (in 7)[b] |
|---|---|---|---|
| Average Bond Distances (Å) | | | |
| Si(1)–H(1) | 1.38 (3) | | |
| Si(1)–$N_{ax}$ | 2.062 (2) | 2.087 (6) | 2.080 (6) |
| Si(1)–N(2) | 1.909 (2) | 1.89 (1) | 1.747 (6) |
| Si(1)–N(8) | 1.731 (2) | 1.728 (8) | 1.773 (6) |
| Si(1)–N(9) | 1.729 (2) | 1.690 (7) | 1.773 (6) |
| N(2)–C(3) | 1.484 (3) | 1.53 (1) | 1.48 (1) |
| $N_{eq}$–C(7),C(10) | 1.468 (7) | 1.46 (2) | 1.47 (2) |
| C(3),C(7),C(10)–$C_{eq}$ | 1.512 (4) | 1.51 (1) | 1.51 (3) |
| $C_{eq}$–$N_{ax}$ | 1.483 (5) | 1.49 (2) | 1.48 (1) |
| Si(1) to plane of $N_{eq}$ | 0.166 (1) | 0.183 (1) | 0.179 (2) |
| $N_{ax}$ to plane of $C_{eq}$ | 0.427 (1) | 0.515* | 0.455* |
| Average Bond Angles (deg) | | | |
| H(1)–Si(1)–N(2),N(8) | 94 (2) | | |
| H(1)–Si(1)–N(9) | 99 (1) | | |
| H(1)–Si(1)–$N_{ax}$ | 175 (1) | | |
| $N_{ax}$–Si(1)–N(2) | 82.5 (1) | 84.3 (3) | 84.3 (2) |
| $N_{ax}$–Si(1)–N(8)–N(9) | 85.6 (8) | 83.9 (3) | 84.1 (2) |
| N(2)–Si(1)–N(8) | 117.3 (1) | 116.8 (3) | 118.9 (3) |
| N(2)–Si(1)–N(9) | 111.7 (1) | 111.7 (7) | 119.3 (3) |
| N(8)–Si(1)–N(9) | 128.4 (1) | 128.4 (5) | 118.7 (3) |
| Si(1)–N(2)–C(3) | 115.5 (2) | 113.5 (8) | 120.3 (3) |
| Si(1)–$N_{eq}$–C(7),C(10) | 118.8 (7) | 121.5 (14) | 118.8 (7) |
| $N_{eq}$–C(3),C(7),C(10)–$C_{eq}$ | 107.4 (13) | 107.3 (12) | 106.9 (12) |
| C(3),C(7),C(10)–$C_{eq}$–$N_{ax}$ | 107.2 (3) | 107.4 (9) | 107.6 (10) |
| $C_{eq}$–$N_{ax}$–$C_{eq}$ | 112.1 (3) | 112.0 (8) | 111.7 (10) |
| $C_{eq}$–$N_{ax}$–Si(1) | 106.7 (25) | 106.8 (14) | 107.1 (7) |

[a] This work. [b] Reference 8.

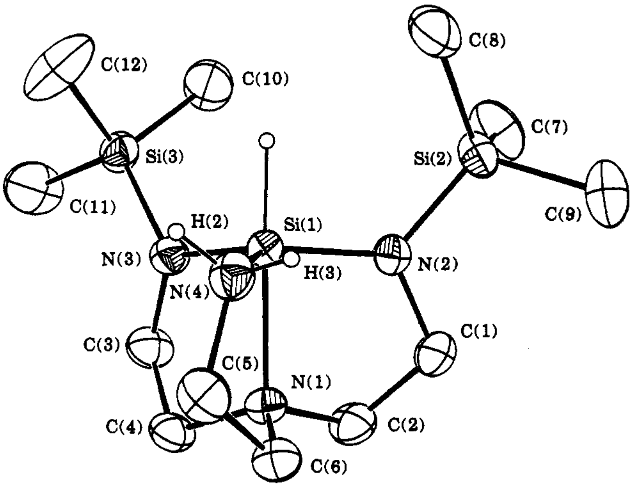
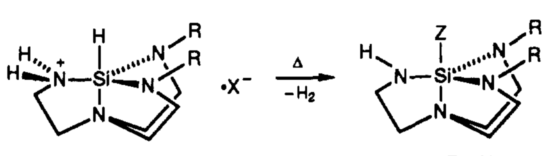


Figure 1. ORTEP drawing of 10, with ellipsoids drawn at the 50% probability level.

bond in **10** is indeed observed to be significantly longer than the two other Si(1)–$N_{eq}$ bonds in this cation and also longer than all three of the Si–$N_{eq}$ bonds in the parent **5a**, which cocrystallized with **6** in compound **7**. As can also be seen in Table V, protonation of an $N_{eq}$ atom of azasilatrane **5a** has a profound effect on the $N_{eq}$–Si(1)–$N_{eq}$ angles. In cation **6**, the N(8)–Si(1)–N(9) bond angle, opposite to the protonation site, is ca. 9° larger than in **5a**, the N(2)–Si(1)–N(9) bond angle is ca. 7° smaller than in **5a**, and the N(2)–Si(1)–N(8) bond angles are equal within experimental error. Since the C–$N_{ax}$–C angles in **5a** and **6** are equal within experimental error, the main structural distortion occurring upon protonation of **5a** to **6** is a framework deformation, involving a ca. 9° rotation of the Si(1)–N(9) bond around the pseudo-3-fold axis of **5a** toward the Si(1)–N(2) bond, combined with simultaneous torsion of the N(9)–C(10) and C(10)–C(11) bonds. The observation that all three $N_{eq}$–Si(1)–$N_{eq}$ bond angles in cations **6** and **10** are identical within experimental error suggests that this type of cage deformation may originate from rehybridization and redistribution of electron density induced by the protonation of $N_{eq}$, rather than from steric repulsion between the substituents at N(8) and N(9) or from differences in the packing of the lattices of **7** and **10**.

As seen in Table V, the H(1)–Si(1)–$N_{ax}$ fragment in **10** is slightly, though significantly, bent. The extent of this bending in **10** appears to be greater than in 1-phenylazasilatrane, in which the $N_{ax}$–Si(1)–$C_{ax}$ bond angle formed by the Si(1) atom and the two axial substituents is 177.5 (2)°.[7a] It is interesting to notice that the spatial orientation of the $N_{ax}$–Si(1)–H(1) plane in **10** is different from that of the $N_{ax}$–Si(1)–$C_{ax}$ plane in 1-phenylazasilatrane. In the latter compound[7a] the $N_{ax}$–Si(1)–$C_{ax}$ fragment is bent in the $N_{ax}$–Si–N(2) plane, with the Si–$C_{ax}$ bond pointing away from the N(8) and N(9) atoms (the N(8)–Si(1)–$C_{ax}$, N(9)–Si(1)–$C_{ax}$, and N(2)–Si(1)–$C_{ax}$ angles being 98.5 (2), 99.0 (2), and 96.2 (2)°). In cation **10**, on the other hand, the $N_{ax}$–Si(1)–H(1) fragment is bent in the $N_{ax}$–Si(1)–N(9) plane with an H(1)–Si(2)–N(9) angle of 99 (1)°. This places H(1) in proximity to one of the two protons on N(2) (see Figure 1). In view of the close proximity of the structural parameters of cations **6** and **10**, the spatial orientation of the $N_{ax}$–Si(1)–H(1) fragment in **6** is likely to be the same as in **10**. The proximity of H(1) and one of the two protons at N(2) in **6** and **10** could explain why both of these cations easily eliminate hydrogen on heating **7** and **10** to yield **8** and **13**, respectively, in good yields. Whether this process is facilitated by prior nucleophilic attack of the anion or by initial elimination of hydrogen gas to form a cationic intermediate is yet unclear. In a recent publication[8] we noted that one of the nitrogen atoms of the azide ion in **6** lies within hydrogen bonding distance of the protonated nitrogen atom N(2). The existence of such a hydrogen bridge is confirmed in the structure of **10**, in which the distance of the proton H(2) to the S atom of the $SCN^-$ ion (2.69 ± 0.03 Å) is well below the sum of the van der Waals radii (3.05 Å)[12] of sulfur and hydrogen. The N(2)–H(2)–S angle is 151.6 (3)°. Conceivably, hydrogen bonding may facilitate cleavage of the N(2)–H(2) bond during the elimination of hydrogen upon pyrolysis of cations **6** and **10**.



(2)

**6**: R = H, X = $N_3$
**10**: R = $SiMe_3$, X = SCN
**8**: R = H, Z = $N_3$
**13**: R = $SiMe_3$, Z = SCN

In the thermolysis of **10**, both $Me_3Si$ substituents are lost largely as $Me_3SiNCS$. Pyrolysis of moist **10** reproducibly gives a 2:1 mixture of isomers **13** and **14** in low yield.

The C–S (1.641 (2) Å) and C–N (1.146 (3) Å) distances within the $SCN^-$ ions for **10** are intermediate between those reported[13] for the free thiocyanate ion (S–C, 1.59 Å; C–N, 1.25 Å) and for covalently S-bonded SCN groups (S–C, 1.71 Å; C–N, 1.10 Å) in $NH_4Ag(SCN)_2$.

**IR Spectroscopy.** The IR spectra of **5a**,**b**, **7**, **8**, and **10**–**13** are given in Table I. These spectra were assigned by following a vibrational analysis of the silatrane cage reported earlier.[14] As we have noted elsewhere,[4,15] the IR spectra of azasilatranes having Si–$N_{ax}$ bonds are very similar to those of 1-H- and 1-methylsilatrane (**1a**; Z = H, Me, respectively), in displaying three characteristic medium to strong IR absorption bands at ca. 960 ($\nu_2$), 920 ($\nu_3$), and 620 $cm^{-1}$ ($\nu_4$) (see Table I) attributable to vibrations in which the potential energy contribution from the Si–$N_{ax}$ bond stretching coordinate is significant (10%). In the IR spectra of azasilatranes with less robust Si–$N_{ax}$ bonds, these bands are much weaker or may even be absent.[4] According to this criterion, all the azasilatranes listed in Table I should have substantial Si–$N_{ax}$ bonding interactions. Though the IR spectrum of **13** lacks an absorption band at ca. 960 $cm^{-1}$, the absorption band at 926 $cm^{-1}$ is observed to be unusually strong, suggesting that the latter may be borrowing intensity from the absorption band expected at ca. 960 $cm^{-1}$. Such a process is allowed, because the $\nu_2$ and $\nu_3$ absorption bands are of the same symmetry (see Table I). In the IR spectra of azasilatranes with less robust Si–$N_{ax}$ bonds, the absorption band at ca. 620 $cm^{-1}$ ($\nu_4$) is usually absent or extremely weak.[4] In the IR spectrum of **13**, on the other hand, this band is present in appreciable intensity. The presence of substantial Si–$N_{ax}$ bonding in the azasilatranes listed in Table I is consistent with the observed $^{29}Si$ chemical shifts (see next section). The structural metrics in Table V for **5a** (in **7**), **6** (in **7**), and **10** also point to substantial Si–$N_{ax}$ interaction.

As can be seen in Table I, protonation of **5a** to cation **6** causes $\nu$(SiH) to increase from 1967 $cm^{-1}$ in **5a** to 2023 $cm^{-1}$ in **7** along with a reduction in the intensity of the absorption band by a factor of 2–3. This indicates that the Si–H bond in cation **6** is stronger, and less polar, than in **5a**. This result is reasonable if the Si–H bond in **6** possesses greater silicon s character than in **5a**, a conclusion requiring a nonlinear H(1)–Si(1)–$N_{ax}$ framework. Although the hydrogens were not located in **6**, it is not unreasonable to assume that, as in **10**, the $N_{ax}$–Si(1)–H(1) fragment in **6** is bent.

The $\nu$(SiH) values (Table I) of cations **6** and **10** are significantly lower than those of the cations **18** and **19** (2075–2080 $cm^{-1}$)[15] or of the tetrahedral $HSi[N(n\text{-}Pr)_2]_3$ (2115 $cm^{-1}$),[16] indicating that the distortions of the Si(1) atom in cations **6** and **10** from ideal TBP geometry are probably not as dramatic as in **18** and **19**, and certainly not as great as in the tetrahedral model compound.

The presence of covalently bonded $N_3$, SCN, and NCS groups in compounds **8**, **13**, and **14**, respectively, is easily

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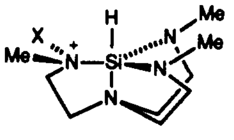
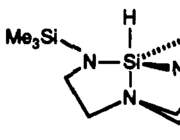


**18**: X = Me
**19**: X = $Me_3Si$



**20**

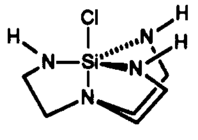
and unambiguously deduced from their IR spectra. The presence of a covalently bonded azido group in **8** is signaled by an N≡N stretching frequency which is 67 $cm^{-1}$ higher than that observed for the azide ion of compound **7**. A similar difference is observed in the $\nu$(C≡N) values of the $SCN^-$ ion in **10** and the S-bonded SCN group in **13** (Table I). As in free $SCN^-$ ions, the C≡N bond of an N-bonded SCN group should possess appreciable double-bond character, and hence the $\nu$(C≡N) values for these species should be similar and well below that of a covalently S-bonded SCN group. Accordingly, the absorption band at 2071 $cm^{-1}$ in the IR spectrum of a mixture of **13** and **14** was assigned to 1-(isothiocyanato)azasilatrane (**14**) and that at 2104 $cm^{-1}$ to 1-(thiocyanato)azasilatrane (**13**).

**$^{13}$C and $^{29}$Si NMR Spectra.** The $^{13}$C and $^{29}$Si NMR chemical shift values of compounds **5a,b**, **7**, **8**, and **10–14** are given in Table II. Most of the data were obtained from solid-state NMR experiments, because of the instability of the cations **6**, **10**, and **11** in solution and because of the low solubility of the azide salts **7** and **11** as well as of the neutral compounds **13** and **14** in common NMR solvents.

The $^{29}$Si chemical shift values ($\delta_{Si}$) of solid **5a,b** (Table II) are below the corresponding $\delta_{Si}$ values (−82.3 ppm for **5a**,[16] −68.4 ppm for **5b**[16,17]) in solution. A similar phenomenon was observed[18] with silatranes of type **1a**, for which the $\delta_{Si}$ values in the solid state are up to 5 ppm lower than in solution. The effect has been attributed[18] to strengthening of the Si-$N_{ax}$ bond under the influence of crystal-packing forces. This conclusion gains support from our recent crystal structure determination of **5a**,[19] which displays a Si-$N_{ax}$ bond length of 2.109 (3) Å. This parameter for **5a** in **7** (2.080 (6) Å, Table V) is smaller, but only barely outside of experimental error (i.e., 3(esd)). The $\delta_{Si}$ values of the cations **6** and **11** and of the cocrystallized, conjugate base in compounds **7** and **12** are seen in Table II to be very close to those of the corresponding pure azasilatranes **5a,b**, indicating the presence of essentially five-coordinate silicon and strong Si-$N_{ax}$ bonds in these compounds. Furthermore, in both **7** and **12**, the $\delta_{Si}$ value of the cation **6** or **11** is assigned to be lower than that of the cocrystallized conjugate base, which is consistent with a higher positive charge expected at the Si(1) atom of the cation **6** or **11**, relative to the cocrystallized conjugate base.

In comparison with the $\delta_{Si}$ value reported for the related compound **20** in solution (−70.8 ppm in $CDCl_3$),[2a] that of the Si(1) atom in cation **10** (Table II) appears to be exceptionally low. The $\delta_{Si}$ value of the Si(1) atom in cation **10** is, however, consistent with the crystal structure (Table V), which indicates that the distortion of the Si(1) atom in cation **10** from perfect TBP geometry is virtually the same as in cation **6**. The fact that cation **10** does not possess a plane of symmetry because the $SCN^-$ ion binds to H(2) (Figure 1) is reflected in the inequivalency of the two trimethylsilyl substituents in the $^{29}$Si MAS NMR spectrum (Table II).

Silatranes of type **1a**[1a] have been reported to display decreasing $\delta_{Si}$ values with increasing electronegativity of the axial substituent at the Si(1) atom. While the chemical shift order **5b** > **5a** > **21** (−85.2 ppm, $CDCl_3$[2a]) reflects the electronegativity order of the axial substituents H > Me > Cl, the $\delta_{Si}$ value for **14** (−85.6 ppm) lies surprisingly close to that of **21**, whereas those for **8** (−92.4 ppm) and **13** (−97.0 ppm) are anomalously low, considering that the NCS, $N_3$, and SCN substituents are all expected to have lower electronegativities than Cl. Interestingly, $\delta_{Si}$ for **13** is quite close to that of 1-fluorosilatrane (**1a**, X = F; $\delta_{Si}$ = −101.5 ppm[18]). It thus appears for azasilatranes that the electronegativity of the axial substituent alone cannot rationalize the observed trend in the $\delta_{Si}$ values of these compounds. Such a rationalization presumably requires a more rigorous approach, as in a quantum-mechanical calculation, in which both the dia- and paramagnetic contributions[20] to the $^{29}$Si chemical shift are evaluated.



**21**

The $^{13}$C MAS NMR spectra of **7**, **8**, and **10–13** display two broad (line width ≅400 Hz) NMR signals at ca. 35 and 50 ppm, characteristic of the cage carbon atoms C(3), C(7), C(10) and C(4), C(6), C(11), respectively.[2-4] These values compare favorably with those reported for **5a,b** (Table II).[2a] The solution $^{13}$C chemical shifts of the cage carbon atoms in compounds **13** and **14** are nearly equal, as might be expected. In the case of **7**, **8**, and **11**, the $^{13}$C signal at ca. 50 ppm displays a shoulder at ca. 48 ppm, reflecting the magnetic inequivalence of the carbon atoms within the sets C(3), C(7), C(10) and C(4), C(6), C(11) and/or the presence of inequivalent lattice sites within the crystal. Due to enhanced conformational mobility (in combination, of course, with MAS) the $^{13}$C NMR signals of the methyl substituents in compounds **5b** and **10–12** are much narrower (line width ≅20 Hz) than those of the cage carbons. Thus, the $^{13}$C NMR absorptions due to the methyl groups of the cation and of the neutral molecule in compound **12** were resolved into two singlets at 5.39 and 11.6 ppm, respectively, in a 3:1 intensity ratio. As can be seen in Table II, the agreement between the $\delta_C$ values of the cation in compounds **11** and **12** is excellent, thereby confirming unambiguously the assignment of the $^{13}$C NMR signal at 11.6 ppm in the spectrum of compound **12** to the methyl group of the cocrystallized conjugate base. This result suggests that, at least as far as the hybridization state of the methyl carbon atom of these species is concerned, the structure of cocrystallized **5b** in **12** ($\delta_C$(Me) 11.6 ppm) differs considerably from that of pure **5b** ($\delta_C$(Me) 2.12 ppm). The occurrence of spinning side bands, exclusively on the low-field side of the $^{13}$C NMR resonance of the SCN group in crystalline **10** and **12–14**, indicates the presence of essentially linear, axially symmetric SCN groups in all four compounds. In the case of compound **10**, this conclusion is supported by the crystal structure in which a linear $SCN^-$ ion occurs (SCN angle 179.2 (2)°). The proximity of the $\delta_C$ values does not allow discrimination between covalently bonded and ionic SCN groups in these compounds. As mentioned earlier, however, this differ-

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entiation was readily and unambiguously made on the basis of the FT-IR spectra of compounds **10** and **12**–**14**.

**Conclusions.** The equatorially protonated azasilatrane cations **6** and **11**, which could not be isolated by direct protonation of **5a**,**b** with strong acids,[8] can be prepared by the reaction of these azasilatranes with the weakly electrophilic $Me_3SiN_3$ or $Me_3SiNCS$. The concomitant formation of N-trimethylsilylated azasilatranes indicates that formation of these cations involves free $HN_3$ or HSCN, liberated in situ through nucleophilic attack of $N_{eq}$ of the azasilatrane on the silicon of the $Me_3SiX$ reagent. The nature and the stoichiometry of the crystalline end product appears to be governed by delicate differences in crystal-packing forces. The crystal structure of **10** confirms two earlier conclusions[8] concerning the structure of cation **6**, namely that the Si–$N_{eq}$ bond to the protonation site is significantly longer than the other two Si–$N_{eq}$ bonds and that one of the protons at the protonation site is engaged in a hydrogen bond with the counterion. In cation **10** (and presumably in **6**), the Si–H bond points toward one of the protons at the protonation site, which could account for the ease with which hydrogen is eliminated in their thermolysis reactions to give **13** and **8**, respectively.

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**Supplementary Material Available:** Tables of anisotropic thermal parameters, bond lengths and bond angles, torsional angles, least-squares planes, and general displacement parameters (8 pages); a table of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.

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# Preparation and Carbonylation of Ring-Functionalized Methyl Zirconocenes $[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2]_2Zr(CH_3)_{2-n}Cl_n$ ($n$ = 0, 1). Observation and X-ray Structure of a Fluxional "Acyl–Phosphonium" Moiety in the Complex $[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2][(\eta^5\text{-}C_5H_4)P(C_6H_5)_2]Zr[\eta^2\text{-}(OC)CH_3]Cl$

Wayne Tikkanen[*,†] and Joseph W. Ziller[‡]

*Department of Chemistry and Biochemistry, California State University, Los Angeles,*
*Los Angeles, California 90032, and Department of Chemistry,*
*University of California, Irvine, California 92717*

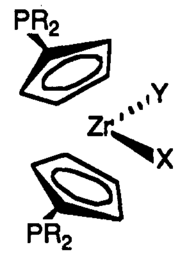
*Received November 30, 1990*

The interaction of $[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2]_2ZrCl_2$ which 2 equiv of methyl Grignard reagent or methyllithium gives $[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2]_2Zr(CH_3)_2$ (I), which is readily converted to $[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2]_2Zr(CH_3)Cl$ (II) by treatment with $^1/_2$ equiv of lead(II) chloride. No acyl complex is observed in the reaction of these methyl zirconocenes with CO, but a product that results from attack of the ring-bound phosphine on a transient acyl complex is obtained. The complex $[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2][(\eta^5\text{-}C_5H_4)P(C_6H_5)_2]Zr[\eta^2\text{-}(OC)CH_3]Cl$ (III) can be isolated from the action of CO on II, and this formulation is verified by the single-crystal X-ray study. III crystallizes from dichloromethane/diethyl ether in a monoclinic system (space group $P2_1/c$) with $Z$ = 4, $a$ = 12.3056 (12) Å, $b$ = 18.5738 (18) Å, $c$ = 13.5718 (15) Å, $\beta$ = 101.285 (8)°, $V$ = 3042.0 (5) Å$^3$, and $R$ = 3.6% ($R_w$ = 4.3%) for 4851 observed reflections. Variable-temperature NMR studies indicate that the carbonylation products are fluxional and undergo intramolecular attack by the phosphorus on the other cyclopentadienyl ring. An activation enthalpy of 61 kJ/mol was observed for this process with III in dichloromethane-$d_2$.

## Introduction

This group[1,2] and others[3] have been interested in the use of phosphinocyclopentadienides as bifunctional ligands. Our work has focused on the zirconocenes $[(\eta^5\text{-}C_5H_4)PR_2]_2ZrXY$ (A) as chelating ligands for the formation of heterobinuclear complexes.

We have reported the preparation of such compounds A where X = Y = Cl and R = $C_6H_5$, $CH_3$ as well as their complexes with the $Mo(CO)_4$ fragment.[1,2] Our interest in these metallo ligands is that one can tune the electrophilicity and/or steric bulk of the zirconium center by changing the substituents X and Y from halide to different alkyl groups. Here we present the synthesis and characterization of methyl derivatives of $[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2]_2ZrXY$ (X = Y = $CH_3$, I; X = $CH_3$, Y = Cl, II) and



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† California State University, Los Angeles.

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