Synthetic, Structural, and Theoretical Studies of Diphenyltetrazene Complexes of Silicon and Germanium

Glenn A. Miller, Soon W. Lee, and William C. Trogler*

Department of Chemistry, D-006, University of California at San Diego, La Jolla, California 92093

Received July 25, 1988

The reaction between dilithium 1,4-diphenyltetrazenide (1) and $SiCl(CH_3)_3$ or $GeCl(CH_3)_3$ in toluene yields *trans*-$(Ph)(Me_3Si)NN{=}NN(Ph)(SiMe_3)$ (**3**) and *trans*-$(Ph)(Me_3Ge)NN{=}NN(Ph)(GeMe_3)$ (**5**). Bis(trimethylsilyl)aniline and bis(trimethylgermyl)aniline are formed as by products of fragmentation of $(Ph)(Me_3E)N_4(Ph)^-$ to $Ph(Me_3E)N^-$ and phenyl azide, where E = Si or Ge. Crystals of **3** belong to the triclinic space group $P\bar{1}$ with $a = 6.337$ (2) Å, $b = 7.986$ (2) Å, $c = 10.713$ (2) Å, $\alpha = 76.52$ (2)°, $\beta = 89.59$ (2)°, $\gamma = 86.02$ (2)°, $V = 529.9$ (2) Å^3, and $Z = 1$. Refinement of 153 least-squares variables for 1431 unique reflections of $I > 2\sigma(I)$ led to $R = 0.032$ and $R_w = 0.050$. Crystals of **5** belong to the monoclinic space group $P2_1/n$ with $a = 9.363$ (2) Å, $b = 9.011$ (3) Å, $c = 12.595$ (3) Å, $\beta = 106.96$ (2)°, $V = 1016.3$ (4) Å^3, and $Z = 2$. Refinement of 138 least-squares variables on 2202 unique reflections of $I > 3\sigma(I)$ led to $R = 0.034$ and $R_w = 0.038$. Both **3** and **5** adopt a planar trans structure with a planar bent N(1)–N(2)–N(2a)–N(1a) chain. For **3** N(1)–N(2) = 1.394 (2) Å and N(2)–N(2a) = 1.254 (3) Å. For **5** N(1)–N(2) = 1.377 (3) Å and N(2)–N(2a) = 1.260 (4) Å. The chief difference between the structures is that the phenyl rings in **3** are 54.7° out of conjugation with the N_4 π system, whereas in **5** the phenyl rings are in partial resonance (27.9° out of plane) with the N_4 π system. This is consistent with the longer Ge–N(1) bond of 1.912 (3) Å in **5** (Si–N(1) = 1.781 (1) Å in **3**) reducing repulsions between the $GeMe_3$ and Ph substituents. Addition of **1** to $SiCl_2Me_2$ produced the cyclic species $Me_2\overline{SiN(Ph)N{=}NN}(Ph)$ (**6**) and $(PhNSiMe_2)_2$ (**7**). Compound **6** crystallizes in the monoclinic space group $C2/c$ with $a = 19.408$ (3) Å, $b = 6.704$ (1) Å, $c = 11.815$ (2) Å, $\beta = 111.77$ (2)°, $V = 1427.5$ (4) Å^3, and $Z = 4$. Refinement of 120 least-squares variables converged to $R = 0.032$ and $R_w = 0.049$ for 1417 unique reflections with $I > 3\sigma(I)$. The structure contains a planar $\overline{SiN(1)\text{–}N(2)\text{–}N(2a)\text{–}N}(1a)$ ring with Si–N(1) = 1.755 (1) Å, N(1)–N(2) = 1.392 (1) Å, and N(2)–N(2a) = 1.267 (2) Å. SCF–DV–Xα calculations for the model complexes *trans*-$(H_3Si)HNN{=}NNH(SiMe_3)$ and $H_2\overline{SiN(H)N{=}NN}(H)$ are presented to compare the bonding in the planar acyclic and cyclic tetrazenes. Good agreement was observed between the observed electronic absorption spectra of **3** and **6** and that calculated for the model complexes. In **3** and **6** the lowest electronic transition arises from a $\pi_3 \rightarrow \pi_4$ transition of the N_4 π system at 3.97 eV in **3** (3.95 eV, calculated) and 4.11 eV in **6** (4.35 eV calculated).

Introduction

We recently reported[1,2] the preparation of several transition-metal tetrazene (also called tetraazadiene, tetraazabutadiene, or tetrazenido) compounds from the readily available tetrazenido dianion 1 (eq 1).[1] This reagent has

$$PhNHLi + PhN_3 \rightleftarrows Ph(H)NN{=}NN(Ph)Li \xrightarrow{\text{base}} \underset{\textbf{1}}{Ph(Li)NN{=}NN(Ph)Li} \quad (1)$$

permitted the synthesis of tetrazene complexes for Ni, Pd, and Pt allowing for the first time a comparison of metal–tetrazene bonding within a triad. Main-group tetrazene compounds may also be useful as precursors to interesting materials, such as ceramics and semiconducting nitrides.[3] Structural studies of the main-group systems aid in the analysis of bonding within the N_4 backbone of the tetrazene ligand in transition-metal complexes.[4] Donation from dπ orbitals on the metal to tetrazene π^* orbitals may be important in transition-metal complexes but should be diminished in main group analogues.

The few known main-group tetrazene complexes have been prepared by an oxidative coupling of hydrazine derivatives, by coupling lithiated hydrazines with aryldiazonium salts, or by the [2 + 3]-cycloaddition reaction between azides and substituted silaketimines.[5] Herein we describe metathesis reactions with main-group substrates, which suggest 1 offers a convenient entry to the synthesis of main-group tetrazene compounds of group 14.

Experimental Section

Reactions were performed with standard Schlenk and cannula filtration techniques using a nitrogen atmosphere. Solids were manipulated under nitrogen in a Vacuum Atmospheres glovebox equipped with an HE-493 drytrain. Glassware was either oven-dried or flame-dried before use. Benzene, ethers, and hydrocarbon solvents were refluxed over sodium or potassium benzophenone ketyl and distilled under nitrogen or by vacuum transfer. Benzene-d_6 was freeze–thaw–degassed before use and stored under nitrogen. NMR-grade carbon tetrachloride was distilled from P_2O_5, degassed, and stored under nitrogen. The silane and germane precursors (Alfa, Strem) were used as received. The dianion $[Li(THF)_x]_2[PhNN{=}NNPh]$ (1), was prepared by the literature procedure.[1] Photolyses used the output from a 200-W Hg-Xe arc lamp filtered through a 10-cm distilled water filter and the walls of the quartz reaction flask.

^1H NMR spectra were obtained with use of a Varian EM-390 instrument, and IR spectra were obtained either with an IBM IR/32 or with a Perkin-Elmer 1320 spectrometer. UV–vis spectra of solutions contained in a 1-cm quartz vacuum cell were obtained with use of an IBM UV9420 spectrophotometer. Mass spectra were performed by the Mass Spectrometry Facility at the University of California, Riverside, CA. Elemental analyses were performed by Galbraith Analytical Laboratory. Melting points were determined in sealed capillaries under a nitrogen atmosphere.

Synthesis of *N*,*N*-Bis(trimethylsilyl)aniline (2) and 1,4-Diphenyl-1,4-bis(trimethylsilyl)-2-tetrazene (3). A solution of 0.71 g of 1 in 25 mL of THF at −80 °C was treated with 2.0

---

[1] Lee, S. W.; Miller, G. A.; Campana, C. F.; Trogler, W. C. *Inorg. Chem.* **1988**, *27*, 1215.

[2] Lee, S. W.; Miller, G. A.; Campana, C. F.; Maciejewski, M. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1987**, *109*, 5050.

[3] Seyferth, D. *Actual. Chim.* **1986**, 71; *Ultrastructure Processing of Ceramics, Glasses, and Composites*; Hench, L. L., Ulrich, D. R.; Eds.; Wiley: New York, 1984. Narula, C. K.; Paine, R. T.; Schaeffer, R. *Mater. Res. Soc. Symp. Proc.* **1986**, *73*, 383. Interrante, L. V.; Carpenter, L. E.; Whitmarsh, C.; Lee, W. *Ibid.* **1986**, *73*, 359.

[4] Gross, M. E.; Trogler, W. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 192. Trogler, W. C.; Johnson, C. E.; Ellis, D. E. *Inorg. Chem.* **1981**, *20*, 980. Gross, M. E.; Ibers, J. A.; Trogler, W. C. *Organometallics* **1982**, *1*, 530. Maroney, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1984**, *106*, 4144.

[5] Wiberg, N. *Adv. Organomet. Chem.* **1985**, *24*, 179.

0276-7333/89/2308-0738$01.50/0

mL (4.0 mmol) of a 2 M benzene solution of trimethylsilyl chloride, dropwise with vigorous stirring. The solution was stirred for 1 h at −80 °C and then warmed slowly to room temperature. The volatiles were removed, and the residue was extracted with 3 × 30 mL of pentane. The filtrate was concentrated to saturation and cooled slowly to −40 °C overnight. The red supernatant was decanted away from colorless crystalline blocks. The product was recrystallized by cooling a concentrated pentane solution to −80 °C to yield compound **3** (241 mg, 6.7 mmol, 42%): ^{1}H NMR (CCl_4) δ 7.3–6.9 (m, Ph), 0.13 (s, Me); IR, (mineral oil) 3060 (sh), 3020 (sh), 2030 (w), 1585 (m), 1480 (sh), 1260 (sh), 1250 (vs), 1165 (w), 1154 (w), 1070 (sh), 1051 (s), 1025 (sh), 1000 (w), 950 (m), 895 (w), 840 (vs, br), 760 (m), 700 (m), 685 (m), 630 (m), 520 (sh), 450 (sh) cm^{-1}; UV (pentane) 312 nm (ϵ 21 000), 258 (21 000); mp 79–80 °C; MS (EI), *m/e* 356 (32), 251 (100), 164 (59), 73 (73), 59 (30). Anal. Calcd for $C_{18}H_{28}N_4Si_2$: C, 60.61; H, 7.93; N, 15.71. Found: C, 60.71; H, 7.54; N, 15.77.

Distillation of the red supernatant afforded $PhN(SiMe_3)_2$ (**2**; 160 mg, 6.7 mmol, 42%) which was spectroscopically identical with a sample prepared by a literature procedure.[6] Higher reaction temperatures or the use of DME as solvent results in high yields of $PhN(SiMe_3)_2$ with little or no $Ph_2N_4(SiMe_3)_2$ observed.

Synthesis of 1,1-Dimethyl-2,5-diphenylsila-2-tetrazoline (6). Treatment of 1.3 g of **1** in 20 mL toluene at −80 °C with 3.7 g (29 mmol) of dichlorodimethylsilane gave a light yellow solution over a white precipitate. The mixture was slowly warmed to room temperature and filtered through a Celite pad, and the volatiles were removed. The residue was extracted with warm pentane, and the filtrate was concentrated to saturation and cooled slowly to −80 °C. The white crystals were collected and dried under vacuum for several hours (0.70 g, 26 mmol, 90%): ^{1}H NMR (C_6D_6) δ 7.3–6.7 (m, Ph), 0.14 (s, Me); IR (KBr) 3060 (vw), 3030 (w), 2120 (w, br), 2090 (sh), 1590 (vs), 1480 (vs), 1458 (sh), 1435 (sh), 1385 (w), 1320 (sh), 1312 (vs), 1295 (s), 1280 (sh), 1258 (s), 1149 (w), 1109 (s), 1090 (s), 1079 (m, sh), 1060 (m), 1037 (m, sh), 1019 (vs), 1000 (s), 978 (vs, br), 960 (sh), 890 (m), 860 (m, br), 805 (s), 776 (w), 750 (s), 738 (sh), 690 (s), 650 (w), 513 (sh), 500 (m), 440 (w), 390 (w), 370 (vw), 340 (sh), 330 (w), 320 (w), 298 (w), 270 (w), 260 (sh), 240 (m) cm^{-1}; UV (pentane) 302 nm (ϵ 20 000), 281 (18 000), 220 (sh), 206 (22 000); mp 111–113 °C; MS, exact mass *m/e* 268.1148 (calcd *m/e* 268.1144, Δ = 1.5 ppm); EI, *m/e* 268 (20), 240 (2), 225 (27), 149 (100). Anal. Calcd for $C_{14}H_{16}N_4Si$: C, 62.58; H, 6.01; N, 20.95. Found: C, 62.83; H, 5.92; N, 20.65.

Synthesis of Tetramethyl-*N*,*N*′-diphenylcyclodiazadisilane (7). If near stoichiometric amounts of dichlorodimethylsilane were used in the preceding synthesis, $(PhNSiMe_2)_2$ (**7**) was isolated (up to 50% yield) rather than the tetrazene. This material was purified by sublimation (180 °C, 0.001 mmHg): mp 250–252 °C (lit.[7] mp 252.5 °C); MS, exact mass *m/e* 298.1325 (calcd *m/e* 298.1322, Δ = 1.2 ppm); EI, *m/e* 298 (81), 283 (100), 149 (18).

Synthesis of *N*,*N*-Bis(chlorodimethylsilyl)aniline (8). Distillation of the recrystallization supernatant from the preceding two syntheses gave the *N*,*N*-bis(chlorodimethylsilyl)aniline (**8**; up to 24% yield): ^{1}H NMR (CCl_4) δ 7.3–7.0 (m, 5 H, Ph), 0.42 (s, 12 H, Me); bp 55–56 °C (0.001 mmHg); MS, exact mass *m/e* 277.0279 (calcd for ^{35}Cl *m/e* 277.0277, Δ = 0.7 ppm); EI, *m/e* 277 (43), 262 (64), 242 (12), 226 (23), 149 (100) (all but the last ion fragment have expected isotope pattern(s) for one or two chlorines). Anal. Calcd for $C_{10}H_{17}Cl_2NSi_2$: C, 43.16; H, 6.17. Found: C, 42.96; H, 6.58. The material is extremely reactive toward moisture and glassware.

Synthesis of *N*,*N*-Bis(trimethylgermyl)aniline and 1,4-Diphenyl-1,4-bis(trimethylgermyl)-2-tetrazene (5). A yellow slurry of 0.33 g of **1** in toluene (30 mL) was treated with 0.4 mL (4 mmol) of Me_3GeCl. After the solution was stirred overnight, the white suspension was concentrated by 50%, filtered, and concentrated under reduced pressure to an oil, which crystallized on being kept under vacuum overnight. Recrystallization from pentane gave white crystals of **5** (61 mg, 0.14 mmol, 18%): ^{1}H NMR (CCl_4) δ 7.3–6.8 (m, Ph), 0.42 (s, Me); IR (mineral oil) 1550 (m, br), 1270 (m, br), 1250 (sh), 1240 (sh), 1170 (w), 1152 (w), 1085 (mw), 1060 (m), 1020 (sh), 910 (w), 885 (w), 820 (w), 750 (m), 720 (w), 700 (m), 680 (m), 610 (sh), 600 (m), 565 (w), 520 (sh) cm^{-1}; mp 116–118 °C; MS, exact mass *m/e* 440.0815 (calcd ^{70}Ge *m/e* 440.0799, Δ = 3.6 ppm). Anal. Calcd for $C_{18}H_{28}N_4Ge_2$: C, 48.51; H, 6.35; N, 12.57. Found: C, 48.12; H, 6.38; N, 11.94.

Table I. Crystallographic Data and Summary of Data Collection and Structure Refinement

	$Ph_2N_4(SiMe_3)_2$ (3)	$Ph_2N_4SiMe_2$ (6)	$Ph_2N_4(GeMe_3)_2$ (5)
cryst size, mm	0.5 × 0.5 × 0.4	0.52 × 0.44 × 0.40	0.35 × 0.4 × 0.5
fw, g/mol	356.68	268.11	445.68
lattice	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P2_1/n$
a, Å	6.337 (2)	19.408 (3)	9.363 (2)
b, Å	7.986 (2)	6.704 (1)	9.011 (3)
c, Å	10.713 (2)	11.815 (2)	12.595 (3)
α, deg	76.52 (2)	90	90
β, deg	89.59 (2)	111.77 (1)	106.96 (2)
γ, deg	86.02 (2)	90	90
V, Å^3	529.9 (2)	1427.5 (4)	1016.3 (4)
d_{calcd}, g/cm^3	1.13	1.25	1.46
Z	1	4	2
T, °C	23	−100	−100
total reflctns	1759	1656	3369
unique reflctns ($I > n\sigma(I)$)	1431 (n = 2)	1417 (n = 3)	2202 (n = 3)
angles, deg	$4 < 2\theta < 50$	$4 < 2\theta < 55$	$3 < 2\theta < 60$
hkl	$+h,\pm k,\pm l$	$\pm h,+k,+l$	$+h,+k,\pm l$
no. of parameters	153	120	138
R	0.032	0.032	0.034
R_w	0.050	0.049	0.038
GOF	1.73	2.09	1.15

Distillation of the recrystallization supernatant yields primarily $PhN(GeMe_3)_2$ (180 mg, 0.55 mmol, 74%) whose boiling point and IR and NMR spectra were identical with those of an authentic sample prepared by a literature route.[8]

X-ray Structure Determinations. All X-ray data were collected with use of a Nicolet R3m/V automated diffractometer equipped with a Mo source (Mo Kα, λ = 0.710 73 Å) and a graphite crystal monochromator. Details on crystal data and intensity data are given in Table I. The orientation matrix and unit cell parameters were determined from 50 machine centered reflections with 15° < 2θ < 30°. Axial photographs were measured as a check of axis lengths and unit-cell symmetry. Intensities of three check reflections were monitored after every 50 reflections during data collection ($\theta/2\theta$ scan). Data were corrected for minor decay and Lorentz and polarization effects. No absorption corrections were applied. All calculations were carried out on a MicroVax II computer with use of the SHELXTL PLUS program package.

A room-temperature data collection of $Ph_2N_4SiMe_2$ was frustrated by rapid decomposition of the crystals in the X-ray beam. Therefore, a clear colorless block of $Ph_2N_4SiMe_2$ was sealed in a glass capillary under a dry nitrogen atmosphere and cooled to −100 °C. The cell parameters and systematic absences, hkl ($h + k = 2n + 1$), $h0l$ ($l = 2n + 1$), and $0k0$ ($k = 2n + 1$), indicated two possible space groups: Cc and $C2/c$. A statistical analysis suggested a centric space group and only the $C2/c$ solution converged. The silicon atom was located by direct methods, and all non-hydrogen atoms were found by difference Fourier syntheses and least-squares refinements. Anisotropic refinement and a difference Fourier synthesis then revealed the hydrogen atoms. Finally, two further cycles of least-squares refinements converged; the largest shift/esd was less than 0.03 and the largest residual peak in the difference Fourier map was 0.26 e/Å^3.

A clear colorless block of $Ph_2N_4(SiMe_3)_2$ was cut from a large plate and sealed into a glass capillary under nitrogen. Unit-cell parameters suggested a triclinic lattice. Data collection proceeded normally until the check reflections dropped dramatically. The structure was solved by direct methods as described above in both $P1$ and $P\bar{1}$, but only the solution for the latter space group converged. All protons were refined isotropically with a fixed thermal

---

[6] Abel, E. W.; Willey, G. R. *J. Chem. Soc.* **1964**, 1528. Wannagat, V. U.; Krüger, C.; Niederprüm, H. *Z. Anorg. Chem.* **1962**, *314*, 80.

[7] Fink, W. *Helv. Chim. Acta* **1964**, *47*, 498. Fink, W. *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 760.

[8] Wiberg, N.; Karampatses, P.; Kim, C.-K. *Chem. Ber.* **1987**, *120*, 1213.

Table II. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10⁴) for $Ph_2N_4(SiMe_3)_2$, $Ph_2N_4SiMe_2$, and $Ph_2N_4(GeMe_3)_2$

	x	*y*	*z*	*U*(eq)[a]
		$Ph_2N_4(SiMe_3)_2$ (**3**)		
Si(1)	4375 (1)	2716 (1)	7912 (1)	480 (10)
N(1)	4007 (3)	473 (2)	8453 (1)	520 (10)
N(2)	4470 (3)	−428 (2)	9710 (1)	500 (10)
C(1)	3101 (4)	3408 (3)	6296 (2)	630 (10)
C(2)	3021 (5)	3952 (3)	8993 (2)	690 (10)
C(3)	7200 (5)	3096 (3)	7772 (3)	810 (10)
C(11)	2692 (3)	−461 (2)	7824 (1)	430 (10)
C(12)	806 (3)	−1030 (2)	8347 (2)	560 (10)
C(13)	−486 (4)	−1878 (3)	7698 (2)	670 (10)
C(14)	106 (4)	−2142 (3)	6517 (2)	680 (10)
C(15)	1967 (4)	−1604 (3)	6004 (2)	680 (10)
C(16)	3284 (4)	−775 (2)	6648 (2)	570 (10)
		$Ph_2N_4SiMe_2$ (**6**)		
Si	0	1775 (1)	7500	224 (2)
N(1)	−456 (1)	−153 (2)	7948 (1)	247 (4)
N(2)	−247 (1)	−2058 (2)	7731 (1)	274 (4)
C(1)	647 (1)	3349 (2)	8710 (1)	336 (5)
C(11)	−1038 (1)	−110 (2)	8398 (1)	247 (4)
C(12)	−1605 (1)	−1533 (2)	8035 (1)	299 (5)
C(13)	−2162 (1)	−1473 (3)	8505 (2)	357 (5)
C(14)	−2165 (1)	−5 (3)	9328 (2)	396 (6)
C(15)	−1609 (1)	1422 (3)	9677 (2)	395 (6)
C(16)	−1045 (1)	1377 (2)	9219 (1)	322 (5)
		$Ph_2N_4(GeMe_3)_2$ (**5**)		
Ge(1)	1426 (1)	1724 (1)	3751 (1)	238 (1)
C(1)	304 (4)	3535 (4)	3777 (4)	387 (13)
C(2)	3178 (4)	1531 (4)	5023 (3)	336 (11)
C(3)	2140 (5)	1661 (6)	2454 (4)	500 (16)
N(1)	124 (3)	66 (3)	3669 (2)	234 (8)
N(2)	−249 (3)	−423 (3)	4590 (2)	225 (8)
C(12)	−869 (4)	−2300 (4)	2789 (3)	250 (10)
C(13)	−1519 (4)	−3110 (4)	1829 (3)	300 (10)
C(14)	−1826 (4)	−2460 (4)	792 (3)	324 (11)
C(15)	−1515 (4)	−960 (4)	715 (3)	326 (12)
C(16)	−905 (4)	−128 (4)	1671 (3)	281 (10)
C(11)	−543 (3)	−790 (3)	2717 (3)	218 (9)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

parameter. Finally, two cycles of least-squares refinements converged; the largest shift/esd was 0.1 and the largest residual peak in the difference Fourier map was 0.16 e/Å³.

A block of $Ph_2N_4(GeMe_3)_2$ was sealed in a glass capillary under a dry nitrogen atmosphere and cooled to −100 °C. The cell parameters and systematic absences, $h0l$ ($h + l = 2n + 1$) and $0k0$ ($k = 2n + 1$), uniquely determined the space group to be $P2_1/n$. The germanium atom was located by direct methods, and all non-hydrogen atoms were found by difference Fourier synthesis and least-squares refinements. Hydrogen atoms were placed in calculated positions. All non-hydrogen atom thermal parameters were made anisotropic, and subsequent least squares refinements converged; the largest shift/esd was less then 0.04, and the largest residual peak in the difference map was 0.8 e/Å³.

Table II contains final atomic positional and isotropic thermal parameters; complete tables of distances and angles, hydrogen atom positions, anisotropic thermal parameters, and observed and calculated structure factors are available as supplementary material. Selected bond distance and angles are given in Tables III and IV.

Theoretical Studies. Electronic structure calculations were performed with a DEC MicroVax II computer and used the self-consistent field discrete variational Xα (SCF–DV–Xα) method.[9] Numerical atomic orbitals from exact Hartree–Fock–Slater calculations were used as basic functions, assuming the α values of Schwartz.[10] For Si the atomic orbitals through 3d were included. For N, a minimal 1s, 2s, 2p basis was used. For H, a 1s, 2s, 2p basis set was used. Core orbitals (1s, 2s, 2p) were frozen and orthogonalized against valence orbitals. The Mulliken[11] scheme was used to compute atomic orbital populations. The molecular Coulomb potential was calculated by using a least-squares fit[12] of the model electron density to the true density. Seven radial degrees of freedom were allowed in the expansion of the density, in addition to the radial atomic densities. For the molecular exchange potential, we set $\alpha = 0.716$. The transition-state approximation[13] was used to compute electronic transition energies. For the calculations *trans*-$(H_3Si)HN_4H(SiH_3)$ and $H_2\overline{\mathrm{SiN(H)NNN}}\mathrm{(H)}$ were idealized to C_{2h} and C_{2v} symmetry, respectively, from the structures of **3** and **6** with N–H = 1.04 Å and Si–H = 1.43 Å.

Results and Discussion

Treatment of **1** with protic solvents results in the

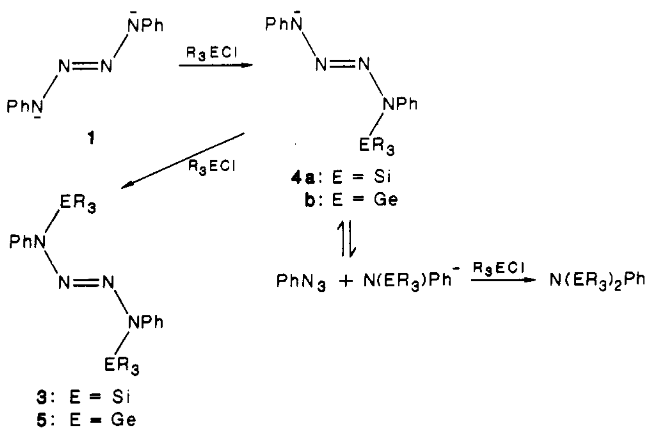
Table III. Selected Bond Distances (Å) for $Ph_2N_4(SiMe_3)_2$, $Ph_2N_4SiMe_2$, and $Ph_2N_4(GeMe_3)_2$

$Ph_2N_4(SiMe_3)_2$ (**3**)		$Ph_2N_4SiMe_2$ (**6**)		$Ph_2N_4(GeMe_3)_2$ (**5**)	
Si(1)–N(1)	1.781 (1)	Si–N(1)	1.755 (1)	Ge(1)–N(1)	1.912 (3)
Si(1)–C(1)	1.862 (2)	Si–C(1)	1.845 (1)	Ge(1)–C(1)	1.946 (4)
Si(1)–C(2)	1.858 (2)	N(1)–N(2)	1.392 (1)	Ge(1)–C(2)	1.937 (3)
Si(1)–C(3)	1.835 (3)	N(2)–N(2a)	1.267 (2)	Ge(1)–C(3)	1.937 (4)
N(1)–N(2)	1.394 (2)	N(1)–C(11)	1.416 (2)	N(1)–N(2)	1.377 (3)
N(2)–N(2a)	1.254 (3)	C(11)–C(12)	1.398 (2)	N(2)–N(2a)	1.260 (4)
N(1)–C(11)	1.426 (2)	C(11)–C(16)	1.394 (2)	N(1)–C(11)	1.410 (4)
C(11)–C(12)	1.377 (3)	C(12)–C(13)	1.389 (2)	C(11)–C(12)	1.403 (4)
C(12)–C(13)	1.385 (3)	C(13)–C(14)	1.385 (2)	C(12)–C(13)	1.391 (5)
C(13)–C(14)	1.375 (3)	C(14)–C(15)	1.386 (3)	C(13)–C(14)	1.383 (5)
C(14)–C(15)	1.352 (3)	C(15)–C(16)	1.390 (2)	C(14)–C(15)	1.393 (5)
C(15)–C(16)	1.382 (3)			C(15)–C(16)	1.392 (5)
C(16)–C(11)	1.385 (2)			C(16)–C(11)	1.394 (4)

Table IV. Selected Bond Angles (deg) for $Ph_2N_4(SiMe_3)_2$, $Ph_2N_4SiMe_2$, and $Ph_2N_4(GeMe_3)_2$

$Ph_2N_4(SiMe_3)_2$ (**3**)		$Ph_2N_4SiMe_2$ (**6**)		$Ph_2N_4(GeMe_3)_2$ (**5**)	
C(1)–Si–C(2)	108.6 (1)	N(1)–Si–N(1a)	85.2 (1)	C(1)–Ge–C(2)	113.1 (2)
C(2)–Si–C(3)	111.4 (1)	Si–N(1)–N(2)	114.0 (1)	C(2)–Ge–C(3)	106.1 (2)
C(3)–Si–C(1)	109.3 (1)	Si–N(1)–C(11)	131.3 (1)	C(3)–Ge–C(1)	111.1 (2)
N(1)–Si–C(1)	106.0 (1)	C(1)–Si–N(1)	117.5 (1)	N(1)–Ge–C(1)	108.5 (1)
N(1)–Si–C(2)	110.5 (1)	N(1)–N(2)–N(2a)	113.4 (1)	N(1)–Ge–C(2)	110.3 (1)
N(1)–Si–C(3)	110.9 (1)	C(1)–Si–C(1a)	112.4 (1)	N(1)–Ge–C(3)	107.6 (2)
Si–N(1)–N(2)	122.0 (1)	C(11)–N(1)–N(2)	114.5 (1)	Ge–N(1)–N(2)	121.3 (2)
Si–N(1)–C(11)	124.4 (1)			Ge–N(1)–C(11)	126.2 (2)
N(2)–N(1)–C(11)	111.2 (1)			N(2)–N(1)–C(11)	112.5 (2)
N(1)–N(2)–N(2a)	111.5 (1)			N(1)–N(2)–N(2a)	111.9 (2)

Scheme I



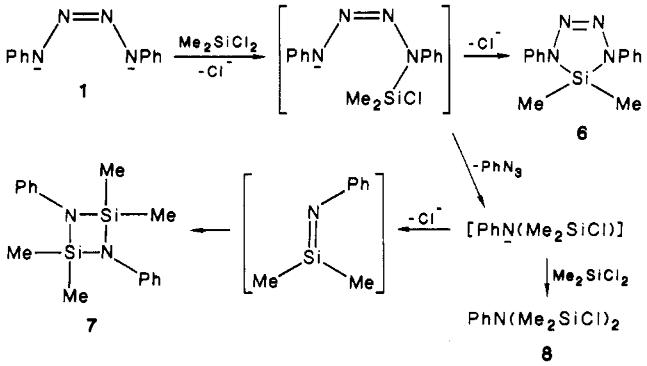
cleavage of the N_4 backbone to generate quantitatively aniline (NMR analysis), phenyl azide (IR analysis), and approximately 3 mol of THF (NMR), the latter stoichiometry varied with sample age and length of time under vacuum during its preparation. No evidence of Ph(H)-NN=NN(H)Ph was observed when **1** was treated with 2 equiv of various protic sources in benzene; only aniline (NMR) and phenyl azide (IR) were observed. It is not clear whether the product decomposed rapidly via a 1,4-hydrogen shift or whether the monoprotonated dianion fragmented before accepting the second proton (see below). Treatment of **1** with 2 equiv of MeI produces Ph(Me)-NN=NN(Me)Ph in 60% yield.[2] Other halocarbon substrates (CH_2Br_2, CH_2Cl_2, CH_3Cl, CCl_4, CH_2BrCH_2Br) gave complex mixtures.

The reaction between **1** and Me_3SiCl is solvent-dependent. In THF or DME solvent, $PhN(SiMe_3)_2$ (**2**) is isolated in up to 65% yield. When toluene is used, the expected tetrazene $Ph(Me_3Si)NN{=}NN(SiMe_3)Ph$ (**3**) is obtained in 40% yield in addition to a 40% yield of **2**. This suggests that the monosilated dianion **4** reacts according to Scheme I. The equilibrium between the delocalized anion and localized silated anilide anion would be expected to be solvent-dependent so that less polar solvents would disfavor fragmentation as was observed.

The preparation of the germanium derivative $Ph(Me_3Ge)NN{=}NN(GeMe_3)Ph$ (**5**) was analogous to that of **3**, except the yield of **5** was lower. Apparently the fragmentation of **4b** to $PhN(GeMe_3)Li$ (Scheme I) is enhanced compared to the reaction with Me_3SiCl. Compound **5** is as stable as **3** under the reaction and workup conditions; hence, the decreased yield of **5** does not result from rearrangement of **5** to PhN_3 and $PhN(GeMe_3)_2$.

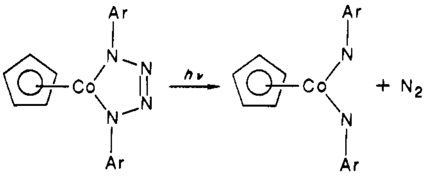
A similar solvent dependency on the course of reaction was observed with dichlorodimethylsilane. Treatment of **1** with an excess of Me_2SiCl_2 in benzene or toluene gives a mixture of products, including $PhNN{=}NN(Ph)SiMe_2$ (**6**), $PhNSi(Me)_2N(Ph)SiMe_2$ (**7**), and $PhN(SiMe_2Cl)_2$ (**8**) (Scheme II); use of THF, DME, or a stoichiometric amount of Me_2SiCl_2 decreases the yield of **6** to negligible amounts. Compound **6** can be separated readily from the other two compounds. The corresponding reaction with Me_2GeCl_2 proceeds to a similar reaction mixture as observed by NMR spectroscopy, but we were unable to separate the products. The work of Klingebiel and co-workers,[14] on the elimination of LiF from $LiSiFR_2$ compounds, provides precedent for the proposed iminosilane intermediate of Scheme II and for its dimerization to **7**. An alternative mechanism that involves nucleophilic attack of $N(Ph)(SiMe_2Cl)^-$ on $(Ph^-NN{=}NNPh)SiMe_2Cl$, followed by loss of PhN_3 and ring closure, cannot be excluded.

Scheme II



From these observations we conclude that compound **1** can act as a source of "PhN^{2-}", which is less harsh than $PhNLi_2$. Treatment of $PhNLi_2$ (generated by treating aniline with excess BuLi in diethyl ether) with Me_2SiCl_2 yields a complex mixture with small amounts of **7** and **8** present (NMR analysis). The utility of **1** as a source of the nitrene PhN^{2-} is being explored.

Photochemical extrusion of N_2 from certain transition-metal tetraazadiene complexes (eq 2) provides a route to



(2)

Ar = C_6H_5, C_6F_5, $o\text{-}C_6(CH_3)_2H_3$

metal bis(nitrene) reactive intermediates.[15] These species even react with C–F bonds, a rarity in the thermal chemistry of metal complexes.[16] Because few routes to metal bis(nitrenes) are known,[17] the behavior of **3** and **6** on UV photolysis was examined.

Photolysis of **3** in pentane or benzene gives PhN_3 and $PhN(SiMe_3)_2$ quantitatively by NMR. Such 1,4-silyl shifts have been reported previously[5] for linear tetrazenes. Photolysis of **5** gave similar results and thermolysis of **5** at 50 °C also produced PhN_3 and $PhN(GeMe_3)_2$ by NMR analysis. Surprisingly, photolysis of **6** gives a complex mixture with no evidence (IR, NMR) of the products expected for the corresponding 1,4 shift or [2 + 3] cycloreversion: PhN_3 and $PhNSi(Me)_2N(Ph)SiMe_2$ (**7**). This contrasts with the work of Wiberg and co-workers,[5,18] who examined the thermolysis of $Me_2SiN(R)NNN(R)$ for R =

---

[9] Ellis, D. E.; Painter, G. S. *Phys. Rev. B* **1970**, *2*, 2887. Delley, B.; Ellis, D. E. *J. Chem. Phys.* **1982**, *76*, 1949.

[10] Schwartz, K. *Phys. Rev. B* **1972**, *5*, 2466.

[11] Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.

[12] Delley, B.; Ellis, D. E.; Freeman, A. J.; Baerends, E. J.; Post, D. *Phys. Rev. B.* **1983**, *27*, 2132.

[13] Slater, J. C. *The Self Consistent Field For Molecules and Solids*; McGraw-Hill: New York, 1974; p 51.

[14] Stalke, D.; Keweloh, N.; Klingebiel, U.; Noltemeyer, M.; Sheldrick, G. *Z. Naturforsch.* **1987**, *42B*, 1237. Hesse, M.; Klingebiel, U. *Angew. Chem.* **1986**, *98*, 638.

[15] Gross, M. E.; Trogler, W. C. *J. Organomet. Chem.* **1981**, *209*, 407. Gross, M. E.; Johnson, C. E.; Maroney, M. J.; Trogler, W. C. *Inorg. Chem.* **1984**, *23*, 2968. Trogler, W. C. *ACS Symp. Ser.* **1986**, *No. 307*, 177.

[16] Richmond, T. G.; Osterberg, C. E.; Arif, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 8091; Richmond, T. G.; King, M. A.; Kelson, E. P.; Arif, A. M. *Organometallics* **1987**, *6*, 1995.

[17] Barner, C. J.; Collins, T. J.; Mapes, B. E.; Santarsiero, B. D. *Inorg. Chem.* **1986**, *25*, 4322.

[18] Wiberg, N.; Vasisht, S. K.; Fischer, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 236. Wiberg, N.; Karampaties, P.; Kim, Ch.-K. *Chem. Ber.* **1987**, *120*, 1213.

Table V. Least-Squares Planes in $Ph_2N_4SiMe_2$, $Ph_2N_4(SiMe_3)_2$, and $Ph_2N_4(GeMe_3)_2$

plane no.		atoms in plane	equations of planes[a] A	B	C	D	av, displacement, Å
1	($Ph_2N_4SiMe_2$)	N1,N2,N1A,N2A	7.980	0.000	8.200	6.1502	0.006
2	($Ph_2N_4SiMe_2$)	N1,Si,C11	6.777	0.428	8.728	6.6218	0
3	($Ph_2N_4SiMe_2$)	C11-C16	5.490	-3.924	7.092	5.4238	0.003
4	($Ph_2N_4SiMe_2$)	Si,C1,C1A	-17.033	0.000	9.105	6.8285	0
5	($Ph_2N_4(SiMe_3)_2$)	N1,N2,N1A,N2A	5.172	-3.438	-4.372	-1.7858	0
6	($Ph_2N_4(SiMe_3)_2$)	N1,Si,C11	4.809	-2.366	-6.537	-3.7107	0
7	($Ph_2N_4(SiMe_3)_2$)	C11-C16	-2.562	6.104	-2.770	-3.1472	0.006
8	($Ph_2N_4(GeMe_3)_2$)	N1,N2,N1A,N2A	7.458	-4.824	0.457	0.2287	0
9	($Ph_2N_4(GeMe_3)_2$)	N1,Ge,C11	7.054	-5.541	0.040	0.0657	0
10	($Ph_2N_4(GeMe_3)_2$)	C11-C16	9.089	-2.107	-4.211	-1.4828	0.010

Dihedral Angles (deg) between Planes

plane no.	plane no.	angle	plane no.	plane no.	angle
1	2	5.3	5	6	16.3
1	3	36.1	5	7	54.7
1	4	85.6	6	7	70.4
2	3	39.5	8	9	5.9
2	4	81.9	8	10	27.9
			9	10	30.4

[a] The equations are of the form $Ax + By + Cz = D$.

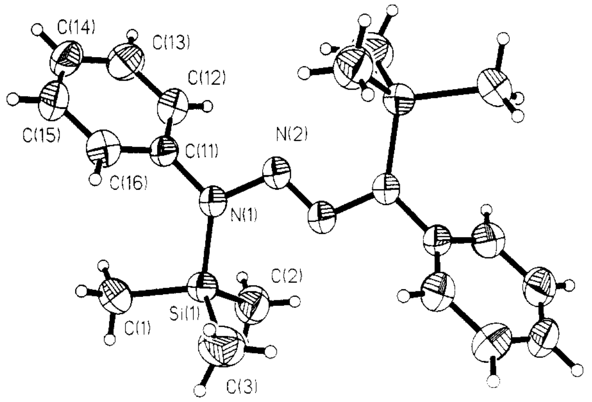


Figure 1. ORTEP plot and atom labeling scheme for *trans*-Ph(Me_3Si)NN=NN($SiMe_3$)Ph.

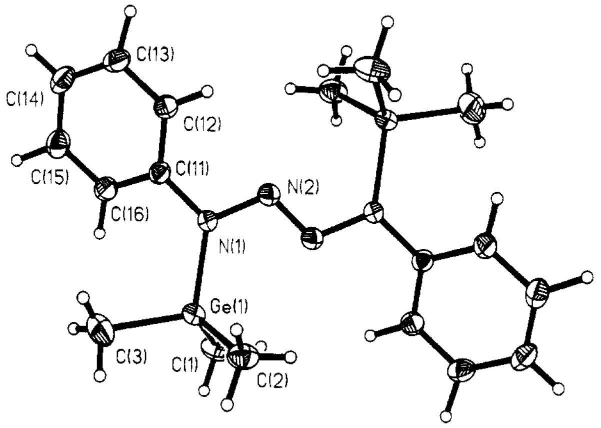


Figure 2. ORTEP plot and atom labeling scheme for *trans*-Ph(Me_3Ge)NN=NN($GeMe_3$)Ph.

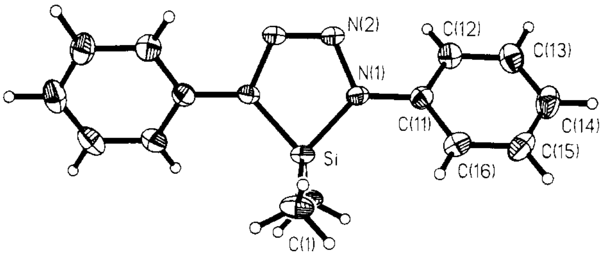


Figure 3. ORTEP plot and atom labeling scheme for $Me_2\overline{SiN(Ph)N=NN}(Ph)$.

Si(t-Bu)Me_2 and Si(t-Bu)$_2$Me. These compounds decompose cleanly to RN_3 and the reactive species Me_2Si=NR, which subsequently dimerized.

Molecular Structures of *trans*-(Ph)(Me_3Si)NNNN(Ph)($SiMe_3$), *trans*-(Ph)(Me_3Ge)NNNN(Ph)($GeMe_3$), and $Me_2\overline{SiN(Ph)NNN}(Ph)$. The molecular structures with atomic numbering schemes for **3**, **5**, and **6** are shown in Figures 1–3. Compound **6** has a crystallographic C_2 axis passing through the symmetric unit, bisecting the N(2)–N(2a) bond, while **3** and **5** lie on crystallographic inversion centers (between N(2) and N(2a)). The coordination sphere around Si in **6** is essentially tetrahedral with a dihedral angle of 85.6° between the planes defined by the metallacyle and SiC_2 fragment. The metallacycle ring is nearly planar with N(2) having the maximum displacement of 0.008 Å from the least-squares plane. In all three structures the N_4 fragments are planar and the phenyl groups are not coplanar with the N_4 fragment. The terminal nitrogen of **3**, however, is displaced 0.14 Å from the substituent plane, which forms a 16° dihedral angle with the N_4 fragment. In contrast to the Si derivative, the phenyl substituent in the Ge derivative **5** becomes nearly coplanar with the N_4 chain for Ge, probably resulting from a relief of steric crowding (longer N–Ge bonds) that permits more π conjugation between the phenyl ring and N_4 π system. The terminal nitrogen in **5** exhibits a trigonal-planar geometry and lies close to being coplanar with the N_4 moiety (dihedral angle 5.9°, Table V). This suggests π conjugation between the terminal-nitrogen lone pair and the central –N=N– fragment. The N(1)–N(2) bond lengths in the N_4 moieties (**6**, 1.392 (1) Å; **3**, 1.394 (2) Å, **5**, 1.377 (3) Å) correspond to N–N single bonds, and the N(2)–N(2a) bonds lengths (**6**, 1.267 (2) Å; **3**, 1.254 (3) Å; **5**, 1.260 (4) Å) correspond to N–N double bonds. The value for **3** closely resembles that of 1.268 (7) Å for the central N=N bond in tetrakis(trimethylsilyl)tetrazene.[19] A similar long–short–long bond pattern was observed in cyclic Pt and Pd diphenyltetrazenido complexes[1] consistent with the description of these molecules as similar to **6**: tetrazenido or tetrazene complexes (A) and not tetraazadiene complexes (B). In type A compounds,

---

[19] Veith, M. *Acta Crystallogr., Sect. B* **1975**, *B31*, 678.

Table VI. Valence Orbitals of *trans*-($(H_3Si)HN_4H(SiH_3)$) and Their Atomic Composition

orbital energy, eV		atomic character[a] Si (3s, 3p)	Si (3d)	N_α (2s, 2p)	N_β (2s, 2p)	H_α	H_{Si}
$9b_u$	0.383	33	13		10	31	14
$3b_g$	−1.330		5	20	71		2
$3a_u$	−4.802		4	63	25	1	2
$9a_g$	−6.047	9		10	77		3
$2b_g$	−6.822	12	2	42	12		33
$2a_u$	−7.656	39			10		50
$8b_u$	−7.683	32	2		5		60
$8a_g$	−7.836	35	1	2	2	1	59
$1b_g$	−8.375	32		40	3		25
$7b_u$	−9.003	17		36	33	1	9
$7a_g$	−10.350	25	1	39	7	4	22
$1a_u$	−10.433	3		22	75		

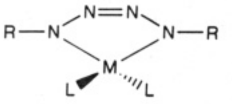
[a] N_α denotes N directly bound to Si and N_β denotes other two equivalent nitrogens. H_α and H_{Si} denotes hydrogen atoms bound to nitrogen and silicon, respectively.

Table VII. Valence Orbitals of $H_2\overline{SiN(H)NNN}H$ and Their Atomic Character

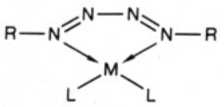
orbital energy, eV		atomic character[a] Si (3s, 3p)	Si (3d)	N_α (2s, 2p)	N_β (2s, 2p)	H_α	H_{Si}
$7b_2$	−0.997	43	22	10	6	9	1
$2a_2$	−1.910		4	25	70	1	
$3b_1$	−5.703		5	56	22		17
$6b_2$	−7.672	6		22	72		
$1a_2$	−7.889		1	82	17		
$8a_1$	−8.222	18		20	56	2	4
$2b_1$	−8.884	44	1	2	13		41
$5b_2$	−10.762	9	1	77	6	6	
$7a_1$	−11.097	32		10	25		31
$1b_1$	−11.420	4		25	71		

[a] N_α denotes N directly bound to Si and N_β denotes other two equivalent nitrogens. H_α and H_{Si} denotes hydrogen atoms bound to nitrogen and silicon, respectively.

the tetrazene ligand can be viewed as a dianionic ligand with little π-bonding character.



A



B

Theoretical Studies of Silyltetrazenes. To compare the bonding in the acyclic and cyclic tetrazenes SCF–Xα–DV calculations of the model complexes *trans*-$(H_3Si)HN_4H(SiH_3)$ and $H_2\overline{SiN(H)NNN}H$ were performed Tables VI and VII). In both complexes the lowest unoccupied orbital $3b_g$ or $2a_2$ is an empty π* orbital of the N_4 fragment (Figure 4). Three π orbitals, $1a_u$, $2b_g$, and $3a_u$ for the acyclic case and $1b_1$, $1a_2$, and $3b_1$ for the cyclic example, are occupied, and the planarity of the silicon bound nitrogens can be attributed to delocalized π bonding within the N_4 framework. The $3b_g$ and $3a_u$ (or $2a_2$ and $3b_1$) orbitals correspond to π* orbitals (π_3 and π_4) of a four-atom π system, such as butadiene, where $1a_u$ and $2b_g$ (or $1b_1$ and $1a_2$) correspond to π-bonding orbitals (π_1 and π_2). Because three of the four orbitals are filled, this corresponds to one net double bond and the tetrazene structure observed. There is surprisingly little difference in the bonding in the acyclic and cyclic tetrazenes. The orbitals in the cyclic compound (Figure 4) lie at lower energy than in the acyclic case. This probably arises from the difference between having one electropositive silyl group shared with two nitrogens versus a silyl group for each terminal nitrogen.

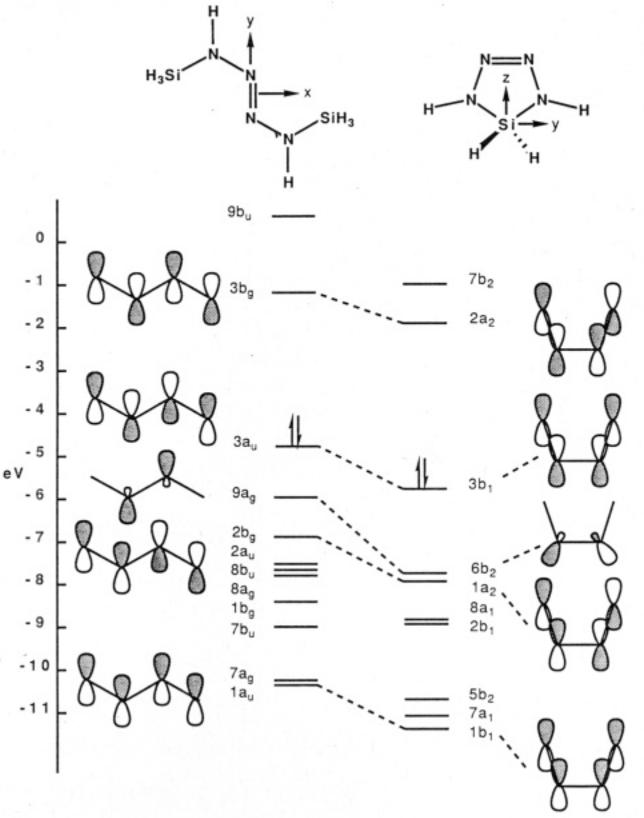


Figure 4. Molecular orbital diagrams showing results of SCF–DV–Xα calculations for *trans*-$(H_3Si)HN_4(SiH_3)H$ and $H_2\overline{SiN(H)NNN}(H)$. Orbitals associated with the N_4 π system and nitrogen lone pairs are depicted.

Table VIII. Calculated Transition Energies

trans-$(H_3Si)(H)N_4(H)(SiH_3)$ transitn	calcd energy, eV	$H_2\overline{SiN(H)NNN}(H)$ transitn	calcd energy, eV
$3a_u \rightarrow 3b_g$	3.95	$3b_1 \rightarrow 2a_2$	4.35
$9a_g \rightarrow 3b_g$	4.73[a]	$6b_2 \rightarrow 2a_2$	5.80
$2b_g \rightarrow 3b_g$	6.22[a]	$1a_2 \rightarrow 2a_2$	6.01
$3a_u \rightarrow 9b_u$	5.56[a]	$3b_1 \rightarrow 7b_2$	5.16[a]

[a] Dipole-forbidden transition.

From the modest contribution of Si to these occupied π orbitals (Tables VI and VII) we conclude that Si–N π bonding is relatively unimportant. These results agree well with previous CNDO/S calculations[20] for acyclic N_4H_4. This contrasts with the bonding in cyclic transition-metal tetraazadiene complexes, where calculations show the more energetically accessible d orbitals to mix strongly with the N_4 π system. In $(OC)_3\overline{FeN(H)NNN}(H)$ and in $(\eta\text{-}C_5H_5)\overline{CoN(H)NNN}(H)$ an N_4 π orbital similar to $3a_u$ or $3b_1$ of Figure 4 was also found[4] to be the highest occupied orbital. As Figure 4 shows, the second highest occupied orbitals $9a_g$ and $6b_2$ can be attributed to the antisymmetric combination of lone-pair orbitals on the nitrogen atoms connected by a double bond. Similar high-lying lone-pair orbitals on nitrogen are found in the cyclic transition-metal tetraazadienes[4] and probably account for the acid lability of tetrazenes.[5]

The calculations also provide a tentative assignment for the absorption spectra of **3** and **6**. As can be seen in Table VIII only one low-energy transition, $3a_u \rightarrow 3b_g$ ($\pi_3 \rightarrow \pi_4$),

---

[20] Kroner, J.; Wiberg, N.; Bayer, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 178.

is dipole-allowed for the planar acyclic tetrazene. This agrees with the absorption spectrum observed for **3**, whose lowest energy absorption at 312 nm or 3.97 eV (ϵ = 21 000) matches well with the 3.95 eV calculated for the HOMO–LUMO transition in $(H_3Si)(H)N_4(H)(SiH_3)$. A similar assignment has been proposed for the lowest energy absorption in N_4H_4 (4.7 eV)[20] and other tetrazenes.[21] The only other transition, found at 258 nm or 4.81 eV (ϵ = 21 000) in the absorption spectrum of **3** probably results from the characteristic[22] π–π^* transitions of the two phenyl substituents in **3**. For $H_2SiN(H)NNN(H)$ the $3b_1 \rightarrow 2a_2$ ($\pi_3 \rightarrow \pi_4$) HOMO–LUMO transition is predicted to be blue shifted from that in the linear isomer. Again there is good agreement between the calculated value of 4.35 eV and the experimental value for **6** (302 nm or 4.11 eV ($\epsilon \sim$ 20 000)). Assignment of the three other intense features in the UV spectrum of **6** (at 4.41, 5.60, and 6.02 eV) is problematic since both the $6b_2 \rightarrow 2a_2$, $1a_2 \rightarrow 2a_2$ transitions, and those originating from the phenyl substituents should occur in this region. The photochemical activity toward fragmentation of the N_4 group noted earlier is consistent with the antibonding character of the $3b_g$ or $2a_2$ orbital populated on electronic excitation.

Acknowledgment. This work is based on research sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant AFOSR-86-0027. We thank the DoD University Research Instrumentation Program (Grant DAAL03-87-G-0071) for funds to purchase an X-ray diffractometer.

Registry No. 1, 109719-17-7; 2, 4147-89-1; 3, 118399-12-5; 5, 118399-13-6; 6, 109639-46-5; 7, 3284-06-8; 8, 109639-47-6; Me_3SiCl, 75-77-4; Me_2SiCl_2, 75-78-5; Me_3GeCl, 1529-47-1; $PhN(GeMe_3)_2$, 13361-71-2.

Supplementary Material Available: Tables of positional parameters for hydrogen atoms, thermal parameters, and bond angles for these complexes (9 pages); listings of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

---

[21] Wiberg, N.; Vasisht, S. K.; Bayer, H.; Meyers, R. *Chem. Ber.* 1979, *112*, 2718.

[22] Dyer, J. R. *Applications of Absorption Spectroscopy of Organic Compounds*; Prentice-Hall: New York, 1965; p 18.

Base-Induced Migrations of Germyl, Stannyl, and Plumbyl Groups to the Cyclopentadienyl Ligand in the System $(\eta^5\text{-}C_5H_5)M(CO)_nER_3$ (M = Fe, Mo, W; *n* = 2, 3; E = Ge, Sn, Pb; R = Me, Ph)[1]

Jorge Cervantes,[†] Steven P. Vincenti,[‡] Ramesh N. Kapoor,[‡] and Keith H. Pannell*[,‡]

Departments of Chemistry, Universidad Autonoma Metropolitana, Iztapalapa, Mexico D.F., Mexico, and The University of Texas at El Paso, El Paso, Texas, 79968

Received July 26, 1988

Treatment of the general class of complex $(\eta^5\text{-}C_5H_5)M(CO)_nER_3$ (M = Fe, Mo, W; *n* = 2, 3; E = Ge, Sn, Pb; R = Me, Ph) with lithium diisopropylamide (LDA) gives rise to deprotonation of the cyclopentadienyl ring followed by migration of the ER_3 group to the cyclopentadienyl ring. The resulting metalate anion may be quenched with methyl iodide to yield $(\eta^5\text{-}C_5H_4ER_3)M(CO)_nMe$. In the case of the EPh_3 complexes this is the only chemistry observed for all three transition metals and group 14 elements, with the exception of $(\eta^5\text{-}C_5H_5)Fe(CO)_2PbPh_3$. For the trimethyl derivatives only the Ge complexes undergo this chemistry in high yield, while the Sn and Pb complexes exhibit both the migration reaction and direct base-induced cleavage of the transition metal–Sn(Pb) bond to yield the transition metalate $[(\eta^5\text{-}C_5H_5)M(CO)_n]^-$. The use of *n*-butyllithium in place of LDA produces considerably more M–E cleavage except for the germanium complexes where migration chemistry is observed.

Introduction

In the course of a study on the formation of carbene derivatives of molybdenum and tungsten containing germanium and tin, Dean and Graham observed that migrations of Ph_3Ge groups from both Mo and W to the cyclopentadienyl ring in the system $(\eta^5\text{-}C_5H_5)M(CO)_3GePh_3$ (M = Mo, W) occurred upon reaction of the complexes with alkyllithium reagents.[2] The degree that such migrations were observed depended upon the basicity of the alkyllithium. When *tert*-butyllithium was used significant amounts of migration were observed, especially when the metalate anions formed were trapped with $(CH_3)_3OPF_6$, whereas with methyllithium only methoxycarbene complexes were obtained upon quenching, e.g. $(\eta^5\text{-}C_5H_5)Mo(CO)_2(GePh_3)C(OMe)Me$. Related alkoxycarbene derivatives of triphenyltin complexes were also synthesized, but no tin migrations to the cyclopentadienyl ring were observed.

Following the Dean and Graham report several groups have studied such reactions. It has been shown that related base-induced migrations occur with silyl,[3,4] oligosilyl,[5]

[†] Universidad Autonoma Metropolitana.

[‡] The University of Texas at El Paso.

[1] Organometalloidal Derivatives of the Transition Metals. 19. For part 18 see: Pannell, K. H.; Rozell, J. R.; Lii, J.-C.; Tien-Mayr, S.-Y. *Organometallics*, in press.

[2] Dean, W. K.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1060.

[3] Berryhill, S. R.; Clevenger, G. L.; Burdurli, Yu. P. *Organometallics* **1985**, *4*, 1509.

[4] Thum, G.; Riews, W.; Greissinger, D.; Malisch, W. *J. Organomet. Chem.* **1983**, *252*, C67.

[5] Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. P. *Organometallics* **1986**, *5*, 1056.

0276-7333/89/2308-0744$01.50/0