Preparation, spectroscopic characterization, and deprotonation reactions of Si(NHR)₄ (R = *i*-Pr, *t*-Bu, *p*-tolyl) — EPR identification of persistent radicals formed by oxidation of polyimidosilicates

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Abstract: Treatment of $Cl_2Si(NH-t-Bu)_2$ (**6a**) with *t*-BuNH₂ in boiling toluene yields trisamino(chloro)silane $ClSi(NH-t-Bu)_3$ (**7**); formation of the tetraaminosilane $Si(NH-t-Bu)_4$ is not observed. The reaction of $SiCl_4$ with 4 equiv. of LiNHR produces the corresponding tetraaminosilanes $Si(NHR)_4$ (**2a**, R = i-Pr; **2b**, R = t-Bu; **2c**, R = p-tol) in good yields. When the sterically demanding adamantyl derivative LiHNAd is employed, only disubstitution occurs to form $Cl_2Si(NHAd)_2$ (**6b**). Oxidation of the dimeric imidosilicates $\{Li_3[Si(NR)_3(NHR)]\cdot THF\}_2$ (**3a**, R = i-Pr; **3b**, R = t-Bu) with 1 mol of iodine produces the persistent radicals $\{Li_2[Si(NR)_3(NHR)]\cdot LiI\cdot3THF\}$, which, on the basis of EPR spectra, exist as SiN_3Li_3I cubes in solution. The spirocyclic tetraimidosilicate monoanion radical $\{[(THF)_2Li(\mu-Nnaph)_2Si(\mu-Nnaph)_2Li(THF)_2]\}^{--}$ (**10**) is formed upon oxidation of the tetralithiated species $\{Li_4[Si(Nnaph)_4]\cdot4Et_2O\}$ (**1**) and $\{[Li(12-crown-4)]_2[(Et_2O)_2Li(\mu-Nnaph)_2Si(\mu-Nnaph)_2Li(Et_2O)_2]\}$ (**8**) with iodine. The spectroscopic characterization of hexa(amino)disiloxane (*t*-BuNH)_3SiOSi(NH-*t*-Bu)_3 (**14**) formed from the reaction of $Cl_3SiOSiCl_3$ with 6 equiv.

Key words: imido ligands, silicate, radicals, EPR spectra, lithium.

Résumé : Le traitement du Cl₂Si(NH-*t*-Bu)₂ (**6a**) par de la *t*-BuNH₂ dans du toluène bouillant conduit à la formation de trisamino(chloro)silane, ClSi(NH-*t*-Bu)₃ (**7**); on n'a pas observé de formation du tétraaminosilane, Si(NH-*t*-Bu)₄. La réaction du SiCl₄ avec quatre équivalents de LiNHR conduit à la formation des tétraaminosilanes correspondants, Si(NHR)₄ (**2a**, R = *i*-Pr; **2b**, R = *t*-Bu; **2c**, R = *p*-tol), avec de bons rendements. Lorsqu'on effectue la réaction avec le LiHNAd, un dérivé de l'adamantane dont les contraintes stériques sont plus grandes, on ne se produit qu'une disubstitution conduisant à la formation du Cl₂Si(NHAd)₂ (**6b**). L'oxydation des imidosilicates dimères {Li₃[Si(NR)₃(NHR)·THF}₂ (**3a**, R = *i*-Pr; **3b**, R = *t*-Bu) avec une mole d'iode conduit à la formation des radicaux persistants {Li₂[Si(NR)₃-(NHR)·LiI·3THF}⁺ qui, sur la base de leurs spectres RPE, existeraient en solution sous la forme de cubes de SiN₃Li₃I. L'oxydation par de l'iode des espèces tétralithiées {Li₄[SiNnaph)₄]·4Et₂O} (**1**) et {Li[12-couronne-4]₂[(Et₂O)₂Li(μ-Nnaph)₂Si(μ-Nnaph)₂Si(μ-Nnaph)₂Li(THF)₂]⁻ (**10**). On discute de la caractérisation spectroscopique de l'hexa(amino)disiloxane (*t*-BuNH)₃SiOSi(NH-*t*-Bu)₃ (**14**) qui se forme par réaction du Cl₃SiOSiCl₃ avec six équivalents de LiNH-*t*-Bu.

Mots clés : ligands imido, silicate, radicaux, spectre RPE, lithium.

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Introduction

An ongoing area of research in main group chemistry is the synthesis and characterization of imido $[NR]^{2-}$ (R = alkyl, aryl) analogues of common *p*-block oxoanions such as sulfate and phosphate (1–3). The chemistry of the tetraimidophosphate trianion $[P(NR)_4]^{3-}$, formally isoelectronic² with orthophosphate $[PO_4]^{3-}$, has been extensively explored. Both main group (4–7) and transition-metal (8) derivatives are known; the coordination behaviour (6, 7) and radical chemistry (6, 7, 9, 10) of this important member of the family of polyimido anions have been examined.

In contrast, the chemistry of the isoelectronic tetraimidosilicate tetraanion ($[Si(NR)_4]^{4-}$) remains essentially unknown; only one example, { $Li_4[Si(Nnaph)_4] \cdot 4Et_2O$ }_x (1), has been characterized (11). This naphthyl derivative was originally targeted because, unlike the majority of primary amines, 1-aminonaphthalene can be doubly deprotonated

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²The original definition of "isoelectronic" (isosteric) compounds restricts the term to species having the *same number of atoms* and the same number of electrons (I. Langmuir. J. Am. Chem. Soc. **41**, 1543 (1919)). Thus, according to this definition, N^{3-} is isoelectronic with O^{2-} . However, nitrides are compositionally different to oxides as a result of the different charges on the anions.



Fig. 1. Solid-state structures of 3a, 4, and 13. The *i*-Pr (3a), *t*-Bu (4a, 13), and Ad (4b) groups are omitted from cluster N atoms for clarity.

(12, 13). The metathesis reaction between dilithiated amide (Li_2Nnaph) and silicon tetrachloride $(SiCl_4)$ in diethyl ether proceeds with the elimination of lithium chloride (LiCl) to yield **1** (eq. [1]) (11).

Unfortunately, it has not proven possible to grow crystals of 1 that are suitable for X-ray analysis; in consequence, the solid-state structure of 1 remains unknown. In an effort to structurally characterize a tetraimidosilicate, the preparation of the isopropyl analogue of 1 was also attempted by the reaction of tetraaminosilane $Si(NH-i-Pr)_4$ (2a) with 4 equiv. of *n*-butyllithium. Regardless of the reaction conditions, only trilithiation was achieved, resulting in the isolation of ${Li_3[Si(N-i-Pr)_3(NH-i-Pr)] \cdot THF}_2$ (3a) (11). This behaviour is reminiscent of observations reported for trisamino(imino)phosphoranes, for which only twofold deprotonation of (i-PrNH)₃PNSiMe₃ is observed under a variety of reaction conditions (10). However, it should be noted that the reaction of the tert-butyl analogue (t-BuNH)₃PNSiMe₃ with n-BuLi yields the tetraimidophosphate [P(N-t-Bu)₃(NSiMe₃)]³⁻ via triple deprotonation under mild reaction conditions (5). Thus, it is of interest to attempt the tetralithiation of Si(NHt-Bu)₄ (2b) to determine whether a similar increase in reactivity over 2a is observed.

An examination of the extant literature (14) regarding **2b** revealed that no practical synthetic route to this compound has been reported, though **2a** is well-known and can be prepared by the reaction of excess isopropylamine with SiCl₄ (15). However, only a 6% yield of the desired product **2b** is recovered from the analogous reaction of SiCl₄ with excess *tert*-butylamine, even at elevated reaction temperatures (14). Thus, the synthesis of **2b** has been reinvestigated, as only minimal experimental detail is available from previous work.

The isoelectronic relationship between the tetraimidosilicate tetraanion $[Si(NR)_4]^{4-}$ of **1** and the tetraimidophosphate trianion $[P(NR)_4]^{3-}$ is especially intriguing in light of the remarkably stable radicals formed upon oxidation of

{Li₃[P(NR)₃(NSiMe₃)]}₂ (4a, R = t-Bu; 4b, R = Ad) with halogens (9, 10). As the synthesis of radicals of the p-block elements is a topical area of research (16), it will, thus, be of interest to examine the one-electron oxidation of 1 to see if similar behaviour is observed. Furthermore, the fact that 3a is isostructural with 4 (Fig. 1) suggests that the oxidation of 3a may well result in the formation of cubic radicals that are isostructural with the tetraimidophosphate radicals {Li₂[P(NR)₃(NSiMe₃)]·LiX·3THF}' (5a, R = t-Bu; 5b, R = Ad; X = Cl, Br, I) described previously (9, 10).

In this contribution, we describe the synthesis and multinuclear NMR spectroscopic characterization of (*i*) the tetraaminosilanes Si(NHR)₄ (**2a**, R = *i*-Pr; **2b**, R = *t*-Bu; **2c**, R = *p*-tol), (*ii*) the aminochlorosilanes Cl₂Si(NHAd)₂ (**6b**) and ClSi(NH-*t*-Bu)₃ (**7**), and (*iii*) the hexa(amino)disiloxane (*t*-BuNH)₃SiOSi(NH-*t*-Bu)₃ (**14**) and the tetraimidosilicate complex {[Li(12-crown-4)]₂[(Et₂O)₂Li(μ -Nnaph)₂Si(μ -Nnaph)₂-Li(Et₂O)₂]} (**8**). We also report the characterization, by EPR spectroscopy, of persistent radicals formed by oxidation of tetramido- and aminotris(imido)-silicates with iodine.

Experimental

Reagents and general procedures

All experiments were carried out under an argon atmosphere using standard Schlenk techniques. Toluene, diethyl ether, and tetrahydrofuran (THF) were dried over Na–benzophenone, distilled, and stored over molecular sieves prior to use. 12-Crown-4 (98%), Cl₃SiOSiCl₃ (>98%), *n*-BuLi (2.5 mol/L solution in hexanes), *tert*-butylamine, and SiCl₄ (99%) were used as received from Aldrich. The lithiated amides LiHNR (R = *i*-Pr, *t*-Bu, *p*-tol) were prepared by standard procedures involving the reaction of the corresponding primary amines with *n*-BuLi in hexane (*i*-Pr, *t*-Bu) or Et₂O (*p*-tol) at -78 °C. Iodine was sublimed prior to use. Compounds 1 (11), 3b (11), and 13 (17) were prepared by the methods reported in the literature.

Instrumentation

¹H, ⁷Li, ¹³C, ²⁹Si, and ³¹P NMR spectra were collected on a Bruker DRX-400 spectrometer with ¹H and ¹³C chemical shifts referenced internally to ¹H impurities and natural abundance ¹³C in the deuterated solvents, respectively; external standards were used for the ⁷Li (LiCl in D₂O), ²⁹Si (SiMe₄ in CDCl₃), and ³¹P (85% H_3PO_4 in D_2O) spectra. All spectra were collected at 22 °C (unless otherwise noted). IR spectra were recorded as Nujol or Fluorolube mulls on KBr plates using a Nicolet Nexus 470 FT IR spectrometer in the range 4000–400 cm⁻¹. Mass spectra were recorded on a Bruker Esquire 3000 ESI ion trap mass spectrometer. Elemental analyses were provided by the Analytical Services Laboratory, Department of Chemistry, University of Calgary, Calgary, Alberta and by Canadian Microanalytical Service Ltd., Vancouver, British Columbia. EPR spectra were recorded at 22 °C on a Bruker EMX 113 spectrometer; spectral simulations were carried out using WINEPR SimFonia; spectra were plotted using WinEPR (18). The g values of the radicals were calculated using the field-frequency ratio of each sample.

Preparation of Si(NH-*i*-Pr)₄ (2a)

SiCl₄ (1.3 mL, 1.93 g, 11.3 mmol) was added dropwise to a white slurry of LiHN-*i*-Pr (3.040 g, 46.74 mmol) in diethyl ether (50 mL) at 0 °C. The reaction mixture was stirred for 3 h, then warmed slowly to 22 °C and stirred for an additional 15 h. The pale yellow slurry was centrifuged; the supernatant liquid was filtered, leaving a colourless filtrate. The solvent was removed in vacuo and the product was washed with hexane (5 mL), giving Si(NH-*i*-Pr)₄ as a white powder (2.292 g, 8.80 mmol, 78%). ¹H NMR (C₆D₆) δ : 3.22 (sept, 1H, CH₃-CH, ³J(H,H) = 7 Hz), 1.10 (d, 6H, CH₃-CH, ³J(H,H) = 7 Hz, Me). ¹³C{¹H} NMR (C₆D₆) δ : 42.65 (s, CH), 28.34 (s, CH₃). Literature values (from ref. 15): ¹H NMR (C₆D₆) δ : 3.21 (sept, 1H, CH₃-CH, ³J(H,H) = 6.7 Hz), 1.10 (d, 6H, CH₃-CH, ³J(H,H) = 6.7 Hz, Me). ¹³C{¹H} NMR (C₆D₆) δ : 42.6 (s, CH), 28.3 (s, CH₃).

Preparation of Si(NH-t-Bu)₄ (2b)

A solution of SiCl₄ (0.79 mL, 6.90 mmol) in diethyl ether (15 mL) was added to a white slurry of LiHN-*t*-Bu (2.191 g, 27.71 mmol) in diethyl ether (50 mL) at 0 °C. The reaction mixture was stirred for 1 h, then warmed slowly to 22 °C and stirred for an additional 3.5 h. The white slurry was filtered, and the solvent was removed from the colorless filtrate in vacuo, giving Si(NH-*t*-Bu)₄ as a white powder (1.830 g, 5.78 mmol, 84%). ¹H NMR (C₆D₆) δ : 1.28 (s, *t*-Bu). ¹³C{¹H} NMR (C₆D₆) δ : 48.69 (s, *CMe*₃), 33.99 (s, *CMe*₃). ²⁹Si{¹H} NMR (C₆D₆) δ : -52.9 (s). MS (EI): 316.6 ([M]⁺). Anal. calcd. for C₁₆H₄₀N₄Si: C 60.70, H 12.73, N 17.70; found: C 60.28, H 11.47, N 17.97.

Preparation of Si(NH-*p*-tol)₄ (2c)

SiCl₄ (0.11 mL, 0.16 g, 0.96 mmol) was added dropwise to a white slurry of LiHN-*p*-tol·Et₂O (0.606 g, 3.723 mmol) in diethyl ether (35 mL) at 0 °C. The reaction mixture was stirred for 2 h, then warmed slowly to 22 °C and stirred for an additional 15 h. The pale orange slurry was centrifuged; the supernatant liquid was filtered, leaving a yellow filtrate. The solvent was removed in vacuo, giving Si(NH-*p*-tol)₄ as a pale orange powder (0.338 g, 0.747 mmol, 78%). ¹H NMR (C₆D₆) δ : 6.90, 6.71 (d of d, 4H, C₆H₄, ²J(¹H, ¹H) = 76.8 Hz, ³J(¹H, ¹H) = 8.2 Hz), 3.80 (s, 1H, NH), 2.11 (s, 3H, *p*-CH₃). ¹³C{¹H} NMR (C₆D₆) δ : 142.66 (s, *C*-NH), 130.22 (s, *o*-CH), 128.53 (*m*-CH), 117.59 (*C*-CH₃), 20.53 (CH₃). ²⁹Si{¹H} NMR (C₆D₆) δ : -52.9 (s). Anal. calcd. for C₂₈H₃₂N₄Si: C 74.29, H 7.13, N 12.38; found: C 73.22, H 7.13, N 11.91.

Preparation of Cl₂Si(NH-t-Bu)₂ (6a)

A solution of SiCl₄ (4.0 mL, 34.9 mmol) in diethyl ether (20 mL) was added to a solution of *t*-BuNH₂ (25.0 mL, 0.238 mol) in diethyl ether (150 mL) at 22 °C over 5 min, resulting in a dense white slurry. The reaction mixture was stirred for 16 h, then filtered through a sintered glass frit, yielding a clear colourless filtrate. The white solid (*t*-BuNH₃)Cl was washed with diethyl ether (100 mL). The solvent was removed from the filtrate in vacuo, giving Cl₂Si(NH-*t*-Bu)₂ as a colourless liquid (7.024 g, 28.88 mmol, 83%). ¹H NMR (C₆D₆) δ : 1.48 (br, N*H*), 1.11 (s, *t*-Bu). ¹³C{¹H} NMR (C₆D₆) δ : -38.9 (s). Literature values (from ref. 18): ¹H NMR (C₆D₆) δ : 1.49, 1.11. ¹³C{¹H} NMR (C₆D₆) δ : 50.6, 32.5.

Preparation of Cl₂Si(NHAd)₂ (6b)

SiCl₄ (0.26 mL, 2.27 mmol) was added to a white slurry of LiHNAd (0.714 g, 4.54 mmol) in toluene (30 mL) at 0 °C. The reaction mixture was allowed to warm to 22 °C and stirring was continued for 28 h. The reaction mixture was filtered and the solvent was removed from the filtrate in vacuo, giving Cl₂Si(NHAd)₂ as a white solid (0.731 g, 1.83 mmol, 81%). ¹H NMR (C₆D₆) δ : 1.90 (br, 1H, *CH*), 1.79 (d, 2H, *CH*₂-C-NH), 1.49 (t, 2H, CH-*CH*₂-CH). ¹³C{¹H} NMR (C₆D₆) δ : 51.20 (s, *C*-NH), 46.25 (s, *CH*), 36.45 (s, *CH*₂-C-NH), 30.35 (s, CH-*CH*₂-CH). ²⁹Si{¹H} NMR (C₆D₆) δ : -38.8 (s). Anal. calcd. for C₂₀H₃₀N₂SiCl₂: C 60.13, H 8.07, N 7.01; found: C 59.85, H 8.24, N 7.13.

Preparation of ClSi(NH-t-Bu)₃ (7)

tert-Butylamine (10.0 mL, 95.16 mmol) was added to a solution of Cl₂Si(NH-*t*-Bu)₂ (3.078 g, 12.65 mmol) in toluene (20 mL) at 22 °C, resulting in a clear colorless solution. The reaction mixture was refluxed at 113 °C for 24 h. The resulting white slurry was cooled to 22 °C and filtered through a sintered glass frit, resulting in a clear colorless filtrate. The white solid (*t*-BuNH₃·HCl) was washed with toluene (5 mL). The solvent was removed from the filtrate in vacuo, giving spectroscopically pure ClSi(NH-*t*-Bu)₃ as a colourless liquid (3.138 g, 11.21 mmol, 89%). ¹H NMR (C₆D₆) δ : 1.20 (s, *t*-Bu). ¹³C{¹H} NMR (C₆D₆) δ : 49.47 (s, *C*Me₃), 33.28 (s, *CMe₃*). ²⁹Si{¹H} NMR (C₆D₆) δ : -45.2 (s).

Preparation of $\{[Li(12\text{-}crown-4)]_2[(Et_2O)_2Li(\mu-Nnaph)_3Si(\mu-Nnaph)_3Li(Et_2O)_3]\}$ (8)

n-Butyllithium (4.65 mL, 11.62 mmol) was added to a solution of 1-aminonaphthalene (0.833 g, 5.817 mmol) in diethyl ether (30 mL) at -78 °C and stirred for 1 h. SiCl₄

(0.17 mL, 1.484 mmol) was added to the reaction mixture dropwise. After 30 min, the reaction mixture was warmed to 22 °C and stirred for an additional 24 h. The resulting yellow slurry was then filtered, yielding a clear yellow solution. 12-Crown-4 (0.48 mL, 3.024 mmol) was added to the solution at 22 °C, resulting in a yellow slurry, which was stirred for 1 h. The solvent was then removed in vacuo, giving 8 as a bright yellow powder (1.489 g, 1.166 mmol, 80%). ¹H NMR (*d*₈-THF) δ: 8.5 (br), 8.10 (d, 4H), 7.44 (d, 4H), 7.09 (t, 4H), 7.02 (t, 4H), 6.90 (t, 4H), 6.40 (t, 4H), 3.40 (q, 16H, Et₂O), 3.33 (s, 24H, 12-crown-4), 1.14 (t, 24H, Et₂O). ¹³C{¹H} NMR (d_8 -THF) δ : 162.37, 137.44, 128.61, 128.24, 127.06, 124.63, 124.19, 120.70, 108.46, 106.92, 68.82 (s, (s, 12-crown-4), 65.52 $(CH_3CH_2)_2O),$ 14.59 (s, $(CH_3CH_2)_2O$). ⁷Li NMR (d_8 -THF) δ : 0.63 (s). Anal. calcd. for C₇₂H₁₀₀N₄SiO₁₂Li₄: C 68.12, H 7.94, N 4.41; found: C 67.20, H 8.00, N 4.83.

Preparation of (t-BuNH)₃SiOSi(NH-t-Bu)₃ (14)

A solution of Cl₃SiOSiCl₃ (1.479 g, 5.191 mmol) in diethyl ether (10 mL) was added to a white slurry of LiHN-t-Bu (2.463 g, 31.15 mmol) in diethyl ether (40 mL) at 0 °C. After 30 min, the white slurry was warmed to 22 °C and stirred for an additional 15 h. The resulting pale yellow slurry was filtered and the solvent was removed from the filtrate in vacuo, giving (t-BuNH)₃SiOSi(NH-t-Bu)₃ as a pale yellow solid (1.770 g, 3.505 mmol, 68%). Sublimation of the crude product at 135 °C under reduced pressure resulted in the isolation of a white powder (1.177 g, 2.331 mmol, 45%). IR (cm⁻¹) v: 3412 (m, (N-H)), 1230 (vs, (Si-O-Si)). ¹H NMR (C_6D_6) δ : 1.34 (s, *t*-Bu), 1.31 (s, *t*-Bu, minor resonance) (relative intensities ca. 5:1), 1.21 (NH). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (C₆D₆) δ: 49.10 (s, CMe₃), 33.84 (s, CMe₃), 48.80, 33.87 (minor resonances). ²⁹Si{¹H} NMR (C₆D₆) δ : -54.5 (s). Anal. calcd. for C₂₄H₆₀N₆Si₂O (14): C 57.09, H 11.98, N 16.64; $C_{28}H_{71}N_7Si_2O(14 + t-BuNH_2)$: C 58.17, H 12.38, N 16.96; found: C 56.32, H 12.19, N 15.99, Cl < 0.3.

Results and discussion

Preparation and NMR characterization of $Cl_2Si(NHAd)_2$ (6b), $ClSi(NH-t-Bu)_3$ (7), and $Si(NHR)_4$ (2a, R = *i*-Pr; 2b, R = *t*-Bu; 2c, R = *p*-tol)

With only limited information available (14) regarding previous attempts to synthesize 2b, the reaction of SiCl₄ with t-BuNH₂ was reinvestigated. As reported in the literature (19), treatment of SiCl₄ with an excess of tertbutylamine at room temperature results in the aminolysis of two silicon-chlorine bonds and the formation of 6a in 83% yield. Further treatment of **6a** with an excess of *t*-BuNH₂ in boiling toluene resulted in the formation of 7, a colourless liquid, in 89% yield. While several physical properties of 7 have been determined, including the boiling point and refractive index (14), no spectroscopic data for this compound have been reported. The tert-butyl ¹H NMR resonance of 7 (1.20 ppm) is shifted slightly downfield as compared with that of **6a** (1.11 ppm), while the ²⁹Si NMR signal (-45.2 ppm) of 7 appears at higher field than the corresponding resonance of **6a** (-38.9 ppm). The α -carbon signal in the ¹³C NMR spectrum of 7 is shifted to higher field (49.5 vs. 50.6 ppm), while the methyl groups resonate at lower field (33.3 vs. 32.6 ppm).

Attempts to prepare 2b by the reaction of 7 with an excess of tert-butylamine at elevated temperatures were unsuccessful; in all cases, no reaction could be detected by ¹H NMR spectroscopy. In consequence, an alternative synthetic route, based on the method by which the trisamino(imino)phosphoranes $(RNH)_3PNSiMe_3$ (R = *i*-Pr, Cy, *t*-Bu, Ad) have been prepared (5, 10) (eq. [2]), was adopted whereby SiCl₄ was treated with 4 equiv. of LiHN-t-Bu at 22 °C (eq. [3]). This reaction proceeds with the elimination of 4 equiv. of LiCl and produces the desired compound **2b** in 84% yield. The identity of **2b** was established by multinuclear NMR, mass spectrometry (M⁺ at 316.6), and elemental (C, H, N) analysis. The trends in multinuclear NMR data that were observed on moving from the bisamino compound 6a to the trisamino species 7 continue with this tetraaminosilane: the ¹H NMR signal is at still lower field (1.28 ppm) as is the CMe_3 peak in the ¹³C NMR spectrum (34.0 ppm), while the second ¹³C NMR resonance (48.7 ppm) and the ²⁹Si NMR signal (-52.9 ppm) appear at higher field. No trace of contamination from unreacted 6a or 7 was detected in the NMR spectra of this compound.

[2]
$$Cl_3PNSiMe_3 + 3LiHNR$$

 $\xrightarrow{Et_2O} (RNH)_3PNSiMe_3 + 3LiCl$

$$[3] \qquad \text{SiCl}_4 + 4\text{LiHN-}t\text{-Bu} \\ \xrightarrow{\text{Et}_2\text{O}}{0 \ ^{\circ}\text{C}} \text{Si(NH-}t\text{-Bu)}_4 + 4\text{LiCl}$$

The ease with which this reaction (eq. [3]) occurs indicates that electronic effects rather than the steric influence of the bulky *t*-BuNH₂ group, as previously postulated (14), preclude the formation of **2b** in solvothermal reactions between SiCl₄ and *t*-BuNH₂. The formation of LiCl presumably provides a sufficient driving force for complete aminolysis to occur. The utility of this synthetic approach is not limited to the *tert*-butyl group: the known derivatives **2a** and **2c** have also been prepared in ca. 80% yields by this procedure and identified by multinuclear NMR spectra.

Following the success of this synthetic methodology for producing **2b**, it was of interest to determine whether other, perhaps even more sterically hindered tetraaminosilanes, could be prepared in the same manner. To that end, the synthesis of "Si(NHAd)₄" (**2d**) was attempted via the analogous reaction of SiCl₄ with lithium adamantylamide (LiHNAd). However, the disubstituted compound **6b** was isolated in 81% yield in this case. As the electron-withdrawing effects of NHAd and NH-*t*-Bu groups are expected to be quite similar to one another, this failure to generate tris- or tetra-(adamantylamino)silanes must be attributed to the greater steric bulk of the adamantyl cages as compared with that of the *tert*-butyl substituents of **2b**.

Attempted preparation of $\{Li_4[Si(NR)_4]\}$ (R = t-Bu, ptol) — Synthesis and NMR characterization of $\{[Li(12-crown-4)]_2[(Et_2O)_2Li(\mu-Nnaph)_2Si(\mu-Nnaph)_2Li(Et_2O)_2]\}$ (8)

With an efficient synthetic route to $Si(NH-t-Bu)_4$ established, an attempt to tetralithiate this species with *n*-BuLi was carried out. The two reagents were combined in hexane at 22 °C. The ¹H NMR spectrum of the product of this reaction, a fine white powder, contained two *t*-Bu resonances at 1.64 and 1.48 ppm in a 1:3 ratio, as well as a broad signal attributable to a NH fragment; unreacted *n*-BuLi was also detected. These spectroscopic data are consistent with the formation of a trilithiated species {Li₃[Si(N-*t*-Bu)₃(NH-*t*-Bu)]}₂ (**3b**) (11), which is isostructural with **3a**. The reaction was repeated under various conditions. In all cases, a significant amount of unreacted *n*-BuLi was observed in the ¹H NMR spectrum of the product, along with a broad signal that was attributed to a NH fragment, the presence of which was confirmed by IR spectroscopy. Reactions between **2b** and Mg-*n*-Bu₂ under a variety of conditions also resulted in incomplete deprotonation, as revealed by sharp N–H stretching vibrations in the IR spectra of the products.

In light of the limited reactivity of **2b** toward *n*-BuLi, it was decided to undertake similar reactions with Si(NH-p-(2c), as the increased acidity of the NH protons of arylamino substituents compared with that of alkylamino groups has been observed to facilitate complete lithiation in related trisamino(thio)phosphate systems (20). The spectroscopic data obtained from these experiments were inconclusive, but did not provide any strong evidence to support the formation of "{Li₄[Si(N-p-tol)₄]}". Based on these results, it is proposed that fourfold deprotonation of $Si(NHR)_4$ (R = alkyl, aryl) is not possible using alkyl lithium reagents, as they are not sufficiently basic to effect the removal of the fourth proton. The synthesis of 1 requires the double deprotonation of 1-aminonaphthalene prior to reaction with $SiCl_4$ (11); since H₂Nnaph is the only primary amine that can be dilithiated, the naphthyl derivative 1 may be a unique example of a tetralithiated tetraimidosilicate.

With the library of viable R groups thus curtailed, the preparation of a crown ether complex of 1 was undertaken, with the expectation that the resulting material would be more crystalline than the diethyl etherate 1. The synthesis of 1 by the literature procedure (11) was modified by the addition of 2 equiv. of 12-crown-4 after filtration to remove the LiCl by-product. The resulting bright yellow powder was characterized by ¹H and ¹³C NMR spectroscopy, as well as by an elemental (C, H, N) analysis. The overlapping multiplets in the aromatic region of the ¹H NMR spectrum of the product render it difficult to interpret. However, only 10 distinct signals were observed in the aromatic region (106.9–162.4 ppm) of the ¹³C NMR spectrum, in addition to the resonances for 12-crown-4 and diethyl ether ligands, indicating the equivalence of the four Nnaph substituents. Based on these data, this novel tetraimidosilicate complex is thought to exist in a spirocyclic conformation {[Li(12 $crown-4)]_{2}[(Et_{2}O)_{2}Li(\mu-Nnaph)_{2}Si(\mu-Nnaph)_{2}Li(Et_{2}O)_{2}]\} (8),$ with two Li⁺ cations sequestered by 12-crown-4; the remaining two Li^+ cations are each N,N-chelated by the naphthylimido groups and bis-solvated by two diethyl ether ligands.

Though single crystals of 8 are readily obtained from THF-hexane solutions, they are not of sufficient quality for X-ray analysis; thus, the proposed structure of 8 has not been confirmed in the solid state. However, the proposed



spirocyclic geometry has been observed in the solid state for the isoelectronic tetra(naphthylimido)phosphate {[Li(TH- $F)_4$][(THF)₂-Li(μ -Nnaph)₂P(μ -Nnaph)₂Li(THF)₂]} (**9a**) (4) and in solution for the *tert*-butyl analogue {[Li(THF)₄]{Li(TH- $F)_2$](μ -N-*t*-Bu)₂P(μ -N-*t*-Bu)₂]Li(THF)₂} (**9b**) (10).



Surprisingly, only one signal (0.63 ppm) was observed in the ⁷Li NMR spectrum of 8 in d_8 -THF, indicating that the chemically inequivalent lithium cations exchange rapidly in solution despite the presence of 12-crown-4. This can be rationalized by taking into account the presence of four highly nucleophilic imido groups and the large negative charge of the tetraimidosilicate tetraanion. These two factors combine to render chelation by the $[Si(Nnaph)_4]^{4-}$ preferable to, or at least competitive with, an η_4 mode of coordination by the crown ether. A variable-temperature ⁷Li NMR study in d_8 -THF showed that the spectrum is highly dependent upon temperature, confirming that the lithium cations are in dynamic equilibrium in solution. The single resonance broadens significantly even at 0 °C, then resolves into several sharp resonances at lower temperatures (-45 to -60 °C). It is expected that further lowering of the temperature would eventually result in two singlets in a 1:1 ratio attributed to the N,N-chelated lithium ions and the $[Li(12-crown-4)]^+$ cations. However, this resolution could not be achieved above the temperature at which the NMR solvent began to gel.

Formation and EPR characterization of persistent polyimidosilicate radicals

Oxidation reactions of the tetraimidosilicate **1** were explored to determine whether **1** is capable of forming stable radicals,³ in a manner similar to that reported for the isoelectronic tetraimidophosphates {Li₃[P(NR)₃(NSiMe₃)]}₂ (**4a**, R = *t*-Bu; **4b**, R = Ad) (6, 9, 10). The addition of 0.5 mol of iodine to a bright yellow solution of **1** in THF resulted in a deep green-brown solution, indicating the formation of a paramagnetic species, presumably a lithiated derivative of trianion radical [Si(Nnaph)₄]^{3-.} An EPR spectrum of this solution (Fig. 2) at 22 °C displayed a single broad resonance (ca. 15 G), with no resolved hyperfine coupling (HFC) to the four nitrogen nuclei of the tetraimidosilicate radical. Though this was initially surprising, it

³ In this article, a "stable" radical is one that is inherently stable as an isolated species and does not decompose under an inert atmosphere at room temperature (16). A "persistent" radical is one that has a relatively long lifetime under the conditions that are used to generate it; radical less stable than this are termed "transient".

Fig. 2. Experimental EPR spectra of iodine-oxidized 1 (top) and 10 (middle); simulated EPR spectrum of 10 (bottom).



should be noted that extensive line broadening is often observed in fluxional radical systems: the variable-temperature ⁷Li NMR data obtained for the related crown ether complex **8** are certainly indicative of considerable solution dynamics, and lithium exchange is expected to occur still more readily in the absence of any crown ether.

In an attempt to resolve the nitrogen and lithium HFCs in the EPR spectrum of the $[Si(Nnaph)_4]^{3-}$ radical, the crown ether complex **8**, believed to be less fluxional than **1**, was oxidized with iodine. An EPR spectrum (Fig. 2) of this darkgreen reaction mixture revealed a nine-line pattern, which is consistent with coupling to four equivalent ¹⁴N (I = 1, 99.6%) nuclei; the g value of this radical is 2.0037. The pronounced "S-curve" shape of the spectrum and the broadness of the spectral lines are attributed to unresolved HFC (21) to the lithium cations (⁷Li, I = 3/2, 92.6%) in the spirocyclic radical monoanion {[(THF)₂Li(µ-Nnaph)₂Si(µ-Nnaph)₂Li(THF)₂]}⁻⁻ (**10**).

A good simulation of this spectrum (Fig. 2) was obtained by using hyperfine coupling constants (HFCCs) of 3.8 G to four nitrogen atoms and 0.7 G to two lithium cations. These HFCCs are slightly smaller than those observed for the isostructural tetraimidophosphate radical [(THF)₂Li(μ -N-*t*-Bu)_2P(μ -N-*t*-Bu)Li(THF)₂]' (11) for which the corresponding HFCCs are 4.30 G (¹⁴N) and 1.08 G (⁷Li) (10). However, the value of the ⁷Li HFCC for 10 should be regarded as approximate, since the broadness of the spectral lines precludes diScheme 1. Oxidation of 3a by iodine to form two cubic radicals 12 (R = i-Pr).



rect measurement of this coupling. The striking difference between the line widths produced by the two symmetrical spirocyclic radicals **10** (ca. 3 G) and **11** (ca. 0.5 G) is thought to be caused by spin delocalization into the naphthyl groups of **10**, and the resultant presence of numerous inequivalent ¹H hyperfine couplings. This is not an unreasonable hypothesis, since Li₂Nnaph is reported to be paramagnetic and the EPR spectrum contains sufficiently large ¹H HFCCs to produce a signal that is approximately 17 G in width (12).

While the green colour formed upon oxidation of **1** and **8** persists for more than 24 h in both instances, the EPR signals were surprisingly weak, indicating the presence of only a small amount of paramagnetic material in the solutions. This observation suggests that either the tetraimidosilicate radical has only a short lifetime or that radical formation is not quantitative, i.e., that the radical **10** is not the exclusive product of these oxidation reactions. Attempts to isolate the tetraimidosilicate radical were unsuccessful owing to the limited stability of this persistent radical. Overall, the stability of **10** is comparable to that of the isostructural neutral radical **11** (10).

Previous work with tetraimidophosphate radicals has shown that cubic derivatives are significantly more stable than spirocycles such as 10 and 11 (6, 7, 9, 10). Oxidation of the dimeric aminotris(imido)silicate 3a with iodine is expected to proceed in an analogous fashion to oxidations of the structurally similar cluster 4. As depicted in Scheme 1, this process can be viewed to involve disruption of the Li₆N₆ core of 3a, yielding two molecules of the cubane radical $\{Li_2[Si(N-i-Pr)_3(NH-i-Pr)]\cdot LiI\cdot 3THF\}$ (12). In practice, the addition of 1 equiv. of I_2 to a slurry of **3a** in THF yields an intensely yellow solution that gives rise to a somewhat stronger EPR signal than do the products of the corresponding reactions with 1 and 8. The EPR spectrum of the reaction mixture is primarily a seven-line pattern with multiple smaller HFCs present as well (Fig. 3); the g value of this radical is 2.0044. The best simulation of this spectrum was obtained by including HFCCs to three equivalent nitrogen atoms (8.1 G), one unique nitrogen atom (2.0 G), three lith-







ium cations (0.9 G), and an iodine atom (0.4 G) (Fig. 3). Thus, this EPR spectrum is consistent with the formation of the cubic radical 12 and confirms that 3a undergoes an analogous reaction to 4 when oxidized.

Like the tetraimidosilicate radical 10, the amidotris(imido)silicate 12 is considered to be a persistent radical, since it decomposes in solution within 72 h.³ This is somewhat surprising, as cubic tetraimidophosphate radicals are more stable than related spirocyclic species and they can be isolated and structurally characterized in the solid state (6, 7, 9, 10). However, it must be noted that the isopropyl substituents of 10 provide only modest steric protection to prevent dimerization of the radical: stable tetraimidophosphate radicals occur only when bulkier tert-butyl or adamantyl groups are in place (10). Thus, oxidation of the tert-butyl derivative 3b with 1 mol of iodine was undertaken, with the expectation that a highly persistent or stable radical would result. Surprisingly, the paramagnetic species generated from this reaction was found to be even less stable than 12, persisting in solution for only a few seconds. An EPR spectrum of the reaction mixture produced a very weak signal, consisting of a poorly resolved seven-line pattern. While this suggests HFC of the unpaired electron to three equivalent ¹⁴N nuclei, consistent with the formation of a cubic radical, the experimental parameters used to acquire this spectrum were not optimal owing to the low sample concentration. Oxidation of the related dimer $\{Li_3[PhSi(N-t-Bu)_3]\}_2$ (13) (17), an organic derivative of a trisimidosilicate that exists as a Li₆N₆ hexagonal prism bicapped by the two Si-Ph units (cf. 3a in Fig. 1), also yielded a transient radical. The lower stability of this radical as compared with that of 12 can be attributed to a combination of the smaller steric bulk of the phenyl group (cf. the NH-i-Pr unit), combined with the fewer number of electronegative (i.e., N) atoms over which the unpaired electron can be delocalized. However, no explanation can be given at the present time as to why the oxidation of the more sterically protected **3b** leads to less stable radicals than the corresponding reactions of the isopropyl derivative **3a**.

Preparation and characterization of (*t*-BuNH)₃-SiOSi(NH-*t*-Bu)₃ (14)

As an alternative precursor to polyimidosilicate radicals, we targetted hexa(*tert*-butylamino)disiloxane (*t*-BuNH)₃-SiOSi(NH-*t*-Bu)₃ (14), which was synthesized by the reaction of hexachlorodisiloxane with 6 equiv. of LiHN-*t*-Bu at 0 °C in diethyl ether (eq. [4]) and purified by sublimation. The resultant white powder was characterized by IR and multinuclear NMR spectra, GC–MS, and elemental analyses.

$$[4] \qquad Cl_{3}SiOSiCl_{3} + 6LiHN-t-Bu$$
$$\xrightarrow{Et_{2}O} (t-BuNH)_{3}SiOSi(NH-t-Bu)_{3} + 6LiCl$$

The ¹H NMR spectrum of the product exhibits a minor resonance at 1.31 ppm in addition to the major peak at 1.34 ppm. The integrated relative intensities of these two resonances exhibit an approximately 1:5 ratio. The ¹³C NMR spectrum is consistent with this observation, showing one major set of tert-butyl resonance (49.10 and 33.84 ppm) and a second set of minor resonances at 48.80 and 33.87 ppm. These minor resonances, with the same relative intensities, persist in the NMR spectra of samples purified by either sublimation or recrystallization. The ²⁹Si NMR spectrum of the product exhibits a single sharp resonance at -54.6 ppm. Furthermore, the GC-MS revealed only a single component. Since the two signals in the ¹H NMR spectrum are very close together, the integration of the relative intensities must be regarded as approximate, and we have considered the possibility that the ratio of the intensities is 1:6 with the smaller resonance attributed to a component with a single *t*-BuN group. The possible candidates for the "single t-BuN" species include t-BuNHLi, t-BuNH₂, or [t-BuNH₃]Cl, each of which could form a hydrogen-bonded adduct with the O atom of 14. The product shows no resonance in the ^{7}Li NMR spectrum, thus ruling out *t*-BuNHLi as an additional component. Elemental analyses show that the product contains insignificant amounts of Cl (<0.3%), thus excluding [t-BuNH₃]Cl as an impurity. Although we cannot count out the possibility of one molecule of t-BuNH₂ as a hydrogenbonded component of the product, the IR spectrum (Fluorolube mull) shows only extremely weak, broad bands in the 3120-3240 cm⁻¹ region, which could be assigned to hydrogen-bonded t-BuNH₂, in addition to a sharp, mediumintensity band at 3412 cm⁻¹ attributed to v(N-H) of 14. We also note that the CHN analyses are in better agreement with the calculated values for 14 than with the alternative (14 + t) $BuNH_2$). We are led to the tentative conclusion, therefore, that the best explanation of the combined spectroscopic and analytical data for 14 involves some sort of intermolecular interaction in solution that leads to inequivalence of one of the N-t-Bu groups. Unfortunately, numerous crystals of 14 obtained by recrystallization or sublimation were only weakly diffracting, and consequently, we have been unable to obtain a solid-state structure by X-ray crystallography. In view of the uncertainty about the structure of 14, we have not pursued the hexalithiation.

Conclusions

The reaction of $SiCl_4$ with lithiated primary amides LiHNR (R = alkyl, aryl) in diethyl ether provides a versatile

and efficient route to tetraaminosilanes Si(NHR)₄. Fourfold deprotonation of Si(NHR)₄ does not appear to be possible using either *n*-BuLi or MgBu₂, suggesting that the preparation of tetraimidosilicates $[Si(NR)_4]^4$ can only be achieved if the amine is doubly deprotonated prior to reaction with SiCl₄, i.e., by the use of Li₂NR. EPR studies of the products of the one-electron oxidation of tetraimido or amidotris(imido)silicates with iodine indicate the formation of persistent spirocyclic and cubic radicals, respectively. The reasons for the lower stability of these polyimidosilicate radicals as compared with that of the analogous tetraimidophosphate radicals are not yet fully understood and merit further investigation.

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