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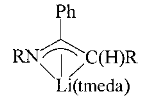
A 1-Aza-2-silacyclobut-3-ene and an Alkyne from [Li{Si(SiMe$_3$)$_3$}(thf)$_3$] and the Isocyanide 2,6-Me$_2$C$_6$H$_3$NC

Peter B. Hitchcock, Michael F. Lappert,* and
Marcus Layh

The interaction of a trimethylsilylmethyllithium reagent Li[CH$_{3-n}$(SiMe$_3$)$_n$] ($n = 1$, 2, or 3) and an α-H-free nitrile R′CN can yield a 1-azaallyl-, β-diketiminato-, or 1,3-diazaallyllithium, depending on n, the nature of R′, the stoichiometry, and the absence or presence of a neutral coligand. Examples of such products from LiCHR$_2$ (R = SiMe$_3$) and PhCN are **A**,[1] **B**,[2] **C**,[3] or **D**,[1] each formed by initial insertion of PhCN into the Li–C bond of Li(CHR$_2$) and a 1,3-Me$_3$Si shift from C to N, followed for **B**–**D** by insertion of a further PhCN molecule into an Li–N or Li–C bond of **A** and a final 1,3-Me$_3$Si N→N or C→N shift. This chemistry was extended to the lithium silyl and germyl congeners of LiCR$_3$. Thus, [Li(SiR$_3$)(thf)$_3$] with 2,6-Me$_2$C$_6$H$_3$CN (ArCN) yielded the zwitterionic 3-sila-β-diketiminatolithium complex **E**, a process involving a hitherto unprecedented 1,3-Me$_3$Si shift from Si to N.[4] We also previously demonstrated that from LiCHR$_2$ and an isocyanide R′NC, a similar diversity of products **F**–**H** is available, each formed via successively the 1:1 adduct and the lithioaldimine **I**.[1] Compound **I**, by a 1,2-Me$_3$Si C→C shift, is transformed into **F**, which by a similar sequence generates **G** and **H**.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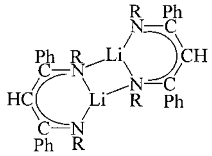
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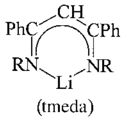
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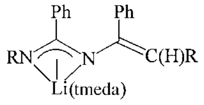
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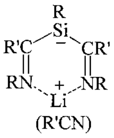
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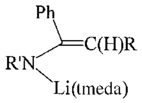
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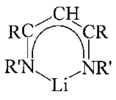
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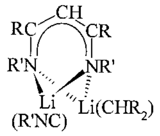
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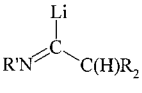
I

We now report the results presented in Scheme 1: Treatment of [Li(SiR$_3$)(thf)$_3$] [5] with the isocyanide ArNC yields

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[**] We thank EPSRC for a fellowship for M.L. and other support.

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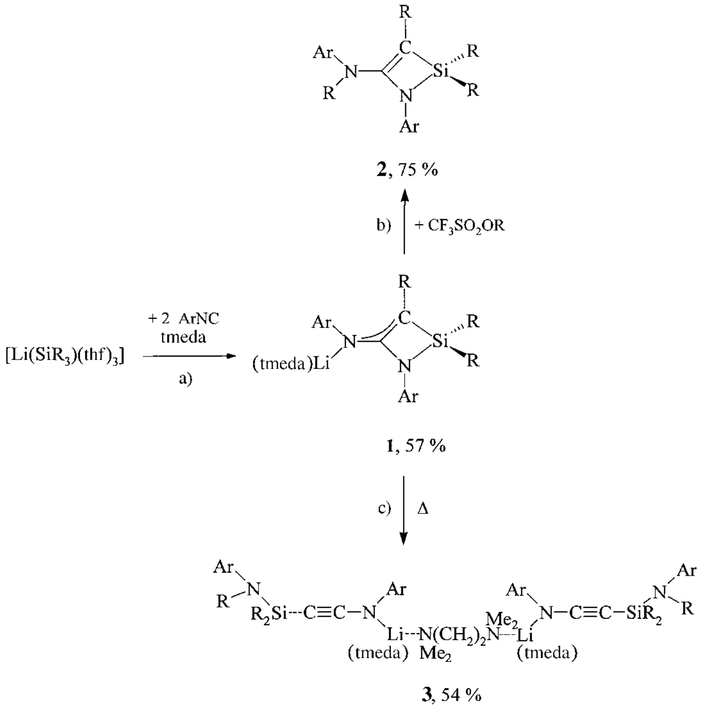


Scheme 1. Synthesis of compounds **1**–**3**; R = SiMe$_3$, Ar = 2,6-Me$_2$C$_6$H$_3$, tmeda = *N,N,N′,N′*-tetramethylethylenediamine. See text for details.

the novel, crystalline 4-aryl(lithio)amino-1-aza-2-silacyclobut-3-ene derivative **1** (step a), which upon being quenched with trimethylsilyl triflate was converted into **2** (step b). In contrast, heating **1** in refluxing benzene afforded the crystalline alkyne derivative **3** (step c), the C≡C fragment of which remarkably arises from the ArNC units. Moreover, we present X-ray crystallographic data which establish the molecular structures of the crystalline amidolithium compounds **1** and **3**.

The formation of **1** was independent of whether one or two equivalents of ArNC were employed and of solvent (pentane or Et$_2$O). The conversion of **1** into **3** (Scheme 1, step c) was monitored by ^{1}H NMR spectroscopy on a sample of **1** in C$_6$D$_6$ in a sealed NMR tube; quantitative conversion was achieved at 80 °C in 14 h if tmeda (0.5 mol) was added. On a preparative scale, optimal results from **1** alone were achieved by heating in benzene at 80 °C for 2 h.

Each of the compounds **1**–**3** gave satisfactory elemental analyses and multinuclear NMR spectra, and for **1** and **2** acceptable EI mass spectra were also obtained (see Experimental Section). In addition, single-crystal X-ray diffraction data revealed the molecular structures of crystalline **1** and **3** (see Figure 1). The unusual structure of **1** was maintained in solution, as established by a series of NOE difference NMR spectra.

Compound **1** is a monomer, in which the atoms of the four-membered heterocyclic ring and the exocyclic N atom N1 are essentially coplanar and the geometry at N1 and each of the ring atoms N2, C1, and C2 is almost planar (Figure 1, left). Of the endocyclic bond angles, only C2-C1-N1 is obtuse (105.2(5)°), and of the remainder only that at Si1 (76.9(3)°) deviates significantly from 90°. The Li atom is directly bonded only to N1 and the two nitrogen atoms of tmeda, having no close contacts to C1 or C2, although the N1–C1 (1.331(7) Å) and C1–C2 (1.411(8) Å) bond lengths indicate significant delocalization of π-electron density between these three atoms. In this respect, the situation resembles that in [Li{N(R)C(4-BrC$_6$H$_4$)=CR$_2$}(thf)], which has a structure such as that of **F**[6] and corresponding N–C (1.35(1) Å) and C–C (1.40(2) Å) bond lengths similar to those of **1**; but the azaallyl differs from **1** in having relatively close Li···C contacts of 2.23(2) and 2.32(2) Å.[6] We conclude that **1** is best described as a resonance hybrid of the enamidolithium structure **1a** and the dipolar **1b**. As far as we are aware, only two SiNCC heterocycles have previously been crystallographically characterized, both being 1-aza-2-silacyclobutanes with C–C single bond lengths of 1.541(5) Å in Si(*t*Bu)$_2$N(Si*t*Bu$_2$Ph)-C{H(OEt)}CH$_2$[7] and 1.569(5) Å Si(Ph)$_2$N(SiMe$_2$Ph)C-{H(Ph)}CH*i*Pr.[8] In silacyclobutenes, the C=C bond lengths are unexceptional; [9, 10] they lie in the range 1.34–1.37 Å, for

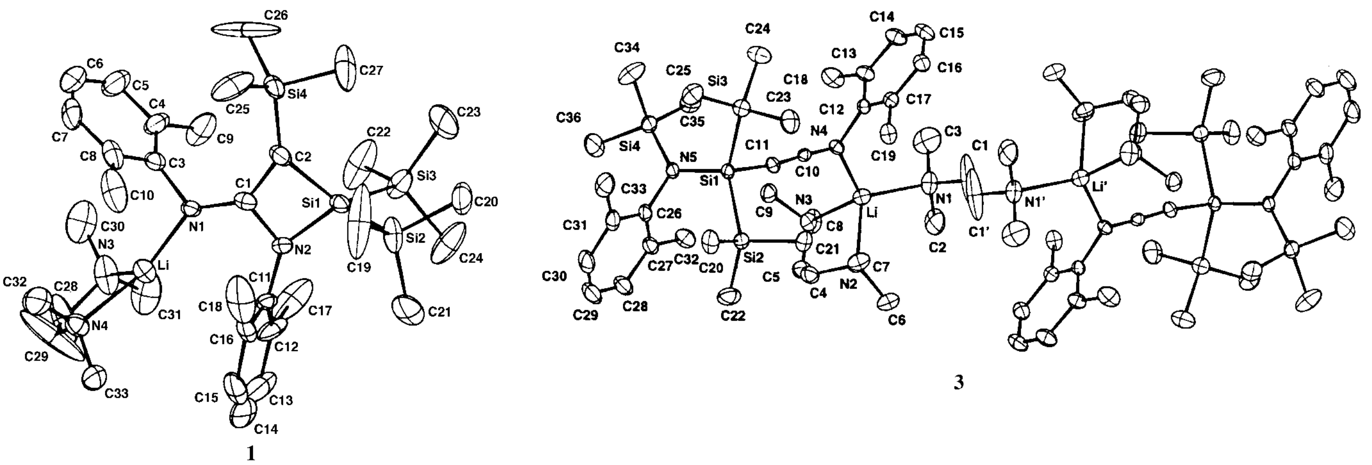
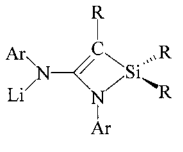


Figure 1. Crystal structures and atomic labeling schemes of **1** and **3**. Selected bond lengths [Å] and angles [°]: **1**: Li–N1 1.958(11), Li–N3 2.119(12), Li–N4 2.162(11), Si1–N2 1.785(5), Si1–C2 1.831(7), Si1–Si3 2.346(3), Si1–Si2 2.353(3), N1–C1 1.331(7), N2–C1 1.421(7), C1–C2 1.411(8); N2-Si1-C2 76.9(3), C1-N2-Si1 89.7(3), C1-C2-Si1 88.1(4), C2-C1-Si1 105.2(5), C1-N1-Li 134.1(5). **3**: Li–N1 2.241(6), Li–N2 2.175(6), Li–N3 2.210(6), Li–N4 2.029(6), N4–C10 1.317(4), C10–C11 1.221(4), Si1–C11 1.796(3), Si1–N5 1.769(3); C11-C10-N4 175.3(3), C10-C11-Si1 171.5(3).



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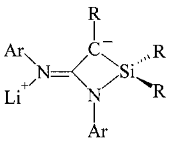
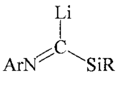


Ib

example,[9] 1.338(4) Å in (2,4,6-$i\mathrm{Pr_3C_6H_2})\overline{\mathrm{Si(Me)C(H){=}C(Ph)C}}$-($\mathrm{SiMe_2OSiMe_3}$)Ad (Ad = adamantyl). The very different electronic environments at C1 and C2 of **1** are also evident from their $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR chemical shifts in $\mathrm{C_6D_6}$: $\delta = 168.4$ and 48.6, respectively.

The crystalline lithioaminoalkyne **3** is a dimer (Figure 1, right), in which a bridging tmeda molecule links the two mononuclear fragments. (It is somewhat rare for tmeda to behave in this fashion; previous selected examples are given in ref. [11].) Features typical for an alkyne include the short C10–C11 bond of 1.221(4) Å and the near linearity at C10 (175.3(3)°) and C11 (171.5(3)°). The $\mathrm{C_{sp}}$–Si bond length of 1.796(3) Å is slightly shorter than those of trimethylsilylalkynes (1.84 Å[12]), while the C–N bond length of 1.317(4) Å can be compared with that of 1.344(3) Å in the aminoalkyne $\mathrm{C_{12}H_8N{-}C{\equiv}C{-}NC_{12}H_8}$.[13] As expected, the Li–N4 distance of 2.029(6) Å in the four-coordinate lithium compound **3** is longer than that of the three-coordinate complex **1**.

The initial two steps in the reaction pathway from $[\mathrm{Li(SiR_3)(thf)_3}]$ and ArNC to **1** probably resemble those in the corresponding $\mathrm{Li(CHR_2)}$/ArNC system. Thus, initial formation of the lithioaldimine **4** (cf. **I**[4]) is followed by a 1,2-$\mathrm{Me_3Si}$ Si → C shift that converts **4** into the isomer **5** (cf. **F**[4]). An electrocyclic cycloaddition of ArNC to **5** (see **6**) yields **1**. The transformation of **1** into **3** requires a 1,3-$\mathrm{Me_3Si}$ shift from C2 to N2 (facilitated by the partial carbanionic character of C2 (see **1b**) and N2–C1 ring scission.



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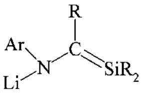

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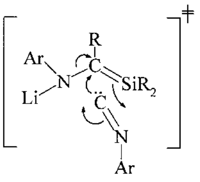

6

The head-to-head coupling of two isocyanide molecules to generate an alkyne has a precedent, the transformation of the isocyanide R′NC into the alkyne $\mathrm{PhMe_2Si(R')NC{\equiv}CN}$-$\mathrm{(R')SiMe_2R''}$ (**J**) by successive treatment with $\mathrm{LiSiMe_2Ph}$ and $\mathrm{R''Me_2SiCl}$ (R′ = *cyclo*-$\mathrm{C_6H_{11}}$, *s*Bu, or *i*Pr; R″ = Me or Ph).[14] While the molecular formulas and the presence of the alkyne moiety in **J** were unambiguously established, the present results suggest that an isomeric (aminosilyl)(silylamino)alkyne structure should be considered.

Compounds **1** and **3** have potential as ligand-transfer reagents, and **2** contains a hitherto unknown $\overline{\mathrm{C{=}CSiN}}$ ring system. The reactions of isocyanides with trimethylsilylmethyl or -silyl compounds are being extended to -germyls and -stannyls and to isoelectronic analogues of the Group 15 elements.

Experimental Section

1: 2,6-$\mathrm{Me_2C_6H_3NC}$ (0.40 g, 3.01 mmol) was added at −80 °C to a solution of $[\mathrm{Li\{Si(SiMe_3)_3\}(thf)_3}]$ (0.67 g, 1.53 mmol) in pentane (50 mL) and tmeda (0.23 mL, 1.55 mmol). The reaction mixture was stirred for 1 h, then allowed to warm slowly to room temperature, and stirred for 24 h. All volatile components were removed in vacuo, the residue was extracted with pentane (40 mL) and filtered, and the filtrate was concentrated and cooled. After 1 d colorless crystals of **1** (0.55 g, 57 %) were obtained. M.p. 124 °C (decomp.); elemental analysis calcd for $\mathrm{C_{35}H_{61}LiN_4Si_4}$: C 62.6, H 9.71, N 8.84; found: C 62.6, H 9.57, N 8.53; EI-MS: *m/z* (%): 523 (10) [M^+]; ^{1}H NMR ($\mathrm{C_6D_6}$, 300.1 MHz): $\delta = 0.15$ (s, CSi*Me*$_3$), 0.43 (s, SiSi*Me*$_3$), 1.09 (s, $\mathrm{NCH_2}$), 1.33 (s, NMe), 2.54 (s, Me (LiNAr)), 2.59 (s, Me (NAr ring)), 6.71 (t, 1 H, *J* = 7.4 Hz, Ph), 6.83 (d, 2 H, *J* = 7.4 Hz, Ph) (both NAr rings), 6.94 (t, 1 H, *J* = 7.5 Hz, Ph), 7.11 (d, 2 H, *J* = 7.5 Hz, Ph) (both LiNAr units); ^{7}Li NMR ($\mathrm{C_6D_6}$, 116.6 MHz): $\delta = -0.59$; ^{29}Si NMR ($\mathrm{C_6D_6}$, 99.4 MHz): $\delta = -21.2$ (s, C*Si*Me$_3$(C)), −20.0 (s, Si(*Si*Me$_3$)$_2$), 8.0 (s, *Si*(SiMe$_3$)$_2$); ^{13}C NMR ($\mathrm{C_6D_6}$, 75.5 MHz): $\delta = 0.5$ (s, Si(Si*Me*$_3$)$_2$), 3.9 (s, CSi*Me*$_3$), 20.8, 20.9 (s, Me), 45.1 (s, NMe), 48.6 (s, *C*SiMe$_3$), 56.5 (s, $\mathrm{NCH_2}$), 121.7, 122.8 (s, *p*-Ph), 128.5, 128.8 (s, *m*-Ph), 134.1, 137.0, 144.2, 150.9 (s, *ipso*-C), 168.4 (s, $\mathrm{CN_2}$).

2: $\mathrm{CF_3SO_3SiMe_3}$ (0.1 mL, 0.87 mmol) in pentane (10 mL) was slowly added to a solution of **1** (0.55 g, 0.87 mmol) in pentane (30 mL) at −40 °C. The mixture was allowed to warm to room temperature and was stirred for 6 h. Removal of the volatile substances in vacuo and extraction of the residue with pentane (20 mL), filtration and concentration of the filtrate gave, upon cooling, colorless crystals of **2** (0.38 g, 75 %). M.p. 205 °C (decomp.); elemental analysis calcd for $\mathrm{C_{30}H_{54}N_2Si_5}$: C 61.8, H 9.33, N 4.80; found: C 61.5, H 9.33, N 4.84; EI-MS: *m/z* (%): 582 (57) $[M]^+$, 567 (42) $[M-\mathrm{Me}]^+$, 509 (100) $[M-\mathrm{SiMe_3}]^+$; ^{1}H NMR ($\mathrm{C_6D_6}$, 300.1 MHz): $\delta = -0.20$, −0.22 (s, 9 H, $\mathrm{SiMe_3}$), 0.22 (s, 18 H, $\mathrm{SiMe_3}$), 2.39, 2.60 (s, Me), 6.85 (s, 3 H, Ph), 6.91 (s, 3 H, Ph); ^{29}Si NMR ($\mathrm{C_6D_6}$, 99.4 MHz): $\delta = -19.2$ (s, $\mathrm{CSiMe_3}$), −17.9 (s, Si(*Si*Me$_3$)$_2$), 9.3 (s, *Si*(SiMe$_3$)$_2$), 13.8 (s, $\mathrm{NSiMe_3}$); ^{13}C NMR ($\mathrm{C_6D_6}$, 75.5 MHz): $\delta = 0.5$ (s, Si(Si*Me*$_3$)$_2$), 2.7, 2.8 (s, $\mathrm{SiMe_3}$), 20.5, 21.0 (s, Me), 76.7 (s, *C*SiMe$_3$), 123.8, 129.6 (s, *p*-Ph), 129.5, 129.8 (s, *m*-Ph), 134.4, 138.5, 143.7, 143.9 (s, *ipso*-C), 162.8 (s, $\mathrm{CN_2}$).

3: **1** (0.64 g, 1.01 mmol) was dissolved in benzene (5–10 mL) and heated for 2.5 h to 80 °C. The volatile substances were removed in vacuo. The residue was extracted with pentane (60 mL), and the extract filtered to remove a small amount of precipitate. The filtrate was concentrated and cooled to give colorless crystals of **3** (0.4 g, 54 %). Elemental analysis calcd for $\mathrm{C_{72}H_{138}Li_2N_{10}Si_8}$: C 62.6, H 10.06, N 10.13; found: C 62.4, H 9.76, N 9.99; the mass spectrum showed only peaks due to fragmentation of the ligands; IR (Nujol) $\tilde{\nu} = 2032\ \mathrm{cm^{-1}}$ (C≡C); ^{1}H NMR ($\mathrm{C_6D_6}$, 300.1 MHz): $\delta = 0.29$ (s, Si(Si*Me*$_3$)$_2$), 0.37 (s, $\mathrm{NSiMe_3}$), 1.60 (s, $\mathrm{NCH_2}$), 1.78 (s, NMe), 2.54, 2.61 (s, Me), 6.88 (m, Ph), 7.01 (d, Ph), 7.13 (d, Ph); ^{7}Li NMR ($\mathrm{C_6D_6}$): $\delta = 0.93$; ^{29}Si NMR ($\mathrm{C_6D_6}$, 99.4 MHz): $\delta = 4.5$ ($\mathrm{NSiMe_3}$), −19.1 (Si(*Si*Me$_3$)$_2$), −42.2 (*Si*(SiMe$_3$)$_2$); ^{13}C NMR ($\mathrm{C_6D_6}$, 75.5 MHz): $\delta = 1.5$ (s, Si(Si*Me*$_3$)$_2$), 3.5 (s, NSi*Me*$_3$), 20.4, 21.7 (s, Me), 44.9 (s, NMe), 47.9 (s, C≡C), 56.1 (s, $\mathrm{NCH_2}$), 119.6, 123.8 (s, *p*-Ph), 128.5, 128.6 (s, *m*-Ph), 130.8, 137.7, 149.6, 150.9 (s, *ipso*-C).

Crystal data for **1**: $\mathrm{C_{33}H_{61}LiN_4Si_4}$, $M_r = 633.2$, monoclinic, space group $P2_1/n$ (No. 14), $a = 13.196(1)$, $b = 18.965(2)$, $c = 17.006(2)$ Å, $\beta = 110.10(1)°$, $V = 3996.7(7)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.05\ \mathrm{Mg\,m^{-3}}$, $F(000) = 1384$, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, $\mu = 0.17\ \mathrm{mm^{-1}}$; for **3**: $\mathrm{C_{72}H_{138}Li_2N_{10}Si_8(C_5H_{10})}$, $M_r = 1454.7$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.519(2)$, $b = 13.944(2)$, $c = 18.074(3)$ Å, $\alpha = 108.36(1)$, $\beta = 90.58(1)$, $\gamma = 111.69(1)°$, $V = 2313.8(7)$ Å^3, $Z = 1$, $\rho_{\mathrm{calcd}} = 1.04\ \mathrm{Mg\,m^{-3}}$, $F(000) = 800$, $\lambda\ (\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, $\mu = 0.16\ \mathrm{mm^{-1}}$. Data were collected at 173(2) K on a Enraf-Nonius CAD4 diffractometer in the $\omega/2\theta$ mode for the range of $2 > \theta > 22°$ (**1**) and $2 > \theta > 25°$ (**3**). The structure was solved by direct methods (SHELXS 86) and refined by full-matrix least-squares methods on all F^2 (SHELXL 93). All non-hydrogen atoms were anisotropic, and hydrogen atoms were included in the riding mode with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2\,U_{\mathrm{eq}}(\mathrm{C})$ or $1.5\,U_{\mathrm{eq}}$. The *o*-methyl groups of the phenyl rings were fixed for **1** at idealized geometry but with refinement of the torsion angle defining the H atom positions. Final residuals for **1** (**3**) for 4876 (8144) independent reflections were $R_1 = 0.137$ (0.097), $wR_2 = 0.200$ (0.164) and for the 3131 (5584) reflections with $I > 2\sigma(I)$, $R_1 = 0.085$ (0.059), $wR_2 = 0.166$ (0.139), GOF = 1.021 (1.034); parameters refined 383 (447); largest difference peak 0.55 (0.70) e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-102645 (**1**) and CCDC-102646 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Received: August 6, 1998 [Z12263IE]
German version: *Angew. Chem.* **1999**, *111*, 562–565

Keywords: heterocycles · insertions · lithium · silicon

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Selective Vesicle Formation from Calixarenes by Self-Assembly**

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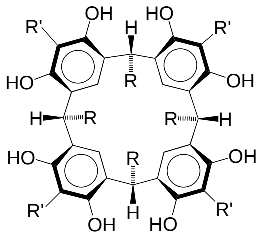
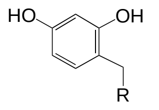
All living systems are compartmentalized by vesicles, in which various membrane proteins including channel proteins are incorporated, and thus specific biological functions can be carried out. The characterization of the shape, size, and properties of vesicles formed from various amphiphiles, including some synthetic ones, is crucial not only for the study of the structure and function of model membranes,[1] but also for the potential application of these membrane system as sensors and in technologies such as drug entrapment and release, and photochemical solar energy conversion.[2] Previously we reported that a simple polyhydroxy macrocyclic amphiphile, calix[4]resorcarene (**1**), behaves as an artificial potassium ion channel when embedded in planar bilayers of soybean lecithin.[3] The cylindrical macrocycle formed by four benzene rings and four extended alkyl chains provides the channel pore for ion passage through the lipid bilayer.[3] One would expect that amphiphiles such as **1** and calix[4]pyrogallolarene (**2**) would be aggregated in water and yield a specific self-assembled structure. Here we describe the selective formation of vesicles from the polyhydroxy macrocyclic amphiphiles **1** and **2**.[4]



1 R = $CH_3(CH_2)_{16}$, R' = H
2 R = $CH_3(CH_2)_{16}$, R' = OH



3 R = $CH_3(CH_2)_{16}$

Injection of a solution of **1** or **2** (6.7 mM) in tetrahydrofuran (0.4–2.0 mL) into a buffer (HEPES–Tris 5 mM, 4 mL, pH 7.0; HEPES = 2-[4-(hydroxyethyl)piperazine-1-yl]ethanesulfonic acid, Tris = tris(hydroxymethyl)aminomethane) at 60 °C immediately gave a dispersion of amphiphiles.[5] The dispersion was a slightly white suspension and remained in this form for more than a few months. Several characteristics of typical self-assembled structures have been observed for the dispersion obtained.

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[**] We are grateful to Dr. K. Nakazato (PRESTO, JST) for the TEM analyses and helpful discussions. We also thank Dr. M. Mehta, Prof. T. Fujinami, W. Tomoda, Prof. S. Kaneko, and Prof. H. Suzuki (Shizuoka University) for helpful discussions.