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Synthesis of Sila-Macrocycles, New Type of Metal Ligands

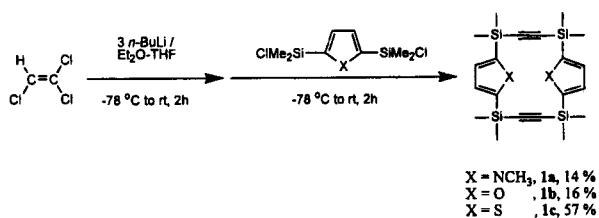
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Cyclic species with alternating silicon and acetylenic units have been studied by many groups due to their unusual orbital interactions and potential coordination capabilities.¹ Sila-calixarenes were also synthesized to investigate the binding properties towards metal ions.² Carbon is commonly used as the bridging element in macrocycles such as porphyrins or calixarenes. Introduction of silicon as a bridge instead of carbon can give new binding properties absent in the carbon analogues.³ Since the C-Si bond lengths are longer than C-C bonds, smaller rings become less strained when silicon is introduced. Many groups have studied macrocycles because the pocket size and shape can be adjusted easily for the inclusion processes. We report the synthesis of new sila-macrocycles containing both $\text{C}\equiv\text{C}$ bonds and heteroaromatics, and the metal complexation behavior of these compounds.

As shown in Scheme 1, dilithioacetylene was generated from trichloroethylene quantitatively according to the literature procedure.⁴ Slow addition of the corresponding 2,5-bis(chlorodimethylsilyl)heteroaromatics⁵ gave readily the macrocycles which have rigid structures and will stack easily. The $\text{C}\equiv\text{C}$ bond was inserted to give new coordination site. If we can bind both of the $\text{C}\equiv\text{C}$ bond in a single molecule with some metal, the product would be either a metal complex or a ladder polymer with defined nanostructure. The X-ray structure analysis of **1c** (Figure 1) reveals that the overall structure is similar to the tetrathiasila-calix[4]arene.² It has C_2 axis of symmetry and thiophene ring is twisted from the plane composed of four silicon atoms to relieve steric crowding of the two sulfur atoms.



Scheme 1. Syntheses of macrocycles **1a**, **1b** and **1c**.

Corriu *et al.*⁷ reported the synthesis of linear polymer having the same repeat unit as the thiophene derivative **1c** using 2,5-dilithiothiophene and bis(chlorodimethylsilyl)-acetylene. The difference can be explained by the fact that the reactivity of the dianions towards chlorosilane reagents differ. The less reactive dilithioacetylene allowed time for intramolecular α - ω elimination of LiCl rather than reacting with another molecule to give linear polymer.

To further enhance the binding possibility by control of the ring size, a diacetylene unit was introduced as shown in Scheme 2. Dilithiobutadiyne was generated from hexachlorobutadiene by Barton's method,⁶ and subsequent reaction with 2,5-bis(chlorodimethylsilyl)heteroaromatics gave the cyclization products. As a whole, product yields are poor because

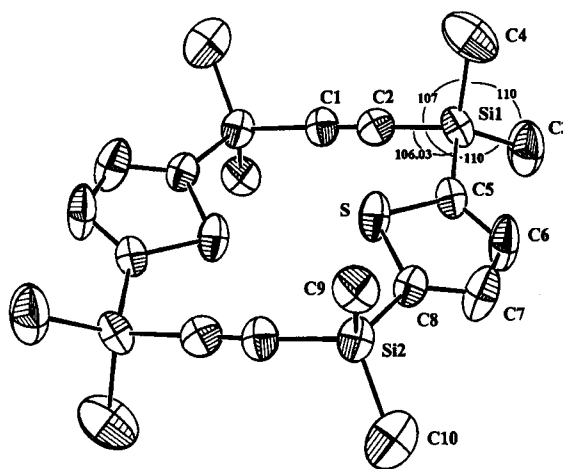
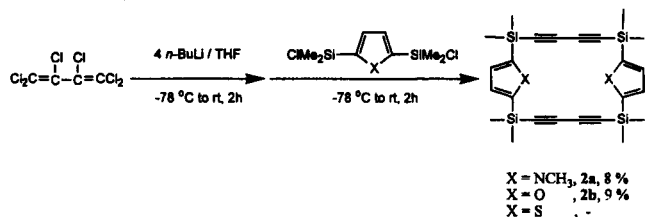


Figure 1. ORTEP view of $[\text{C}_{20}\text{H}_{28}\text{S}_2\text{Si}_4]$ with selected bond lengths (Å) and angles ($^\circ$): Si(1)-C(2) 1.853(4), Si(1)-C(5) 1.860(6), C(1)-C(2) 1.201(6), C(5)-C(6) 1.364(6), C(6)-C(7) 1.422(10), C(5)-S 1.708(6); C(2)C(1)Si(2) 175.0(5), C(2)Si(1)C(5) 106.0(3), C(2)Si(1)C(3) 110.4(2), C(2)Si(1)C(4) 107.6(2), C(3)Si(1)C(4) 110.8(4), Si(1)C(5)S 122.7(2), Si(1)C(5)C(6) 128.1(5), C(5)C(6)C(7) 112.9(6). Selected dihedral angles ($^\circ$): C(2)Si(1)C(5)S -36.84, C(2)Si(1)C(5)C(6) 146.56, C(5)Si(1)C(2)C(1) 52.63, C(8)SC(5)Si(1) -177.05.



Scheme 2. Syntheses of macrocycles **2a** and **2b**.

the reactivity of dilithiobutadiyne is lower than that of dilithioacetylene and the larger ring size is also certain to contribute to lower yields because there should be a less chance for the two terminal parts to meet to give cyclization products in the large rings. Nevertheless, it is surprising that the sulfur analogue could not be obtained even in trace amounts.

Sakurai *et al.*¹ reported that the highly strained hexamethyl-3,6,9-trisilacyclonona-1,4,7-triyne is thermally and oxidatively stable. The same was true for compounds **1a**, **1b**, and **1c**. Although having distorted C≡C bonds, these compounds are thermally stable because ring strain is relieved due to the bulkier silicon atom. To the contrary, compounds with diacetylene bonds (**2a** and **2b**) was crosslinked without melting.

As a preliminary study on the metal binding of these macrocycles, complexation of **1c** with CuX (X=Cl, Br) was tested. In both cases, complexation could be seen clearly in the FT-IR spectra. A new sharp peak appeared at 1960 cm⁻¹ resulting from the weakened C≡C bond by complexation.⁸ The ²⁹Si solid-state CP/MAS NMR spectrum of **1c** showed a single peak at -27.7 ppm because all four Si atoms are equivalent. On the other hand, after complexation, a new peak at -22.9 ppm appeared in addition to the previous one indicating that there are Si atoms surrounded by two different environments, that is, Si atoms adjacent to the complexed and uncomplexed C≡C bond as shown in the plausible structure depicted in Figure 2. Thus, the preliminary study described indicates these macrocycles to be promising metal ligands.

Selected spectral data. ¹H NMR (200 MHz, CDCl₃), ¹³C NMR (50 MHz, CDCl₃). **1a**: White solid; mp 286 °C. ¹H NMR δ 0.42 (s, 24H); 3.78 (s, 6H), 6.37 (s, 4H), ¹³C NMR δ -1.3; 37.2, 114.4, 118.9, 135.5, MS (70 eV), 438 (M⁺). **2a**: White solid; crosslinking without melting. ¹H NMR δ 0.46 (s, 24H); 4.00 (s, 6H), 6.39 (s, 4H), ¹³C NMR δ -1.5; 37.7, 84.5, 89.5, 119.6, 134.5, MS (70 eV), 486 (M⁺). **1b**: Colorless needle-like crystals; mp 205 °C. ¹H NMR δ 0.42 (s, 24H); 6.61 (s, 4H), ¹³C NMR δ -1.8; 111.7, 120.3, 161.6, MS (70 eV), 412 (M⁺). **1c**: Colorless plate-like crystals; mp 276 °C. ¹H NMR δ 0.48 (s, 24H); 7.30 (s, 4H), ¹³C NMR δ -0.0; 113.5, 134.9, 143.5, MS (70 eV), 444 (M⁺). **2b**: White solid; crosslinking without melting. ¹H NMR δ 0.42 (s, 24H); 6.63 (s, 4H), ¹³C NMR δ -2.5; 83.0, 89.3, 120.9, 160.9, MS (70 eV), 460 (M⁺).

Crystal data was collected at 293 K on an Enraf-Nonius

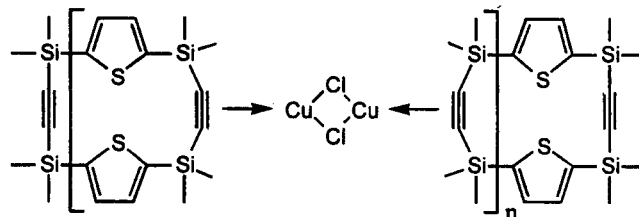


Figure 2. Suggested complex structure of **1c**-CuCl complex.

CAD4 diffractometer using graphite-monochromated Mo-Kα radiation (λ=0.71073 Å) by the ω-2θ method. The structure was solved using the SHELXS-86 and refined by full-matrix least squares (SHELXL-93) using 817 independent reflections with *I* > 2σ(*I*).

Crystal data for 1c. C₂₀H₂₈S₂Si₄, M=444.9, monoclinic, space group P112₁/a, *a*=9.4038(7), *b*=11.0941(10), *c*=12.1827(9) Å, γ=97.609(9)°, *V*=1259.8(2) Å³, *Z*=2, *D*_c=1.173 g cm⁻³, *R*₁=0.0404 (w*R*₂=0.0815).

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