Separation of Cis and Trans Isomers of 1,4-Disilacyclohexadienes and Related 9,10-Dihydro-9,10-disilaanthracenes[1]

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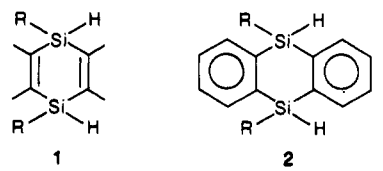
Methods for the preparation of 1,4-dihydrohexamethyl-1,4-disilacyclohexa-2,5-diene and 9,10-dimethyl-9,10-dihydrodisilaanthracene give mixtures of cis and trans isomers which cannot be separated by standard chromatographic methods. Treatment of the corresponding cis and trans dichloro derivatives with *cis*-2-butene-1,4-diol (Et_3N/THF) gives monomolecular, bridging dialkoxy adducts. These are readily purified by elution over silica gel or recrystallization. Bridging of the pseudoaxial positions by the diol is confirmed by spectroscopic data. Reduction of the adducts with $LiAlH_4/Et_2O$ under mild conditions provides the cis isomers of the dihydrodisilacyclohexadiene and the dihydrodisilaanthracene in pure form. The separated hydrosilanes provide entries to other specifically substituted derivatives.

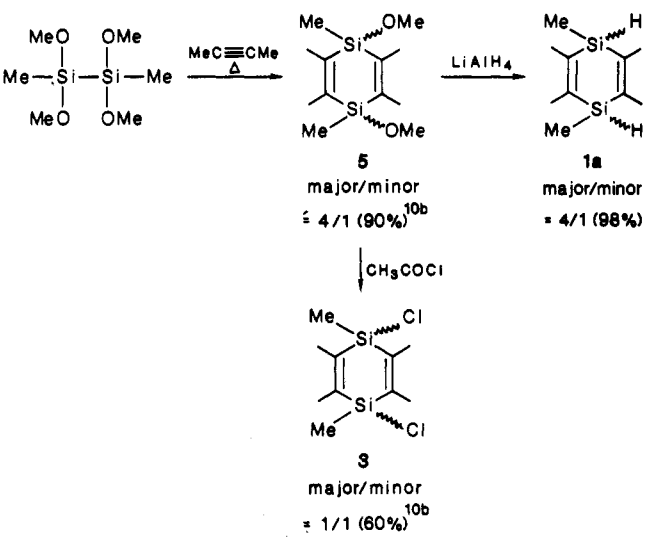
Introduction

The silicon analogues of carbocyclic aromatic species have been the subject of several recent reports.[3] Two interesting goals in this series are 1,4-disilabenzene[4,5] and the related 9,10-disilaanthracene. An attractive route to these intermediates involves the thermal extrusion of H_2 from dihydrides such as **1** and **2**. Pyrolysis of 1,4-disilacyclohexa-2,5-diene at 800 °C followed by trapping in an argon matrix provides a species whose spectroscopic properties are consistent with those of 1,4-disilabenzene, the simplest member of the series.[5] Since Maier[6] has presented convincing evidence that the elimination reaction leading to silabenzene by extrusion of hydrogen from 1-sila-2,5-cyclohexadiene is a concerted process, it is probable that this pathway also operates in the formation of 1,4-disilabenzene. The stability of disilabenzene and disilaanthracene species may be improved by placement of bulky substituents at the silicon centers or by appropriate substituents at carbon in **1** or in positions ortho to silicon in **2**. Such tactics have already proved successful in the formation of silenes and disilenes.[3] Prior to the report of Maier[5] our preliminary thermolysis study of a 1:4 isomeric mixture of **1a** (R = Me) demonstrated that only a 10% conversion to the expected disilabenzene had occurred.[7] Analysis of the thermolysis products showed that the minor isomer but not the major isomer had reacted. By analogy to Maier's results, the minor isomer was assigned the cis structure. Clearly, to simplify the study of the formation of disilabenzenes and disilaanthracenes a source of pure (or enriched) cis precursors would be an advantage.



1 **2**

Scheme I



The synthetic routes that generate **1a** (R = Me) and **2a** (R = Me) provide products with an isomer ratio of 1:4 and 1:2, respectively. While the major isomer of **1a** and **2a**[8] can be obtained by recrystallization, it is the major isomer of **1a** that was found to be unreactive in thermolysis reactions[7] and was therefore assigned the trans structure. The isolation of the cis isomers, in pure form, has proved to be a challenging problem. Conventional methods such as crystallization, column chromatography, and preparative gas chromatography all failed to produce the separation.

We wish to report a novel method for isolation of the cis isomers of **1a** and **2a**. The approach is based on the synthesis of the dichloride analogues of **1** and **2** followed by reaction with a diol that can bridge the two silicon centers. The diol adducts are easily separated from the oligomeric products formed from the trans isomers. Subsequent reduction with lithium aluminum hydride

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(2) Author to whom correspondence should be addressed.
(3) For a comprehensive review, see: Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.
(4) Rich, J. D.; West, R. *J. Am. Chem. Soc.* **1982**, *104*, 6884.
(5) Maier, G.; Schottler, K.; Reisenauer, H. P. *Tetrahedron Lett.* **1985**, *26*, 4079.
(6) Maier, G.; Mihm, G.; Baumgartner, R. O. W.; Reisenauer, H. P. *Chem. Ber.* **1984**, *117*, 2337.
(7) Welsh, K. M.; West, R.; Michl, J., Presented at the XIX Organosilicon Symposium, Baton Rouge, LA, April 1985.
(8) McCarthy, W. Z.; Corey, J. Y.; Corey, E. R. *Organometallics* **1984**, *3*, 255.

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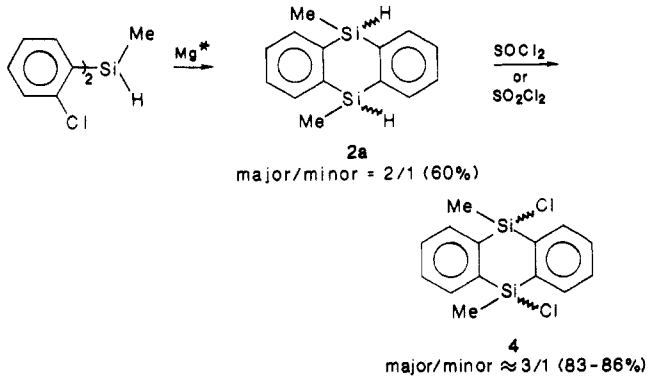
Scheme II

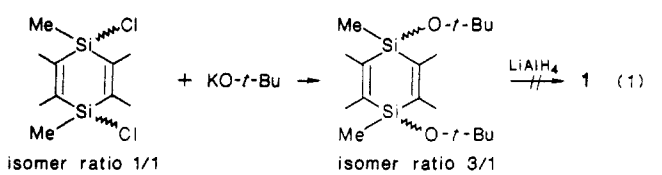


regenerates pure *cis*-**1** and *cis*-**2**.

Results

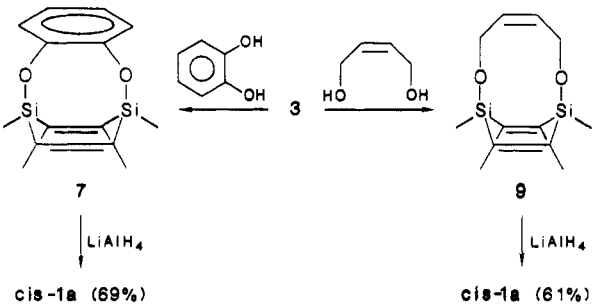
Scheme I outlines the synthesis of the isomers of 1,4-dihydrohexamethyl-1,4-disilacyclohexa-2,5-diene, **1a**. Static thermolysis of *sym*-dimethyltetramethoxydisilane with 2-butyne at 250 °C provides a 4/1 isomeric mixture of 1,4-dimethylhexamethyl-1,4-disilacyclohexa-2,5-diene, **5**,[9] which provides **1a** on reduction with lithium aluminum hydride. The synthesis of the isomers of **2a** is outlined in Scheme II.[8] The Grignard reagent generated from bis(*o*-chlorophenyl)methylsilane, **6**, and activated magnesium (prepared from $MgBr_2$, K, and KI) when treated with methylchlorosilane provides isomeric 9,10-dimethyl-9,10-dihydrodisilaanthracene in a ratio of about 1:2. The major (trans) isomers of both **2a** and **5** are obtained by repeated recrystallization from ethanol[8] and chloroform, respectively. Careful reduction of the major isomer of **5a** with LAH gives a single isomer of **1a**. The isomeric purity of these major (or trans) isomers of **1a** and **2a** was confirmed by ^1H NMR spectroscopy.

An attempt was made to prepare and separate the cis and trans isomers of **1** through introduction of bulky substituents at silicon. It was anticipated that such substitution could enhance the resolution of the two isomers under preparative VPC conditions. Treatment of the dichloride **3** with KO-*t*-Bu (eq 1) gives the di-*tert*-butoxide in a 3:1 isomeric ratio which could indeed be separated by preparative VPC. However, the bulky alkoxide groups could not be reduced with LAH and this approach was abandoned.



The method developed to separate the cis from the trans isomers in both **1a** and **2a** exploits the unique reactivity of a cis dichlorides relative to the trans isomer. It was assumed that diols such as catechol or *cis*-2-butene-1,4-diol could span the two silicon centers of *cis*-**3** or *cis*-**4** forming a monomolecular complex whereas reaction of the corresponding trans isomers might be expected to give oliomeric products. Hexamethyl-1,4-dichloro-1,4-disilacyclohexa-2,5-diene, **3**, is obtained by treatment of **5** with refluxing acetyl chloride.[10] Halogenation of an isomeric mixture

Scheme III



Scheme IV

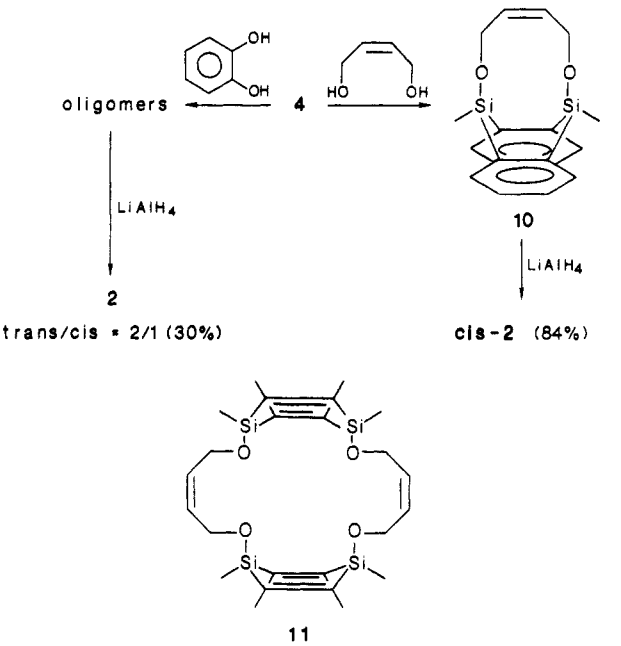


Figure 1.

of **2a** with either sulfuryl chloride in refluxing carbon tetrachloride or neat thionyl chloride gives **4** as a mixture of isomers. To maximize the formation of the 1:1 adduct the solutions of the dichlorides and of the diols were simultaneously added dropwise to a THF or Et_2O solution of Et_3N. The results are summarized in Schemes III and IV. When catechol is added to **3**, the product formed in greater that 70% yield is spectroscopically consistent with the 1:1 adduct **7**, but **4** gives oligomeric (or polymeric) products from both isomers. Attempts to separate the catechol adducts of **4** by distillation, column chromatography, or recrystallization failed. The best overall results were achieved from reaction of **3** or **4** with *cis*-2-butene-1,4-diol to give the adducts **9** and **10** in greater than 50% yield (Schemes III and IV). The adducts **7**, **9**, and **10** are monomeric as verified by high-resolution mass spectroscopy and have been characterized by ^1H and ^{13}C NMR as well as chemical analyses. If dilute conditions were not employed in the reaction of the dichloride **3** with *cis*-2-butenediol, a dimer, **11**, is isolated whose spectroscopic properties are consistent with the structure shown in Figure 1. In a related system, dimers and monomers have also been reported from the reaction of butane-1,4-diols with Ph_2SiCl_2.[11]

Reduction of **7**, **9**, and **10** with $LiAlH_4$ proceeds smoothly at room temperature to give >95% isomerically pure dihydrides **1a** and **2a** in 60–80% yield. The spectroscopic

(9) Atwell, W.; Weyenberg, D. *J. Am. Chem. Soc.* **1968**, *90*, 3438.
(10) (a) Wudl, F.; Allendoerfer, R. D.; Demirgian, J.; Robbins, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 3160. (b) Rich, J. D.; West, R. *J. Am. Chem. Soc.* **1983**, *105*, 5211.
(11) Cragg, R. H.; Lane, R. D. *J. Organomet. Chem.* **1985**, *289*, 23.

properties correspond to the *minor* isomers of **1a** and **2a** as synthesized according to Schemes I and II. When the reduction of **7** and **9** was carried out in refluxing THF, a significant loss of stereospecificity was observed.

Discussion

Generation of disilabenzenes and disilaanthracenes will require functional groups on each silicon center in the precursor. It is anticipated that reactions that will produce the unsaturated systems will require the cis isomer. The synthetic methods that have been developed for 1,4-disilacyuclohexadienes include (1) reaction of a silylene or silylene precursor with acetylene,[9,12] (2) thermal or metal-catalyzed dimerization of silacyclopropene,[13] and (3) thermal or metal-catalyzed addition of acetylenes to disilacyclobutene.[12,14] Of these methods, only the silylene addition to an acetylene has been used to prepare silicon-functional 1,4-disilacyclohexadienes, and this route generates a mixture of geometrical isomers. Likewise, of the methods that have been developed for generation of the 9,10-dihydro-9,10-disilaanthracene framework[8,15] only the preparative method utilized in this study provides a single functionality at both silicon centers, and this route also provides both cis and trans isomers. In both systems a mixture of geometrical isomers is generated in which the trans form is the major isomer. The major isomer can be isolated for both **2** and **5** by fractional recrystallization. In the related 1,4-dihydro-1,4-diphosphacyclohexadiene mixtures produced from addition of $R'PH_2$ to $RP(C{=}CH)_2$, the major isomer was also isolated by fractional recrystallization (10 times), although in this system the cis isomer predominates.[16] The purpose of this investigation was to demonstrate that a chemical route could be employed to separate the geometrical isomers and provide reasonable quantities of the cis form of **1** and **2**.

Once the framework is generated, the basic sequence to produce *cis*-**1a** and *cis*-**2a** involves three steps in each case: (a) generation of an isomeric mixture of chlorides; (b) reaction with a diol to obtain the monomeric "adduct" selectively from the cis isomer; and (c) reduction of diol adduct with LAH to give the desired cis isomers. An unexpected advantage of this sequence was the enrichment of the desired cis isomer after completion of the three steps. This implies an isomerization process in either or both the chlorination and the alcoholysis steps (Schemes I through IV). Conversion of R_3Si^*Cl with MeOH to R_3Si^*OMe in pentane occurs by either retention or inversion mechanisms,[18] but the stereochemistry of the chlorinations of SiOMe with CH_3COCl and of SiH by $SOCl_2$ or SO_2Cl_2 has not been reported. Therefore, either the chlorination or the reaction with the diol could involve a combination of retention and inversion processes which would lead to a different ratio of cis to trans isomers in either **3** and **4** or the adducts **7**, **9**, and **10**. The reduction of acyclic R_3Si^* OR with LAH in Et_2O takes place with retention of configuration but with loss of stereochemistry in THF.[17] If it is assumed that the reduction of **7**, **9**, and **10** occurs with the same stereochemistry at both silicon centers, only a single isomer will be produced; therefore the method is independent of a retention or an inversion mechanism in the last step.

The diols that were selected to react with the chlorosilanes represent two somewhat different structural types. The oxygen atoms of the diol must bond to the two silicon atoms of **1** and **2** at different ends of the molecule. The catechol represents a rigid diol in which the distance between the two oxygen atoms is approximately 2.7 Å (from models). An eight-membered ring is formed in the monomeric product when the catechol reacts with the cis form of **3** or **4**. In the *cis*-2-butene-1,4-diol the alcohol groups are obviously constrained to the same side of the double bond, but the intervening methylene groups allow considerable flexibility in the distance that the oxygen atoms can span. Models show that the distance between the two oxygen atoms in the adducts **9** and **10** are approximately 3.7 Å in the ten-membered ring formed in the diol adduct. Since derivatives of **2** may be nearly planar in solution,[8] the distance that the diol must span in this case may be too large to provide monomeric products in the reaction with catechol. Although this should be considered a tentative conclusion since a planar form of 1,4-disilacyclohexadiene and both planar and nonplanar forms of 9,10-dihydro-9,10-disilaanthracene are known in the solid.[19] A boat form for 1,1,4,4-tetrafluoro-1,4-disilacyclohexa-2,5-dienes in solution has been claimed.[14] The disilacyclohexadiene or disilaanthracene framework in the diol adducts **7**, **9**, and **10** could be either planar or nonplanar as well. Attempts to determine the solid-state structure of **10** have not yet been successful.[20] Other diols may also be effective in this type of isomer separation, but it is likely that more rigid diols will be more successful in spanning the two different centers in a 1,4-diheterocyclohexadiene and related dihydroanthracene derivative.

The thermal extrusion of H_2 from **1** or **2** is not the only synthetic route possible for generation of disilabenzenes and disilaanthracenes. Since conditions for the stereospecific conversion of SiH bonds to other functional groups such as SiCl or SiOR have been developed,[17] the isolation of *cis*-**1a** and *cis*-**2a** will provide access to other silicon-functional 1,4-disilacyclohexadienes and 9,10-dihydrodisilaanthracenes. Thus, other routes to the unsaturated derivatives may be developed. This approach to isomer separation is not restricted to the specific silicon compounds studied in this report. Variations of the organic exocyclic substituents at silicon as well as at carbon should be possible. The basic approach could be applicable to other related derivatives where silicon is replaced by heavier members of group IV (14[22]). The cis isomer of 1,4-diphospha-1,4-cyclohexadiene reacts with 1,2-dibromoethane to give the bridged diphosphonium salt that is the analogue of **9**.[16] Thus extension of this general approach was reported after our work on the silicon systems had been completed.

Experimental Section

General Data. All reactions unless otherwise noted were carried out under an atmosphere of dry nitrogen. Solvents were dried by using standard techniques, and all glassware was thoroughly dried in an oven at 110–120 °C prior to use.

Methods for the preparation of *sym*-dimethyltetramethoxydisilane,[21] 1,4-dimethoxyhexamethyl-1,4-disilacyclohexa-2,5-diene,[9]

(12) Barton, T. J.; Kilgour, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 7746.
(13) (a) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879. (b) Ishikawa, M., Fuchikami, T.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1977**, 352. (c) Ishikawa, M., Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1977**, *142*, C45.
(14) Liu, C.-S.; Cheng, C.-W. *J. Am. Chem. Soc.* **1975**, 97, 6746.
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(18) (a) Corriu, R. J. P.; Royo, G. *J. Organomet. Chem.* **1968**, *14*, 291. (b) Corriu, R. J. P.; Larcher, F.; Royo, G. *J. Organomet. Chem.* **1976**, *104*, 161.
(19) D'yachenko, O. A.; Atovmyan, L. O. *Zh. Strukt. Khim.* **1983**, *24*, 775.
(20) Corey, E. R., unpublished results.
(21) Childs, M. E.; Weber, W. P. *J. Organomet. Chem.* **1975**, *86*, 169.

5, and 1,4-dichlorohexamethyl-1,4-disilacyclohexa-2,5-diene,[10] 3, have been previously described. All other reagents are commercially available and, unless otherwise noted, were used without further purification.

^{1}H NMR spectra were recorded on a Bruker WP-270 (270 MHz) or a Varian XL 300 (300 MHz) spectrometer. ^{13}C NMR spectra were obtained on a JEOL FX-200 (200 MHz) spectrometer. All NMR spectra were recorded at ambient temperatures. Mass spectra and exact mass determinations were performed on a Kratos MS-80 mass spectrometer operating at an ionizing voltage of 30 eV. A Hewlett-Packard 5890 gas chromatograph with an FID and a 10 m × 0.56 mm i.d. megabore column coated with 5% phenylmethylsilicone was used for analytical gas chromatography. Preparative gas chromatography was performed on a Gow Mac Model 550P gas chromatograph using a thermal conductivity detector and helium as the carrier gas.

Elemental analyses were performed by Galbraith Laboratories, Inc.

***trans*-1,4-Dimethoxyhexamethyl-1,4-disilacyclohexa-2,5-diene, 5.** 1,4-Dimethoxyhexamethyl-1,4-disilacyclohexa-2,5-diene[10] (2.50 g) as a 1:4 mixture of isomers was dissolved in a minimal amount of refluxing chloroform (approximately 5 mL). The solution was slowly cooled (to prevent oiling out of the isomeric mixture) to room temperature and then chilled to −10 °C. The dimethoxide was allowed to crystallize at this temperature for several hours to give *trans*-**5** (1.10 g, 44%; 95% isomeric purity) as clear, colorless crystals; mp 84.5–87.0 °C (the original mixture of isomers exhibited a melting range of 68–76 °C); ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.31 (s, 6 H, OCH_3), 1.85 (s, 12 H, C=CCH_3), 0.14 (s, 6 H, $SiCH_3$).

1,4-Dihydrohexamethyl-1,4-disilacyclohexa-2,5-diene, 1. To a stirred solution of LAH (0.2 g, 0.005 mol) in THF (25 mL) was added an isomeric mixture of **5** (1.0 g, 0.0038 mol) in THF (25 mL). The mixture was stirred at room temperature for 12 h. After the mixture was cooled in an ice bath, the excess LAH was destroyed by the dropwise addition of a saturated aqueous solution of NH_4Cl. Following the addition of hexane (150 mL) the salts were removed by filtration. Removal of the solvents gave a viscous residue which was passed through a 5-cm activated silica gel column with hexane as eluent to give 0.73 g (98%) of **1**. Analytical gas chromatography indicated the presence of the cis and trans isomers in a 1:4 ratio: ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.96 (unresolved q, 2.5 H, cis and trans Si–H), 1.72 (s, 15 H, cis and trans C=CCH_3), 0.09 (d, J = 3.2 Hz, 6 H, trans $SiCH_3$), 0.07 (d, J = 3.2 Hz, 1.5 H, cis $SiCH_3$); MS (30 eV), m/e (relative intensity) 196 (M^+, 32), 181 (100), 141 (30, 127 (38); exact mass determination calcd for $C_{10}H_{20}Si_2$ 196.1103, measd 196.1104.

***trans*-1,4-Dihydrohexamethyl-1,4-disilacyclohexa-2,5-diene, 1.** The preparation of the pure trans isomer of **1** is similar to that of the mixture of **1**. A sample of crystalline *trans*-**5** (0.50 g, 1.95 mmol) was treated with $LiAlH_4$ (0.10 g, 2.6 mmol) to give *trans*-**1**: 0.24 g (63%); ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.96 (q, J = 3.2 Hz, 2 H, SiH), 1.72 (s, 12 H, C=CCH_3), 0.09 (d, J = 3.2 Hz, 6 H, $SiCH_3$).

1,4-Di-*tert*-butoxyhexamethyl-1,4-disilacyclohexa-2,5-diene. A solution of potassium *tert*-butoxide (2.0 g, 18 mmol) in THF (25 mL) was added dropwise with stirring over a period of 1 h to **3** (2.0 g, 7.5 mmol) in THF (50 mL). After the addition was complete, the mixture was refluxed for 4 h. The KCl salts were removed by filtration, and solvent was stripped by rotary evaporation, leaving 2.45 g of 1,4-di-*tert*-butoxyhexamethyl-1,4-disilacyclohexa-2,5-diene as a viscous oil which slowly solidified on standing. The solid was then purified by sublimation (85 °C, 0.1 torr): yield 2.27 g (88%); mp 74–84 °C; MS (30 eV), m/e (relative intensity) 340 (M^+, 10), 269 (7), 227 (76), 213 (100); exact mass determination calcd for $C_{18}H_{36}O_2Si_2$ 340.2244, measd 340.2255. Anal. Calcd for $C_{18}H_{36}O_2Si_2$: C, 63.47; H, 10.65. Found: C, 63.37; H, 10.52.

(22) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-trasition elements comprise gorups 3 through 12, and the p-block elements comprise groups 13-18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Gas chromatographic analysis indicated the presence of two isomers in a 1:3 ratio which were separable by preparative gas chromatography using a 6 ft × 0.25 in. column packed with 5% SE-30 on Chromosorb W. Minor isomer: mp 108–109 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.80 (s, 12 H, C=CCH_3), 1.14 (s, 18 H, CCH_3), 0.02 (s, 6 H, $SiCH_3$). Major isomer: mp 85–87 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.79 (s, 12 H, C=CCH_3, 1.18 (s, 18 H, CCH_3), −0.02 (s, 6 H, $SiCH_3$).

9,10-Dimethyl-9,10-dihydrodisilaanthracene, 2. Samples of **2** prepared from bis(*o*-chlorophenyl)methylsilane, **6**,[8] and activated Mg generated from commercial, anhydrous $MgCl_2$ and K followed by quenching with dichloromethylsilane sometimes contained minor impurities after distillation as indicated by a broad multiplet just upfield and/or downfield of SiMeH resonances (apparent triplet centered at δ 0.59 in the ^{1}H NMR spectrum). These samples were purified by chromatography (silica gel, hexanes as eluant) prior to halogenation.

The synthesis of **2** is improved by reaction of **6** with $MgBr_2$ prepared from magnesium and ethylene dibromide. To dried Mg shavings (2.50 g, 104 mmol) and THF (25 mL) was added $BrCH_2CH_2Br$ (8.0 mL, 92 mmol) dissolved in THF (75 mL), and the resultant was heated at reflux for 1 h. Approximately 70 mL of THF was distilled at atmospheric pressure and the resultant slurry evacuated without heating until no solvent was observed. The solid residue was finally heated gently under vacuum for 30 min. After the mixture was cooled to room temperature, the residue was brought to atmospheric pressure under Ar, and THF (200 mL), K (6.0 g, 150 mmol), and KI (7.0 g) were added. The slurry was heated at reflux for 1 h, the heat source removed, and a solution of **6** (10.1 g, 37.8 mmol) in THF (50 mL) added rapidly. After being heated at reflux for 3 h, a solution of dichloromethylsilane (4.0 mL, 38 mmol) in THF (40 mL) was added dropwise and the slurry stirred overnight. After the usual workup, Kugelrohr distillation provides 5.4 g (60%) of **2** as a colorless oil, bp 98–110 °C (0.05 mm) [lit.[8] bp 90–138 °C (0.05 mm)]. There are no impurities in the silicon–methyl region detectable in the ^{1}H NMR spectrum. Samples solidify when seeded. The ^{1}H NMR spectrum (300 MHz) shows two SiMe doublets approximate ratio of 1 (δ 0.69)/2 (δ 0.65).

9,10-Dichloro-9,10-dimethyl-9,10-disilaanthracene, 4. A mixture of **2** (4.04 g, 16.8 mmol), CCl_4 (2 mL), and $SOCl_2$ (4.0 mL) was heated at reflux for 24 h or until disappearance of the SiH signal (multiplet centered at δ 4.9) in the ^{1}H NMR spectrum. After removal of the volatiles, Kugelrohr distillation gave 4.49 g (86%) of crude **4**, as a 3:1 mixture of isomers, bp 99–110 °C (0.04 mm), which solidifies on standing.

The ratio of the two isomers varies slightly from run to run and ranges from about 3 (δ 0.96)/1 (δ 0.91) for 20-h halogenations to 4/1 for 60-h reactions.

In a separate run, distilled **4** (2.57 g; ratio of isomers is about 2/1) was heated under N_2 with dried hexane and the solution decanted from the waxy solid that remained. On being cooled to room temperature, the solution was again decanted from the small amount of yellow solid that precipitated and the decantate cooled to −10 °C. The precipitate that formed was filtered in a drybag under N_2 and washed with a minimal quantity of hexane. The white solid (1.12 g) has a melting point of 94–98 °C: ^{1}H NMR (100 MHz, $CDCl_3$, internal Me_4Si) δ 8.0–7.0 (m, arom, 7.9), 0.89, 0.79 (s, SiMe, 6.1). Ratio of isomers is about 3 (δ 0.88)/1 (δ 0.79).

In a similar fashion, SO_2Cl_2 (5 mL) was added dropwise to a solution of **2a** (isomeric ratio, 2:1; 4.06 g, 16.8 mmol) in CCl_4 (3 mL). Reaction becomes very vigorous after 40% of the SO_2Cl_2 has been added. The reaction mixture was stirred for about 0.5 h after completion of the addition, and volatiles were removed. Kugelrohr distillation provided 4.36 g (83%) of crude **4** as a 3:1 mixture of isomers: bp 135–155 °C (0.4 mm), which solidifies on standing: mp 86–96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.0–7.4 (m, arom, 9.00), 0.96, 0.91 (s, SiMe, 5.0); exact mass determination calcd for $C_{14}H_{14}Si_2Cl_2$ 308.0011, measd 308.0010.

Reduction of 4 with LAH. Reduction of an isomeric mixture of **4** (0.799 g, 2.58 mmol) with $LiAlH_4$ (0.527 g, 13.0 mmol) in Et_2O (50 mL) for 1.5 h followed by workup with saturated NH_4Cl solution provided 0.509 g (81%) of **2**, bp 105–120 °C (0.15 mm). The ^{1}H NMR spectrum shows a cis/trans ratio of 1:2, similar to that prepared from condensation of **6** with $MeSiHCl_2$.

Catechol Derivative 7. A solution of **3** (1.09 g, 4.14 mmol) in Et_2O (225 mL) and a solution of freshly sublimed catechol (0.45 g, 4.14 mmol) in Et_2O (225 mL) were simultaneously added dropwise with rapid stirring to a solution of triethylamine (4 mL) in Et_2O (250 mL). A white precipitate (Et_3NHCl) began to form immediately. Once the addition was complete (approximately $2–2^1/_2$ h), stirring was continued at room temperature for another 8 h. The salts were removed by filtration, and the solvent and excess amine were stripped by rotary evaporation leaving a brown viscous oil (1.56 g). Addition of hexane (200 mL) and removal of insoluble materials followed by treatment with activated charcoal resulted in the isolation of the catechol derivative, 0.99 g (79%) of **7**, as a slightly yellow, very viscous oil: ^1H NMR (270 MHz, $CDCl_3$) δ 6.80 (br s, 4 H, ArH), 1.80 (s, 12 H, C=$COCH_3$), 0.59 (s, 6 H, $SiCH_3$); MS (30 eV), *m/e* (relative intensity) 302 (M^+, 12), 287 (27), 225 (56), 211 (77); exact mass determination calcd for $C_{16}H_{22}O_2Si_2$ 302.1158, measd 302.1161.

Reaction of 4 with Catechol. A sample of **4** (3.60 g, 11.7 mmol) in THF (30 mL) and freshly sublimed catechol (1.28 g, 11.6 mmol) in THF (30 mmol) were added simultaneously to a refluxing solution of Et_3N (3.3 mL, 24 mmol) in THF (100 mL). A precipitate forms immediately. After 2.5 h, a GC trace of an aliquot shows that only one component is present. The mixture was stirred at room temperature for an additional 12 h after which the precipitate of $Et_3NH^+Cl^-$ (2.79 g, 87%) was removed and the filtrate stripped to give an opaque liquid (4.76 g). Distillation of a portion of the crude product (3.3 g) provided catechol [sublimes below 50 °C (0.05 mm), 0.37 g] and 0.78 g of a volatile portion, bp 100–230 °C (0.05 mm), which contains no identifiable product.

To the portion that remained after the distillation (2.18 g) dissolved in THF (50 mL) was added $LiAlH_4$ (1.0 g), and the mixture was refluxed for 8.5 h followed by stirring at room temperature overnight. After workup, the residue was distilled to give catechol (0.56 g) and 0.46 g of oil, bp 90–120 °C (0.01 mm), whose ^1H NMR spectrum is identical with the original starting isomeric mixture of **2** (30%).

An attempt to elute the remainder of the original isolated semisolid over silica gel with methylene chloride provided no identifiable monomeric product.

***cis*-2-Butenediol Derivative 9.** A solution of **3** (1.04 g, 3.9 mmol) in diethyl ether (225 mL) and a solution of *cis*-2-butene-1,4-diol (0.35 g, 3.9 mmol) in diethyl ether (225 mL) were added with rapid stirring in a slow simultaneous manner to a flask containing a solution of triethylamine (10 mL) in diethyl ether (250 mL). After an initial induction period of approximately 10 min a white precipitate (Et_3NHCl) began to form. After the addition, which required 3 h, was complete the slurry was stirred at room temperature overnight. The ammonium salts were removed by filtration, and the solvent and amine were stripped by rotary evaporation. Hexane (200 mL) was added, and the insoluble material was removed by filtration. The solution was then treated with activated charcoal. Removal of the hexane gave 0.67 g (61%) of **9** as a clear, colorless liquid: ^1H NMR (270 MHz, C_6D_6) δ 5.42 (t, 2 H, -HC=CH), 4.09 (d, 4 H, C=CCH_2), 1.80 (s, 1 H, C=CCH_3), 0.31, (s, 6 H, $SiCH_3$); ^{13}C NMR (200 MHz, C_6D_6) δ 149.8, 129.0, 58.4, 16.2, -3.6; MS (30 eV), *m/e* (relative intensity) 280 (M^+, 7), 265 (26), 211 (52); exact mass determination calcd for $C_{14}H_{24}O_2Si_2$ 280.1315, measd 280.1312.

If the reaction is performed at higher concentrations from **3** (1.0 g) in diethyl ether (25 mL) and *cis*-2-butenediol (0.35 g) in diethyl ether (25 mL) added simultaneously to a solution of triethylamine (10 mL) in diethyl ether (125 mL), a "dimeric" adduct, **11**, consisting of two disilacyclohexadiene units and two diols is obtained: 0.27 g (12%); mp 240 °C dec; ^1H NMR (270 MHz, $CDCl_3$) δ 5.52 (t, J = 4.3 Hz, 4 H, C=CH), 3.83 (d, J = 4.3 Hz, 8 H, C=CCH_2), 1.80 (s, 24 H, C=CCH_3), 0.14 (s, 12 H, $SiCH_3$); ^{13}C NMR (200 MHz, C_6D_6) δ 149.4, 129.8, 58.7, 15.7, -3.8; MS (30 eV), *m/e* (relative intensity) 560 (M^+, 20), 405 (11), 383 (35), 367 (18), 211 (100), 195 (52); exact mass determination calcd for $C_{28}H_{48}O_4Si_4$ 560.2630, measd 560.2621.

The *cis*-2-Butenediol Derivative of 10. A solution of **4** (3.98 g, 12.9 mmol) in THF (225 mL) and a solution of *cis*-2-butene-1,4-diol (1.20 mL, 14.5 mmol) in THF (225 mL) were added over 2.5 h to a stirred solution of Et_3N (5.0 mL, 36 mmol) in THF (250 mL) at room temperature. After completion of addition the slurry that formed was stirred for 4 h and filtered to remove $Et_3NH^+Cl^-$ (3.35 g, 95%). Removal of solvent from the filtrate provided a gum which was dissolved in CH_2Cl_2/hexane and reduced in volume to the point of crystallization. On cooling, filtration provided solid **10**, 1.61 g. A second slightly gummy crop, 0.81 g (combined yield, 58%), was obtained from reduction of the filtrate. Recrystallization from toluene provided purified **10**, as a colorless solid: mp 229–232 °C; ^1H NMR ($CDCl_3$, 270 Hz) δ 7.81–7.45 (m, arom 7.8), 5.20–5.08 (t, CH=CH, 1.9), 4.09–3.96 (q, CH_2, 4.2), 0.70 (s, SiMe, 6.1); ^{13}C NMR ($CDCl_3$) δ 142.6, 133.5, 129.20, 129.14, 58.6, 2.9; exact mass determination calcd for $C_{18}H_{20}O_2Si_2$ 324.1002, measd 324.1010. Anal. Calcd for $C_{18}H_{20}O_2Si$: C, 66.62; H, 6.21. Found: C, 66.42; H, 6.49.

After removal of hexane-insoluble material, the volatiles were stripped from the filtrate to give a yellow-brown gum.

Reduction of 7 and 9 To Give *cis*-1,4-Dihydrohexamethyl-1,4-disilacyclohexa-2,5-diene (1a). The procedure for the LAH reduction of **7** is identical with that for **9**. In a typical experiment, **7** (1.58 g, 5.2 mmol) in THF (50 mL) was added to a solution of LAH (0.40 g, 11 mmol) in THF (50 mL). After being stirred at room temperature for 4 h, the mixture was placed in an ice bath and the excess LAH was destroyed by the careful addition of a saturated solution of ammonium chloride. After the addition of 150 mL of hexane, the solution was worked up in the usual manner. The solvent was stripped, and the residue was passed through a 5-cm column of activated silica gel using hexane as eluent giving *cis*-**1a** (>95% isomeric purity; 0.70 g, 69%): ^1H NMR (270 MHz, $CDCl_3$) δ 4.08 (q, J = 3.2, 2 H, SiH), 1.82 (s, 12 H, C=CCH_3), 0.20 (d, J = 3.2, 6 H, $SiCH_3$). MS (30 eV), *m/e* (relative intensity) 196 (M^+, 34), 181 (100).

In a similar fashion, reduction of **9** (0.60 g, 2.1 mmol) with LAH (0.10 g, 2.6 mmol) provided 0.25 g of **1a** (61%).

Reduction of *cis*-Butenediol Complex 10. A mixture of **10** (2.61 g, 80.6 mmol) and $LiAlH_4$ (1.17 g, 30.8 mmol) in ether (100 mL) was stirred overnight. After workup with NH_4Cl (aqueous, saturated), the ether layer was removed and dried over $MgSO_4$ and the volatiles were removed. Kugelrohr distillation gave **2a** (1.62 g, 84%), bp 95–100 °C (0.04 mm). The oil crystallized to a white solid: mp 39–40 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.85–7.45 (m, arom, 7.9), 5.08–5.04 (q, SiH, 1.8, J_{SiHCH} = 3.9 Hz), 0.75 (d, $SiCH_3$, 6.3, J_{SiHCH} = 3.9 Hz).

Addition of *cis*-**2** to an isomeric mixture of **2** [SiMe doublets centered at δ 0.69 (minor) and 0.64 (major)] enhanced the intensity of the lower field doublet and shifted these resonances slightly to δ 0.70 and 0.65.

Reduction of the *cis*-Butenediol Product of *trans*-4. The solvent was removed from the filtrate obtained after removal of the hexane-insoluble **10** (2.42 g) from the reaction of **4** (3.98 g, 12.9 mmol) and *cis*-butenediol (1.20 mL, 14.5 mmol). The gummy residue was dissolved in ether (50 mL), $LiAlH_4$ (0.5 g) added, and the mixture stirred at room temperature overnight. After aqueous workup, Kugelrohr distillation of the oil obtained from the organic layer gave a fraction (0.57 g), bp 85–95 °C (0.05 mm). The fraction contains three components with the major product equivalent in GC retention time to that of an authentic sample of **2**. An ^1H NMR spectrum shows that the cis isomer of **2** is the major isomer present.

Chlorination of *cis*-2. A mixture of *cis*-**2** (2.70 g, 11.3 mmol), $SOCl_2$ (3.0 mL, 41 mmol), and CCl_4 was heated at reflux for 4 days. After removal of the volatiles, Kugelrohr distillation of the residue gave a thick oil, which solidified: bp 99–105 °C (0.04 mm); mp 98–100 °C; 2.83 g (81%); ^1H NMR (100 MHz, $CDCl_3$) δ 7.6–7.0 (m, arom, 8.5), 0.89 (s, $SiCH_3$, 5.5).

An attempt to recrystallize the dichloride resulted in decomposition.

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Registry No. *cis*-**1a**, 108167-69-7; *trans*-**1a**, 108167-70-0; *cis*-**2a**,

87938-61-2; *trans*-**2a**, 87938-51-0; *cis*-**3**, 83447-54-5; *trans*-**3**, 83447-55-6; *cis*-**4**, 108167-72-2; *trans*-**4**, 108150-17-0; *trans*-**4** *cis*-2-butene derivative, 108150-18-1; *cis*-**5**, 85977-35-1; *trans*-**5**, 85977-36-2; **6**, 87938-58-7; **7**, 108167-73-3; **9**, 108167-74-4; **10**, 108167-76-6; **11**, 108167-75-5; $MgBr_2$, 7789-48-2; potassium *tert*-butoxide, 865-47-4; *cis*,4-di-*tert*-butoxyhexamethyl-1,4-disilacyclohexa-2,5-diene, 108189-52-2; *trans*-1,4-di-*tert*-butoxyhexamethyl-1,4-disilacyclohexa-2,5-diene, 108167-71-1; ethylene dibromide, 106-93-4; dichloromethylsilane, 75-54-7; catechol, 120-80-9; *cis*-2-butene-1,4-diol, 6117-80-2.

Coordination Chemistry of Group 14 Metalloles. 3.[1] Synthesis and Reactivity of 1,1-Dimethyl- and 1,1,3,4-Tetramethylsilole and 1,1,3,4-Tetramethylgermole Complexes[2]

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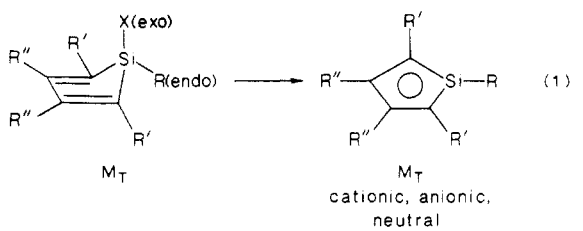
Silacyclopentadienes and germacyclopentadienes (metalloles) without phenyl substituents are effective ligands for transition-metal complexes. Direct displacement of carbonyl ligands from $Fe_2(CO)_9$, $Ru_3(CO)_{12}$, or $Co_2(CO)_8$ results in stable complexes (η^4-metallole)$M(CO)_3$ (M = Fe, Ru), (η^4-metallole)$Co_2(CO)_6$, and [(η^4-metallole)$Co(CO)_2]_2$. (η^4-metallole)$Fe(CO)_3$ undergoes carbonyl replacement with PPh_3. Cleavage of the cobalt–cobalt bond is achieved with both iodine and sodium amalgam; the anions obtained react with Ph_3SnCl. Displacement of 1,5-cyclooctadiene in $(1,4\text{-COD})_2Ni$ affords (η^4-silole)NiCOD. Displacement of COD in (1,5-COD)$M(CO)_4$ (M = Cr, Mo, W) leads to (η^4-metallole)$M(CO)_4$ and also (η^4-metallole)$_2M(CO)_2$. In iron complexes, the exo methyl is cleaved by $SnCl_4$. Chlorine can be displaced by some nucleophiles (CH_3Li, PhLi, H_2O, alcohols). No evidence for the formation of η^5-silacyclopentadienyl complexes has been obtained.

Introduction

Since the first silacyclopentadiene, 1,1,2,3,4,5-hexaphenyl-1-silacyclopentadiene (hexaphenylsilole), was prepared in 1959 by Braye and Hübel,[3] the chemistry of siloles has been considerably developed; in particular their use as ligands with transition metals.[4] Interest has been directed to the similarities between cyclopentadienes and siloles, especially for the preparation of the silacyclopentadienyl anion[5] and the η^5-silacyclopentadienyl ligand. The observation of the latter in mass spectrometry has been suggested[6,7] without any further evidence, however.

Functionalization at silicon could be an efficient way for the transformation of η^4-silole to η^5-silolyl (eq 1).



(1)

M_T = transition metal; R = hydrocarbon radical; R' = Ph; R'' = Ph, H; X = functional group

Functional complexes have been obtained both by cleavage of the exo methyl[8] and complexation of functional siloles.[1] Unfortunately, neither of these ways led to the expected η^5-silolyl complex. In the case of the parent germole, a cationic species coordinated to iron has been obtained but shown to be an η^4-complex with the positive charge mainly localized at the germanium atom.[9] Also a μ-germylene complex was formed from reaction of germole with diiron enneacarbonyl, instead of the expected (η^5-germolyl)dicarbonyliron dimer.[10] These facts contrast with the recent development of the chemistry of the η^5-phospholyl complexes[11] since one would expect similar behavior for silole (or germole) and phosphole. Since all these attempts have been carried out with *C*-phenyl-substituted siloles, the failure to obtain the η^5-system could be explained by the observation of Pauson et al.,[12,13] who pointed out that phenyl substitution on the ring rendered the formation of η^5-cyclopentadienyl more difficult.

Recently, some of us have reported the synthesis of C-unsubstituted siloles[14,15] as well as of 3,4-dimethylsilacyclopentadienes[16,17] and their iron tricarbonyl com-

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