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# Novel disilane chemistry: silyl radical catalyzed cyclo-trimerization of alkynes, synthesis of 1,4-disilacyclohexa-2,5-dienes and silicon hypercoordination studies

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# Novel disilane chemistry: silyl radical catalyzed cyclo-trimerization of alkynes, synthesis of *1,4*-disilacyclohexa-*2,5*-dienes and silicon hypercoordination studies

by

Jinchao Yang

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirement for the degree of
DOCTOR OF PHILOSOPHY

Major: Inorganic Chemistry
Major Professor: John G. Verkade

Iowa State University
Ames, Iowa
2000

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**Major Professor**

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**For the Major Program**

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**For the Graduate College**

# DEDICATION

To My Wife Ying Fu, My Daughter Catherine BeiBei Yang

My Father and My Mother

## TABLE OF CONTENTS

# CHAPTER 1. GENERAL INTRODUCTION

## Dissertation organization

This dissertation consists of a general introduction (chapter 1), four papers (presented as four separate chapters) and a proposal on future research (chapter 6). The first two papers represent published research, the third and fourth papers are in preparation and will be submitted for journal publication soon. Literature citations, tables and figures pertain only to the paper in which they are included. Preceding the first paper is a brief general introduction. Following the proposed research chapter is a general summary (chapter 7) and the acknowledgments. Supplemental materials consisting of X-ray diffraction data are provided in appendices which follow the references of the corresponding papers.

## Introduction

The initial goal of this research was to develop a synthesis of a series of *1,4*-disilacyclohexa-*2,5*-dienes as potential precursors to the corresponding disilabenzenes. Four disilanes [*hexakis*(dimethylamino)disilane, *pentakis*(dimethylamino)chlorodisilane, *symmetric-tetrakis*(dimethylamino)dichlorodisilane and *symmetric-bis*(dimethyl-amino)dichloro-di-*tert*-butyldisilane] were synthesized and reacted with diphenylacetylene in sealed tubes to give the corresponding products *1,1,4,4*-

*tetrakis*(dimethylamino)-*2,3,5,6*-tetraphenyl-*1,4*-disilacyclohexa-*2,5*-diene, *1,4*-*bis*(dimethylamino)-*1,4*-dichloro-*2,3,5,6*-tetraphenyl-*1,4*-disilacyclohexa-*2,5*-diene and *1,4*-dichloro-*1,4*-di-*tert*-butyl-*2,3,5,6*-tetraphenyl-*1,4*-disilacyclohexa-*2,5*-diene in moderate yields.[1] The reaction pathway was found to be a process which includes silylene generation (by successful trapping with *1,4*-diphenyl-*1,3*-butadiene) together with by-product formation via disproportionation, silylene/diphenylacetylene reactions and product formation steps. Disilanes with different groups attached were found to have different reactivities presumably because of varying Si-Si bond energies. Disilanes with electron withdrawing groups (Cl and OMe) were found to be capable of catalytically cyclo-trimerizing alkynes into their corresponding benzene derivatives.[2] The most effective disilane for such trimerization was found to be hexachlorodisilane, which trimerizes phenylacetylene into isomeric triphenylbenzenes and *1*-decyne into isomeric trioctylbenzenes in 100% conversions. Other alkynes can also be trimerized into benzene derivatives in moderate to high yields. Such heretofore unreported catalytic properties of disilanes may be due to the combined effect of the weakness of their Si-Si bond and the strength of Si-X (X = Cl, OMe) bonds. A radical pathway proposed for these catalytic reactions was supported by experimental results. Attempts to create heterogeneous catalysts with $Si_2Cl_6$ led to the discovery of thermal dimerizations of alkynes. This type of reaction was found to be most effective with terminal conjugated alkynes. A radical reaction pathway was also suggested for these reactions.

In an attempt to use quinones as radical traps, we discovered that disilanes bearing electron withdrawing groups react with *1,2*-quinones and *p*-quinones at room temperature in the presence of a solvent (or at *ca.* 100 °C in the absence of a solvent) to form disilylated products in quantitative yields. Because these reactions were not catalyzed by a transition metal catalyst, as was heretofore the case,[3,4] it was necessary to consider a different reaction pathway. A pathway involving the formation of highly reactive hypercoordinated silicon species was proposed which was supported by experimental results.

Each of the four papers deals with an aspect of the disilane reactions, the first being a short communication already published in the Journal of American Chemical Society, and the second constituting a full paper containing a thorough description of the radical reactions, the catalytic properties of several disilanes, and the thermal cyclodimerizations of some terminal conjugated alkynes. The third paper describes the synthesis of some *1,4*-disilacyclohexa-*2,5*-dienes using a more convenient and general approach. The fourth paper discusses the hypercoordination properties of disilanes bearing electron withdrawing groups. Finally, a proposal on disilane chemistry is given as a possible extension of the current research.

## References

1. Yang, J.; Verkade, J. G. *J. Am. Chem. Soc.* **1998**, 120, 6834.

2. Yang, J.; Verkade, J. G. *Organometallics* **2000**, 19, 893.

3. Yamashita, H.; Reddy, N. P.; Tanaka, M. *Organometallics* **1997**, 16, 5223.

4. (a) Chuit, C.; Corriu, R. J. P.; Young, J. C. *Chem. Rev.*, **1993**, 93, 1371. (b) Holmes, R. R. *Chem. Rev.*, **1996**, 96, 927.

# CHAPTER 2. DISILANE-CATALYZED TRIMERIZATION OF ACETYLENES

A paper published in the Journal of American Chemical Society[1]

Jinchao Yang[2,3] and John G. Verkade[2,4]

## Abstract

$Si_2Cl_6$ is shown to be a catalyst for the cyclo-trimerization of both terminal and non-terminal alkynes between 160-200 °C, e.g., cyclo-trimerization of $PhC\equiv CPh$ gave $C_6Ph_6$ in 60% yield. The reaction involves formation of $SiCl_3$ radicals. $Si_2(OMe)_6$ also catalyzes the cyclotrimerization of alkynes, but with lower conversions (yields). This represents the second example of such reactions facilitated by a non-metallic catalyst, as well as the first example proceeding by a radical pathway.

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3. Primary researcher and author.

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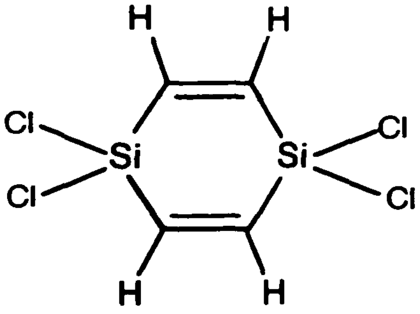
Eighty-two years after the discovery by Bertholet in 1866 that acetylene thermally trimerizes to benzene in low yield at temperatures in excess of 400 °C,[1] Reppe reported that this reaction is catalyzed near room temperature in solutions of nickel complexes.[2] Since then, alkyne trimerization has become one of the most intensely studied synthetically useful transformations, and many transition-metal systems including salts, oxides, organometallic derivatives, and zerovalent metals have been found to catalyze this reaction via a mechanism involving alkyne coordinating to the metal.[3] In 1980 it was reported that the nonmetallic compound diethylamine catalyzes the cyclotrimerization of aryl ethynyl ketones to *1,3,5*-triaroyl benzenes.[4] Evidence for an ionic mechanism was put forth in 1994 for this reaction in which Michael addition of diethylamine to the CH carbon of the triple bond to form an eneamineone was followed by addition of two aryl ethynyl ketone molecules with subsequent regeneration of diethylamine by elimination from trimer.[5] Because this reaction depends on the formation of an enamineone resonance-stabilized by an aroyl carbonyl, this cyclotrimerization appears to be restricted to aroylethynes. We report here the second example of alkyne cyclotrimerizations catalyzed by a non-metal compound and the first example of a catalyst that operates by a free-radical mechanism. The alkynes in the reactions reported herein include disubstituted as well as monosubstituted ethynes.

In 1971 it was reported that the gas-phase reaction of acetylene with hexachlorodisilane at 450 °C gave **1** in 30% yield, presumably via $SiCl_2$ diradicals produced by the disproportionation of $Si_2Cl_6$.[6] When we allowed



**1**

diphenylacetylene to react with $Si_2Cl_6$ in a sealed tube at this temperature, only an insoluble black solid was formed. However, by lowering the temperature, hexaphenylbenzene was obtained in reasonable yield (eq 1).[7]

$$\mathrm{PhC{\equiv}CPh} \xrightarrow[\text{2 d, 60\%}]{\mathrm{Si_2Cl_6}\text{ (60 mol \%), 170-180 °C}} \mathrm{C_6Ph_6} \qquad (1)$$

That $Si_2Cl_6$ acted as a procatalyst that undergoes no net change in our reaction was shown by the single $^{29}Si$ NMR peak at δ 12.52 ppm for $Si_2Cl_6$ in the reaction mixture, which was confirmed by recording this spectrum after addition of authentic $Si_2Cl_6$. Further confirmation was secured by quantitatively converting the $Si_2Cl_6$ in the reaction mixture to $Si_2(NMe_2)_6$ with excess $HNMe_2$ followed by comparison of the $^1H$ NMR, $^{13}C$ NMR, and EI mass spectra with those of an authentic sample. Recycling the same sample of

$Si_2Cl_6$ five times in separate reactions with diphenylacetylene revealed no loss in $C_6Ph_6$ yield.

While the formation of **1** from acetylene and $Si_2Cl_6$ at 450 °C was attributed to $SiCl_2$ diradical formation,[6] it is reasonable to suppose that, under our milder conditions, $SiCl_3$ radicals induce the trimerization of PhC≡CPh by an addition-elimination pathway depicted in Scheme 1. The presence of radicals in eq 1 was substantiated by the lack of detectable product when 20% (molar) of hydroquinone or *9,10*-dihydroanthracene was added to the reaction mixture as radical traps. Acid-catalyzed cyclo-trimerization of diphenylacetylene by HCl formed by hydrolysis of $Si_2Cl_6$ in the presence of adventitious water was ruled out by failure of the reaction with HCl (in $Et_2O$) or $SiCl_4$ that had been partially hydrolyzed by exposure to moist air. That silicon tetrachloride by itself is ineffective as a catalyst in our reactions is reasonable in view of its exceedingly high first dissociation energy (*ca.* 111 kcal/mol[8]). Because the dissociation energy of $SiCl_3$ (that is generated from $Si_2Cl_6$) to $SiCl_2$ is only *ca. 66* kcal/mol, [8] $SiCl_2$ as a reactive intermediate cannot be ruled out a *priori*. However, the products obtained under our experimental conditions, when compared with the more drastic conditions resulting in the formation of **1**,[6] favor the relatively simple pathway involving $SiCl_3$ radicals depicted in Scheme 1. Although attempts to trap one or more of the intermediates **A-D** in Scheme 1 with hydrogen donors such as *9,10*-dihydroanthracene or *9,10*-dihydrophenylanthrene failed, we were able to detect $HSiCl_3$ and the corresponding aromatized hydrogen donor dehydrogenated product by $^1H$ NMR spectroscopy. This result further substantiates the formation of $SiCl_3$ radicals via Si-Si bond cleavage. Trichlorosilane and anthracene were also detected when a mixture consisting only of $Si_2Cl_6$ and *9,10*-dihydroanthrancene was heated to 190 C for 80 h. As noted earlier, the presence of *9,10*-dihydroanthranceen in Scheme 1 inhibited hexaphenylbenzene formation (reaction 1). However, when 1-decyne was employed in the presence of this hydrogen donor or *9,10*-dihydrophenanthrene, quantitative trimerization was detected as well as the formation of $HSiCl_3$ and aromatization of the hydrogen donor. This result is consistent with the idea that alkyl ethynes are more competitive for $SiCl_3$ radicals (even at low concentrations) than diphenylacetylene.

Equation 1 has been extended to other alkyne substrates, among which are those shown in eqs 2-5. Apparently terminal alkynes undergo cyclo-trimerization in high conversion more easily than nonteriminal examples for steric reasons. At 20 mol % $Si_2Cl_6$, eq 2 gave 30% conversion after 2 days, and for reasons that are not clear, this conversion was not appreciably increased after 6 days. Equation 3 gives an 80% conversion to products even at 5 mol % $Si_2Cl_6$ after 30 h. To rule out catalysis by the walls of the steel pressure vessel in eq 5, the readction was run in the absence of $Si_2Cl_6$, whereupon only starting material was recovered. Interestingly, in the absence of $Si_2Cl_6$, phenylacetylene was found to give mainly dimerized products (α and β-phenyl naphthalene) along with an isomeric mixture of trimers under the conditions of eq 4, whereas *3*-hexyne and *1*-decyne were thermally stable in the absence of $Si_2Cl_6$.[9]

$$\mathrm{EtC{\equiv}CEt} \xrightarrow[\text{2 d, 45\%}]{\mathrm{Si_2Cl_6}\text{ (49 mol \%), 200 °C}} \mathrm{C_6Et_6} \qquad (2)$$

$$\mathrm{CH_3(CH_2)_7C{\equiv}CH} \xrightarrow[\text{230 h, 100\%}]{\mathrm{Si_2Cl_6}\text{ (10 mol \%), 190 °C}}$$

$$\text{1,3,5 and 1,2,4-}\mathrm{C_6H_3(n\text{-}Oct)_3} \qquad (3)$$
$$\text{(~1:1 ratio)}$$

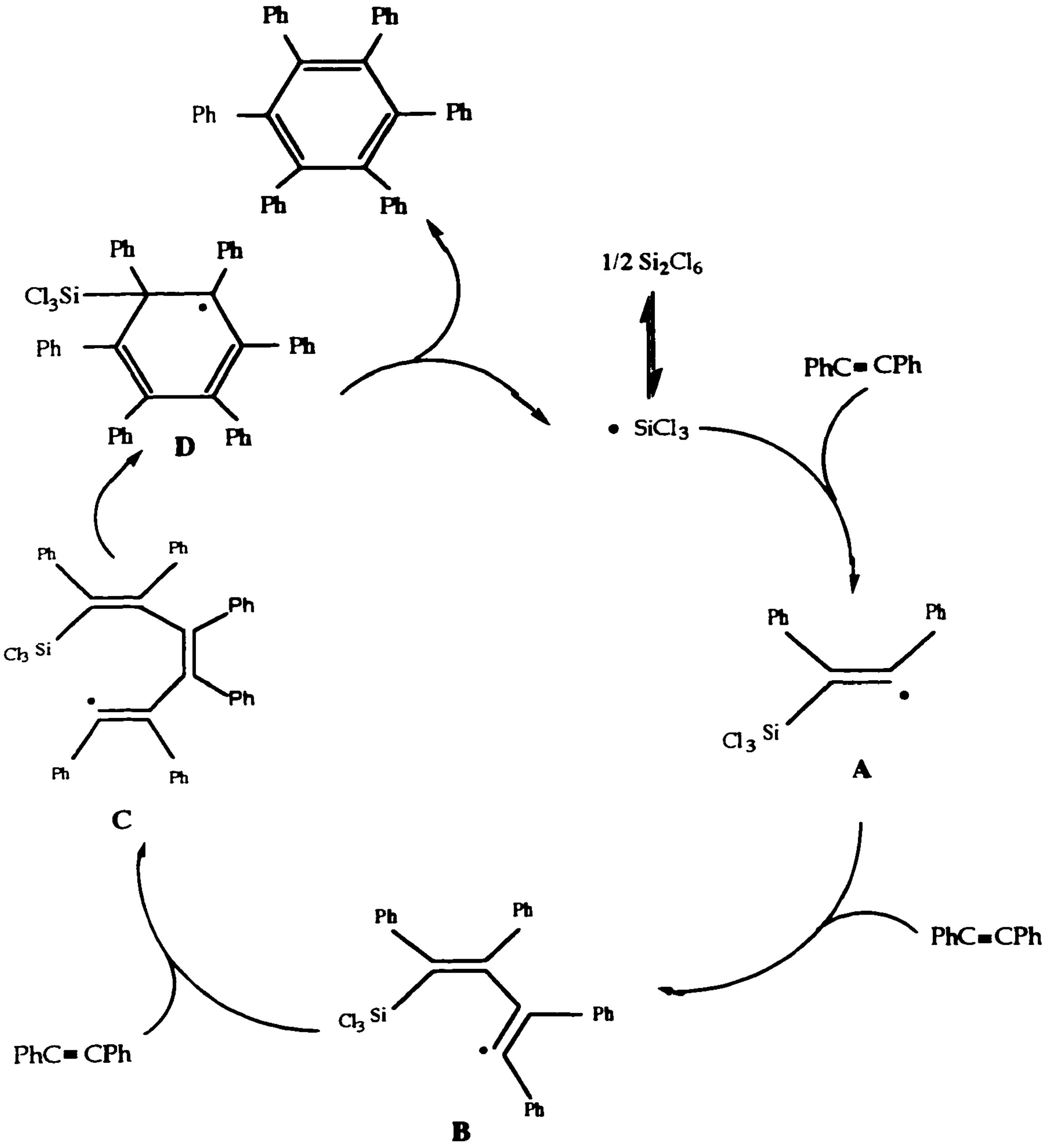
$$\mathrm{PhC{\equiv}CH} \xrightarrow[\text{15 h, 100\%}]{\mathrm{Si_2Cl_6}\text{ (17 mol \%), 200 °C}} \text{1,3,5 and 1,2,4-}\mathrm{C_6H_3Ph_3} \qquad (4)$$
$$\text{(~1:1 ratio)}$$

$$\mathrm{HC{\equiv}CH} \xrightarrow[\text{vessel, 2 d, 90\%}]{\mathrm{Si_2Cl_6}\text{, 210 °C, pressure}} \mathrm{C_6H_6} \qquad (5)$$

We found that $Si_2(OMe)_6$ also catalyzes alkyne cyclo-trimerization, although conversions are substantially lower than with $Si_2Cl_6$ under the same conditions (e.g., 40% and 30% conversion in eq 3 and 4, respectively). On the other hand, no reactions were detected using $Si_2Me_6$ as a potential procatalyst, even when present in high molar ratios and in reactios lasting up to 150 h. We suggest that the decreasing catalytic activity in the order $Si_2Cl_6 > Si_2(OMe)_6 > Si_2Me_6$ is attributable to an accompanying decrease in the electron-withdrawing power of the silicon substituents. Such an electronic effect can be expected to strength the Si-Si bond, thus diminishing thermal product of silyl radicals. In all three of the above disilanes, the substituent-silicon bonds[8,10] are considerably stronger than the Si-Si linkage.[10] Interestingly, the reaction of $Si_2(NMe_2)_6$ with alkynes follows a stiochiometric course leading to *1,1,4,4-tetrakis*(dimethylamino)-*1,4*-disilacyclohexa-*2,5*-diene.[9]

In Scheme 1, cleavage of an Si-substituent bond in intermediate **A** by an $SiCl_3$ radical to give $SiCl_4$ and $SiCl_2$ is apparently less favored than sequential attack of A by two additional PhC≡CPh molecules. When intermediate C is formed, the drive to a stable aromtic product causes an $SiCl_3$ to be excluded from this intermediate. Further substantiation for Si-Si bond cleavage in the action of $Si_2Cl_6$ and $Si_2(OMe)_6$ in these reactions was sought by heating a mixture of these compounds in hopes of forming the crossover product $Cl_3SiSi(OMe)_3$. Only a complicated mixture of $Si_2Cl_{6-x}(OMe)_x$ products could be detected by $^1H$ NMR spectroscopy, however.

Scheme 1



Others have reported that $Me_3SiCl$ and Pd/C (10% palladium on carbon) is a catalyst for cyclo-trimerizing alkynes to the corresponding benzene derivatives.[11] It was found in this system that both trimethylchlorosilane and palladium were necessary for the reaction to occur. Although the authors suggest that the seemingly heterogeneous process might in fact be a homogeneous one (possibly through the formation of a soluble catalytic palladium species), they were not able to detect or isolate an intermediate. To determine if silyl radicals produced under these conditions could be catalyzing the cyclo-trimerization, we repeated the reaction with $Si_2Cl_6$ and 1-octyne at 140 C using a mixture of $Si_2Cl_6$ and 10% palladium on carbon, and also an $Si_2Cl_6/PdCl_2$ mixture. Surprisingly, the conversions to trimers were only 7.00% for $Pd/C/Si_2Cl_6$ system and 11.0% for $PdCl_2/Si_2Cl_6$ system; much less than $Si_2Cl_6$ by itself under the same conditions (70% conversion). At the higher temperature these palladium catalysts apparently act as radical traps, perhaps by an oxidative addition process-a possibility we are current examining.

Experiments are underway to evaluate the scope and limitations of the alkynes and group 14 procatalysts congeneric with disilanes that can be employed in these novel reactions.

**Acknowledgements**

The authors are grateful to NSF and the Iowa State Center for Advanced Technology Development for grant support. Helpful discussions with T. J. Barton and (the late) G. A. Russell are gratefully acknowledged.

## References

1. Bertholet, M. C. R. Held. *Seances Acsd. Sci.* **1866**, 905.
2. Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Liebigs Ann. Chem.* **1948**, *560*, 1.
3. See, for example: (a) Takahashi, T.; Xi, Z.; Yamazaki, A.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1998**, *120*, 1672. (b) Yokota, T.; Sakurai, Y.; Sakaguchi, S.; Ishii, Y. *Tetrahedron Lett.* **1997**, *38*, 3923. (c) Marx, H. W.; Moulines, F.; Wagner, T.; Astruc, D. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1701. (d) Bose, R.; Matzger, A. J.; Mohler, D. L.; Vollhardt, K. P. C. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1478. (e) Bianchini, C.; Caulton, K. G.; Chardon, C.; Doublet, M. L.; Eisenstein, O.; Jackson, S. A.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Streib, W. E.; Vacca, A.; Vizza, F. *Organometallics* **1994**, *13*, 2010. (f) Vollhardt, K. P. C. *Pure Appl. Chem.* **1993**, *65*, 153. (g) Baidossi, W.; Goren, N.; Blum, J. *J. Mol. Catal.* **1993**, *85*, 153. (h) Smith, D. P.; Strickler, J. R.; Gray, S. D.; Bruck, M. A.; Holmes, R. S.; Wigley, D. E.; *Organometallics* **1992**, *11*, 1275. (I) Bianchini, C.; Caulton, K.; Chardon, C.; Eisenstein, O.; Folting, K.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Rauscher, D. J.; Streib, W. E.; Vizza, F. *J. Am. Chem. Soc.* **1991**, *113*, 5127. (j) Dutoit, C. J.; Du Plessis, J. A, K.; Lackmann, G. *J. Mol. Catal.* **1989**, *53*, 67. (k) Borrini, A.; Dweisi, P.; Ingrosso, G.; Luckermi, A.; Serra, G.; *J. Mol. Catal.* **1985**, *30*, 181. (l) Tysoe, W. T.; Nyberg, G. L.l Lambert, R. M. *J. Chem. Soc., Chem. Commun.* **1983**, *11*, 623.
4. Balasubramanian, K.; Selvaraj, P.; Venkataramani, S. *Synthesis* **1980**, 29.

5. (a) Matsuda, K.; Inoue, K.; Koga, N.; Nakamura, N.; Iwamura, H. *Mol. Cryst. Liq. Cryst.* **1994**, *253*, 33. (b) Matsuda, K.; Nakamura, N.; Iwamura, H. *Chem. Lett.* **1994**, 1765.
6. Chernyshev, E.A.; Komalenkova, N.G.; Bashkuova, S.A. *Zh. Obshch. Khim.* **1971**, *41*, 1175.
7. In a thick-walled quartz tube was placed diphenylacetylene (0.50 g, 2.8 mmol) followed by 0.50 g (1.8 mmol) of hexachlorodisilane which was added under nitrogen by a syringe. The tube was cooled in liquid nitrogen and was flame sealed under vacuum. The tube was heated to 170 -180 °C in an oil bath for 2 days, during which time the color of the solution changed to brown after 1 h, and then to black after 1 day. Single crystals were observed to form at the bottom of the tube. After allowing the tube to cool to room temperature, it was opened and the solid product was washed with 3 x 0.5 mL $CHCl_3$ and dried under vacuum to give 0.3 g (60% yield) of crystalline product which was identified as hexaphenylbenzene. Mp: 455 - 457 °C. $^1H$ NMR (300 MHz, $C_6D_6$): δ 6.69-7.15 (m, $C_6H_5$, 30H); $^{13}C$ NMR (75 MHz, $C_6D_6$): δ 140.60, 140.28, 131.41, 126.55, 125.16. MS (EI, 70 eV): m/z (ion, relative intensity) 534.2 ($M^+$, 22.53), 457.2 ($M^+$-$C_6H_5$, 0.80). Elemental analyses: Calcd. for $C_{42}H_{30}$ C 94.38%, H 5.62%. Found: C 93.25%, H 5.73%. The NMR data are identical to those reported in *The Aldrich library of $^{13}C$ and $^1H$ FT NMR Spectra*, 1st ed. Milwaukee: Aldrich Chemical Co.: Milwaukee, WI, **1993**.
8. Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 247.

9. Yang, J.; Verkade, J. To be published.

10. Moeller, T. *Inorganic Chemistry*; John Wiley & Sons: New York, **1982**.

11. Jhingan, A. K.; Maier, W. F. *J. Org. Chgem.* **1987**, *52*, 1161.

# CHAPTER 3. DISILANE-CATALYZED VERSUS THERMALLY INDUCED REACTION OF ALKNES: A COMPARISON

A paper published in Organometallics[1]

Jinchao Yang[2,3] and John G. Verkade[2,4]

## Abstract

The alkynes $RC\equiv CR$ (R = H, Et, Ph), $RC\equiv CH$ (R = $Me(CH_2)_5$, $Me(CH_2)_7$, Ph, $Me_3Si$, $EtO_2C$) and $RC\equiv CR'$ (R = Ph, R' = $C_6F_5$; R = Me, R' = Ph) trimerize to corresponding benzene derivatives in 30-100% yields in the presence of $Si_2Cl_6$ as a procatalyst at 170-200 °C over 20-48 hours. These reactions represent only the second example of non-metal-catalyzed alkyne trimerizations. The unsymmetrical alkynes $Me_3SiC\equiv CH$, $EtO_2CC\equiv CH$ and $PhC\equiv CC_6F_5$ gave symmetrical *1,3,5*-substituted benzenes, while the others led to isomeric mixtures. A 1:2 molar mixture of $PhC\equiv CH$ and $PhC\equiv CPh$ provided an isomeric mixture (45% yield) consisting mainly of *1,2,4,5*-tetraphenylbenzene. While $Si_2(OMe)_6$ also catalyzed alkyne trimerizations (though not as efficiently as $Si_2Cl_6$) $Si_2Me_6$ did not, suggesting an electronegativity influence in the

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2. Graduate student and professor, respectively, Department of Chemistry, Iowa State University.
3. Primary research and author.
4. Author for correspondence.

formation of the $Cl_3Si\bullet$ radicals shown to be involved in these reactions. Somewhat unexpectedly, however, neither $Si_2F_6$ nor *sym*-$Si_2Me_2Cl_4$ catalyzed alkyne trimerizations. Experimental support for the radical pathway proposed for the alkyne trimerization observed herein is presented. In the absence of disilane procatalyst, $PhC\equiv CH$ gave an isomeric mixture of dimers, *p*-$MeC_6H_4C\equiv CH$ afforded predominantly a single dimer, *1*-ethynyl-*1*-cyclohexene provided exclusively a single dimer, whereas $RC\equiv CH$ (R = alkyl) and $PhC\equiv CMe$ did not react upon heating under the same conditions.

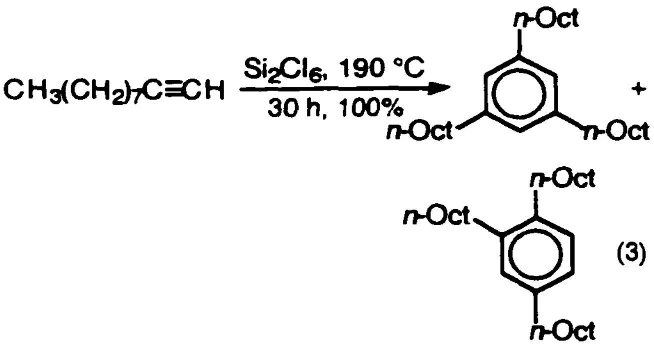
## Introduction

For a variety of reasons, polysubstituted benzene compounds bearing up to six carbon substituents have been of substantial interest during the past two decades.[1] For example, polyalkynyl benzenes are useful as synthons for supramolecular assemblies,[1b,c] electronic devices,[1b,c] and they have potential applications to transition metal catalyst construction[1c] and in functioning as precursors to discotic liquid crystals,[1d] unusual polymers[1e] and carbon allotropes.[1e] Hexaalkyl benzenes containing one or more oxygen or sulfur donor atoms in the alkyl substituents are novel polypodands possessing unusual phase transfer properties toward metal ions and neutral organic molecules.[1f] Hexakis alkynyl and hexakis alkenyl benzenes have been synthesized by the palladium-catalyzed six-fold alkynylation and alkenylation reactions, respectively, of hexabromobenzene.[1a] Moreover hexaalkyl benzenes have been made by alkylating hexamethylbenzene activated as a Cp*Fe complex.[1f]

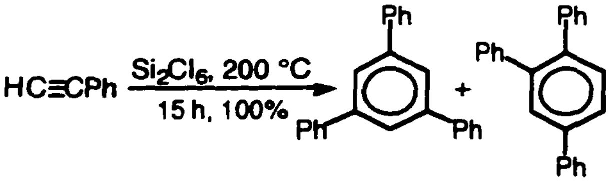
In a recent communication[2] we reported reactions 1-5 as illustrations of only the second example of alkyne cyclotrimerizations catalyzed by a nonmetallic species and disclosed for the first time examples of such transformations demonstrated to proceed by a free radical mechanism. To our knowledge the only other nonmetal-catalyzed reaction of a similar

$$\mathrm{PhC{\equiv}CPh} \xrightarrow[\text{2 d, 70\%}]{\mathrm{Si_2Cl_6},\ 170\text{-}180\ ^\circ\mathrm{C}} \mathrm{C_6Ph_6} \tag{1}$$

$$\mathrm{EtC{\equiv}CEt} \xrightarrow[\text{2 d, 45\%}]{\mathrm{Si_2Cl_6},\ 200\ ^\circ\mathrm{C}} \mathrm{C_6Et_6} \tag{2}$$



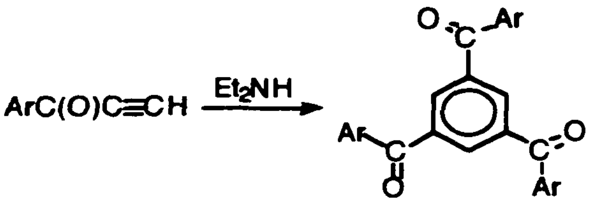
(3)



(4)

$$HC\equiv CH \xrightarrow[2\ d,\ 90\%]{Si_2Cl_6,\ 210\ °C} C_6H_6 \qquad (5)$$

nature is that shown in reaction 6.[3,4] Evidence has been put forth supporting a pathway for reaction 6 involving initial

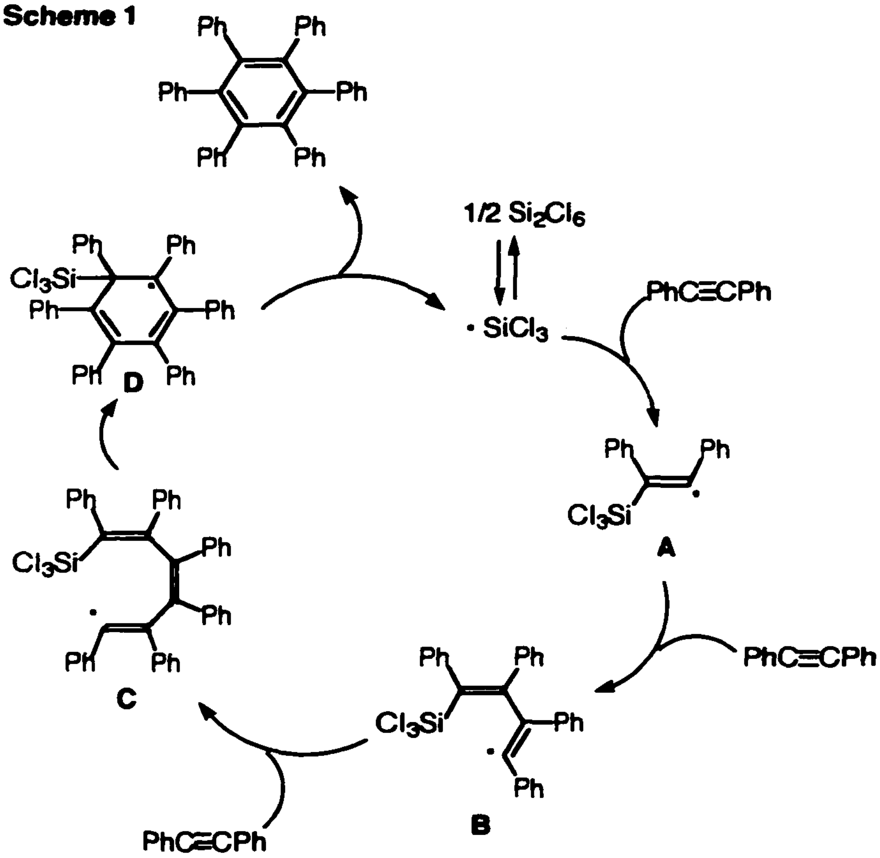


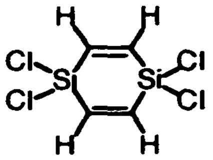
(6)

Michael addition of $Et_2NH$ to the CH carbon of the alkyne to form an eneamine-one, followed by addition of two aryl ethynyl ketone molecules with subsequent regeneration of the catalyst upon trimer formation.[3] By contrast, we adduced evidence that reactions 1-5 transpire via an addition-elimination of $SiCl_3$ radicals as depicted in Scheme 1 for the trimerization of $PhC\equiv CPh$. Here $Si_2Cl_6$ acts as a procatalyst that generates catalytic $SiCl_3$ in an equilibrium dissociation at the temperatures employed for reactions 1-5. At 450 °C, reactions 1 and 5 had earlier been reported to give low yields of **1** and **2**, respectively, presumably via silylenes ($SiCl_2$) intermediates generated in the thermal disproportionation of $Si_2Cl_6$.[5] On the other hand, Bertholet observed in 1866 that acetylene thermally cyclotrimerizes to benzene in low yield at 400 °C.[6]

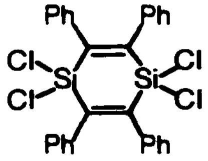
In the present report we extend the scope of our study of $Si_2Cl_6$ as an alkyne trimerization procatalyst to the alkynes $Me_3SiC\equiv CH$, $EtO_2CC\equiv CH$, $C_6F_5C\equiv CPh$, $PhC\equiv CMe$, $CH_3(CH_2)_5C\equiv CH$ and *1*-ethynyl-*1*-cyclohexene. We also describe our results using $Si_2(OMe)_6$ and $Si_2F_6$ as procatalysts. A comparison is then made on the

**Scheme 1**



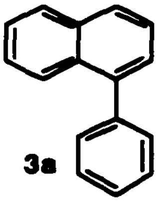


**1**

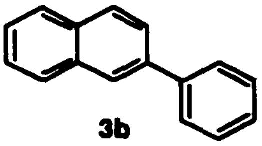


**2**

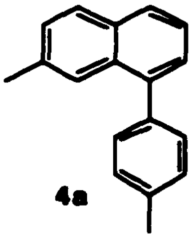
course of the thermal reaction of several conjugated terminal alkynes (wherein isomeric dimers such as **3-5** are formed) with trimerizations of these alkynes catalyzed by $SiCl_3$ radicals.



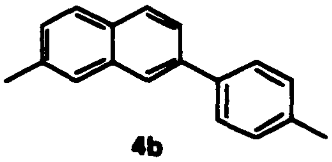
**3a**



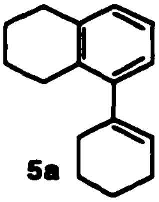
**3b**



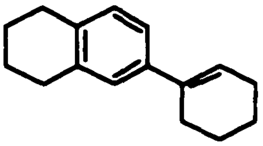
**4a**



**4b**



**5a**



**5b**

## Experimental Section

**General methods.** All reactions were carried out under anhydrous conditions using conventional vacuum lines and Schlenk ware. Diethyl ether, pentane and tetrahydrofuran (THF) were distilled from sodium/benzophenone, and $CHCl_3$ was distilled from $CaH_2$ under nitrogen. Hexachlorodisilane, hexamethyldisilane, *1,2*-dimethyltetrachlorodisilane, diphenylacetylene, *1*-decyne, *1*-octyne, phenylacetylene, *3*-hexyne, *3*-butyn-*2*-one, ethyl propiolate, ethyl-*2*-butynoate, iodopentafluorobenzene, benzene, trimethylsilylacetylene, *4*-ethynyltoluene, pyridine-*2*-bromide, pyridine-*3*-bromide and *1*-ethynyl-*1*-cyclohexene were purchased from Aldrich Chemical Co., and hexamethoxydisilane was purchased from Gelest Inc. All were used as received without further purification. $Si_2F_6$ was synthesized from $SbF_3$ and $Si_2Cl_6$ according to a literature method.[7] Phenyl pentafluorophenylacetylene was synthesized from iodopentafluorobenzene and copper phenylacetylenide[8] and was purified by sublimation. $^1H$ and $^{13}C$ NMR spectra were recorded on a Varian VXR-300 instrument and mass spectra were obtained on a Finnigan 4000 (70 eV EI or CI). GC-MS experiments were carried out using a Finnigan Magnum Ion Trap detector (Finnigan MAT, San Jose, CA) configured in the electron impact ionization mode with automatic gain control. A DB5-MS separation column (30 m, 0.25 mm I.D., 0.25 μm film thickness) was used and the injector and transfer line temperature was fixed at 250 °C. Elemental analyses were performed on a Perkin Elmer series II CHNS/O analyzer by the Instrumental Services unit in our department. Melting points were measured with a Thomas Hoover capillary apparatus and were uncorrected.

**Catalytic synthesis of acetylene.** After $Si_2Cl_6$ (0.27 g, 1.0 mmol) was placed in a steel pressure reactor, it was cooled by liquid $N_2$ and gaseous acetylene (0.26 g, 10 mmol) was introduced. Adventitious acetone was first eliminated from the acetylene with a dry ice trap. The reactor was closed and heated to 210 °C in an oil bath for 48 hrs. The reactor was then cooled to room temperature, vented and opened yielding 0.50 g of a liquid whose $^1H$ and $^{13}C$ NMR spectra indicated that $C_6H_6$ was the only hydrocarbon present (*ca.* 90% conversion). After hydrolyzing the $Si_2Cl_6$ with $H_2O$ at 4 °C, 0.20 g (2.6 mmol, 77% yield) of $C_6H_6$ was isolated upon separation from the aqueous phase. $^1H$ NMR ($CDCl_3$, $\delta$ 7.12) and $^{13}C$ NMR ($CDCl_3$ $\delta$ 128.0) data compared favorably with literature values.[12]

**Catalytic synthesis of hexaphenylbenzene.** The synthesis and characterization of this compound was described in our preliminary communication.[2]

**Catalytic synthesis of hexaethylbenzene.** In a thick-walled quartz tube, *3*-hexyne (0.50 g, 6.1 mmol) was introduced followed by 0.80 g (3.0 mmol) of $Si_2Cl_6$. The tube was argon flushed for a few minutes, and then it was cooled in liquid nitrogen and flame sealed under vacuum. The tube was placed inside a steel pressure reactor which was heated to 200 °C with an oil bath. The pressure was approximately 2 atm during the 48-hour reaction. The reactor was then allowed to cool to room temperature and the tube was opened under nitrogen. The reaction product was analyzed as a mixture of hexaethylbenzene and starting materials. The conversion of *3*-hexyne to product in this reaction was determined to be 51% by $^1$H NMR spectroscopic integration. After dectantation of the $Si_2Cl_6$ and starting materials from the colorless crystals that formed, hexaethylbenzene was obtained in 45% yield after washing with $CHCl_3$ and drying under vacuum. $^1$H NMR ($CDCl_3$): δ 2.65 (q, $CH_2$, 12H), 1.20 (t, $CH_3$, 18H); $^{13}$C NMR ($CDCl_3$): δ 137.8, 22.1, 15.7. HRMS(EI): Calcd. for $C_{18}H_{30}$: 246.23475, found: 246.23480. These data compare favorably with literature values.[9]

**Catalytic synthesis of isomeric trihexylbenzenes.** *1*-Octyne (2.20 g, 20.0 mmol) was added to a thick-walled quartz tube, followed by 1.40 g (5.0 mmol) of $Si_2Cl_6$. The tube was flushed with nitrogen and then it was cooled in liquid nitrogen and flame sealed under vacuum. The tube was heated at 180 °C in an oil bath for 30 hours. After cooling the tube to room temperature, a brown oily material was obtained which was analyzed by GC-MS as a mixture of two isomeric trimers in a *ca.* 1:1 ratio. The conversion of starting material was 100%. Filtration through silica gel gave 2.00 g of a mixture of the two isomers in 90% yield. No attempt was made to separate the two isomers. Bp: ~140 °C/ 0.03 mm. $^1$H NMR of mixture ($CDCl_3$): δ 6.80-7.05 (m, 3H), 0.87-2.56 (m, 39 H); $^{13}$C NMR of the mixture ($CDCl_3$): δ 142.7, 140.3, 140.2, 137.7, 129.2, 128.9, 125.8, 125.7, 36.0, 31.8, 31.6, 31.3, 28.5, 22.6, 22.5, 18.4, 14.1, 14.0. HRMS (EI): Calcd. for $C_{24}H_{42}$: 330.328651, found: 330.3290040. The $^1$H NMR spectrum of this isomeric mixture compares favorably with that found in the literature.[9] No $^{13}$C NMR data were found in the literature for these isomeric compounds.

**Catalytic synthesis of isomeric trioctylbenzenes.** *1*-Decyne (1.00 g, 7.30 mmol) was added to a 25 mL Schlenk flask which had been flushed with argon. $Si_2Cl_6$ (0.20 g, 0.74 mmol) was introduced to the flask and upon mixing, the colorless starting materials became yellow immediately. The flask was cooled in liquid nitrogen and evacuated. The flask was then heated at 190 °C in an oil-bath for 30 hours. After cooling to ambient temperature, a brown oily material was obtained which was found by $^1H$ NMR spectroscopy to be a mixture of *1,3,5*-trioctylbenzene and *1,2,4*-trioctylbenzene. Conversion of *1*-decyne to these products was found to be quantitative, and the two products were found to form in a ca. 1:1 ratio according to GC-MS. $Si_2Cl_6$ was separated by washing the reaction mixture with an aqueous solution saturated with NaOH. No attempt was made to separate the two isomers. Bp: 239-240 °C (2 torr). $^1H$ NMR ($CDCl_3$): $\delta$ 7.06(s), 7.05(s), 6.95(s), 6.92(s), 6.81(s), 2.57 (t, $CH_2$, 6H), 1.57 (br, $CH_2$, 6H), 1.29 (br, $CH_2$, 30H), 0.89 (t, $CH_3$, 9H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 142.7, 140.3, 140.2, 137.3, 129.2, 129.0, 125.8, 125.7, 36.0, 35.6, 32.8, 32.4, 31.9, 31.6, 31.5, 29.9, 29.5, 29.3, 18.4. HRMS(EI): Calcd. for $C_{30}H_{54}$: 414.52255, found: 515.42247. The $^1H$ NMR and MS spectra compared favorably with literature values.[9] To our knowledge, no $^{13}C$ NMR data were reported for the two isomeric compounds.

**Catalytic synthesis of isomeric triphenylbenzenes.** To a 25 mL flask equipped with a magnetic stirrer and a reflux condenser was introduced phenylacetylene (0.75 g, 7.2 mmol). The flask was flushed with argon and then 0.32 g (1.2 mmol) of hexachlorodisilane was added. After stirring the reaction mixture for a few minutes, the flask was stoppered with a septum. The flask was heated to 200 °C in an oil bath and held at that temperature for 15 hours. A liquid (probably hexachlorodisilane, b.p. 144-146 °C) was seen to reflux during reaction. After cooling the reaction mixture to room temperature, a thick brown material was obtained which was dissolved in 10 mL of benzene. A yellow precipitate (0.70 g, 93% yield) formed upon adding 10 mL of pentane to the benzene solution. The precipitate was analyzed by GC-MS as a *ca.* 1:1 mixture of two isomers. The conversion of the starting materials was quantitative since no phenylacetylene starting material was detected by $^1$H and $^{13}$C NMR spectroscopies. No attempt was made to separate the isomers. $^1$H NMR ($CDCl_3$): δ 7.78 (s, central $C_6H_3$), 7.63-7.71 (m, 13H), 7.35-7.55 (m, 21H), 7.14-7.21 (m, 15H); $^{13}$C NMR ($CDCl_3$): δ 142.3, 141.5, 141.1, 141.1, 141.0, 140.6, 140.3, 139.5, 131.1, 129.9, 129.9, 129.8, 129.4, 128.8, 128.8, 127.9, 127.9, 127.5, 127.4, 127.3, 127.1, 127.0, 126.6, 126.5, 126.1, 125.2. HRMS(EI): Calcd. for $C_{24}H_{18}$: 306.14085, found: 306.14060. The NMR data compare favorably with literature values for *1,3,5*-triphenylbenzene and *1,2,4*-triphenylbenzene.[10,13]

**Catalytic synthesis of *1,3,5*-tris(trimethylsilyl)benzene.** In a thick-walled quartz tube, trimethylsilylacetylene (0.30 g, 3.0 mmol) was introduced, followed by hexachlorodisilane (0.31 g, 1.6 mmol). The tube was cooled in liquid nitrogen and flame sealed under vacuum. The tube was placed inside a pressure reactor, which was gradually heated to 190 °C in an oil bath. After 20 hours at that temperature, the reactor was allowed to cool to room temperature. The tube was opened in a hood, and the brown liquid was analyzed by $^1$H, $^{13}$C NMR and MS spectroscopies as a mixture of the title product and starting materials. The conversion of starting materials was determined by $^1$H NMR spectroscopy to be *ca.* 50%. A small quantity of colorless crystals formed in ca. 30% yield after allowing the reaction mixture to remain in a refrigerator for one day. $^1$H NMR ($CDCl_3$): δ 7.67 (s, phenyl, 3H), 0.27 (s, $CH_3$, 27H); $^{13}$C NMR ($CDCl_3$): δ 138.8, 138.2, -1.12. MS (EI): The $^1$H and $^{13}$C NMR data compare favorably with literature values.[11] MS (EI) m/z (ion, relative intensity) 294.1 ($M^+$, 5.60), 279.1 ($M^+$-$CH_3$, 32.07). HRMS (EI) Calcd. for $C_{15}H_{30}Si_3$ 294.16554, found: 294.16559.

**Catalytic synthesis of tetraphenylbenzenes.** A mixture of diphenylacetylene and phenylacetylene in a 2:1 molar ratio [0.520 g (2.92 mmol) of diphenylacetylene and 0.151 g (1.48 mmol) of phenylacetylene] was placed in a thick-walled quartz tube and then 0.50 g (1.8 mmol) of hexachlorodisilane was injected. The tube was cooled in liquid nitrogen, flame sealed under vacuum and heated to 185 °C for 20 hours in an oil bath. Crystals were seen to form during the reaction. After cooling to room temperature, the tube was opened in a hood. A $^1$H NMR spectrum of the mixture revealed 100% conversion of starting material. After the reaction mixture was shaken with 10 mL of chloroform, crystals floating on the surface isolated by filtration were shown to be hexaphenylbenzene by $^1$H and $^{13}$C NMR spectroscopies.[2] The yellow chloroform filtrate was cooled to 4 °C in a refrigerator after which *ca.* 15 mL pentane was added to the solution, giving a yellow precipitate. The precipitate was filtered, washed with 3 x 1 mL of pentane, and dried under vacuum to give 0.30 g of *1,2,4,5-* tetraphenylbenzene (as deduced from the one singlet for the central aromatic ring in the $^1$H NMR spectrum) in 45% yield. $^1$H NMR ($CDCl_3$): δ 7.52 (s, central ring, 2H); 7.22 (s, phenyl, 20H); $^{13}$C NMR ($CDCl_3$): δ 140.9, 139.6, 133.0, 129.9, 127.9, 126.6. MS (EI): m/z (ion, relative intensity) 382.1 ($M^+$, 21.46), 305.3 ($M^+$-$C_6H_5$, 1.51). HRMS (EI) Calcd. for $C_{30}H_{22}$: 382.17215, found: 382.17148. No NMR data were found for *1,2,4,5*-tetraphenylbenzene in the literature.

**Catalytic synthesis of triethyl *1,3,5*-benzenetricarboxylate.** In a thick-walled quartz tube, ethynyl propiolate (0.10 g, 1.0 mmol) was introduced under nitrogen and then $Si_2Cl_6$ (0.14 g, 0.50 mmol) was added. The tube was cooled in liquid nitrogen and flame sealed under vacuum. The tube was placed inside a steel pressure reactor which was then heated to 170 °C for 20 hours. The reaction product was a thick oily material consisting of a mixture of triethyl 1,3,5-benzenetricarboxylate and starting materials as determined by $^1$H and $^{13}$C NMR spectroscopies. Distillation under reduced pressure gave 40 mg of product (40% yield). $^1$H NMR ($CDCl_3$): δ 8.81 (s, $C_6H_3$, 3H), 4.36 (q, $CH_2$, 6H), 1.39 (t, $CH_3$, 9H); $^{13}$C NMR ($CDCl_3$): δ 165.1, 134.4, 131.5, 61.6, 14.2. $^1$H and $^{13}$C NMR data for the *1,3,5*-isomer are in agreement with those obtained from an authentic sample obtained from Aldrich Chemical Co.

**Catalytic synthesis of *1,3,5*-triphenyl-*2,4,6*-tripentafluorophenylbenzene.** Crystalline pentafluorophenylacetylene[8] (0.16 g, 0.60 mmol) was placed inside a thick-walled quartz tube pre-flushed with nitrogen. Hexachlorodisilane (0.20 g, 0.74 mmol) was then added and the tube was cooled in liquid nitrogen and flame sealed under vacuum.

During heating of the tube to 200 °C in an oil bath for two days, the reaction solution was observed to change from light yellow to black, concomitant with the formation of a light yellow precipitate. The tube was opened in a hood and the reaction mixture was shaken with 5 mL of $CHCl_3$. The solid precipitate was separated by filtration and was dried under vacuum to give 0.12 g of the product (75% yield) which was identified as *1,3,5*-triphenyl-*2,4,6*-tripentafluorophenylbenzene. Mp. >300 °C. $^1$H NMR ($CDCl_3$): δ 6.94-7.10 (m, 15H); $^{13}$C NMR ($CDCl_3$): δ 129.2, 128.9, 128.3, 128.2, 128.0, 127.9, 127.7, 127.5, 127.4, 127.3. MS (EI): m/z (ion, relative intensity) 804.2 ($M^+$, 8.28), 637.0 ($M^+$-$C_6F_5$, 0.70); MS (CI/$NH_3$, positive ion) m/z (ion, relative intensity) 804.2 ($M^+$, 1.51); MS (CI/$NH_3$), negative ion) m/z (ion, relative intensity) 804.4 (M, 61.86). Its mass spectrum compared favorably with literature values.[8] No $^1$H, $^{13}$C or $^{19}$F NMR spectral data were found in the literature.

**Synthesis of $Si_2(NMe_2)_xCl_{6-x}$ (x = 2,3,4,5,6).** Syntheses of $Si_2(NMe_2)_5Cl$ and $Si_2(NMe_2)_6$ have been reported elsewhere.[14] Hexachlorodisilane (2.69 g, 10.0 mmol) was added to a 250 mL flask equipped with a magnetic stirrer under nitrogen, followed by the addition of100 mL $Et_2O$. The flask was stoppered by a septum, and the solution was cooled to −178 °C by liquid nitrogen. The flask was weighed and gaseous dimethylamine was then introduced from a cylinder into the flask, which was cooled by liquid nitrogen. A white precipitate was observed to form immediately. The weight of the flask was recorded frequently to make sure the required amount of $HNMe_2$ has been added (1.80 g for $Si_2(NMe_2)_2Cl_4$, 2.70 g for $Si_2(NMe_2)_3Cl_3$, 3.60 g for $Si_2(NMe_2)_4Cl_2$). After the introduction of $HNMe_2$, the flask was allowed to warm up slowly to ambient temperature and the reaction mixture was stirred well for another 20 hours. The precipitate was filtered out from the reaction mixture with a filter, and the solid material ($HNMe_2 \bullet HCl$) was washed with 3 x 30 mL $Et_2O$. The filtrate was evaporated under vacuum. The products $Si_2(NMe_2)_2Cl_4$ and $Si_2(NMe_2)_3Cl_3$ were purified by distillation under vacuum, while $Si_2(NMe_2)_4Cl_2$ was obtained as a solid whose $^{13}C$ and $^{1}H$ NMR spectroscopy indicated that its purity was suitable for subsequent reactions. Product yields: $Si_2(NMe_2)_2Cl_4$ 45%, $Si_2(NMe_2)_3Cl_3$ 70%, $Si_2(NMe_2)_4Cl_2$ 85%. Characterizations of $Si_2(NMe_2)_2Cl_4$: $^{1}H$ NMR ($C_6D_6$): δ 2.31 (s, 6H); $^{13}C$ NMR ($C_6D_6$) δ 36.66. MS ($CI/NH_3$, Positive ion): m/z (ion, relative intensity), 304.4 ($[M+NH_4]^+$, 9.27). Bp 158-160 °C. Elemental analysis: Calcd. for $C_4H_{12}Cl_4N_2Si_2$: C 16.78%; H 4.19%, N 9.79%, Cl 49.65%, Si 19.58%; found: C 16.11%, H 4.40%, N 9.69%, Si 19.50%. The symmetric isomer was assumed here for product $Si_2(NMe_2)_2Cl_4$. $Si_2(NMe_2)_3Cl_3$ $^{1}H$ NMR ($C_6D_6$) δ 2.40 (s, 6H), 2.56 (s, 12H); $^{13}C$ NMR ($C_6D_3$) δ 36.83, 36.78. MS (EI): m/z (ion, relative intensity) 295.0 ($M^+$, 1.30). Bp 220-222 °C. Elemental analysis: Calcd. for $C_6H_{18}Cl_3N_3Si_2$: C 24.45%, H 6.11%, N 14.26%; found: C 23.47%, H 6.41%, N 14.07%. $^{1}H$ $Si_2(NMe_2)_4Cl_2$ NMR ($C_6D_6$) δ 2.46 (s, 24H); $^{13}C$ NMR ($C_6D_6$) δ 37.02. MS (EI): m/z (ion, relative intensity) 302.1 ($M^+$, 0.71). Elemental analysis: Calcd. for $C_8H_{24}Cl_2N_4Si_2$: C 23.76%, H 7.92%, N 18.48%; found: C 22.80%, H 8.31%, N 18,27%. Mp: 70-72 °C. $^{1}H$ and $^{13}C$ NMR data of $Si_2(NMe_2)_4Cl_2$ compare favorably with literature values.[15]

**Catalytic reactions of diphenylacetylene with $Si_2(NMe_2)_xCl_{6-x}$ (x = 2,3,4,5,6).** The sealed tube reactions were carried out under the same conditions as that of $Si_2Cl_6$ with diphenylacetylene. For the $Si_2(NMe_2)_2Cl_4/PhC{\equiv}CPh$ reaction, the dominant product is hexaphenylbenzene (20% conversion), with less than a 2% conversion to isomeric *2,3,5,6*-tetraphenyl-*1,4*-*bis*(dimethylamino)-*1,4*-dichloro-*1,4*-disilacyclohexadienes,[16] as determined by $^1H$ NMR spectroscopy. For the $Si_2(NMe_2)_3Cl_3/PhC{\equiv}CPh$ system, although the main product is again hexaphenylbenzene (10% conversion), the conversion to the isomeric *1,4*-disilacyclohexadienes increased to *ca.* 5%. For the $Si_2(NMe_2)_4Cl_2/PhC{\equiv}CPh$ system, the hexaphenylbenzene conversion decreased to 5% and the conversion to isomeric *1,4*-disilacyclohexadienes rose to 20%. However, in $Si_2(NMe_2)_5Cl/PhC{\equiv}CPh$ and $Si_2(NMe_2)_6/PhC{\equiv}CPh$ systems, the exclusive product is *2,3,5,6*-tetraphenyl-*1,1,4,4*-tetra*kis*(dimethylamino)-*1,4*-disilacyclohexadiene,[16] in about 45% and 20% conversions, respectively.

**UV iradiation of a *1*-octyne/$Si_2Cl_6$ mixture.** A quartz tube (10 mm diameter) was charged with *1*-octyne (2.20 g, 20.0 mmol), followed by 0.25 equivalents of hexachlorodisilane (1.40 g, 5.00 mmol). The mixture was cooled in liquid nitrogen and the tube was flame sealed under vacuum. The reaction mixture was allowed to warm up to room temperature, and was irradiated continuously by a 450 W Hg Hanovia Medium Pressure lamp. During the reaction, the quartz tube was water cooled. The reaction mixture was found to have turned yellow after the 20 hour radiation time. The solution in the tube was analyzed by $^1H$ and $^{13}C$ NMR spectroscopies to be a mixture of starting materials, with barely detectable amounts of the isomeric trimers *1,2,4-* and *1,3,5-*trihexylbenzene. When the reaction time was prolonged to 48 hours, starting materials, together with *ca.* 6% of these isomeric trimerization products (in a 1: 1 ratio) were observed by $^1$H NMR spectroscopy. Removal of the volatiles under vacuum afforded 0.11 g (5%) trimerization products. No attempts were made to isolate the isomers. $^1$H NMR of the isomers ($CDCl_3$) δ 7.03-6.79 (m, 3H), 2.54-0.85 (m, 39H); $^{13}$C ($CDCl_3$) δ 142.69, 140.32, 140.14, 137.67, 129.20, 128.92, 125.80, 125.67, 35.97, 35.60, 32.77, 32.33, 31.75, 31.58, 31.38, 29.52, 29.14, 22.64, 22.62, 14.11. HRMS (EI): Calcd. for $C_{24}H_{42}$: 330.328651, found: 330.3290042. The $^1$H, $^{13}$C NMR and mass spectra compared favorably with the values obtained from the previous $Si_2Cl_6$/*1*-octyne catalytic reaction.

Analogous reactions using $SiCl_4$ or $HSiCl_3$ as catalysts did not afford detectable amounts of trimerization product or any other product. Similarly, irradiating 1-octyne in the absence of $Si_2Cl_6$ failed to provide detectable quantities of any product.

**Reaction of hexachlorodisilane with *2,2*-diphenyl-*1*-picrylhydrazyl.** *2,2*-Diphenyl-*1*-picrylhydrazyl is a well known free radical source.[17] Hexachlordisilane (0.30 g, 11.0 mmol) and *2,2*-diphenyl-*1*-picrylhydrazyl (0.40 g, 10.0 mmol) were added to two NMR tubes under nitrogen, the tubes were cooled in liquid nitrogen and flamed sealed under vacuum. One of the tubes was heated to 190 °C for 20 hours in an oil bath, while the other was kept at ambient temperature. During the reaction of the heated tube, the color of the reaction mixture changed from violet to brown. ESR spectroscopy on both samples revealed that the brown sample was almost ESR silent, with a signal 100 times weaker than that of the unheated sample.

**Thermal formation of *1* and *2*-phenyl naphthalenes, 3a and 3b.** Into a 25 mL flask equipped with a reflux condenser, magnetic stirrer and a nitrogen atmosphere was placed phenylacetylene (2.50 g, 24.5 mmol). The flask was heated to 170 °C for 30 hours in an oil bath, giving a brown viscous material. The product was quite soluble in chloroform, and it was analyzed by GC-MS as a mixture of dimeric isomers (53.6% in a ~10:1 ratio) and trimeric isomers (46.3% *1,3,5*-triphenylbenzene and *1,2,4*-triphenylbenzene in a ~1:1 ratio). The conversion of this reaction by $^1$H NMR spectroscopy was approximately 95% based on the starting material. Separation of the products by preparative TLC (hexane as eluent) gave 0.50 g (20%) of a mixture of **3a** and a trace of **3b** whose presence was indicated by GC-MS. $^1$H NMR ($CDCl_3$): δ 7.85-7.93 (m, 2H); 7.40-7.55 (m, 6H); $^{13}$C NMR: δ 140.7, 140.2, 133.8, 131.6, 130.1, 128.2, 127.6, 127.2, 126.9, 126.0, 125.7, 125.4. HRMS (EI): Calcd for $C_{16}H_{12}$: 204.09390, found: 204.09303. The $^1$H and $^{13}$C NMR data of **3a** compare favorably to literature values.[12]

**Thermal formation of *7*-methyl-*1*-*p*-tolyl-naphthalene, 4a.** In a 10 mL flask equipped with a magnetic stirrer, *4*-ethynyltoluene (2.0 g, 17 mmol) was introduced under nitrogen. The flask was heated in an oil bath to 180 °C for 24 hours. A thick brown material was obtained which was found by GC-MS to consist of a dimer (~85%), along with ~5% of an isomeric dimer and a 10% mixture of isomeric trimers (*1,3,5* and *1,2,4*-tritoluylbenzene) in a ~5:1 ratio. A sample of the major dimer **4a** was purified for

NMR spectroscopy by preparative TLC (hexanes eluent). $^1$H NMR ($CDCl_3$): δ 7.24-7.80 (m, 10H), 2.45 (s, 3H), 2.42 (s, 3H); $^{13}$C NMR ($CDCl_3$): δ 139.5, 138.0, 136.8, 135.6, 132.0, 131.8, 129.9, 128.9, 128.1, 127.9, 127.2, 127.0, 124.9, 124.5, 21.9, 21.3. The GC mass spectrum of the reaction mixture indicated the presence of the aromatic dimers (molecular weight 232) and an HRMS of the mixture confirmed this conclusion. HRMS: Calcd. for $C_{18}H_{16}$ 232.12520, found: 232.12519. The minor dimer is presumed to be **4b** (by analogy with the known structure of **3b**[12]). No $^1$H or $^{13}$C NMR data were found in the literature for isomers **4a** and **4b**.

**Thermal formation of *5*-cyclohex-*1*-enyl-*1,2,3,4*-tetrahydro-naphthalene, 5a.** Into a 10 mL flask equipped with a magnetic stirrer and a reflux condenser was introduced *1*-ethynyl-*1*-cyclohexene (3.00 g, 28.3 mmol) under nitrogen. The flask was heated to 170 °C in an oil bath. After 15 hours, a viscous brown material was obtained which by GC-MS analyzed exclusively as a dimer (M.W. 212) judging from the absence of a singlet $^1$H NMR peak in the reaction mixture expected for the hydrogen at the C(5) position of **5b**. Such a singlet was observed for the analogous minor product **3b** in the **3a/3b** reaction mixture. The conversion of this reaction was found to be quantitative by $^1$H NMR spectroscopy. Compound **5a** was isolated by preparative TLC (hexanes eluent) in 80% yield. NMR: $^1$H NMR ($CDCl_3$): δ 6.98-7.24 (m, 3H), 5.50 (s, 1H), 1.66-2.79 (m, 16H); $^{13}$C NMR ($CDCl_3$): δ 144.8, 138.8, 137.0, 134.4, 127.5, 125.6, 125.2, 125.0, 30.2, 29.9, 27.0, 25.4, 24.4, 23.1, 23.1, 22.2. HRMS: Calcd. for $C_{16}H_{20}$ 212.15650. Found: 212.15662. Elemental Analyses: Calcd. for $C_{16}H_{20}$: C 90.51%, H

9.49%; found: C 88.66%; H 9.63%. No $^1$H or $^{13}$C NMR data were found in the literature for this compound.

In a comparison experiment, $Si_2Cl_6$ (0.20 g, 0.72 mmol) was used as a procatalyst under identical reaction conditions. In addition to the formation of dimer **5a** in 80% conversion (with a trace of **5b**) and two isomeric trimers were found to form in 20% conversion in a ~1:1 ratio as indicated by GC-MS. The presence of compound **5a** and the trimers was confirmed by $^1$H and $^{13}$C NMR spectroscopies.[13] The concentration of **5b**, however, was too low for $^1$H NMR detection.

**Heating *1*-phenyl-*1*-propyne with and without $Si_2Cl_6$.** Equal amounts of *1*-phenyl-*1*-propyne (0.15 g, 0.86 mmol) were added to four thick-wall quartz tubes, and to each of two of them was added (0.20 g, 0.74 mmol) of $Si_2Cl_6$. The tubes were flame sealed under vacuum and were placed inside a pressure reactor which was heated to 180 °C for 40 hours in an oil bath. The two tubes containing the $Si_2Cl_6$ were found to contain the trimerized product *1,3,5*-trimethyl-*2,4,6*-triphenylbenzene in 80% conversion as judged by $^1$H NMR spectroscopy. Colorless crystals that formed after standing at room temperature were used to obtained NMR spectra. $^1$H NMR ($CDCl_3$) $\delta$ 7.2-7.6 (m, 15H), 1.8 (s, 9H); $^{13}$C NMR ($CDCl_3$) $\delta$ 142.0, 131.5, 130.2, 129.7, 128.3, 127.2, 19.3. These data are in good agreement with literature values.[18] The tubes containing no $Si_2Cl_6$ were found by $^1$H and $^{13}$C NMR spectroscopies to contain only starting materials.

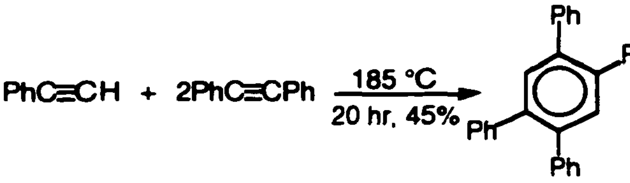
**Thermal reactions of non-conjugated alkynes.** The non-conjugated alkynes *1*-decyne and *1*-octyne were heated at 190-200 °C for 48 hours under nitrogen. Only starting materials were detected by GC-MS and by $^1$H and $^{13}$C NMR spectroscopies.

## Results and Discussion

Our original intent was to synthesize **2**. Although the first low-yield preparation of this compound took place in the gas phase at *ca.* 450 °C,[5b] we attempted to carry out the same reaction in a sealed tube. Because that attempt produced an intractable black char, we repeated the reaction at 170-180 °C and observed the production of $C_6Ph_6$ (reaction 1). It was of interest, therefore, to explore the scope of this novel catalytic alkyne trimerization.

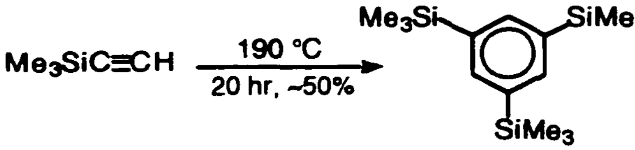
*$Si_2Cl_6$-catalyzed alkyne trimerization.* Like diphenylacetylene, diethyl acetylene was easily converted to colorless crystalline hexaethyl benzene in the presence of $Si_2Cl_6$ (reaction 2). Terminal alkynes such as phenylacetylene, *1*-octyne and *1*-decyne are similarly catalytically cyclotrimerized. Reactions carried out at atmospheric pressure at 170 °C for these alkynes were efficient, leading to 100% conversion of *1*-octyne to isomeric trihexylbenzenes, while conversions of *1*-decyne to trioctylbenzenes and of phenylacetylene to triphenylbenzenes were quantitative with only 10-15 mole % catalyst. In all three reactions, a *ca.* 1:1 mixture of only two isomers (the *1,3,5* and the *1,2,4*-substituted benzenes) was formed while the third isomeric possibility (the most sterically crowded *1,2,3*-substituted product) was not detected. The isomers in all cases

displayed two individual peaks in the GC-MS, and they were further characterized as mixtures by $^{1}$H NMR, $^{13}$C NMR and by high resolution mass spectroscopies. That steric effects prevail in these reactions is also supported by the *ca.* 1:1 ratios of the *1,3,5* and *1,2,4*-substituted products, since statistically this ratio is expected to be 1:3. By employing a mixture of phenylacetylene and diphenylacetylene in a 1:2 ratio, an isomeric tetraphenylbenzene mixture (consisting mainly of the *1,2,4,5*-tetraphenylbenzene isomer) was found to form catalytically in good yield (reaction 7).



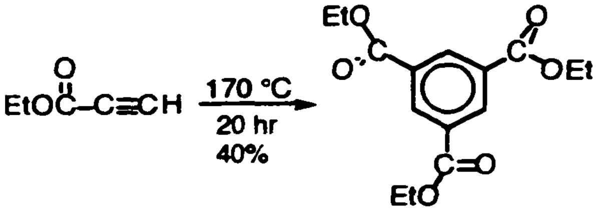
(7)

Other alkyne functionalities apparently survive our catalytic cyclotrimerization process. Reaction 8 proceeds regioselectively, producing only the symmetrical isomer (as indicated by GC-MS and by $^{1}$H and $^{13}$C NMR spectroscopies) probably because of the steric hindrance caused by the crowded trimethylsilyl groups. The cyclo-trimerizations of ethyl propiolate gave triethyl *1,3,5*-benzenetricarboxylate and phenyl



(8)

pentafluorophenylacetylene gave *1,3,5*-phenyl-*2,4,6*-tripentafluorophenylbenzene were also successful (reactions 9 and 10, respectively).



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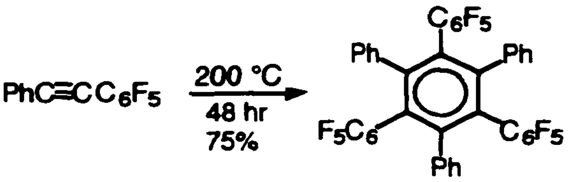


(10)

The regioselectivity of reaction 10 is perhaps somewhat surprising in view of the similarity in size of the substituents relative to those in $Me(CH_2)_5C{\equiv}CH$, $Me(CH_2)_7C{\equiv}CH$ and $PhC{\equiv}CH$, for example, which lead to isomeric mixtures of substituted benzenes. The regioselectivity of reaction 10 may be associated with minimization of coulombic repulsions of the fluorines by alternating $C_6F_5$ with $C_6H_5$ substituents. On the other hand, trimerization was not observed for *p*-$ClC_6F_4C{\equiv}CPh$ or propargyl chloride. Although a reaction did occur with propargyl bromide (as indicated from aromatic signals detected by $^1H$ and $^{13}C$ NMR spectroscopies) the reaction was complicated by the formation of numerous side products that we were unable to separate. As with other metallic and organometallic catalysts,[19] *bis*(trimethylsilyl)acetylene and *bis*(phenylsilyl)acetylene also failed to cyclo-trimerize in the presence of $Si_2Cl_6$. The formation of unidentified oligomers in these cases may be associated with the steric hindrance of the silyl groups and/or steric strain in the cyclo-trimerized products.[20]

In attempts to synthesize triazines from nitriles, reactions of benzonitrile, pentafluorobenzonitrile and acetonitrile with hexachlorodisilane were carried out under conditions similar to those described above. No desired products were detected in the complex reaction mixtures that resulted. Although the strength of the CN triple bond (204 kcal/mol) is quite comparable with that of the $C\equiv C$ bond (200 kcal/mol)[21] the greater polarity of the CN bond apparently does not favor a radical pathway under our conditions.

*Other disilanes.* Hexamethyldisilane was also employed as a potential procatalyst, but no catalytic effect was detected for the aforementioned substrates. Hexamethyoxydisilane was also evaluated as a procatalyst with diphenyl acetylene and with *1*-octyne as substrates. Under the conditions used for the same reactions involving $Si_2Cl_6$, $Si_2(OMe)_6$ led to lower yields of corresponding trimerized products (30% for diphenylacetylene and 40% for *1*-decyne). While it is tempting to speculate that a higher electronegativity of the silicon substituents favors homolysis of the Si–Si bond to form silyl radicals, we were somewhat surprised to observe that $Si_2F_6$ did not catalyze the trimerization of 1-decyne and phenylacetylene under identical conditions in a pressure reactor (170 °C – 200 °C, 2 days, molar ratio of acetylene/catalyst = 100:20). For reasons that are not entirely clear, *sym*-$Si_2Me_2Cl_4$ also did not catalyze alkyne cyclotrimerization.

*Further investigation of the reaction pathway.* Several experiments have been carried out to test the $SiCl_3$ radical pathway for these trimerizations for which we presented evidence earlier.[2] To evaluate the series $Si_2(NMe_2)_xCl_{6-x}$ (x = 0, 2, 3, 4, 5, 6) as catalysts, $Si_2Cl_6$ with the corresponding stoichiometric amount of $HNMe_2$. Here $S_2(NMe_2)Cl_5$ (x = 1) is missing because it could not be obtained in pure form by this method. When the series was reacted with diphenylacetylene under the same reaction condition, interesting reaction product distribution patterns were observed. For x = 0, only the cyclotrimerization product hexaphenylbenzene was obtained. For the disilane in which x = 2, however, the yield of hexaphenylbenzene dropped dramatically to about 20% compared with the 70% yield observed with $Si_2Cl_6$. In addition to the dominant trimerization product, a minor product *2,3,5,6*-tetraphenyl-*1,4*-dichloro-*1,4*-*bis*(dimethylamino)-*1,4*-disilacyclohexadiene was also detected (*ca.* 2% conversion) by $^1H$ NMR. An increased ratio of the same *1,4*-disilacyclohexadiene was observed in the reaction of $Si_2(NMe_2)_3Cl_3$ (x = 3) with diphenylacetylene (hexaphenylbenzene 10%, *1,4*-disilacyclohexadiene 5%). In the reaction of $Si_2(NMe_2)_4Cl_2$ (x = 4) with diphenylacetylene, however, the trimerization product became the minor product (5%), while the formation of the *1,4*-disilacyclohexadiene is dominant (20%). Not surprisingly, reactions of $Si_2(NMe_2)_5Cl$ and $Si_2(NMe_2)_6$ with diphenylacetylene gave only *1,1,4,4*-tetra*kis*(dimethylamino)-*2,3,5,6*-tetraphenyl-*1,4*-disilacyclohexadiene in 45% and 20%

yield, respectively. No cyclotrimerization product was detected in these two cases. We attempt to rationalize these observations on the basis of a process involving reactions in competition as explained below. When only electron-withdrawing Cl groups are present, the homolytic cleavage of the Si-Si bond is favored at a temperature around 200 °C. This result is consistent with the formation of hexaphenylbenzene as the sole product in the $Si_2Cl_6$ case. The introduction of electron-inducting $NMe_2$ groups is expected to inhibit the thermal generation of silyl radicals owing to the greater electron density on the Si atoms and therefore stronger Si-Si bonds. As more $NMe_2$ groups are added on to the dislane, thermal generation of the silylenes $Si(NMe_2)Cl$ and/or $Si(NMe_2)_2$ via disproportionation becomes increasingly favored probably because of the weakness of Si-N bonds compared with Si-Cl bonds.

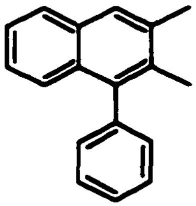
Additional evidence for the $SiCl_3$ radical induced cyclotrimerization of alkynes was obtained from the results of theoretical calculations of electron density on Si for a series of silyl radicals possessing different substituents.[22] It was reported that the electron densities on Si of three silyl radicals pertinent to the present discussion are: $SiMe_3$ (81.0%), $SiCl_3$ (57.3%), and quite surprisingly 84.4% in the case of $SiF_3$. If silyl radical-induced alkyne cyclotrimerization proceeds by electrophilic attack of the radical on the electron rich alkynyl carbons, then this calculation predicts that $SiCl_3$ radicals are more reactive than $SiMe_3$ radicals. The calculations are also consistent with the inertness of $Si_2F_6$ as a procatalyst for alkyne cyclotrimerization despite the greater electronegativity of fluorine compared with chlorine.

Further support for the $SiCl_3$ radical pathway was obtained from UV irradiation of disilane/alkyne mixtures. UV light is well known for its ability to generate radical species.[23] When a mixture of $Si_2Cl_6$ and *1*-octyne (1 : 4 molar ratio) was sealed in a water-cooled quartz tube and irradiated for 20 hours by UV light, a ~1% conversion to the cyclotrimerization products *1,3,5*- and *1,2,4*-trihexylbenzene in a 1:1 ratio (by GC-MS) was detected by $^1H$, $^{13}C$ NMR, and HRMS spectroscopies. When the reaction time was prolonged to 48 hours, a conversion of 6% (with an isolated yield of 5%) was realized. However, reactions under the same conditions in the absence of $Si_2Cl_6$ or in the presence of $HSiCl_3$ (a known $SiCl_3$ radical source[24]) or $SiCl_4$ afforded no detectable cyclotrimerization products, according to $^1H$, $^{13}C$ NMR and GC-MS spectroscopies. When X-ray radiation was utilized (on a Rigaku rotating anode unit using a Mo source, $\lambda = 0.71069$ Å) no cyclotrimerization products were detected even though prolonged radiation times were used and a color change to brown was observed.

In another experiment, a mixture of the stable radical source *2,2*-diphenyl-*1*-picrylhydrazyl and $Si_2Cl_6$ (molar ratio 1.1: 1) was introduced to an NMR tube, followed by flame sealing the tube under vacuum. Upon heating the tube to 190 °C for 20 hours, the initial violet color of the stable free radical was changed to brown, which was taken to indicate radical quenching. Moreover, the intensity of the ESR signal of the reaction mixture was about 100 times weaker, compared with the signal intensity of the unreacted mixture of $Si_2Cl_6$ and *2,2*-diphenyl-*1*-picrylhydrazyl in the same molar ratio. NMR spectroscopic analysis could not be performed owing to the insolubility of the reaction product.

Although it was hoped that $Hg(SiCl_3)_2$ would be a source of $SiCl_3$ radicals upon heating, we were unable to detect any cyclotrimerization product in a sealed tube reaction of $Hg(SiCl_3)_2$ with *1*-decyne (in 1: 5 molar ratio) at 150 °C for 30 hours. On the other hand a search of the literature revealed no example of $Hg(SiCl_3)_2$ serving as a radical source.

*Thermal dimerization of alkynes.* To our knowledge only three reports have appeared that describe the thermal dimerization of alkynes. One of these investigations dealt with high pressure reactions of 30-60% phenylacetylene in MeOH or EtOH which at 220 °C gave the aromatic dimers **3a** and **3b**, three unspecified trimers, and 75% of polymers.[25] The high temperature (700-1100 °C) behavior of phenylacetylene was the subject of a second investigation,[26] in which many products (in addition to dimers and trimers) were produced, in concentrations that are functions of the temperature. In the third study, the formation of the aromatic product **6** from the cyclodimerization of *1*-phenyl-*1*-propyne by γ irradiation in the presence of $Ph_2CO$ was described.[27]



**6**

When we heated phenylacetylene to 170 °C for 15 hours in the absence of solvent and catalyst, a 95% conversion of starting material was observed , with the concommitant formation of 53.6% dimers **3a** and **3b** in a 10:1 ratio, and 46.3% trimers (*1,3,5*-triphenylbenzene and *1,2,4*-triphenylbenzene) in a 1:1 ratio. By analogy, *4*-ethynyltoluene and *1*-ethynyl-*1*-cyclohexene were expected to undergo analogous reactions under similar conditions to give *7*-methyl-*p*-tolyl-naphthalene **4a** and *5*-cyclohex-*1*-enyl-*1,2,3,4*-tetrahydro-naphthalene **5a** as the major products, respectively, and corresponding cyclotrimerization products in comparable but smaller conversion. With *4*-ethynyltoluene, however, we obtained a very viscous reaction mixture after 15 hours at 170 °C which analyzed by GC-MS as 90% dimers **4a** and **4b** in a 17:1 ratio and only 10% trimers (*1,3,5*-tri-*p*-tolylbenzene and *1,2,4*-tri-*p*-tolylbenzene) in a ~5:1 ratio. Interestingly, under the same reaction conditions, *1*-ethynyl-*1*-cyclohexene quantitatively gave only dimer **5a**, with no indication of the presence of the trimers or oligomers by GC-MS and $^1$H and $^{13}$C NMR spectroscopies.

A radical pathway for high-temperature (700-1100 °C) phenyacetylene dimerization has been proposed, wherein adsorption of a free hydrogen atom from the reaction vessel is the initial step.[26] Whether this mechanism applies to our thermolyses at ~200 °C is open to question. Nonetheless, our observation of the formation of **3a**, **4a**, **5a** and small amounts of **3b** and **4b** (owing to steric crowding) is consistent with this mechanism. Surprisingly, the presence of $Si_2Cl_6$ under the conditions used to thermolyze

*1*-ethynylcyclohexene had a relatively minor effect on the formation of dimer **5a**, and resulted in only 20% trimer production.

The existence of conjugated multiple bonds is apparently important to the resonance stabilization of thermally produced radicals and so it is not surprising that *1*-decyne and *1*-octyne, which contain no conjugated multiple bonds, afforded no detectable evidence of reaction even after 40 hours at 200 °C. However, when $Si_2Cl_6$ was present in the above systems, the cyclotrimerization product *1,2,4*/*1,3,5*-trioctylbenzenes and *1,2,4*/*1,3,5*-trihexylbenzenes were formed in good yields as described earlier.

Interestingly, neither *2* nor *3*-ethynyl pyridine dimerize thermally at 200 °C. Only unidentified oligomeric species were detected. When *2*-, and *3*-ethynyl pyridine is heated to 180 °C in the presence of $Si_2Cl_6$, no trimerization product(s) is obtained and only oligomeric species were detected.

The terminal hydrogen of alkynes is apparently essential to thermally induced radical generation and structure rearrangements through hydrogen migration.[27] Thus *1*-phenyl-*1*-propyne heated at 190 °C for 40 hours gave no detectable dimerization product according to GC-MS, $^1H$ and $^{13}C$ NMR spectroscopies.

Although compounds **3a**, **3b**, **4a** and **5a** have been synthesized by means other than those described here, they have not been reported as products of thermal dimerization. Thus **3a** and **3b** have been made by dehydrogenating the corresponding cyclohexenylnaphthalenes.[28] Compound **4a** was synthesized by oxidizing *6*-methyl-*4*-*p*-tolyl-*1,2*-dihydro-naphthalene in the presence of selenium at 280 °C,[29] while **5a** was obtained from *5*-(*2*-hydroxy-cyclohexyl)-tetralin using $ZnCl_2$ as a catalyst.[30] Heretofore, products **4a**, **4b** or **5a** have not been reported to form through thermal dimerization.

Experiments are underway to further clarify the reaction pathways and to evaluate the scope and limitations of novel reactions of this type.

## Acknowledgements

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## Reference

1. (a) Prinz, P.; Lansky, A.; Haumann, T.; Boese, R.; Noltemeyer, M.; Knieriem, B.; de Meijere, A. *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 1289 and references therein. (b) Marx, H.-W.; Moulines, F.; Wagner, T.; Astruc, D. *Angew. Chem. Int. Ed. Engl.* **1996**, 35, 1701. (c) Diercks, R.; Armstrong, J. C.; Boese, R.; Vollhardt, K. P. C. *Angew. Chem. Int. Ed. Engl.* **1986**, 25, 268 and references therein. (d) Praefcke, K.; Kohne, B.; Singer, D. *Angew. Chem. Int. Ed. Engl.* **1990**, 29, 177. (e) Boese, R.; Green, J. R.; Mittendorf, J.; Mohler, D. L.; Vollhardt, K. P. C. *Angew. Chem. Int.*

*Ed. Engl.* **1992**, *31*, 1643 and references therein. (f) Astruc, D. *Top. Curr. Chem.* **1992**, *160*, 47 and references therein.

2. Yang, J.; Verkade, J. G. *J. Am. Chem. Soc.* **1998**, *120*, 6834.
3. Balasubramanian, K.; Selvaraj, P.; Venkataramani, S. *Synthesis* **1980**, 29.
4. (a) Matsuda, K.; Inoue, K.; Koga, N.; Nakamura, N.; Iwamura, H. *Mol. Cryst. Liq. Cryst.* **1994**, *253*, 33. (b) Matsuda, K.; Nakamura, N.; Iwamura, H. *Chem. Lett.* **1994**, 1765.
5. (a) Chernyshev, E. A.; Komalenkova, N. G.; Bashkuova, S. A. *Zh. Obshch. Khim.* **1971**, *41*, 1175. (b) Chernyshev, E. A. *Zh. Obshch. Khim.* **1978**, *48*, 830.
6. Bertholet, M. C. R. *Held. Seances Acad. Sci.* **1866**, 905.
7. Isomura, S.; Takeuchi, K. *J. Fluorine Chem.* **1997**, *83*, 89.
8. Rausch, M. D.; Siegel, A.; Klemann, L. P. *J. Org. Chem.* **1969**, *34*, 468.
9. (a) Amer, I.; Bernstein, T; Eisen, M.; Blum, J.; Vollhardt, K. *J. Mol. Catal.* **1990**, *60*, 313. (b) Eapen, K. C.; Tamborski, C. *J. Org. Chem.* **1988**, *53*, 5564. (c) Robert, W. L. *J. Org. Chem.* **1981**, *46*, 4552. (d) Eapen, K. C.; Dua, S. S.; Tamborski, C. *J. Org. Chem.* **1984**, *49*, 478.
10. Amer, I.; Bernsrein, T.; Eisen, M.; Blum, J. *J. Mol. Catal.* **1990**, *60*, 313.
11. Van der Linden, A.; Schaverien, C. J.; Meijboom, N.; Ganter, C.; Orpen, G. A. *J. Am. Chem. Soc.* **1995**, *117*, 3008.
12. *The Aldrich Library of* $^{13}$*C and* $^{1}$*H FT NMR Spectra*, ed. 1. Aldrich Publishers: Milwaukee, **1993**.

13. Derien, S.; Clinet, J.; Dunach, E.; Perichon, J. *J. Organomet. Chem.* **1992**, *424*, 2.

14. (a) Wan, Y.; Verkade, J. *Inorg. Chem.* **1993**, 32, 431. (b) E. Wiberg et al., *Inorg. Nucl.Chem. Letters*, **1965**, *1*, 33.

15. Wan, Y. *Ph. D. Dissertation*, pp 13, Iowa State University, **1994**.

16. Yang, J.; Verkade, J. to be published.

17. For recent instances see: (a) Valgimigli, L.; Ingold, K.; Lusztyk, J. *J. Org. Chem.* **1996**, *61*, 7947. (b) Tait, A.; Ganzerli, S.; Bella, M. *Tetrahedron*, **1996**, *52*, 12587. (c) Lorimer, J.; Kershaw, D.; Mason, T. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1067. (d) Chan, C.; Cole, E.; Southwell-Keely, P. *Phosphorus, Sulfur Silicon Relat. Elem.* **1991**, *55*, 261.

18. Dietl, H.; Reinheimer, H.; Moffat, J.; Maitlis, P. M. *J. Am. Chem. Soc.* **1970**, *92*, 2276.

19. Rüdinger, C.; Bissinger, P.; Beruda, H.; Schmidbaur, H. *Organometal.* **1992**, *11*, 2867.

20. Sakurai, H.; Ebata, K.; Kabuto, C.; Sekiguchi, A. *J. Am. Chem. Soc.* **1990**, *112*, 1799.

21. March, J. *Advanced Organic Chemistry* (3rd edition). Wiley-Interscience Publishers, **1985**.

22. Maurizio, G. *J. Am. Chem. Soc.* **1993**, *115*, 25.

23. For recent instances see: (a) Cano, M.; Quintana, J.; Julia, L.; Camps, F.; Joglar, J. *J. Org. Chem.* **1999**, *64*, 5096. (b) Mackenzie, S.; Votava, O.; Fair, J.; Nesbitt, D. *J.*

*Chem. Phys.* **1999**, *110*, 5149. (c) Kimura, T.; Fujita, M.; Sohmiya, H.; Ando, T. *J. Org. Chem.* **1998**, *63*, 6719.

24. (a) Walter, H.; Roewer, G.; Bohmhammel, K. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4605. (b) Heinicke, J.; Gehrhus, Barbara. *J. Anal. Appl. Pyrolysis*, **1994**, *28*, 81. (c) Niki, H.; Maker, P.; Savage, C.; Breitenbach, L.; Hurley, M. *J. Phys. Chem.* **1985**, *89*, 3725. (d) Bernard, M.; Ford, W. *J. Org. Chem.* **1983**, *48*, 326.
25. Jarre, W.; Bieniek, D.; Korte, F. *Naturwissenschaften* **1975**, *62*, 391.
26. Hafmann, J.; Zimmermann, G.; Guthier, K. *Liebigs Ann.* **1995**, *4*, 631.
27. Polman, H. *Recl. Trav. Chim. Pays-Bas.* **1973**, *92*, 845.
28. Arnold, R.; Collins, C.; Zenk, W. *J. Am. Chem. Soc.* **1940**, *62*, 983.
29. Baddar, F.; Ei-Assal, L.; Gindy, M. *J. Chem. Soc.* **1948**, 1270.
30. Cook, L. *J. Chem. Soc.* **1936**, 1431.

# CHAPTER 4. SYNTHESIS OF *1,4*-DISILACYCLOHEXA-*2,5*-DIENES

A paper to be submitted for publication to Organometallics

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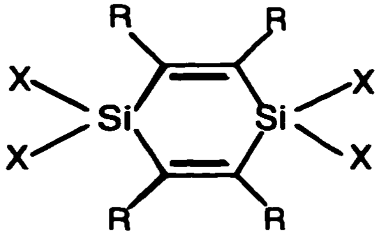
## Abstract

It was discovered that disilanes bearing multiple dimethylamino ($NMe_2$) groups react with alkynes following a pathway that is different from that of $Si_2Cl_6$ and alkyne reactions. Therefore *1,4*-disilacyclohexa-*2,5*-dienes were obtained instead of the cyclo-trimerization products. The reaction product distribution was directly related to the number of dimethylamino groups on the silicon atoms of the disilanes, varying from solely the cyclo-trimerized products (in the absence of dimethylamino groups), to a mixture of cyclo-trimerized products and *1,4*-disilacyclohexa-*2,5*-dienes (with 2-4 dimethylamino groups on the disilane), to only the *1,4*-disilacyclohexa-*2,5*-diene product(s) (with 5-6 dimethylamino groups). The experimental results were explained in terms of electronic effect which determines the strength of the Si-Si bond and the Si-substituent linkages, the steric effect of the reactive intermediates and the apparent competing process of the silyl radical and silylene mechanisms. The *1,4*-disilacyclohexa-*2,5*-dienes obtained could further react with reagents such as $SiX_4$ and $PX_3$ (where X = halogens, alkoxy) to give derivatized *1,4*-disilacyclohexa-*2,5*-dienes. Crystals of six *1,4*-

disilacyclohexa-*2,5*-dienes were obtained and their structures were solved by X-ray diffraction means.

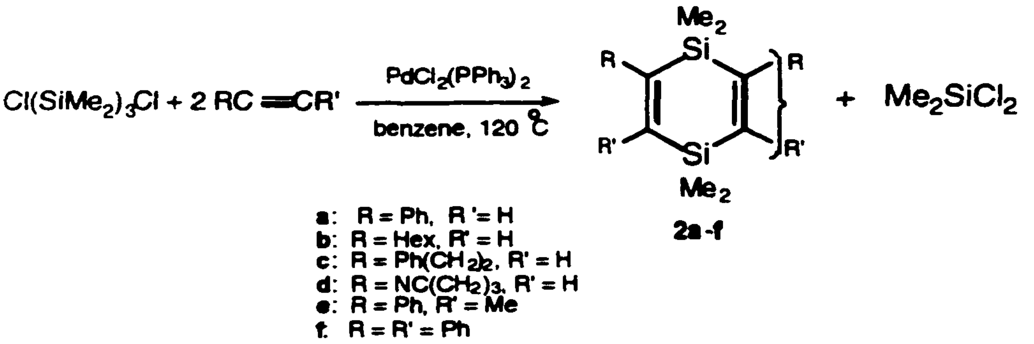
## Introduction

In recent reports[1,2] from our laboratories we reported that disilanes bearing exclusive electron-withdrawing groups (Cl, OMe) catalyze the cyclo-trimerization of alkynes into the corresponding aromatic products in good to excellent yields at *ca.* 200 °C. This contrasts with the behavior of $Si_2Cl_6$ towards acetylene at 450 °C in which *1,4*-disilacyclohexa-*2,5*-diene **1a** was reported by others to form in low yield.[3] Because neither **1a** nor **1b** was detected in the former reaction, it is consistent with a silyl radical mechanism,[1] for which evidence had been adduced.[2] A silylene pathway was proposed to account for the latter reaction.[3] We have shown, however, that chloro disilanes bearing increasing numbers of dimethylamino groups in the presence of diphenylacetylene afford *1,4*-disilacyclohexa-*2,5*-dienes as well as cyclo-trimerized product at 200 °C, until $Si_2(NMe_2)_5Cl$ and $Si_2(NMe_2)_6$ are reached whereupon only *1,4*-disilacyclohexa-*2,5*-diene bearing four $NMe_2$ groups is formed, albeit in low conversion.[2] This relatively mild reaction contrasts to the original synthesis of **1a** at *ca.* 450 °C.[3]

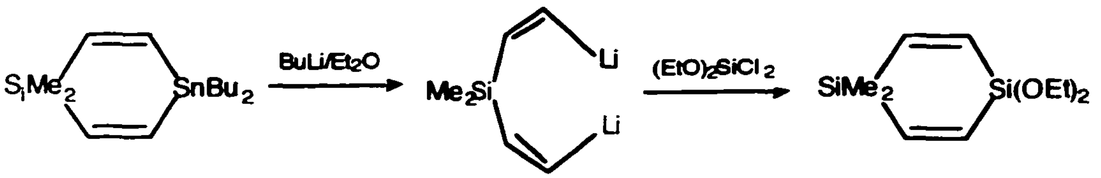


**1a**: R = H, X=Cl
**1b**: R = H, X = OMe

Although gas phase reactions of silylenes with acetylenes at elevated temperature (*ca.* 450 °C) appear to be a traditional route to substituted *1,4*-disilacyclohexa-*2,5*-dienes,[4] approaches involving milder temperatures have been introduced in more recent years. Thus reaction 1 represents an efficient catalytic process that occurs in solution at 120 °C, although it utilizes less accessible trisilanes as a silylene source.[5] Other methods include a Pt-catalyzed hydrosilyation-dimerization of acetylenes containing chelating substitutents[6] and silylation-cyclization of *bis*(organolithium)derivatives (reaction 1).[7] More recently, a new synthetic approach was reported to give **3a-c** as shown in Scheme 1 in which the last step is catalyzed by the metal complex shown.[8] However, the aforementioned approaches did not appear to be suited to us for synthesizing *1,4*-disilacyclohexa-*2,5*-dienes bearing functional groups on the silicon atom which could be easily substituted to form other useful derivatives.

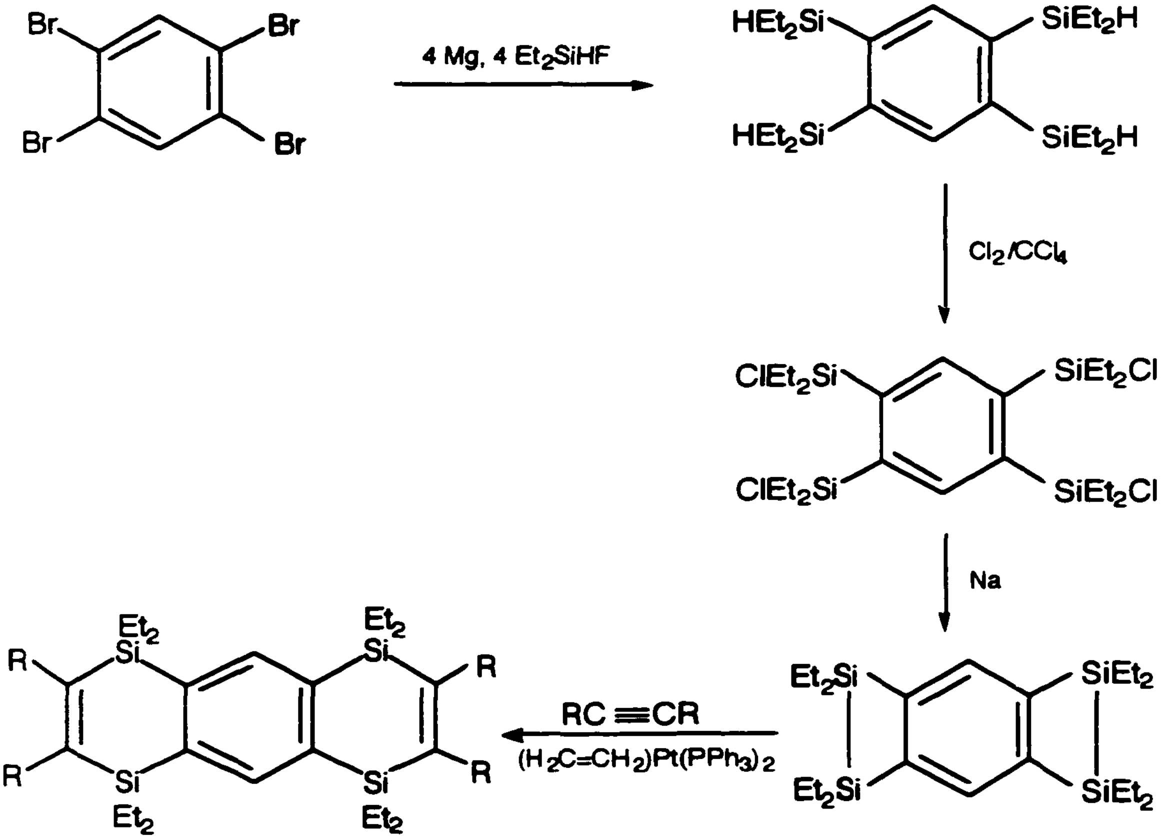


(1)



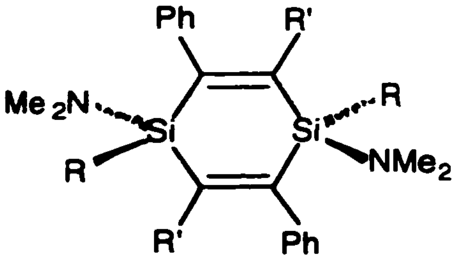
(2)

Scheme 1

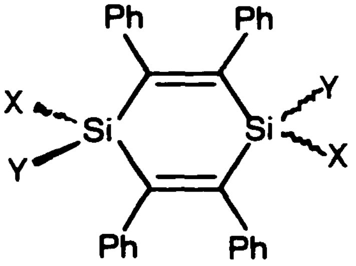


**3a**: R = Ph
**3b**: R = Et
**3c**: R = H

In this paper, we describe synthetic routes by which *1,4*-disilacyclohexa-*2,5*-dienes **4-8**, **9a-e**, **10-13** were obtained in good yields. The molecular structures **4**, **8**, **9c**, 9e, **10** and **13** were determined by X-ray means.



**4**: R = NMe$_2$, R' = Ph
**5**: R = Cl, R' = Ph
**6**: R = Me, R' = Ph
**7**: R = NMe$_2$, R' = Me



**8**: X = Cl, Y = $^t$Bu
**9a**: X = Y = Cl
**9b**: X = Y = Br
**9c**: X = Y = I
**9d**: X = Y = OMe
**9e**: X = Y = OPh
**10**: X = Y = H
**11**: X = Y = OH
**12**: X = Cl, Y = Me
**13**: X = H, Y = $^t$Bu

## Experimental Section

NMR spectra were measured on Bruker AC-200 ($^{29}$Si), Bruker DRX-400 ($^{1}$H and $^{13}$C), Bruker MSL-300 (solid $^{29}$Si) instruments (i.e. magnetic field intensity: 400 MHz for $^{1}$H, 100 MHz for $^{13}$C, 33.3 MHz for $^{29}$Si). The NMR solvent is $CDCl_3$ unless otherwise noted. Chemical shifts references were $CDCl_3$ (δ 7.24 ppm) for $^{1}$H NMR, $CDCl_3$ (δ 77.0 ppm) for $^{13}$C NMR, and $SiMe_4$ (δ 0.00 ppm) for $^{29}$Si NMR. Mass spectra (high and low resolution) measurements and X-ray molecular structure determinations were carried out in the Iowa State University Department of Chemistry Instrument Services laboratories and elemental analysis was carried out by Desert Analytics. Diethyl ether, pentane and tetrahydrofuran (THF) were distilled from sodium/benzophenone, $CHCl_3$ was distilled from $CaH_2$ under nitrogen, and xylenes were distilled under $N_2$ from sodium and dried with molecular sieves. Hexachlorodisilane, dimethyltetrachlorodisilane and hexamethyldisilane were purchased from Aldrich Chem. Co. and hexamethoxydisilane was purchased from Gelest Inc. These reagents were used as received as were benzil, *1*-phenyl-*1,2*-propanedione, anhydrous dimethylamine, *tert*-butylchlorodiphenylsilane, silicon tetrachloride, phosphorus trichloride, phosphorus tribromide, silicon tetrabromide, phosphorus triiodide, diphenylacetylene, phenylacetylene and *1*-phenyl-*1*-propyne were also purchased from Aldrich.

*Symmetric*-dimethyl*tetrakis*(dimethylamino)disilane[10] and di-*tert*-butyltetarphenyldisilane[11] were prepared according to literature methods. Although the syntheses of *hexakis*(dimethylamino)disilane, *pentakis*(dimethylamino)chlorodisilane, *tetrakis*(dimethylamino)dichlorodisilane had been reported,[9, 12] a modified method was used here to achieve higher yields and purities [e.g. by the modified method, the yields for *hexakis*(dimethylamino)disilane (80%), *pentakis*(dimethylamino)chlorodisilane (85%), *tetrakis*(dimethylamino)dichlorodisilane (80%), *symmetric*-di-*tert*-butyl*bis*(dimethylamino)disilane (85%)] as described below for *symmetric*-di-*tert*-butyl*bis*(dimethylamino)disilane as an example. The following method is a general procedure for the synthesis of disilanes bearing multiple dimethylamino groups, which has been improved over the method reported earlier.[9, 12]

**Synthesis of *symmetric*-di-*tert*-butyldichloro*bis*(dimethylamino)disilane (modified method).** In a 250 mL flask equipped with a magnetic stirrer, $Et_2O$ (*ca.* 100 mL) was added, followed by *symmetric*-di-*tert*-butyltetrachlorodisilane (3.12 g, 10.0 mmol). The flask was stoppered by a septum, and the weight was recorded before dimethylamine was introduced. Then the flask was cooled by liquid nitrogen, and dimethylamine was introduced from a gas cylinder through a needle whereupon a white precipitate formed. The flask was weighed frequently to monitor the amount of $HNMe_2$ introduced. Addition of dimethylamine was stopped when 2.70 g (60.0 mmol, 50% in excess) of $HNMe_2$ had been introduced. The mixture was allowed to warm up slowly and it was vigorously stirred for 20 hours at room temperature. After reaction, the unreacted $HNMe_2$ was bled through a needle. The solids (presumably the $[H_2NMe_2]Cl$ salt) was filtered off and washed by 5 x 30 mL of $Et_2O$. The solvent and the volatile materials were removed under reduced pressure and the product was analyzed as a 1:1 mixture of two diasteriomers of *symmetric*-$Si_2{}^tBu_2Cl_2(NMe_2)_2$. $^1H$ NMR ($CDCl_3$): δ 2.65 (s, 12H), 2.61 (s, 12H), 1.04 (s, 18H), 1.01 (s, 18H); $^{13}C$ NMR ($CDCl_3$): δ 39.32, 38.70, 26.90, 26.56, 26.38, 26.22. Mp: 25 °C. HRMS (EI): Calcd. for $C_{12}H_{30}N_2Cl_2Si_2$: 328.132463; found: 328.132848. Elemental analysis: $C_{12}H_{30}N_2Cl_2Si_2$: C 43.90%, H 9.14%, N 8.54%, Cl 21.65%, Si 17.07%; found: C 43.47%, H 9.09%, N 8.12%, Cl 21.38%, Si 17.98%.

For the synthesis of *symmetric*-dichloro*tetrakis*(dimethylamino)disilane, the weight of $HNMe_2$ was carefully controlled so that only the stoichiometric amount of dimethylamine was introduced. The $^1H$ and $^{13}C$ NMR data compare favorably with the literature values.[12] MS (EI): m/z (ion, relative intensity) 302.1 ($M^+$, 0.71). HRMS (EI) Calcd. for $C_8H_{24}Cl_2N_4Si_2$: 302.091661; found: 302.091942. Elemental analysis: Calcd. for $C_8H_{24}Cl_2N_4Si_2$: C 23.76%, H 7.92%, N 18.48%, 23.43%, 18.48%; found: C 22.80%, H 8.31%, 18,27%. Mp: 87-89 °C.

***Symmetric*-di-*tert*-butyltetrachlorodisilane.** This compound was synthesized by a literature method.[11] $^1H$ NMR ($CDCl_3$): δ 1.19 (s, 18H). $^{13}C$ NMR ($CDCl_3$): δ 25.63, 25.11. Mp: 31-32 °C. HRMS (EI): Calcd. for $C_8H_{18}Cl_4Si_2$ 311.967209; found: 311.9675289. Elemental analysis: Calcd. for $C_8H_{18}Cl_4Si_2$: C 30.77%, H 5.77%, Cl 45.51%, 17.95%; found: C 30.96%, H 5.97%, Cl 44.82%, Si 17.83%.

**General method for synthesis of *1,4*-disilacyclohexa-*2,5*-dienes**. The stated amounts of a disilane and an alkyne (either diphenylacetylene or *1*-phenyl-*1*-propyne) were added to a glass sealing and the inside wall of the tube was cleaned by cotton. The tube was then directly flame sealed under vacuum in the case of solid mixtures. For liquid reaction mixtures, the tube was cooled with liquid nitrogen while under vacuum prior to vacuum sealing. In these reactions, the height of the reaction mixture was about one fifth of that of the glass tube. The mixture in the glass tube was heated to *ca.*200 °C for 2 days in an oil bath. Generally crystal formation was observed after the reaction mixture had been cooled to ambient temperature. The tube was quickly opened in a hood, and the liquid portion was decanted, the crystalline product was washed several times by the stated amount of pentane, and was dried under vacuum.

***2,3,5,6*-tetraphenyl-*1,1,4,4-tetrakis*(dimethylamino)-*1,4*-disilacyclohexa-*2,5*-diene (4).** To *pentakis*(dimethylamino)chlorodislane[9, 12] (3.11 g, 10.0 mmol) was added diphenylacetylene (2.05 g, 11.5 mmol, 15% excess). The sealed tube was heated to *ca.* 200 °C for 2 days in an oil bath, during which time the color of the reaction mixture changed to brown. The tube was then allowed to cool to room temperature during which time crystals were observed to form. The tube was opened in a hood and the liquid part was removed by decantation. The crystals (suitable for X-ray analysis) was washed with 5 x 10 mL of pentane. Drying the crystals under vacuum afforded 2.64 g (45% yield) of 4. $^1$H NMR ($CDCl_3$): δ 6.83-7.03 (m, 20H), 2.34 (s, 24H); $^{13}$C NMR ($CDCl_3$) δ 158.43, 143.69, 128.88, 126.95, 124.76, 38.11; $^{29}$Si NMR (solid) δ -33.11. Mp: 260-265 °C. MS (CI/$NH_3$, negative): m/z (relative intensity, ion) 588.2 ($M^-$, 18.83), 544.2 (M-$NMe_2$, 4.04). Elemental analysis: Calcd. for $C_{36}H_{44}N_4Si_2$: C 73.42%, H 7.53%, N 9.51%, found: 72.40%, H 7.53%, N 9.39%. The liquid by-product analyzed for $Si(NMe_2)_3Cl$ by $^1$H, $^{13}$C NMR and MS spectroscopies.

***2,3,5,6*-tetraphenyl-*1,4-bis* (dimethylamino)-*1,4*-dichloro-*1,4*-disilacyclohexa-*2,5*-dienes (5).** In an analogous manner, *symmetric-tetrakis*(dimethylamino) dichlorodisilane (3.03 g, 10.0 mmol) was reacted with diphenylacetylene (2.07 g, 11.5 mmol, 15% excess). After the reaction the liquid [$Si(NMe_2)_3Cl$] was separated from the crystalline material by decantation. According to $^1H$ and $^{13}C$ NMR spectroscopies, the solid consisted of a mixture of two isomeric *1,4*-disila-*2,5*-dienes with one dominant isomer and hexaphenylbenzene as a minor by-product. The crystalline products were washed with 5 x 10 mL of pentane and dried under vacuum, affording 1.43 g solid material which analyzed by $^1H$ NMR spectroscopy as 75% of isomers of **5** and 25% hexaphenylbenzene. Removal of the hexaphenylbenzene was accomplished by recrystallization from $CHCl_2$. Attempts to remove the trace amount of one of the isomer by column chromatography failed. $^1H$ NMR ($CDCl_3$): $\delta$ 7.00-7.08 (m, 20H), 2.33 (s, 12H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 157.30, 140.19, 128.76, 127.33, 125.97, 37.23. Mp: decomposed at 250 °C. MS (CI/$NH_3$, positive): m/z (relative intensity, ion) 571.1 ($M^+$, 20.13), 535.1 ($(M\text{-}Cl)^+$, 6.07, 525.9 ($(M\text{-}NMe_2)^+$, 3.55). HRMS (EI): Calcd. for $C_{32}H_{32}Cl_2N_2Si_2$: 570.14811; found: 570.14931. Crystal suitable for X-ray diffraction spectroscopy were not obtained.

***2,3,5,6*-tetraphenyl-*1,4*-dimethyl-*1,4-bis*(dimethylamino)-*1,4*-disilacyclohexa-*2,5*-dienes (6).** In an analogous manner, *symmetric*-dimethyl*tetrakis*(dimethylamino)disilane (2.62 g, 10.0 mmol) was reacted with diphenylacetylene (2.07 g, 11.5 mmol, 15% excess). The tube was heated to *ca.* 200 °C for 2 days, during which time the reaction mixture was observed to change to light brown. During subsequent cooling of the tube to ambient temperature, crystals were observed to form. The tube was opened in a hood and the liquid portion was removed by decantation. The crystals were washed with 5 x 10 mL of pentane and dried under vacuum giving 3.48 g (7.50 mmol, 75% yield) of one isomer of the product **6**. The other possible isomer was barely detectable by $^1$H NMR spectroscopy product. $^1$H NMR ($CDCl_3$): δ 6.82-7.06 (m, 20H), 2.38 (s, 12H), 0.12 (s, 6H); $^{13}$C NMR ($CDCl_3$): δ 157.40, 143.29, 128.34, 127.08, 124.85, 38.41, -3.36. Mp: 243-245 °C. HRMS (EI) Calcd. for $C_{34}H_{38}N_2Si_2$: 530.257357; found: 530.257848. Elemental analysis: Calcd. for $C_{34}H_{38}N_2Si_2$: C 76.98%, H 7.17%, N 5.28%, Si 10.57%; found: C 77.00%, H 7.26%, N 5.28%, Si 10.75%. Although crystals suitable for X-ray diffraction were obtained by recrystallization from $CH_2Cl_2$, the structure could not be solved completely due to the difficulty in assigning the atoms.

***3,6*-dimethyl-*2,5*-diphenyl-*1,1,4,4*-*tetrakis*(dimethylamino)-*1,4*-disila-cyclohexa-*2,5*-diene** and ***3,5*-dimethyl-*2,6*-diphenyl-*1,1,4,4*-*tetrakis*(dimethylamino)-*1,4*-disilacyclohexa-*2,5*-diene (7).** In an analogous manner, *pentakis*(dimethylamino)-chlorodisilane (3.11 g, 10.0 mmol) was reacted with *1*-phenyl-*1*-propyne (1.11 g, 10.5 mmol, 5% excess). The tube was heated to 200 °C for 2 days in an oil bath during which time the reaction mixture (a brown solution) was observed to reflux. Subsequent cooling to ambient temperature was followed by further cooling to −18 °C in a freezer for one day. The tube was then opened in a hood, and the liquid portion was removed by decantation and the remaining solid was washed with 3 x 10 mL of pentane precooled by dry ice. The product was dried under vacuum, and analyzed for more than 95% of one isomer, presumably the *trans*-conformer of *3,6*-dimethyl-*2,5*-diphenyl-*1,1,4,4-tetra-kis*(dimethylamino)-*1,4*-disilacyclohexa-*2,5*-diene, together with less than 5% of the minor product, judging from the single $^1$H NMR and $^{13}$C NMR peaks observed for the NMe$_2$. Yield: 70%. $^1$H NMR (CDCl$_3$) δ 6.94-7.29 (m, 10H); $^{13}$C NMR (CDCl$_3$) δ 156.25, 152.28, 144.15, 127.90, 127.69, 125.07, 37.80, 18.59. Mp: 168-170 °C. HRMS (EI): Calcd. for $C_{26}H_{40}N_4Si_2$: 464.279155; found: 464.279792. This compound was quite soluble in pentane, which contrasts the solubility behavior of the other *1,4*-disilacyclohexa-*2,5*-diene compounds synthesized herein. The *trans* configuration of 7 is further supported by the reaction of this compound with $SiCl_4$ in refluxing $Et_2O$ for 15 hours wherein only one dominant product was obtained in 90% yield. $^1$H NMR (CDCl$_3$) δ 7.16-7.44 (m, 10 H), 1.91 (s, 6H); $^{13}$C NMR (CDCl$_3$) δ 153.63, 152.22, 136.72, 128.52, 128.16, 127.59, 17.90. The minor product was hardly detectable by $^1$H NMR spectroscopy.

***Trans*-2,3,5,6-tetraphenyl-*1,4*-dichloro-*1,4*-di-*tert*-butyl-*1,4*-disilacyclohexa-*2,5*-diene (8).** In an analogous manner *symmetric*-di-*tert*-butyldichloro-*bis*(dimethylamino)disilane (3.29 g, 10.0 mmol) was reacted with diphenylacetylene (2.13 g, 12.0 mmol, 20% excess). The tube was heated to 210 °C for 3 days, during which time a brown solution was obtained. The tube was allowed to cool to ambient temperature, and then was kept at *ca.* −18 °C in a freezer for 2 days but no crystal formation was observed. The tube was opened in a hood, and pentane (20 mL, precooled by dry ice) was added. The tube was stoppered by a septum and stored in a freezer for 5 hours, during which time a precipitate formed. The solution was removed by a syringe, and the precipitate was washed 5 times with 5 mL pentane. Drying the precipitate under vacuum afforded 0.30 g (0.50 mmol, 5% yield) of **8** as a powder material. When tried at 220 °C for 6 days, a much higher yield (30%) was obtained. The product was confirmed to be a single isomer by $^1H$, $^{13}C$ NMR spectroscopies. $^1H$ NMR ($CDCl_3$): δ 6.52-7.54 (m, br, 20H), 0.51 (s, 18H); $^{13}C$ NMR ($CDCl_3$): δ 156.95, 141.79, 130.01, 127.18 (br), 125.99, 26.70, 22.27. Mp 285-287 °C. HRMS (EI): Calcd. for $C_{36}H_{38}Cl_2Si_2$: 596.188915; found: 596.189827. Elemental analysis: Calcd. for $C_{36}H_{38}Cl_2Si_2$: C 72.48%, H 6.29%, Cl 11.91%, Si 9.40%; found: C 72.26%, H 6.33%, Cl 11.94%, Si 9.01%. Crystals suitable for X-ray diffraction spectroscopy were obtained by recrystallization from chloroform.

**General description of synthesis of *2,3,5,6*-tetraphenyl-*1,1,4,4*-tetrahalogen-*1,4*-disilacyclohexa-*2,5*-dienes 9a-c**. Compound **4** was allowed to react with $SiCl_4$ (or $Si_2Cl_6$, $PCl_3$), $PBr_3$ (or $SiBr_4$) and $PI_3$ in refluxing $Et_2O$ to obtain the corresponding chlorinated, brominated and iodinated derivatives **9a-c** in a good to excellent yields (i.e., 9a and **9b** were obtained both in 95% yield, **9c** was obtained in 70% yield).

***2,3,5,6*-tetraphenyl-*1,1,4,4*-tetrachloro-*1,4*-disilacyclohexa-*2,5*-dienes (9a).** In a 100 mL flask quipped with a magnetic stirrer was added **4** (2.94 g, 5.00 mmol), followed by $Et_2O$ (50 mL). $SiCl_4$ (8.50 g, 50.0 mmol) was introduced via a syringe. The mixture was refluxed at 45 °C for 24 hours, during which time a white precipitate was observed to form. After reaction, the precipitate was filtered under nitrogen and washed with 5 x 10 mL of pentane. Drying the precipitate under vacuum afforded 2.62 g of powdery **9a** in 95% yield. $^1$H NMR ($CDCl_3$): δ 7.07-7.18 (m, 20H); $^{13}$C NMR ($CDCl_3$): δ 155.96, 136.71, 128.93, 127.17. Mp: 287 °C (with decomposition). HRMS (EI): Calcd. for $C_{28}H_{20}Cl_4Si_2$: 553.98282; found: 553.98319. Elemental analysis: Calcd. for $C_{28}H_{20}Cl_4Si_2$: C 60.64%, H 3.61%, Cl 25.63%, Si 10.11%; found: C 60.60%, H 3.54%, Cl 25.47%, Si 10.04%.

***2,3,5,6*-tetraphenyl-*1,1,4,4*-tetrabromo-*1,4*-disilacyclohexa-*2,5*-diene (9b).** This compound was made analogously in 95% yield using $SiBr_4$ (or $PBr_3$). $^1$H NMR ($CDCl_3$): δ 7.07-7.20 (m, 20H); $^{13}$C NMR ($CDCl_3$) δ 155.13, 136.70, 129.26, 127.51, 127.12. Mp: 280 °C (with decomposition). HRMS (EI): Calcd. for $C_{28}H_{20}Br_4Si_2$: 729.78269; found: 729.78284.

***2,3,5,6*-tetraphenyl-*1,1,4,4*-tetraiodo-*1,4*-disilacyclohexa-*2,5*-dienes (9c).** This compound was made analogously in 70% yield by reacting **4** with $PI_3$ in $CH_2Cl_2$ (or refluxing $Et_2O$). $^1$H NMR ($CDCl_3$): δ 7.07-7.19 (m, 20H); $^{13}$C NMR ($CDCl_3$): δ 152.93, 137.50, 129.96, 127.32, 127.00. Mp: decomposed at 200 °C. MS (CI/$NH_3$) m/z (relative intensity, ion): 937.0, 0.67, $[M+NH_3]^+$. Crystals suitable for X-ray diffraction spectroscopy were obtained by recrystallization from $CH_2Cl_2$.

***2,3,5,6*-tetraphenyl-*1,1,4,4*-tetramethoxy-*1,4*-disilacyclohexa-*2,5*-dienes (9d),** Compound 4 (55.4 mg, 0.100 mmol) was placed in an NMR tube followed by 1.2 mL of

$Et_2O$ and hexamethoxydisilane (48.4 mg, 0.20 mmol) which was introduced via a syringe. The mixture was vibrated for 5 h in an ultrasonic bath. The white precipitate that had formed was recovered by evaporating volatile materials under reduced pressure, followed by washing with 3 x 1 mL of pentane. Drying the product under reduced pressure gave 48.2 mg (90% yield) of **9d**. $^1H$ NMR ($CDCl_3$): δ 7.00-7.11 (m, 20H), 3.33 (s, 12H); $^{13}C$ NMR ($CDCl_3$): δ 156.14, 140.82, 128.82, 127.60, 125.89, 50.96. Mp: 188-190 °C. HRMS (EI): Calcd. for $C_{32}H_{32}O_4Si_2$: 536.18392; found: 536.18405.

***2,3,5,6*-tetraphenyl-*1,1,4,4*-tetraphenoxy-*1,4*-disilacyclohexa-*2,5*-dienes (9e).** This synthesis is analogous to that of **9d**, except that $P(OPh)_3$ was used to react with **4** at 140 °C for 15 h in an NMR tube in the absence of a solvent. The product was washed with 3 x 1 mL of pentane followed by drying the product under vacuum which afforded **9e** in 95% yield. $^1H$ NMR ($CDCl_3$) δ 6.68-7.12; $^{13}C$ NMR ($CDCl_3$): δ 157.24, 153.43, 139.16, 129.21, 128.76, 126.26, 122.07, 119.79. MS (EI): m/z (relative intensity, ion): 784.3 (5.26, $M^+$). HRMS (EI) Calcd. for $C_{52}H_{40}O_4Si_2$: 784.246518; found: 784.247446. Elemental analysis: Calcd. for $C_{52}H_{40}O_4Si_2$: C 79.59%, H 5.10%, O 8.16%, Si 7.14%; found: C 79.10%, H 5.19%, Si 7.52%. Crystals suitable for X-ray diffraction spectroscopy were obtained by recrystallization from $CHCl_3$.

***2,3,5,6*-tetraphenyl-*1,4*-disilacyclohexa-*2,5*-diene (10).** Into a 50 mL flask equipped with a magnetic stirrer was introduced **9a** (2.77 g, 5.00 mmol) followed by THF (25 mL). $LiAlH_4$ (0.76 g, 20 mmol) was added and the mixture was refluxed at 75 °C for 24 hours. The excess $LiAlH_4$ was then destroyed with 20 mL of methanol. The mixture was filtered and the volatiles were removed under vacuum. Purification of the product by column chromatography ($CHCl_3$ eluent) afforded 1.45 g (3.00 mmol, 70% yield) of **10**. Sublimation of the compound under vacuum at 200 °C gave crystals suitable for X-ray diffraction. $^1H$ NMR ($CDCl_3$): δ 7.01-7.16 (m, 20H), 4.58 (s, 4H); $^{13}C$ NMR ($CDCl_3$): δ 152.01, 141.67, 128.14, 128.06, 126.34. Mp: 240-242 °C. HRMS (EI): Calcd. for $C_{28}H_{24}Si_2$: 416.141659; found: 416.142209. Elemental analysis: Calcd. for $C_{28}H_{24}Si_2$: C 80.77%, H 5.77%, Si 13.46%; found: C 80.55%, H 5.49%, Si 13.15%.

***2,3,5,6*-tetraphenyl-*1,1,4,4*-tetrahydroxy-*1,4*-disilacyclohexa-2,5-diene (11).** Into a 50 mL flask equipped with a magnetic stirrer was placed **9a** (1.38 g, 2.50 mmol) followed by acetone (25 mL). After **9a** had dissolved, distilled water (0.90 g, 50 mmol) was added dropwise through a syringe while stirring whereupon a white precipitate was observed to form. The reaction mixture was stirred at room temperature for 2 hours, and filtered. The precipitate was washed with 3 x 5 mL of $Et_2O$ , followed by 3 x 5 mL of pentane, and was dried under vacuum giving **11** (1.28 g, 98% yield). $^1H$ NMR ($d_8$-THF): δ 6.88-7.09 (m, 20H), 5.51 (s, 4H); $^{13}C$ NMR ($d_8$-THF): δ 157.21, 143.25, 130.20, 127.62, 125.51. Mp >300 °C. MS (EI): m/z (relative intensity, ion): 480.1 (0.70, $M^+$); (CI/$NH_3$, negative) 479.9 (52.80, $M^-$). HRMS (EI) Calcd. for $C_{28}H_{24}O_2Si_2$: 480.121317; found: 480.122116. Elemental analysis: Calcd. for $C_{28}H_{24}O_2Si_2$: C 70.00%, H 5.00%, O 6.67%, Si 11.67%; found: C 70.57%, H 5.08%, Si 11.74%.

***1,4*-dichloro-*1,4*-dimethyl-*2,3,5,6*-tetraphenyl-*1,4*-disilacyclohexa-*2,5*-diene (12).** The preparation (including workup and isolation) of this compound was analogous to that of **9a**, except that **6** and $SiCl_4$ were used as starting materials. Interestingly, although only one isomer (presumably the *trans*-conformer) of **6** was used in the reaction, a mixture of *cis* and *trans* **12** in a *ca.* 1: 1 ratio was obtained. Attempts to separate these two isomers using sublimation and column chromatography failed. $^1H$ NMR ($CDCl_3$): δ 6.98-7.13 (m, 20H), 0.37 (s, 3H), 0.30 (s, 3H); $^{13}C$ NMR ($CDCl_3$): δ 156.47, 156.44, 128.51, 128.38, 127.66, 127.60, 126.23, 0.40, 0.25. Mp: > 300 °C. HRMS (EI): Calcd. for $C_{30}H_{26}Cl_2Si_2$: 512.095015; found: 512.095967.

***Trans*-*2,3,5,6*-tetraphenyl-*1,4*-dihydro-*1,4*-di-*tert*-butyl-*1,4*-disilacyclohexa-*2,5*-diene (13).** The preparation (including workup and isolation) of this compound is analogous to that of **10** except that **8** and $LiAlH_4$ were used. The total yield of 75%, includes about 10% of a minor diastereomer (presumably the *cis*). Crystals suitable for X-ray diffraction spectroscopy were obtained by recrystallization from $CH_2Cl_2$. $^1H$ NMR ($CDCl_3$): δ 6.82-7.07 (m, 24 H, *cis* and *trans*), 4.97 (s, 2 H, *trans*), 4.50 (s, 0.32 H, *cis*), 0.84 (s, 3.14 H, *cis*), 0.41 (s, 18 H, *trans*); $^{13}C$ NMR ($CDCl_3$) (*trans*-comformer): δ 154.43, 143.59, 129.71, 127.49, 125.59, 28.34, 19.90; $^{13}C$ NMR ($CDCl_3$) (*cis*-comformer): δ 156.69, 140.28, 129.34, 127.02, 125.43, 29.49, 20.00. Mp: 238-240 °C.

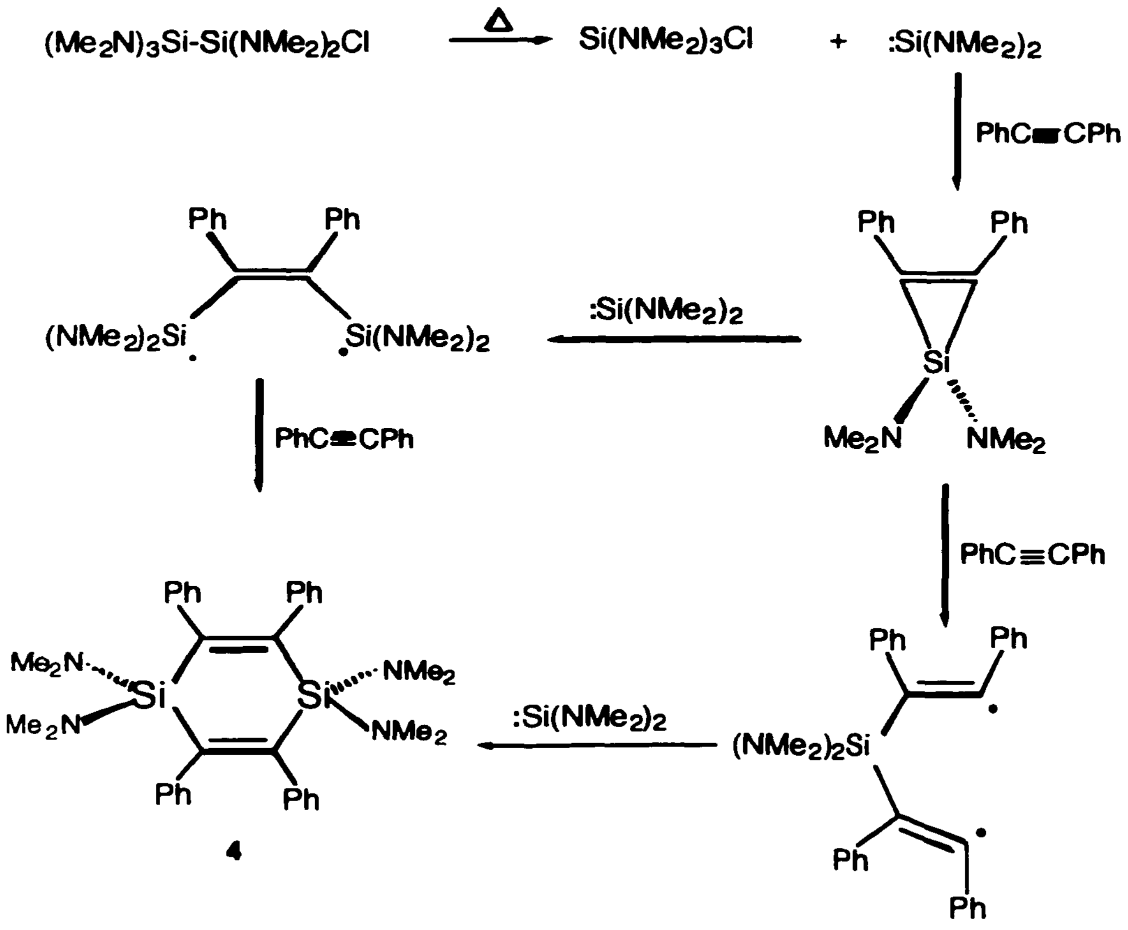
**Variable temperature NMR of 8.** The $^1H$ and $^{13}C$ NMR spectra of compound **8** were measured at different temperatures to investigate the restrictions on the free rotation of the four phenyl groups. $^1H$ NMR at −30 °C ($CDCl_3$): δ 7.52-7.54 (d, 2H), 7.21 (t, 2H), 6.97 (t, 2H), 6.85 (t, 2H), 6.50-6.52 (d, 2H); $^{13}C$ NMR ($CDCl_3$): δ 156.52, 141.55, 129.83, 129.64, 127.34, 126.90, 125.87, 26.47, 22.26. $^1H$ NMR at 25 °C ($CDCl_3$): δ

6.52-7.54 (m, br, 20H), 0.51 (s, 18H); $^{13}$C NMR ($CDCl_3$): δ 156.95, 141.79, 130.01, 127.18 (br), 125.99, 26.70, 22.27. $^{1}$H NMR at 50 °C ($CDCl_3$): δ 6.52-7.54 (br, 20H), 0.46 (s, 18H); $^{13}$C NMR ($CDCl_3$): δ 157.16, 141.92, 130.14, 127.20, 126.04, 26.80, 22.29. At a temperature below 0 °C, five different protons could be observed. At –30 °C, the $^{1}$H NMR clearly showed five well separated signals. Similarly, six distinct $^{13}$C signals were observed at that temperature. At room temperature to 50 °C, the two α-carbons on the phenyl groups tend to coalesce giving a broad peak at 127.20 ppm. Sharpening of this peak was observed as temperature increased from room temperature to 50 °C. Small changes in the chemical shifts of the *tert*-butyl groups also occurred with temperature.

## Results and Discussion

**Synthesis of *1,4*-disilacyclohexa-*2,5*-dienes.** In the reaction of diphenylacetylene with *pentakis*(dimethylamino)chlorodisilane at *ca.* 200 °C the crystalline material **4** (obtained in 45% yield) formed together with a liquid by-product $Si(NMe_2)_3Cl$. When *symmetric-tetrakis*(dimethylamino)dichlorodisilane was used in this reaction, a mixture of *cis* and *trans* isomers of **5** was similarly obtained in about 20% yield, accompanied by *ca.* 5% of the trimerization product hexaphenylbenzene which was separated by recrystallization. One of the isomers occurred in only trace amounts, but neither isomer could be identified spectroscopically, and crystals suitable for X-ray diffraction could not be obtained.

Scheme 1



A pathway for the formation of **4** and **5** is proposed that involves silylene formation as shown in Scheme 1. A similar pathway was proposed in the literature[3, 4, 13] to account for the formation of **1a** and **1b**. To confirm the production of *bis*(dimethylamino)silylene, we attempted to trap this species. Although quinones such as benzil, and dienes such as *1,3*-butadiene are well known traps for $R_2Si$,[14] neither

$Si_2(NMe_2)_5Cl$ nor $Si_2(NMe_2)_4Cl_2$ was found to react with benzil in $CHCl_3$ either at room temperature or at 75 °C. However, when benzil and $Si_2(NMe_2)_5Cl$ were heated to 180 °C in a sealed tube, a brown insoluble material formed. Washing the reaction mixture with pentane gave gray precipitate, which appeared to be an oligomeric material by $^1H$ and $^{13}C$ NMR spectroscopies, and mass spectroscopy also revealed no evidence for the desired product. Experiments using *trans,trans-1,4*-dipheneyl-*1,3*-butadiene as silylene trap succeeded, the trapping product formed was analyzed by HRMS to be consistent with the five-membered ring product **14** (calcd. for $C_{20}H_{26}NSi$: 322.18653; found: 322.186597). This experiment confirms that silylene species were generated from disilanes bearing multiple dimethylamino groups under our aforementioned milder conditions.

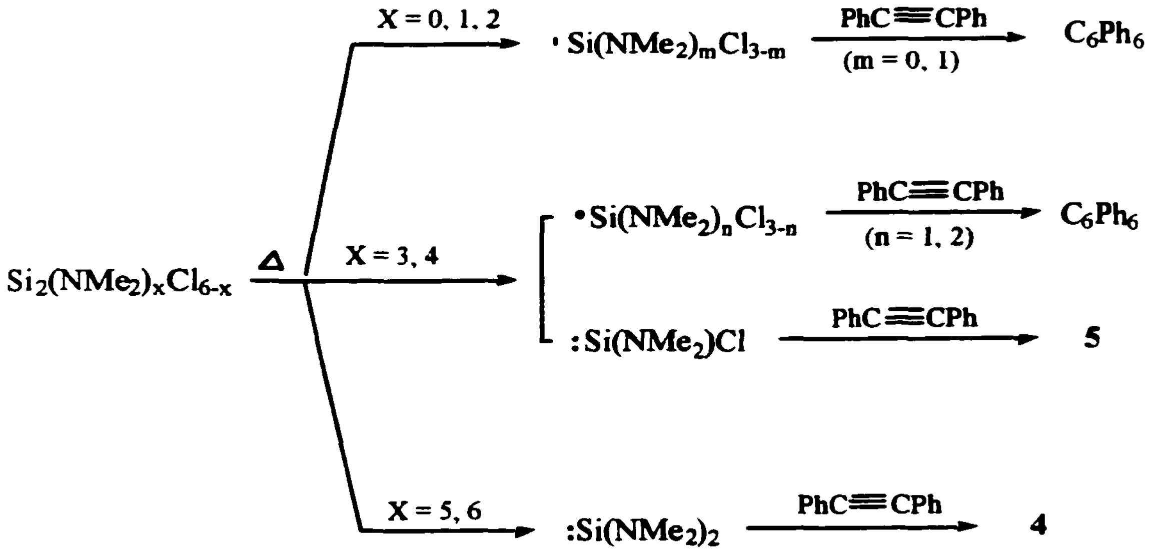
When *hexakis*(dimethylamino)disilane was reacted with diphenylacetylene, the yield of **4** (*ca*. 20%) dropped to less than half of that obtained from the *pentakis*(dimethylamino)chlorodisilane/diphenylacetylene reaction. The better yield of **4** realized with $Si_2(NMe_2)_5Cl$ than with $Si_2(NMe_2)_6$ may be associated with the advantageous formation of $Si(NMe_2)_3Cl$ over $Si(NMe_2)_4$ in the disproportionation of the disilane; the former product featuring a Si-Cl bond which is stronger and less sterically demanding than a Si-$NMe_2$ link, together with a further weakened Si-Si bond in *pentakis*(dimethylamino)chlorodisilane caused by the more electron-withdrawing Cl than the $NMe_2$ group of *hexakis*(diemthylamino)disialne . The presence of both disproportionation products $Si(NMe_2)_3Cl$ and $Si(NMe_2)_4$ was confirmed by $^1H$ NMR,

$^{13}$C NMR and MS spectroscopies.

The non-symmetric alkyne *1*-phenyl-*1*-propyne also reacts with *pentakis*(dimethylamino)chlorodisilane allowing the isolation of an isomeric mixture of **7** (in *ca.* 10: 1 ratio) in 75% yield. Apparently, *symmetric*-dimethy*tetrakis*(dimethylamino)disilane is able to generate unsymmetric silylene species :$SiMe(NMe_2)$ at *ca.* 200 °C since **6** was obtained in 75% yield in the presence of diphenylacetylene. Interestingly, only a trace amount of the *cis*- isomer was detected. Introduction of more bulky *tertiary*-butyl alkyl group in *symmetric-bis*(dimethylamino)-di-*tert*-butyldichlordisilane in the presence of diphenylacetylene led to the formation of **8** in less than 5% yield despite the higher-than-normal temperature of 210 °C for 3 instead of the usual 2 days. Although lower temperature and shorter time for this reaction was not attempted, when prolonged reaction time to 1 week at 220 °C was tried, **8** was obtained in 30% yield. Interesting is the observation that $SiCl^tBu$ species rather than the $Si(NMe_2)^tBu$ species finds its way into the product. This may be associated with the larger steric strain in the latter silylene although the expected disproportionation product $Cl(Me_2N)_2Si^tBu$ might then also be anticipated to be unstable at this temperature. The product formation of **8** in this reaction is also consistent with the previous argument that Si-N linkage is weaker than Si-Cl, therefore only $SiCl^tBu$ silylene species was generated via the aforementioned disproportionation process. The by-product formed from this reaction was analyzed to be $ClSi(NMe_2)_2{}^tBu$ as confirmed by $^1$H, $^{13}$C NMR and mass spectroscopies.

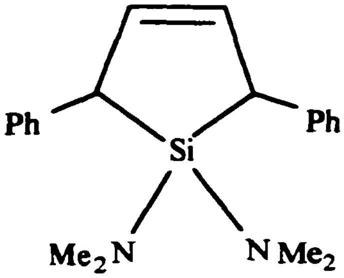
As already mentioned,[2] the reaction pattern was studied by the following testing experiments in which diphenylacetylene was reacted with disilanes with zero, two, three, four, five and six dimethylamino groups.[2] Under the same temperature condition (*ca.* 200 °C) and reaction time (40 hours), we found that the reaction product(s) varied from sole hexaphenylbenzene (in 70% yield) in the case of $Si_2Cl_6$/ $PhC\equiv CPh$, to only **4** in $Si_2(NMe_2)_5Cl/PhC\equiv CPh$ and $Si_2(NMe_2)_5/PhC\equiv CPh$ reactions. A mixture of the cyclotrimerization product and *1,4*-disilacyclohexa-*2,5*-diene could be obtained in various ratios for the disilanes with two to four $NMe_2$ groups. The isolated yields of these reactions were also directly related to the number of the $NMe_2$ groups. We rationalize this observation by the fact that Cl atom is more electron-withdrawing than the $NMe_2$ group, so the Si-Si link in the $Si_2(NMe_2)_5Cl$ is weak, also Si-N bond is weaker than Si-Cl bond, facilitating the disproportination reaction which gives $:Si(NMe_2)_2$ species. However, when fewer Cl atoms are substituted by $NMe_2$ groups, silyl radical generation via homolytic Si-Si cleavage will be increasingly favored, and competing with the disproportionation process, this possibly accounts for the product distributions in the $Si_2(NMe_2)_2Cl_4$ $/PhC\equiv CPh$, $Si_2(NMe_2)_3Cl_3/PhC\equiv CPh$ and $Si_2(NMe_2)_4Cl_2/PhC\equiv CPh$ systems. Although the mono-substituted disilane $Si_2(NMe_2)Cl_5$ was not obtained in pure form, when the impure material was tried, only trimerization product hexaphenylbenzene was obtained with an expected yield of 35% (in-between those of the $Si_2Cl_6/PhC\equiv CPh$ and $Si_2(NMe_2)_2Cl_4/PhC\equiv CPh$ reactions). The *1,4*-disilacyclohexa-*2,5*-diene product **5**, if any, was not detected by NMR spectroscopies. The diagram demonstrating the competition between silyl radical and silylene generation is shown in Scheme 2, where only the reactive species are given.

Scheme 2



Silanes bearing dimethylamino groups, such as *tris*(dimethylamino)chlorosilane and *tetrakis*(dimethylamino)silane, do not form **4** and **5** in the presence of diphenylacetylene at 210 °C for 3 days. This suggests that the relatively weak Si-Si bond in the disilanes used here facilitates the disproportionation reaction that gives rise to silylenes.

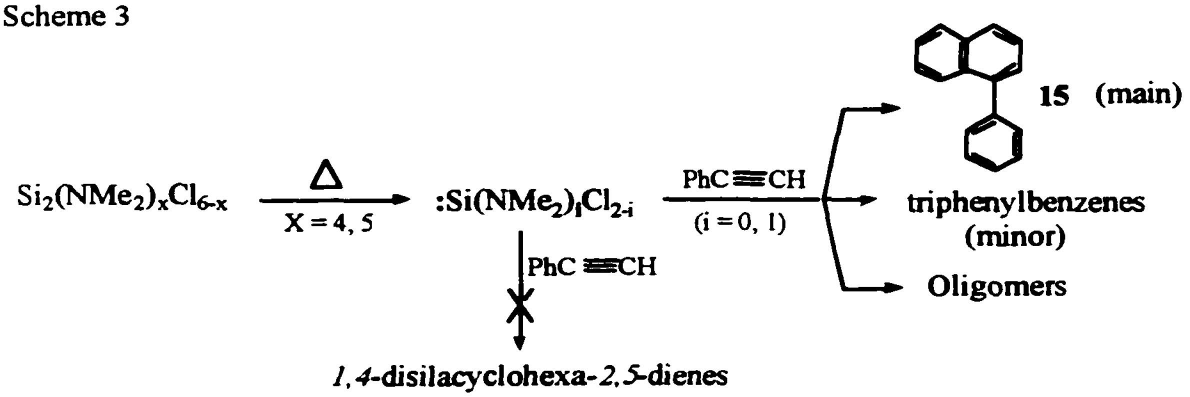
Pyrolysis of either $Si_2(NMe_2)_5Cl$ or $Si_2(NMe_2)_4Cl_2$ at 200 °C in a sealed tube gave oligomer products, together with $Si(NMe_2)_3Cl$, as confirmed by $^1H$, $^{13}C$ NMR and MS spectroscopies. The product of $Si(NMe_2)_3Cl$ in both cases indicates that disproportionation gives rise to $:Si(NMe_2)_2$ and $:Si(NMe_2)Cl$, repspectively. The highly reactive silyene $:Si(NMe_2)_2$ and $:Si(NMe_2)Cl$ are probably responsible for the formation of oligomeric products. The existence of the silylene species $:Si(NMe_2)_2$ was further confirmed by reacting $Si_2(NMe_2)_5Cl$ with *1,4*-dipheneyl-*1,3*-butadiene, in which product **14** was detected to form by HRMS spectroscopy as mentioned above.



**14**

Interestingly, when phenylacetylene (PhC≡CH) was reacted with either *pentakis*(diemthylamino)chlorodisilane or *tetrakis*(dimethylamino)dichlorodisilane, no *1,4*-disilacyclohexa-*2,5*-diene product analogous to **4** or **5** was detected, instead, cyclo-dimerization product **15** was obtained as the dominant product (85% conversion), together with two isomeric trimers *1,3,5*-triphenylbenzene and *1,2,4*-triphenylbenzene (15% conversion) as confirmed by $^1H$, $^{13}C$ NMR and GC-MS spectroscopies, these products were identical to what we reported for the thermal dimerization of terminal conjugated alkynes.[2] Of course, the oligomeric material and $Si(NMe_2)_3Cl$ were also formed from the pyrolysis of the disilanes. Scheme 3 shows the pathway for this reaction, in which phenylacetylene preferentially thermally dimerizes and trimerizes even in the presence of a disilane.

Scheme 3



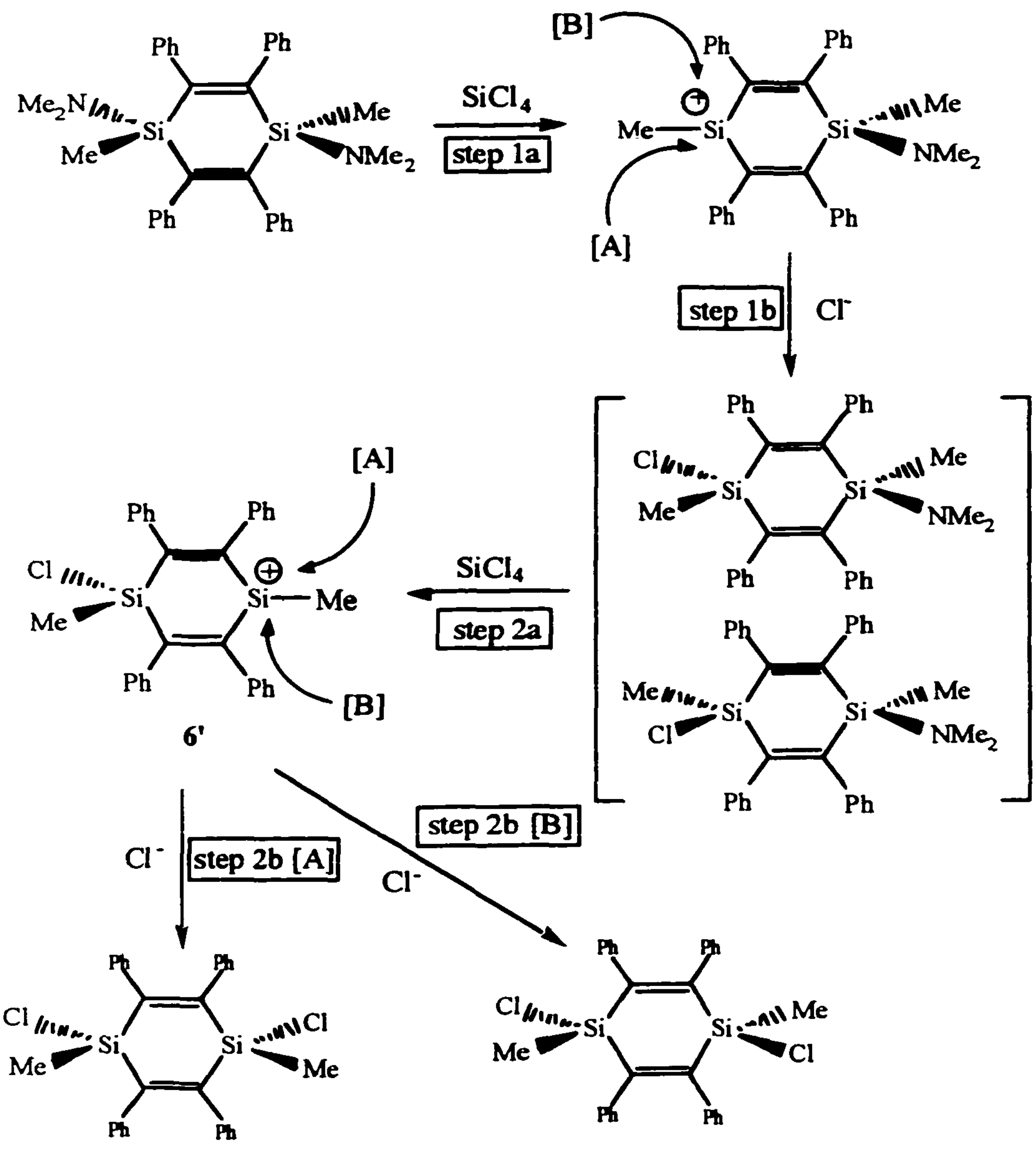
**Substitution reactions with halogens.** It was found that the dimethylamino ($NMe_2$) groups on the *1,4*-disilacyclohexa-*2,5*-dienes such as **4**, **6** and **7** were quite labile to substitution reactions. When **4** was treated with excess $SiCl_4$ at 45 °C in $Et_2O$ for 20 h, the chlorine substituted product **9a** was obtained in 95% yield. Later it was discovered that treatment of **4** with $Si_2Cl_6$ or $PCl_3$ by the same method also afforded **9a**. In an analogous manner, **9b** was obtained in 95% yield in the reaction of $PBr_3$ (or $SiBr_4$) with **4**. Product **9a** and **9b** were characterized by $^1H$, $^{13}C$ NMR, MS spectroscopies and elemental analysis. By the same approach, tetraiodo-substituted product **9c** was obtained in 70% yield using **4** and $PI_3$ in $CH_2Cl_2$ or in refluxing $Et_2O$.

For the *nonsymmetric-1,4*-disilacyclohexa-*2,5*-diene **6**, although one isomer (presumably the *trans*- conformer) was obtained as the dominant product, treatment of **6** with $SiCl_4$ gave two isomers of **12** in a *ca.* 1:1 ratio by $^1H$ NMR. Here we speculate that the halogen substitution reactions proceed by a two-step pathway, of which the first step, a cationic species was generated (by the attack of $SiCl_4$ to form $[Si(NMe_2)Cl_3]Cl^-$) as an intermediate in step 1a. After removal of the dimethylamino group(s) (i.e. after steps 1a, 1b and 2a), the in-coming $Cl^-$ ion can attack both faces of the intermediate with approximately equal possibility, affording two isomeric products in near 1: 1 ratio as illustrated in Scheme 4.

When **4** was allowed to react with excess $Si_2(OMe)_6$ in an ultrasonic bath at room temperature for 5 hours in the presence of $Et_2O$ as the solvent, colorless crystals **9d** formed in 90% yield whose constitution was confirmed by $^1H$, $^{13}C$ NMR and HRMS spectroscopies. the product from reaction $P(OPh)_3$ and **4**. The phenoxy analogue **9e** was obtained as colorless crystals in 95% yield suitable for X-ray diffraction in the reaction of $P(OPh)_3$ with **4** carried out at 140 °C for 15 hours.

Compound **9a** seems to be a useful precursor to other derivatives. When water was added to the solution of **9a** in acetone, a white precipitate formed immediately. After washing the precipitate first with $Et_2O$, followed by pentane, and drying the precipitate under vacuum, a white powdery material **11** was obtained in 90% yield whose

Scheme 4



constitution was confirmed by $^1$H, $^{13}$C NMR and HRMS spectroscopies. This product is very stable towards air and moisture and no decomposition was observed at 200 °C for 3 days. When **11** was treated with CaO at 250 °C under vacuum, *cis*- and *trans*-stilbenes were detected by $^1$H, $^{13}$C NMR and mass spectroscopies. However, a highly thermal stable cross-linked polymer was obtained when the dehydration reaction was carried out in refluxing acetic anhydride.[15]

When **9a** was treated with $LiAlH_4$ in refluxing THF, **10** was obtained in 70% yield. Compound **10** was sufficiently stable enough to be purified by column chromatography. Similarly **13** was obtained by the reduction of **8** with $LiALH_4$.

**$^1$H and $^{13}$C NMR spectroscopy studies.** The $^1$H NMR spectra for **4**, **5**, **6**, **7**, **9a-c**, **10**, **11** and **13** all displayed chemical shifts in the aromatic region as multiple peaks below 7.24 ppm, the chemical shift of $CDCl_3$. For **8**, however, the aromatic proton resonance appeared at room temperature as four almost equally distributed broad singlets (at δ 7.54, 7.18, 6.85, 6.52 ppm), accompanied by a well-resolved triplet at 6.96 ppm (Fig. 1). Four singlets were also observed at room temperature in the $^{13}$C NMR spectrum of **8** (δ 156.95, 141.79, 130.01, 125.99 with some apparent broadening of the latter two resonances, however) along with a severely broadened peak at 127.18 ppm (Fig. 2). Since we did not observe this phenomenon in any other *1,4*-disilacyclohexa-*2,5*-dienes including compound **13**, and because the *tert*-butyl group in **8** represents the most sterically hindered group among all of the silicon substituents in this series, we attributed this apparent differentiation of the phenyl carbons and hydrogens to the restricted rotation of the four phenyl groups caused by the steric hindrance of the *tert*-butyl groups. This phenomenon was not observed in **13** is possibly because its H atoms is a much smaller atom than the Cl atoms in **8**.

$^{1}$H and $^{13}$C NMR spectra of **8** recorded at 50 °C and –30 °C exhibited the expected changes. At –30 °C, free rotation of the phenyl groups is more restricted than at room temperature, thus leading to resolution of the four initially broad peaks. At 50 °C, however, the increased freedom of these groups leads to the appearance of a more conventional spectrum. 2D NMR showing H-C and H-H coupling in **8** are given in Fig. 3 and Fig. 4, respectively.

**Structural features of *1,4*-disilacyclohexa-*2,5*-dienes**. Crystals for compounds **4**, **6**, **8**, **9c**, **9d**, **9e**, **10**, **11** and **13** were obtained and were suitable for X-ray diffraction in all cases except for those of **6**, **11**. All of the other structures were successfully determined and were shown to possess a planar *1,4*- disilacyclohexa-*2,5*-diene six-membered ring, with four phenyl groups perpendicular to the central ring, including that of compound **10**. All possess an inversion center leading to at least a $C_2$ symmetry. However, even for the structures **4** and **9e**, the four substituents are not equivalent in the unit cell, thus precluding a $D_{2h}$ symmetry. Although **10** seems possible to display a $D_{2h}$ symmetry, close inspection indicated that there are two sets of phenyl groups in this compound, thus precluding this possiblity.

The structures for these compounds are shown in Figures 5-10, and some selected bond distances and bond angles for each corresponding structure are given for comparison.in the Appendix at the end of this dissertation.

Compounds **8** and **10** represent the two extremes of this series of *1,4*-disilacyclohexa-*2,5*-dienes, i.e., **8**, the most sterically hindered, while **10** the least. However, the bond distances and bond angles of the central ring of these two structures appear to be very close. For example, the average bond distance of Si-C bond in **8** is 1.8798(17) Å, the C=C bond distance is 1.362(2) Å; while they are 1.8709(13) Å and 1.3550(18) Å, respectively, in **10**. The bond angles on the central ring for each compound are as follows: compound **8**: <C-Si-C' 111.67(7), <Si-C'-C'' 125.25(12); compound **10**: <C-Si-C' 113.38(6), <Si-C'-C'' 124.02(10). The differences in these parameters among the remaining compounds are even smaller. In compound **9e** there are a total of eight phenyl groups, leading to a rather bulky molecule. Here the behavior of the phenoxy groups is of some interest. One set of two such groups is almost parallel to the central *1,4*-disilacyclohexa-*2,5*-diene ring while the other pair is close to being perpendicular to it.

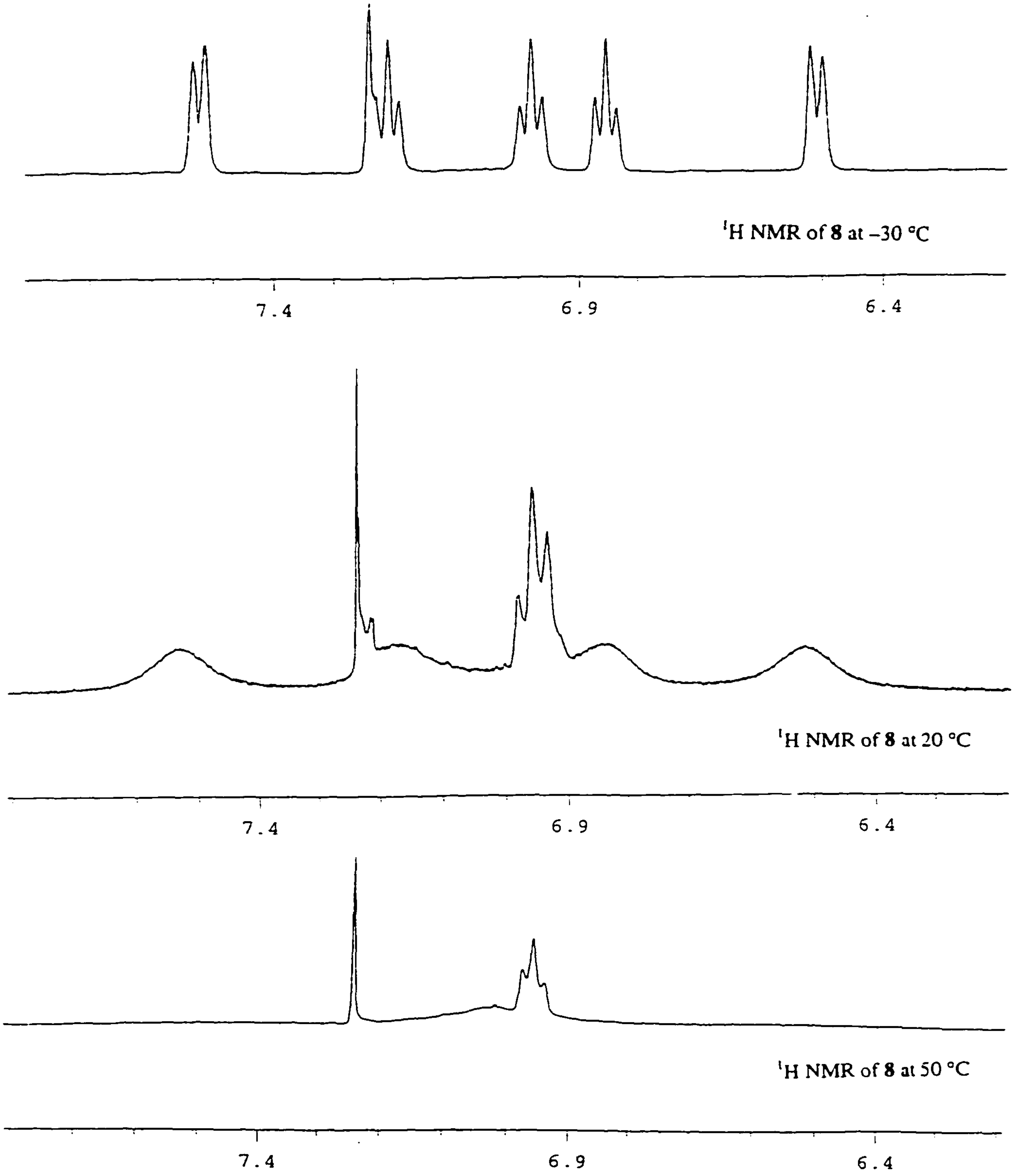
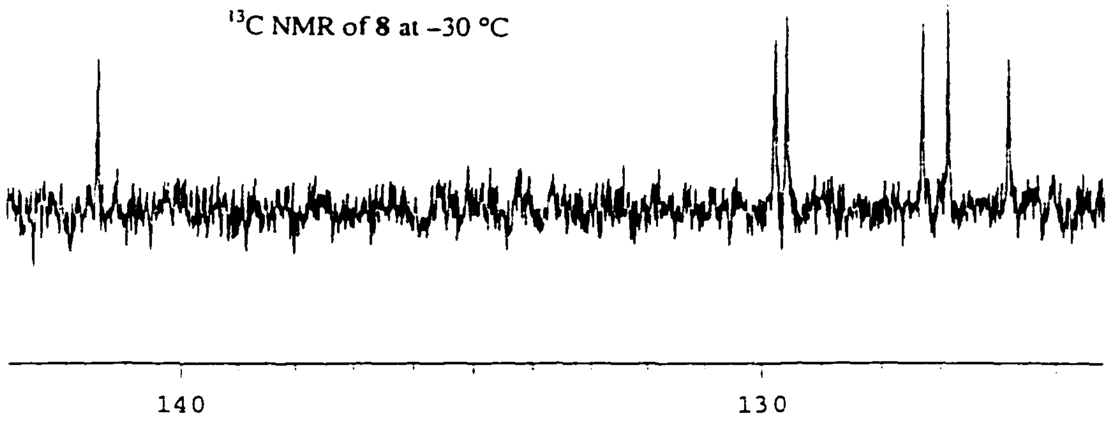
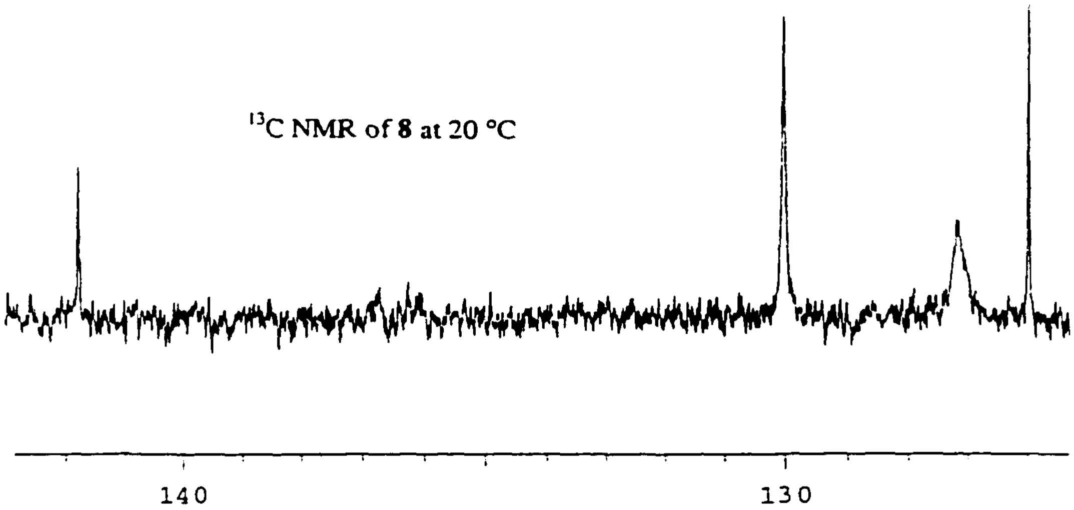


Fig. 1. $^1$H NMR spectrum of **8** at different temperature conditions


$^{13}$C NMR of **8** at –30 °C


$^{13}$C NMR of **8** at 20 °C

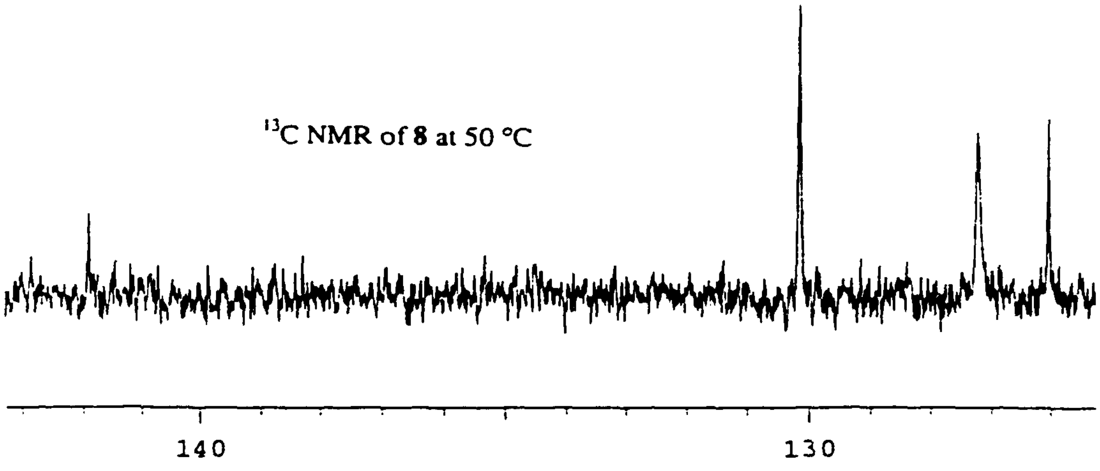

$^{13}$C NMR of **8** at 50 °C

Fig. 2. $^{13}$C NMR spectrum of **8** at different temperature conditions

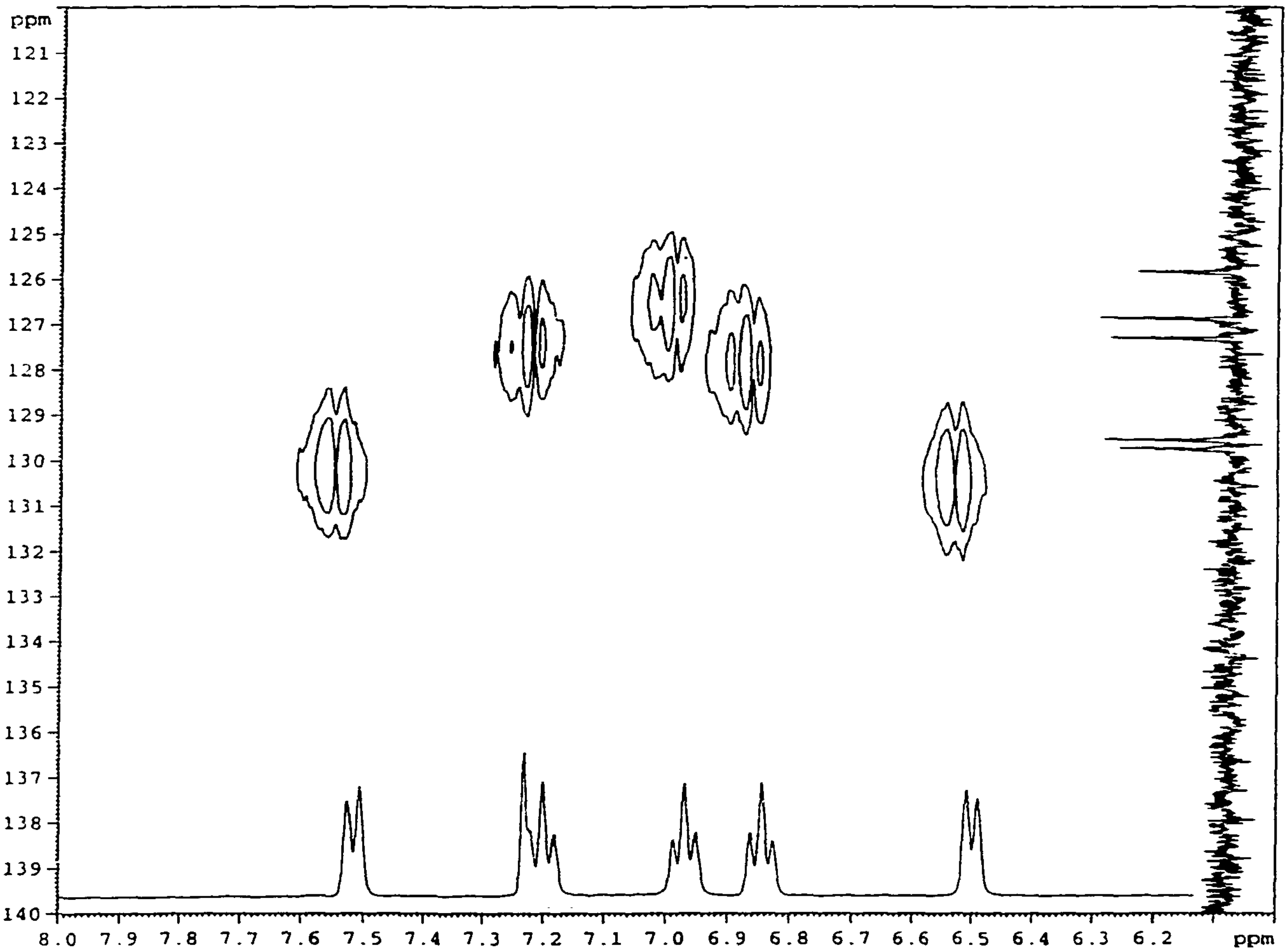


Fig. 3. 2D NMR showing H-C coupling in **8**

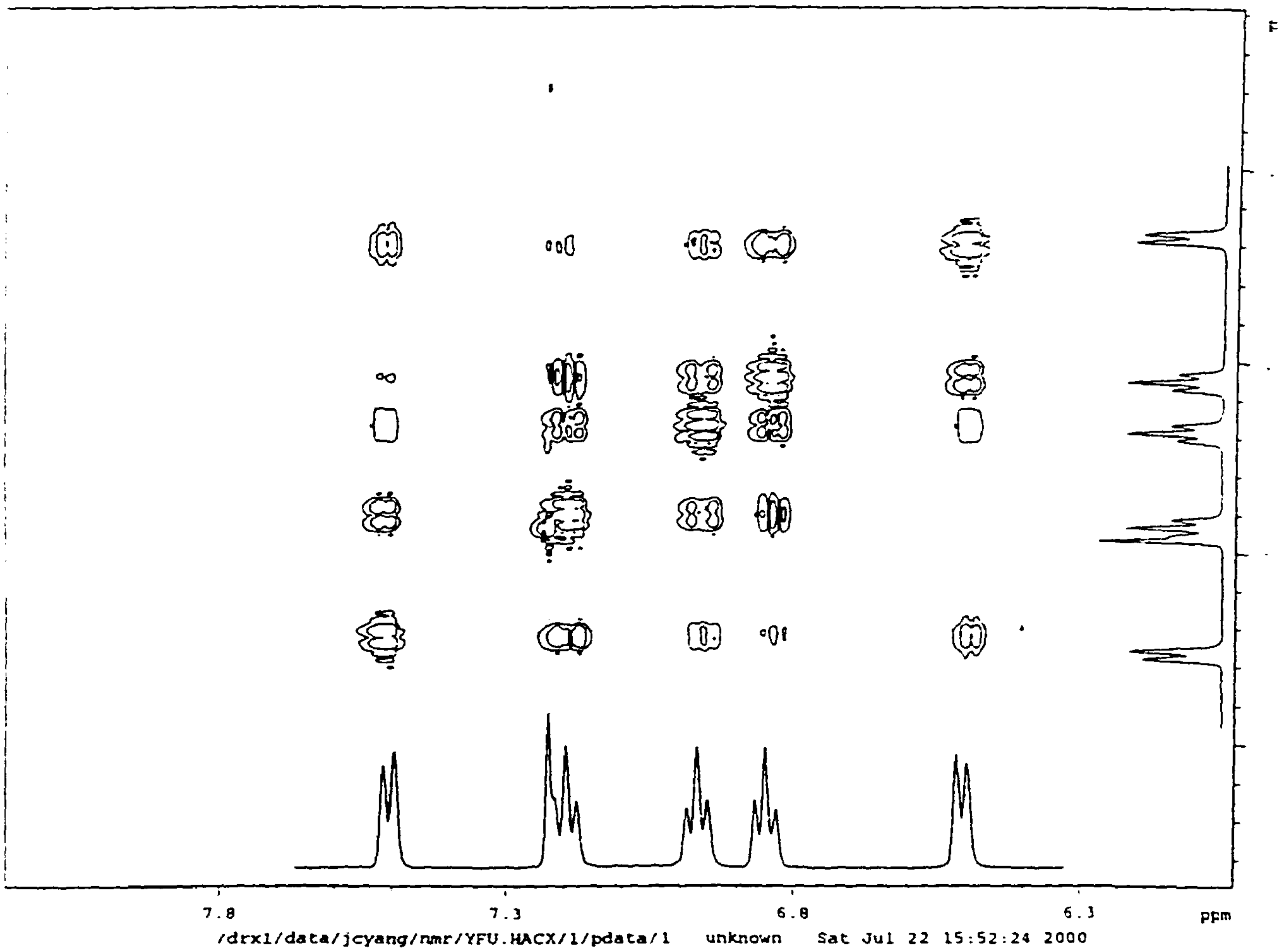


Fig. 4. 2D NMR showing H-H coupling in **8**

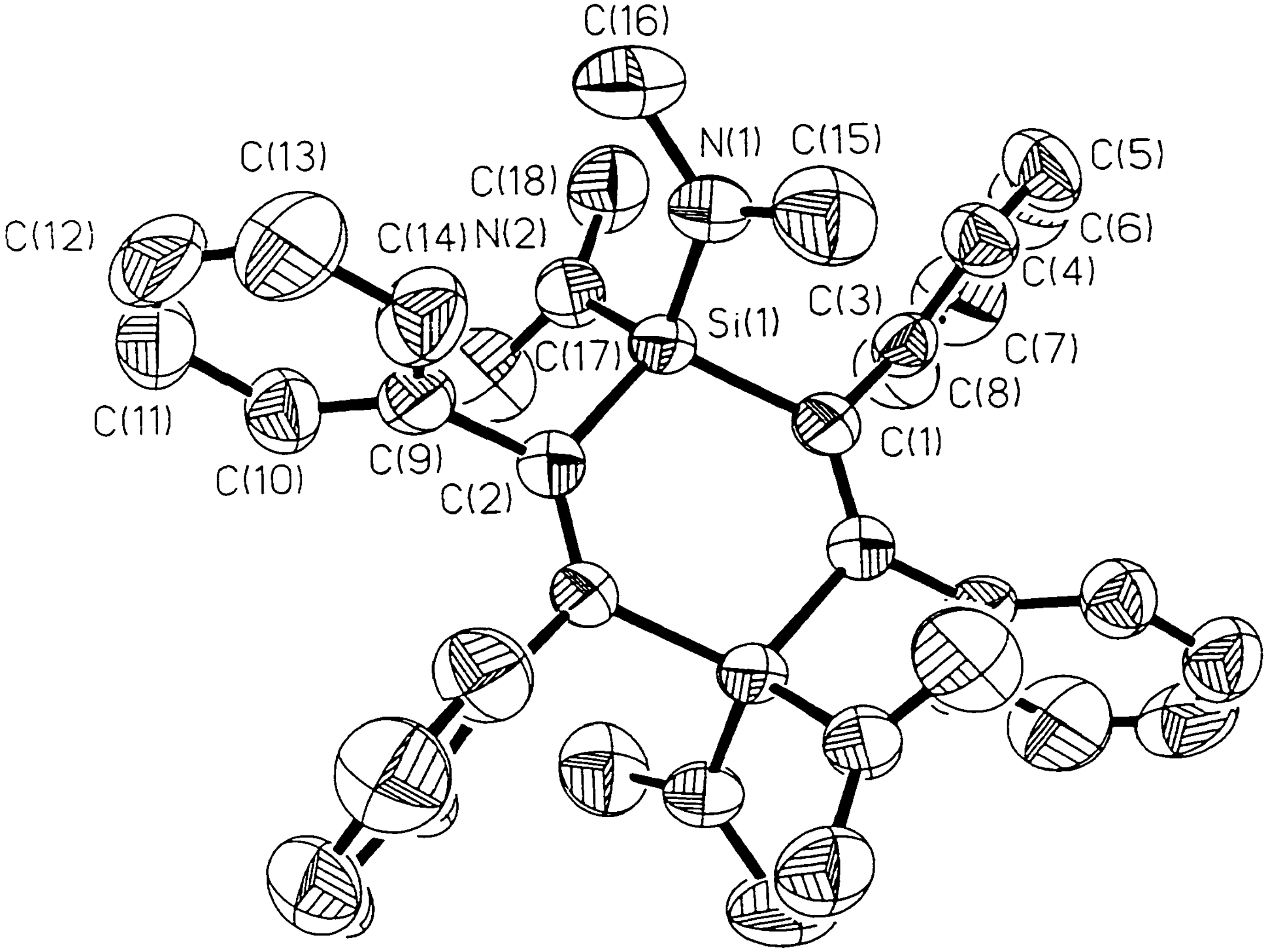


Fig. 5. ORTEP drawing of structure **4**

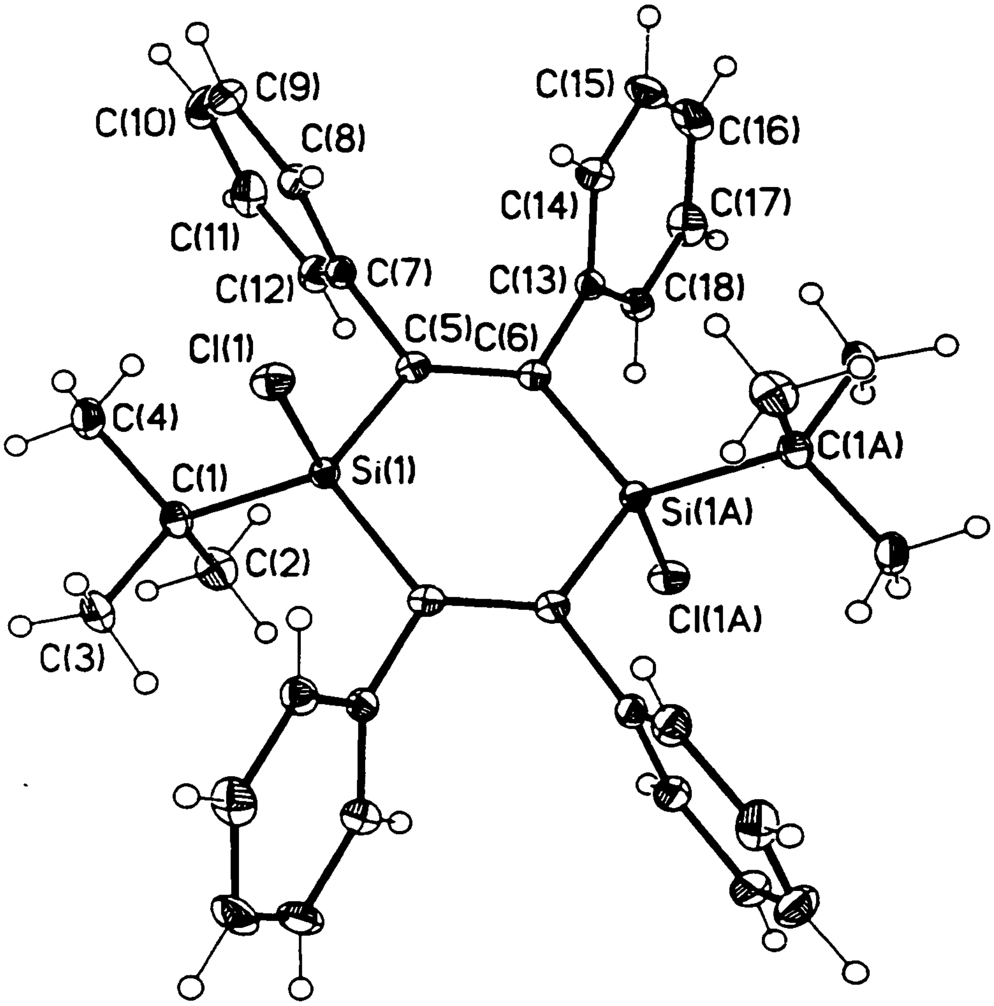


Fig. 6. ORTEP drawing of structure **8**

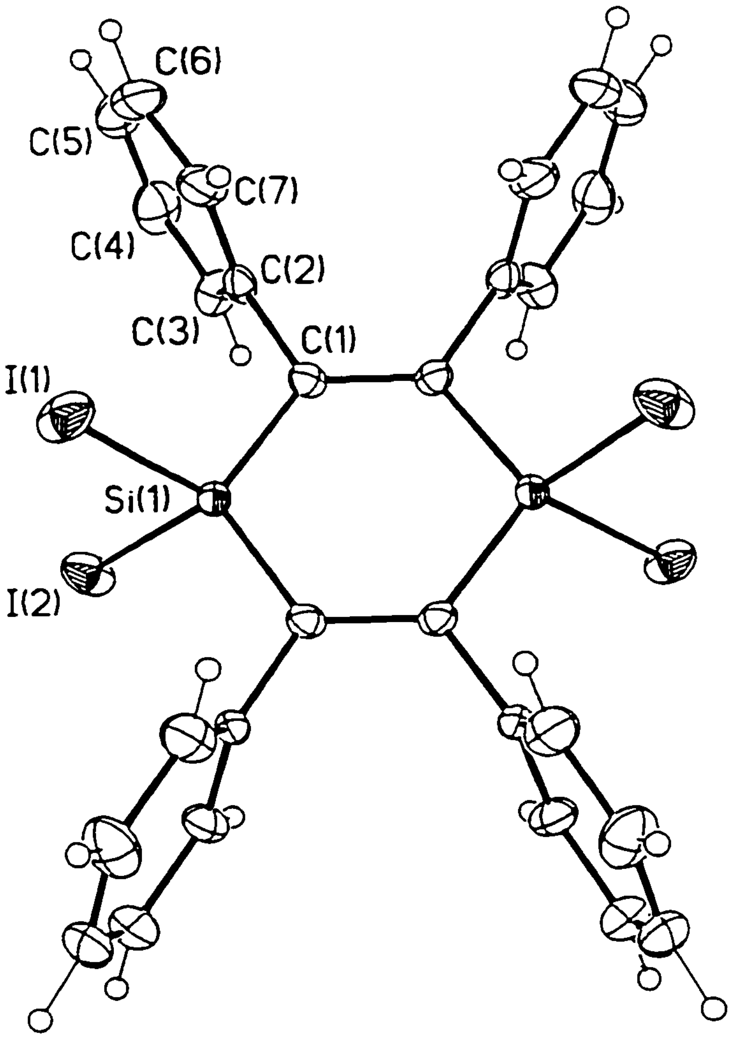


Fig. 7. ORTEP representation of structure **9c**

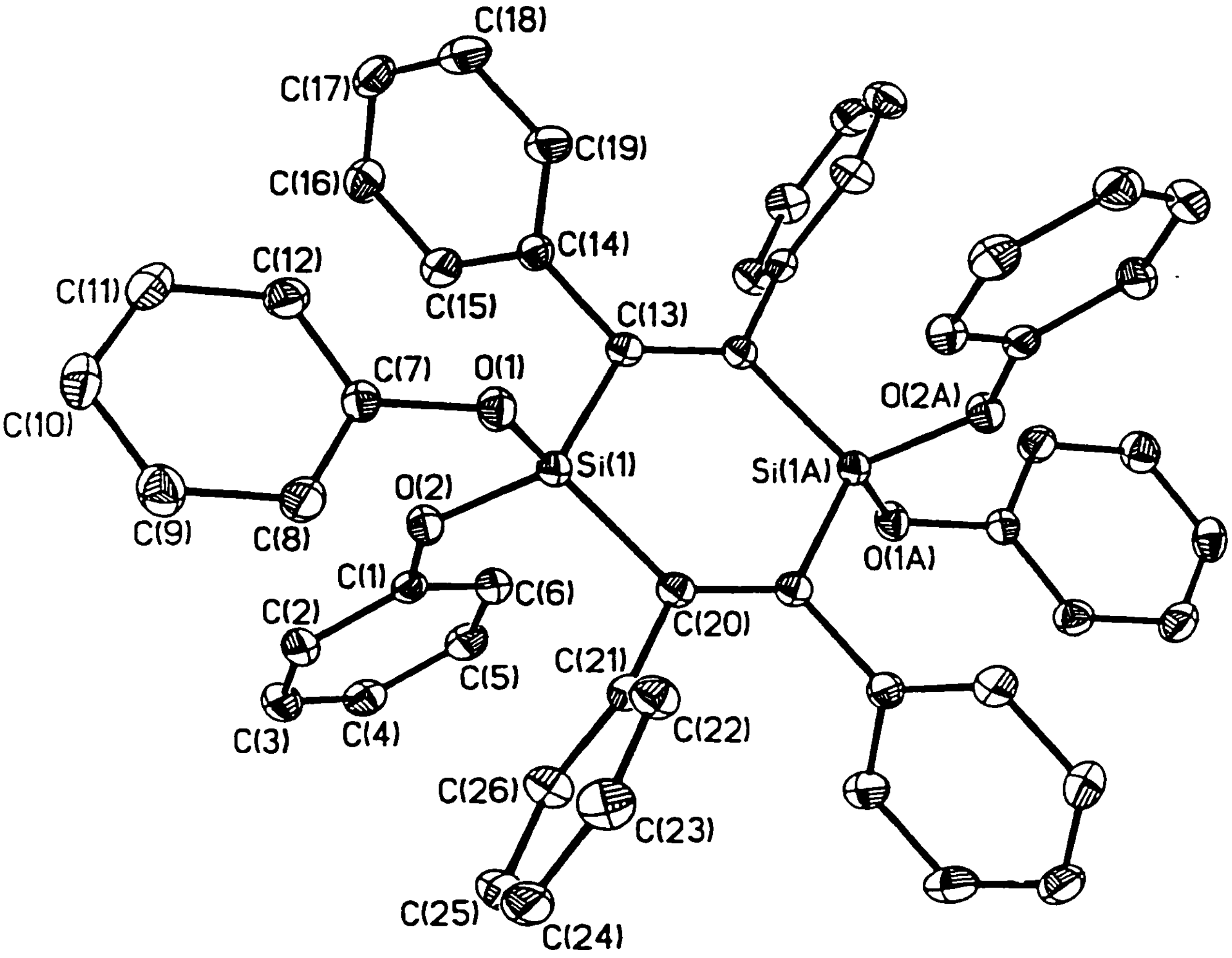


Fig. 8. ORTEP representation of structure **9e**

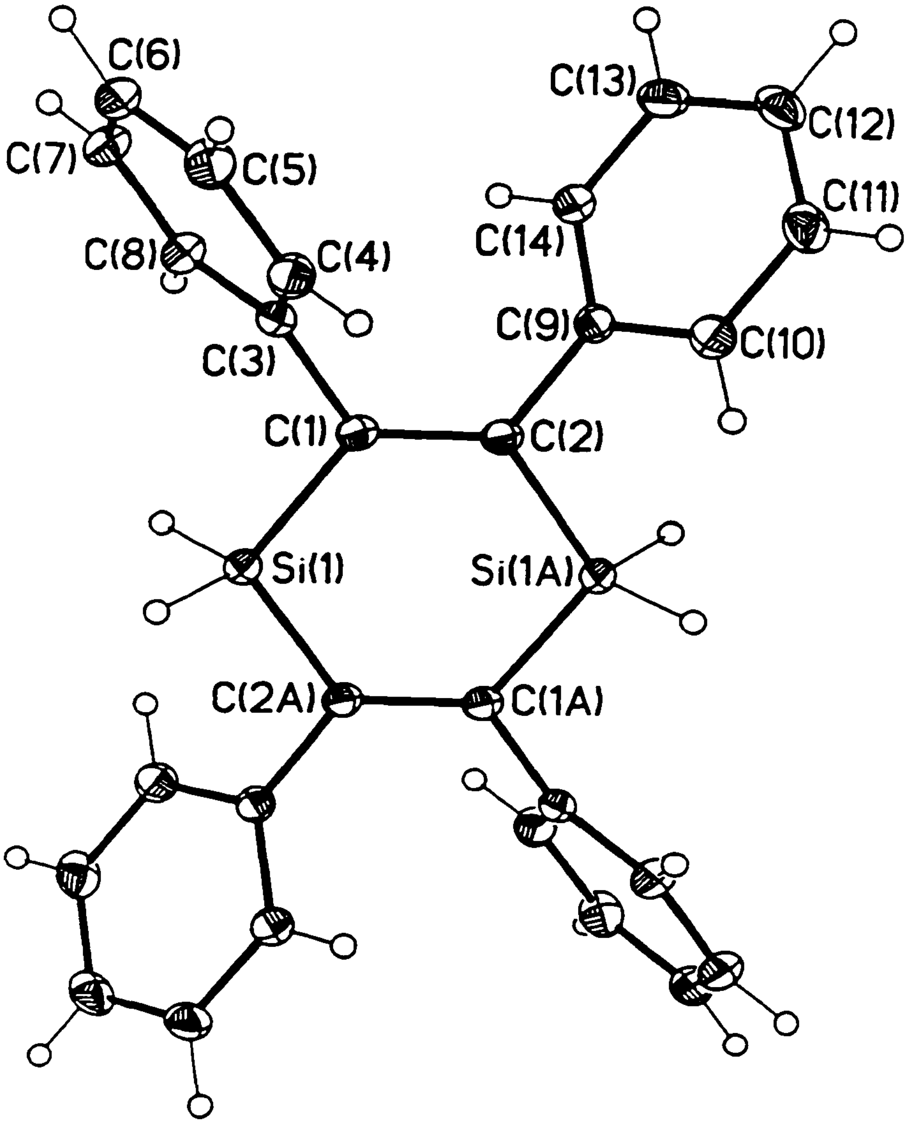


Fig. 9. ORTEP representation of structure **10**

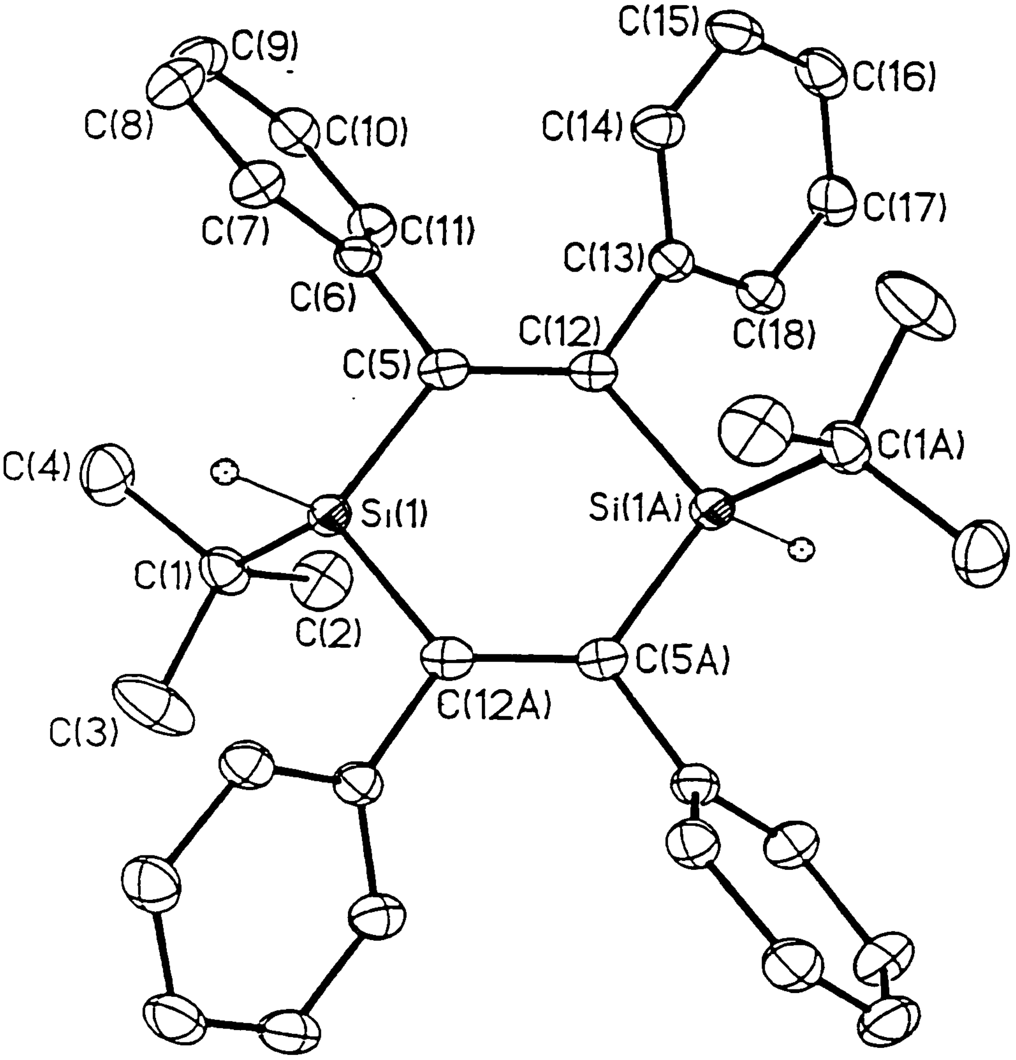


Figure 10. ORTEP representation of structure **13**

## Acknowledgements

The authors thank National Science Foundation (NSF) and Petroleum Research Foundation (PRF) for grant support, also thanks to Dr. Zhigang Wang, a former postdoctor in this research group; Dr. Philip Kisanga for helpful suggestions; Dr. Robson Matos for assistance in obtaining crystals of compound **13** suitable for X-ray diffraction analysis.

## References

1. Yang, J.; Verkade, J.; *J. Am. Chem. Soc.* **1998**, *120*, 6834.
2. Yang, J.; Verkade, J. *Organometallics* **2000**, *19*, 893.
3. Chernyshev, E.; Komalenkova, N.; Bashkirova, S. *USSR Zh. Obshch. Khim.* **1971**, *41*, 1175.
4. (a) Atwell, W.; Weyenberg, D. *J. Am. Chem. Soc.* **1968**, *90*, 3438. (b) Chernyshev, E.; Komalenkova, N.; Bashkirova, S. *J. Gen. Chem. USSR* **1971**, *41*, 1177. (c) Chernyshev, E.; Komalenkova, N.; Bashkirova, S.; Sokolov, V. *J. Gen. Chem. USSR* **1978**, *48*, 757. (d) Welsh, K.; Corey, J. *Organometallics* **1987**, *6*, 1393. (e) Maiser, G.; Reisenauer, H.; Schottler, K.; Wessolek-Kraus, U. *J. Organomet. Chem.* **1989**, *366*, 25. (f) Maiser, G.; Schottler, K.; Reisenauer, H. *Tetrahedron Lett.* **1985**, *26*, 4079.
5. Tanaka, Y.; Yamashita, H.; Tanaka, M. *Organometallics* **1995**, *14*, 530.

6. Medvedeva, A.; Lyashenko, G.; Kozyreva, O.; Voronkov, M. *Russ. J. Gen. Chem.* **1995**, *65*, 145.

7. Sakurai, H.; Koyama, T.; Kira, M.; Hosomi, A.; Nakadaira, Y. *Tetrahedron Lett.* **1982**, *23*, 543.

8. Naka, A.; Yoshizawa, K; Kang, S.; Yamabe, T.; Ishikawa, M. *Organometallics*, **1998**, *17*, 5830.

9. (a) Wiberg, E.; Stecher, O.; Neumaier, A. *Inorg. Nucl. Chem. Letters* **1965**, *1*, 33. (b) Wan, Y.; Verkade, J. *Inorg. Chem.* **1993**, *32*, 431.

10. Hengge, E.; Pletka, H.; Hoefler, F. *Monatsh. Chem.* **1970**, *101*, 325.

11. Reiter, B.; Hassler, K. *J. Organomet. Chem.* **1994**, *467*, 21.

12. Wan, Y. *Ph. D. Thesis*, Iowa State University, **1994**.

13. (a) Barton, T.; Kilgour, J. *J. Am. Chem. Soc.* **1976**, *98*, 7746. (b) Chernyshev, E.;Komalenkova, N.; Bashkirova, S.; Sokolov, V. *USSR. Zh. Obshch. Khim.* **1978**, *48*, 830. (c) Chernyshev, E.; Komalenkova, N.; Bashkirova, S. *USSR. Dokl. Akad. Nauk SSSR* **1972**, *205*, 868.

14. (a) Tsutsui, S.; Sakamoto, K.; Kira, M. *J. Am. Chem. Soc.* **1998**, *120*, 9955. (b) Kwak, Y.; Lee, K. *J. Organomet. Chem.* **1997**, *542*, 219. (c) Lee, D.; Kim, C.; Lee, M. *Phosphorus, Sulfur Silicon Relat. Elem.* **1996**, *119*, 37. And references therein.

15. Yang, J.; Verkade, J. to be published.

# APPENDIX

## SUPPLEMENTAL MATERIAL 1. X-RAY DATA FOR *1,1,4,4-TETRAKIS*(DIMETYLAMINO)-*2,3,5,6*-TETRAPHENYL-*1,4*-DISILACYCLOHEXA-*2,5*-DIENE, 4

A crystal of the compound was mounted on a glass fiber on the Enraf-Nonius CAD4 for a data collection at 293(2) ± 1 K. The cell constant for the data collection were determined from reflections found from a 360 °C rotation photograph. 25 reflections in the range of 7.36-13.76°θ were used to determine precise cell constants. Pertinent data collection and reduction information is given in Table 1.

Lorentz and polarization corrections were applied. A nonlinear correction based on the decay in the standard reflections was applied to the data. A series of azimuthal reflections was collected for the specimen. A semi-empirical absorption correction was applied to the data.

The space group $P2_1/n$ was chosen based on systematic absences and intensity statistics. This assumption proved to be correct ad determined by a successful direct-methods solution[1] and subsequent refinement. All non-hydrogen and hydrogen atoms were placed directly from the E-map. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined individual isotropic displacement parameters. Final refinements were done with SHELXL-93.[2, 3]

Data collection and structure solution were conducted at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment MicroVAX 3100 computer using the SHELXTL-Plus[1] and SHELXL-93.[2]

## REFERENCES

1. SHELXTL-PLUS, Siemens Analytical X-ray Instruments, Inc. Madison, WI.

1. SHELXL-93, G. M. Sheldrick, *J. Appl. Cryst.* In preparation.

1. All X-ray scattering factors and anomalous dispersion terms were obtained from the "International Table for Crystallography", Vol. C, pp. 4.2.6.8 and 6.1.1.4.

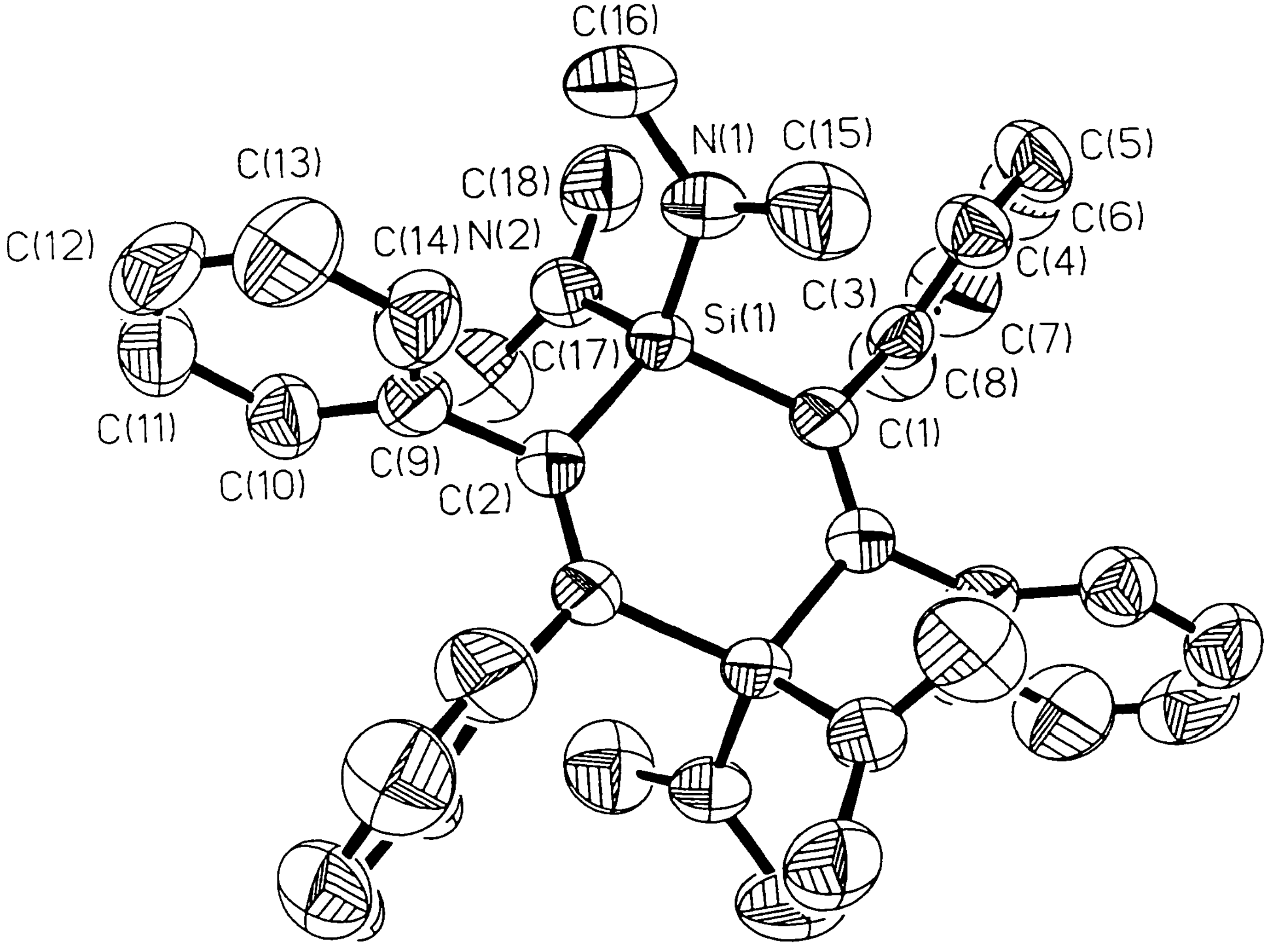


**Figure 1.** Molecular structures of **4**.

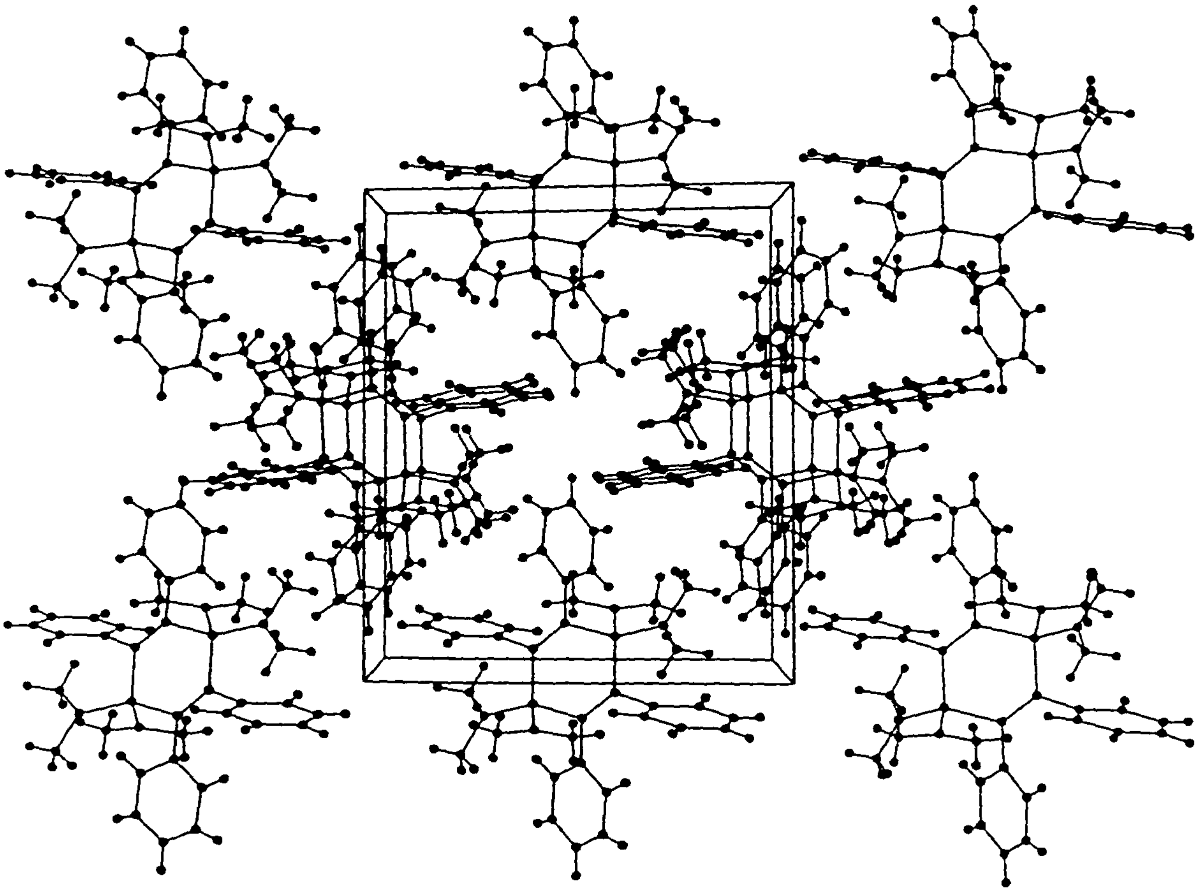


Figure 2. Unit cell drawing for the structure of 4

Table 1. Crystallographic Data for **4**

| | |
|---|---|
| Empirical Formula | $C_{36}H_{44}N_4Si_2$ |
| Color, Habit | Clear, pyramid |
| Crystal Size (mm) | 0.4 x 0.4 x 0.3 |
| Crystal System | Monoclinic |
| Space Group | $P2_1/n$ |
| Unit Cell Dimensions | a = 8.963(2) Å |
| | b = 15.510(3) Å |
| | c = 12.473(2) Å |
| | $\alpha$ = 90 ° |
| | $\beta$ = 98.15(3) ° |
| | $\gamma$ = 90 ° |
| Volume | 1716.4(6) $Å^3$ |
| Z | 2 |
| Formula Weight | 588.93 |
| Density (calc.) | 1.140 $Mg/m^3$ |
| Absorption Coefficient | 0.133 $mm^{-1}$ |
| F (000) | 632 |
| Diffractometer Used | Enraf-Nonious CAD4 |
| Radiation | MoK$\alpha$ ($\lambda$ = 0.71073 Å) |
| Temperature (K) | 293(2) |
| Monochromator | graphite |
| $\theta$ Range | 2.11 to 27.47 ° |
| Scan Type | $omega - 2$theta |
| Standard Reflections | 3 measured every 60 minutes |
| Index Ranges | $-1 \leq h \leq 11$ |
| | $-1 \leq k \leq 20$ |
| | $-16 \leq l \leq 16$ |
| Reflections Collected | 5025 |

Table 1. Continued

| | |
|---|---|
| Independent Reflections | 3937 ($R_{int}$ = 0.0340) |
| Observed Reflections | 2071 ($I \geq 2\sigma(I)$) |
| Max. /Min. Transmission | 0.601/0.552 |
| Absorption Correction | Semi-empirical |
| System Used | SHELXL-93 (Sheldrick, 1993) |
| Solution | direct |
| Refinement Correction | Full-matrix least-squares on $F_2$ |
| Extinction Correction | none |
| Extinction Expression | none |
| Hydrogen Atoms | isotropic |
| Weighting Scheme | w = calc w = $1/[\sigma^2(Fo^2) +$<br>$(0.0860P)^2 + 0.6620P]$<br>where $P = (Fo^2 + 2Fc^2) / 3$ |
| Parameters Refined | 253 |
| Final R Indices [$I \geq 2\sigma(I)$] | R1 = 0.0689, wR2 = 0.1623 |
| R Indices (all data) | R1 = 0.1611, wR2 = 0.2070 |
| GooF, Observed and All Data | 1.147, 1.035 |
| Largest and Mean $\Delta/\sigma$ | 0.227, 0.028 |
| Largest Difference Peak | 0.306 e/Å$^{-3}$ |
| Largest Difference Hole | -0.258 e/Å$^{-3}$ |

$R1 = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$

$wR2 = [\Sigma[\omega (Fo^2 - Fc^2)^2] / \Sigma[\omega (Fo^2)^2]]^{0.5}$

where $w = 1/[\sigma^2(Fo^2) + a * P)^2 + b * P + d + e * sin\theta]$

$GooF = [\Sigma[\omega(Fo^2 - Fc^2)^2] / (n - p)]^{0.5}$

Table 2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for **4**

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Si(1) | 273(1) | 4295(1) | 8993(1) | 43(1) |
| N(1) | -923(4) | 4070(2) | 829(2) | 63(1) |
| N(2) | 1800(3) | 3599(2) | 9013(2) | 57(1) |
| C(1) | 871(4) | 5420(2) | 9004(2) | 43(1) |
| C(2) | -664(3) | 4013(2) | 10215(3) | 43(1) |
| C(3) | 1805(4) | 5648(2) | 8132(3) | 50(1) |
| C(4) | 1176(5) | 694(3) | 7051(3) | 65(1) |
| C(5) | 2062(8) | 5869(3) | 6258(4) | 89(2) |
| C(6) | 3576(8) | 5998(3) | 6515(5) | 97(2) |
| C(7) | 4182(6) | 5944(4) | 7553(6) | 96(2) |
| C(8) | 3336(5) | 5770(3) | 8367(4) | 74(1) |
| C(9) | -1298(4) | 3113(2) | 10190(3) | 51(1) |
| C(10) | -564(5) | 2445(3) | 10789(3) | 67(1) |
| C(11) | -1153(8) | 1608(3) | 10690(5) | 86(2) |
| C(12) | -2448(9) | 1449(4) | 10050(5) | 102(2) |
| C(13) | -3165(8) | 2083(5) | 9486(5) | 112(2) |
| C(14) | -2617(6) | 2912(3) | 9541(4) | 82(1) |
| C(15) | -2173(6) | 4643(4) | 7493(5) | 91(2) |
| C(16) | -1067(7) | 3257(4) | 7245(5) | 106(2) |
| C(17) | 2728(6) | 3391(5) | 9993(5) | 93(2) |
| C(18) | 2577(7) | 3474(4) | 8089(5) | 85(2) |

Equivalent isotropic U defined as one third of the trace of the orthogonalized Uij tensor.

Table 3. Bond Distances (Å) for **4**

| | | | |
|---|---|---|---|
| Si(1) - N(1) | 1.703(3) | C(7) – C(8) | 1.377(6) |
| Si(1) – N(2) | 1.707(3) | C(9) – C(14) | 1.371(6) |
| Si(1) – C(1) | 1.878(3) | C(9) – C(10) | 1.387(5) |
| Si(1) – C(2) | 1.881(3) | C(10) – C(11) | 1.401(7) |
| N(1) – C(15) | 1.444(6) | C(11) – C(12) | 1.335(8) |
| N(1) – C(16) | 1.453(6) | C(12) – C(13) | 1.321(9) |
| N(2) – C(17) | 1.415(6) | C(13) – C(14) | 1.375(7) |
| N(2) – C(18) | 1.441(5) | | |
| C(1) – C(3) | 1.505(4) | | |
| C(2) - C(1)A1 | 1.345(4) | | |
| C(2) – C(9) | 1.506(5) | | |
| C(3) – C(8) | 1.375(6) | | |
| C(3) – C(4) | 1.388(5) | | |
| C(4) – C(5) | 1.381(6) | | |
| C(5) - C(6) | 1.364(8) | | |
| C(6) – C(7) | 1.334(8) | | |

Symmetry transformations used to generate equivalent atoms:

A1 -x, -y+1, -z+2

Table 4. **Bond Angles (degree) of 4**

| | | | |
|---|---|---|---|
| N(1) – Si(1) – N(2) | 108.4(2) | C(9) – C(2) – Si(1) | 112.4(2) |
| N(1) – Si(1) – C(1) | 108.4(2) | (8) – C(3) – C(4) | 117.1(4) |
| N(2) – Si(1) – C(1) | 110.4(2) | C(8) – C(3) – C(1) | 121.3(3) |
| N(1) – Si(1) – C(2) | 110.8(2) | C(4) – C(3) –C(1) | 121.5(3) |
| N(2) – Si(1) – C(2) | 108.42(14) | C(5) – C(4) – C(3) | 120.7(5) |
| C(1) – Si(1) – C(2) | 110.35(14) | C(6) – C(5) – C(4) | 121.0(5) |
| C(15) – N(1) – C(16) | 112.2(4) | C(7) – C(6) – C(5) | 118.2(5) |
| C(15) – N(1) – Si(1) | 120.7(3) | C(6) – C(7) – C(8) | 122.5(5) |
| C(16) – N(1) – Si(1) | 125.3(3) | C(3) – C(8) – C(7) | 120.4(5) |
| C(17) – N(2) – C(18) | 111.7(4) | C(14) – C(9) – C(10) | 116.9(4) |
| C(17) – N(2) – Si(1) | 121.4(3) | C(14) – C(9) – C(2) | 120.9(3) |
| C(18) – N(2) – Si(1) | 123.1(3) | C(10) – C(9) – C(2) | 122.2(3) |
| C(2)A1 – C(1) – C(3) | 121.2(3) | C(9) – C(10) – C(11) | 120.0(5) |
| C(2)A1 – C(1) – Si(1) | 124.3(2) | C(12) – C(11) – C(10) | 120.6(5) |
| C(3) - C(1) – Si(1) | 114.0(2) | C(13) – C(12) – C(11) | 119.8(5) |
| C(1)A1 – C(2) – C(9) | 122.1(3) | C(12) – C(13) – C(14) | 121.7(6) |
| C(1)A1 – C(2) – Si(1) | 125.3(2) | C(13) – C(14) – C(9) | 120.9(5) |

Symmetry transformations used to generate equivalent atoms:

A1 -x, -y+1, -z+2

Table 5. Anistropic displacement parameters (Å$^2$ x 10$^3$) for **4**.

| Atom | U$^{11}$ | U$^{22}$ | U$^{33}$ | U$^{23}$ | U$^{13}$ | U$^{12}$ |
|---|---|---|---|---|---|---|
| Si(1) | 47(1) | 44(1) | 40(1) | −2(1) | 8(1) | −1(1) |
| N(1) | 75(2) | 60(2) | 49(2) | −7(1) | −3(2) | −5(2) |
| N(2) | 64(2) | 55(2) | 56(2) | 5(1) | 22(2) | 13(2) |
| C(1) | 42(2) | 46(2) | 41(2) | 2(1) | 7(1) | 0(2) |
| C(2) | 39(2) | 44(2) | 46(2) | 2(1) | 3(1) | −2(1) |
| C(3) | 56(2) | 41(2) | 56(2) | 0(2) | 18(2) | 5(2) |
| C(4) | 76(3) | 68(3) | 55(2) | 9(2) | 21(2) | 11(2) |
| C(5) | 127(5) | 89(3) | 58(3) | 22(3) | 35(3) | 20(3) |
| C(6) | 125(5) | 84(3) | 99(4) | 18(3) | 79(4) | 10(3) |
| C(7) | 73(3) | 102(4) | 122(5) | 7(3) | 47(4) | −10(3) |
| C(8) | 66(3) | 86(3) | 76(3) | 5(3) | 25(2) | −4(2) |
| C(9) | 57(2) | 48(2) | 52(2) | −4(2) | 21(2) | −7(2) |
| C(10) | 74(3) | 60(3) | 69(3) | 9(2) | 20(2) | −1(2) |
| C(11) | 118(5) | 57(3) | 90(4) | 14(3) | 44(3) | 6(3) |
| C(12) | 155(6) | 57(3) | 106(4) | −19(3) | 59(4) | −44(4) |
| C(13) | 119(5) | 91(4) | 123(5) | −13(4) | 7(4) | −61(4) |
| C(14) | 85(3) | 61(3) | 96(4) | 4(2) | 1(3) | −23(3) |
| C(15) | 82(4) | 96(4) | 86(3) | 7(3) | −24(3) | −12(3) |
| C(16) | 143(6) | 100(4) | 71(3) | −29(3) | 1(4) | −19(4) |
| C(17) | 67(3) | 122(5) | 92(4) | 14(4) | 22(3) | 30(3) |
| C(18) | 98(4) | 72(3) | 97(4) | 5(3) | 49(3) | 20(3) |

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 (h^2 a * U11 + ... + 2hka*b*U12)$

Table 6. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$ x $10^3$) for **4**. Equivalent isotropic U defined as one third of the trace of the orthogonalized Uij tensor.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(4) | 231(39) | 5555(22) | 6869(27) | 0.050 |
| H(5) | 1602(39) | 5885(22) | 5619(28) | 0.050 |
| H(6) | 4161(38) | 6150(21) | 5978(27) | 0.050 |
| H(7) | 5031(42) | 6012(25) | 7767(30) | 0.050 |
| H(8) | 3724(37) | 5676(21) | 9077(27) | 0.050 |
| H(11) | -505(39) | 1324(24) | 11144(28) | 0.050 |
| H(12) | -2853(37) | 902(23) | 10041(25) | 0.050 |
| H(10) | 270(39) | 2579(22) | 11242(27) | 0.050 |
| H(13) | -3912(43) | 2061(26) | 9129(31) | 0.050 |
| H(14) | -3063(39) | 3305(23) | 9112(27) | 0.050 |
| H(15A) | -2106(38) | 5195(23) | 7851(27) | 0.050 |
| H(15B) | -3122(41) | 4389(22) | 7703(26) | 0.050 |
| H(15C) | -2383(36) | 4754(21) | 6716(28) | 0.050 |
| H(16A) | -935(39) | 3354(23) | 6578(28) | 0.050 |
| H(16B) | -369(31) | 2892(18) | 7563(21) | 0.050 |
| H(16C) | -2078(31) | 2992(18) | 7295(21) | 0.080 |
| H(17A) | 3586(41) | 3634(23) | 10002(28) | 0.050 |
| H(17B) | 2932(42) | 2884(23) | 10010(28) | 0.050 |
| H(17C) | 2272(38) | 3487(21) | 10663(26) | 0.050 |
| H(18A) | 3515(39) | 3786(23) | 6146(27) | 0.050 |
| H(18C) | 2757(38) | 2909(24) | 7978(26) | 0.050 |
| H(18B) | 1950(39) | 3690(23) | 7486(27) | 0.050 |

# SUPPLEMENTAL MATERIAL 2. X-RAY DATA FOR *1,4*-DI-*TERT*-BUTYL-*1,4*-DICHLORO-*2,3,5,6*-TETRAPHENYL-*1,4*-DISILACYCLOHEXA-*2,5*-DIENE, 8

A colorless crystal with approximate dimensions 0.46 x 0.40 x 0.10 $mm^3$ was selected from oil under ambient conditions and was attached to the tip of a glass capillary. The crystal was mounted in a stream of cold nitrogen at 173(2) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo Kα (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 5.08 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames at intervals of 0.3° in a 6° range about ω with the exposure time of 10 seconds per frame. A total of 95 reflections was obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 3130 strong reflections from the actual data collection.

The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of 1.2 hemisphere to a resolution of 0.80 Å. A total of 9799 data were harvested by collecting three sets of frames with 0.3° scans in ω with an exposure time 10 second per frame. These highly redundant data sets were corrected for Lorentz and polarization effects. The absorption correction was based on

fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[1]

The systematic absences in the diffraction data were uniquely consistent for the space group $P2_1/c$ which yielded chemically reasonable and computationally stable results of refinement. A successful solution by the direct methods provided the positions of most atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anistropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The molecule occupies a crystallographic inversion center. Final least-squares refinement of 184 parameters against 3241 data resulted in residuals $R$ (based on $F^2$ for $I \geq 2\sigma$) and $wR$ (based on $F^2$ for $I \geq 2\sigma$) of 0.0333 and 0.0782, respectively. The final difference Fourier map was featureless.

## REFERENCES

1. Blessing, R. H. *Acta Cryst.* 1995, A51, 33-38.

1. All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-Ray System, Madison, WI).

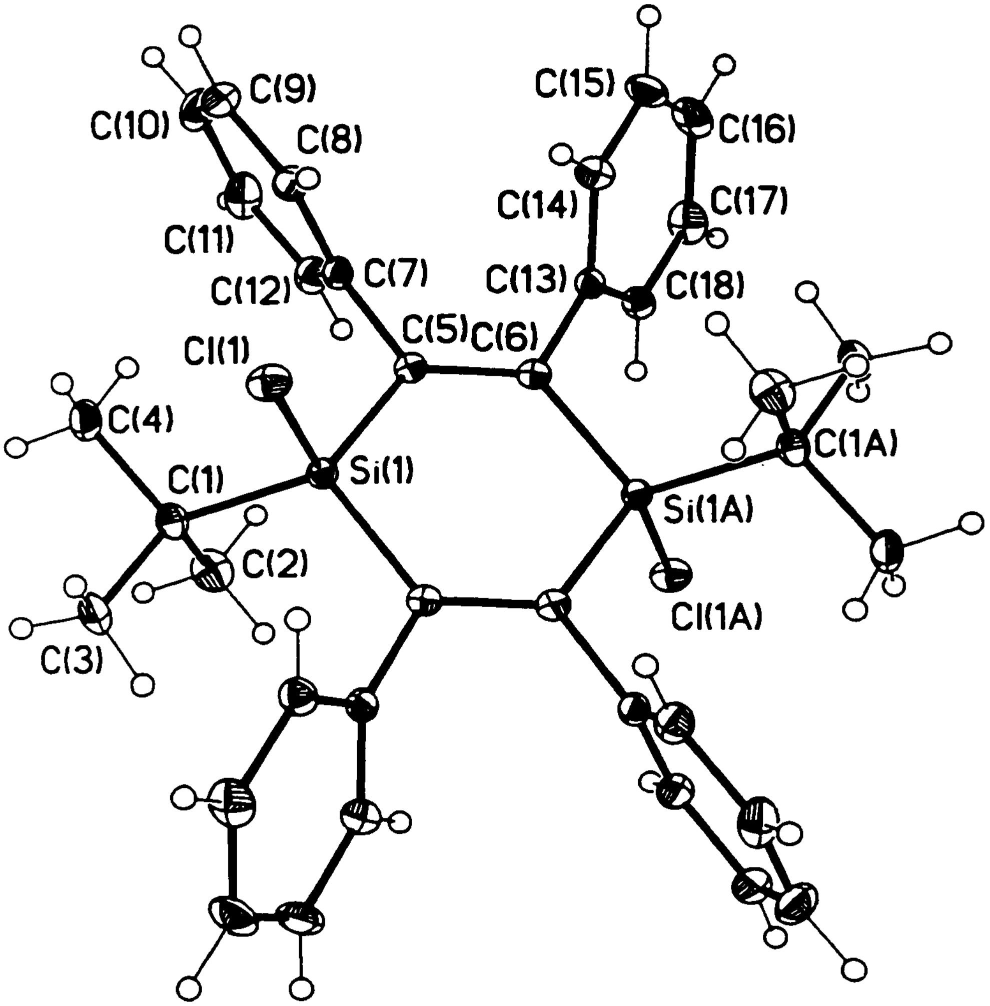


Figure 1. ORTEP drawing of **8**

Table 1. Crystallographic Data for **8**

| | | |
|---|---|---|
| Empirical Formula | $C_{36}H_{38}Cl_2Si_2$ | |
| Formula Weight | 597.74 | |
| Temperature (K) | 173(2) | |
| Wavelength | Mo Kα (λ = 0.71073 Å) | |
| Crystal System | Monoclinic | |
| Space Group | $P2_1/c$ | |
| Unit Cell Dimensions | a = 9.7708(8) Å | α = 90° |
| | b = 9.3984(8) Å | β =103.939(1)° |
| | c = 17.8150(14) Å | γ = 90° |
| Volume | 1587.8(2) $Å^3$ | |
| Z | 2 | |
| Density (calc.) | 1.250 $Mg/m^3$ | |
| Absorption Coefficient | 0.304 $mm^{-1}$ | |
| F (000) | 632 | |
| Crystal Size (mm) | 0.46 x 0.40 x 0.10 | |
| θ Range | 2.36 to 26.37 ° | |
| Index Ranges | -12 ≤ h ≤ 1  10 ≤ k ≤ 11 | |
| | 0 ≤ l ≤ 22 | |
| Reflections Collected | 9799 | |
| Independent Reflections | 3241 (R(int) = 0.0274) | |
| Completeness to theta = 26.37° | 99.8% | |
| Absorption Correction | Semi-empirical | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3241 / 0 / 184 | |
| Goodness-of-fit on $F^2$ | 1.031 | |
| Final R indices [I > 2 sigma(I)] | R1 = 0.0333, wR2 = 0.0782 | |
| R Indices (all data) | R1 = 0.0530, wR2 = 0.0835 | |
| Largest diff. peak and hole | 0.328 and –2.07 e.$Å^{-3}$ | |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for **8**.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Si(1) | 3214(1) | -77(1) | 9554(1) | 20(1) |
| Cl(1) | 1834(1) | 1141(1) | 10018(1) | 29(1) |
| C(1) | 2113(2) | –1025(2) | 8673(1) | 24(1) |
| C(2) | 3145(2) | –1808(2) | 8287(1) | 36(1) |
| C(3) | 1083(2) | –2109(2) | 8882(1) | 32(1) |
| C94) | 1214(2) | 20(2) | 8091(11) | 33(1) |
| C(5) | 4493(2) | 1225(2) | 9297(1) | 20(1) |
| C(6) | 5891(2) | 1312(2) | 9651(1) | 20(1) |
| C(7) | 3883(2) | 2210(2) | 8634(1) | 23(1) |
| C(8) | 2946(2) | 3293(2) | 8704(1) | 28(1) |
| C(9) | 2368(2) | 4163(2) | 8085(1) | 38(1) |
| C(10) | 2696(2) | 3945(2) | 7377(1) | 44(1) |
| C(11) | 3614(2) | 2882(2) | 7301(1) | 39(1) |
| C(12) | 4222(2) | 2106(2) | 7926(1) | 30(1) |
| C(13) | 6769(2) | 2482(2) | 9430(1) | 21(1) |
| C(14) | 6418(2) | 3896(2) | 9527(1) | 29(1) |
| C(15) | 7214(2) | 4999(2) | 9343(1) | 37(1) |
| C(16) | 8386(2) | 4717(2) | 9060(1) | 40(1) |
| C(17) | 8747(2) | 3321(2) | 8961(1) | 36(1) |
| C(18) | 7952(2) | 2213(2) | 9140(1) | 26(1) |

Equivalent isotropic U defined as one third of the trace of the orthogonalized Uij tensor.

Table 3. Bond lengths (Å) and bond angles (°) for **8**.

| | | | |
|---|---|---|---|
| Si(1)-C(6)#1 | 1.8772(16) | C(7)-C(8) | 1.395(2) |
| Si(1)-C(5) | 1.8824(17) | C(8)-C(9) | 1.381(2) |
| Si(1)-C(1) | 1.8971(17) | C(9)-C(10) | 1.388(3) |
| Si(1)-Cl(1) | 2.0853(6) | C(10)-C(11) | 1.370(3) |
| C(1)-C(2) | 1.538(2) | C(11)-C(12) | 1.391(2) |
| C(1)-C(4) | 1.540(2) | C(13)-C(14) | 1.394(2) |
| C(1)-C(3) | 1.540(2) | C(13)-C(18) | 1.398(2) |
| C(5)-C(6) | 1.362(2) | C(14)-C(15) | 1.382(2) |
| C(5)-C(7) | 1.505(2) | C(15)-C(16) | 1.383(2) |
| C(6)-C(13) | 1.504(2) | C(16)-C(17) | 1.381(3) |
| C(6)-Si(1)#1 | 1.8772(16) | C(17)-C(18) | 1.382(2) |
| C(7)-C(12) | 1.392(2) | | |

| | | | |
|---|---|---|---|
| C(6)#1-Si(1)-C(5) | 111.67(7) | C(6)#1-Si(1)-C(1) | 113.71(8) |
| C(5)-Si(1)-C(1) | 112.49(7) | C(5)-C(6)-C(13) | 119.61(14) |
| C(6)#1-Si(1)-Cl(1) | 105.54(5) | C(5)-C(6)-Si(1)#1 | 123.06(12) |
| C(5)-Si(1)-Cl(1) | 105.67(5) | C(13)-C(6)-Si(1)#1 | 117.28(11) |
| C(1)-Si(1)-Cl(1) | 107.07(5) | C(12)-C(7)-C(8) | 118.75 |
| C(2)-C(1)-C(4) | 109.40(14) | C(12)-C(7)-C(5) | 119.69(16) |
| C(2)-C(1)-C(3) | 109.21(15) | C(8)-C(7)-C(5) | 121.52(15) |
| C(4)-C(1)-C(3) | 106.54(14) | C(9)-C(8)-C(7) | 120.78(17) |
| C(2)-C(1)-Si(1) | 107.01(11) | C(8)-C(9)-C(10) | 119.91(19) |
| C(4)-C(1)-Si(1) | 112.03(12) | C(11)-C(10)-C(9) | 119.85(18) |
| C(3)-C(1)-Si(1) | 112.62(11) | C(10)-C(11)-C(12) | 120.69(18) |
| C(6)-C(5)-C(7) | 119.33(14) | C(11)-C(12)-C(7) | 119.99(18) |
| C(6)-C(5)-Si(1) | 125.25(12) | C(14)-C(13)-C(18) | 117.92(16) |
| C(7)-C(5)-Si(1) | 115.41(11) | C(14)-C(13)-C(6) | 119.46(15) |
| C(18)-C(13)-C(6) | 122.60(15) | C(17)-C(16)-C(15) | 119.24(18) |
| C(15)-C(14)-C(13) | 121.08(17) | C(16)-C(17)-C(18) | 120.74(17) |
| C(14)-C(15)-C(16) | 120.36(19) | C(17)-C(18)-C(13) | 120.66(18) |

Symmetry transformations used to generated equivalent atoms: #1 -x+1, -y, -z+2.

Table 4. Anistropic displacement parameters ($Å^2$ x $10^3$) for **8**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 hka^*b^*U^{12}]$

| Atom | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Si(1) | 16(1) | 20(1) | 22(1) | 1(1) | 4(1) | 0(1) |
| Cl(1) | 28(1) | 27(1) | 36(1) | 1(1) | 14(1) | 5(1) |
| C(1) | 21(1) | 27(1) | 24(1) | -2(1) | 5(1) | -3(1) |
| C(2) | 35(1) | 38(1) | 37(1) | -10(1) | 2(1) | -2(1) |
| C(3) | 27(1) | 35(1) | 31(1) | -3(1) | 2(1) | -11(1) |
| C(4) | 27(1) | 39(1) | 27(1) | 2(1) | -4(1) | -6(1) |
| C(5) | 20(1) | 19(1) | 21(1) | 0(1) | 6(1) | 2(1) |
| C(6) | 22(1) | 18(1) | 22(1) | -1(1) | 8(1) | 1(1) |
| C(7) | 19(1) | 24(1) | 23(1) | 5(1) | 1(1) | 5(1) |
| C(8) | 24(1) | 26(1) | 30(1) | 3(1) | 3(1) | -1(1) |
| C(9) | 30(1) | 29(1) | 50(1) | 7(1) | -2(1) | 2(1) |
| C(10) | 34(1) | 48(1) | 43(1) | 24(1) | -5(1) | -3(1) |
| C(11) | 31(1) | 57(2) | 27(1) | 11(1) | 5(1) | -12(1) |
| C(12) | 22(1) | 38(1) | 30(1) | 6(1) | 5(1) | -5(1) |
| C(13) | 22(1) | 22(1) | 18(1) | 2(1) | 1(1) | -4(1) |
| C(14) | 32(1) | 25(1) | 29(1) | 1(1) | 8(1) | -2(1) |
| C(15) | 50(1) | 22(1) | 36(1) | 1(1) | 7(1) | -8(1) |
| C(16) | 44(1) | 37(1) | 37(1) | 8(1) | 10(1) | -20(1) |
| C(17) | 30(1) | 47(1) | 33(1) | 6(1) | 12(1) | -10(1) |
| C(18) | 25(1) | 27(1) | 25(1) | 1(1) | 6(1) | -3(1) |

Table 5. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$ x $10^3$) for **8**.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | 3691 | -2500 | 8650 | 54 |
| H(2B) | 3786 | -1118 | 8140 | 54 |
| H(2C) | 2614 | -2304 | 7824 | 54 |
| H(3A) | 492 | -2518 | 8407 | 48 |
| H(3B) | 482 | -1631 | 9173 | 48 |
| H(3C) | 1617 | -2869 | 9199 | 48 |
| H(4A) | 653 | -512 | 7649 | 49 |
| H(4B) | 1834 | 689 | 7910 | 49 |
| H(4C) | 582 | 546 | 8343 | 49 |
| H(8) | 2702 | 3433 | 9184 | 33 |
| H(9) | 1747 | 4911 | 8142 | 46 |
| H(10) | 2286 | 4530 | 6947 | 52 |
| H(11) | 3837 | 2735 | 6816 | 46 |
| H(12) | 4869 | 1293 | 7869 | 36 |
| H(14) | 5617 | 4106 | 9723 | 34 |
| H(15) | 6956 | 5956 | 9412 | 44 |
| H(16) | 8936 | 5475 | 8936 | 48 |
| H(17) | 8551 | 3121 | 8767 | 43 |
| H(18) | 8211 | 1259 | 9065 | 31 |

# SUPPLEMENTAL MATERIAL 3. X-RAY DATA FOR *1,1,4,4*-TETRAIODO-*2,3,5,6*-TETRAPHENYL-*1,4*-DISILACYCLOHEXA-*2,5*-DIENE, 9c

A colorless crystal with approximate dimensions 0.35 x 0.35 x 0.30 mm$^3$ was selected from oil under ambient conditions and was attached to the tip of a glass capillary. The crystal was mounted in a stream of cold nitrogen at 173(2) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K$\alpha$ ($\lambda$ = 0.71073 Å) radiation and the diffractometer to crystal distance of 5.08 cm.

The initial cell constants were obtained from three series of $\omega$ scans at different starting angles. Each series consisted of 20 frames at intervals of 0.3° in a 6° range about $\omega$ with the exposure time of 10 seconds per frame. A total of 106 reflections was obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 4805 strong reflections from the actual data collection.

The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of 1.2 hemisphere to a resolution of 0.80 Å. A total of 29948 data were harvested by collecting three sets of frames with 0.3° scans in $\omega$ with an exposure time 20 second per frame. These highly redundant data sets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[1]

The systematic absences in the diffraction data were uniquely consistent for the space groups $P4_2/mnm$, $P4nm$, and $P4_2nm$. The E-statistic was skewed due to the location of heavy atoms on special positions. Only the non-centrosymmetric space group $P4_2$nm yielded chemically reasonable and computationally stable results of refinement.[2] A successful solution by the direct methods provided the positions of most atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anistropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The molecule of the complex occupies a crystallographic two fold axis and two crystallographic mirror planes intersecting in the center of the six-membered ring. Atoms I(1), I(2), and Si(1) reside on a mirror plane. There is also one molecule of solvate chloroform per molecule of complex present in the lattice. This chloroform molecule is equally disordered over two positions over the intersection of a crystallographic two-fold axis and two mirror planes. Atom Cl(1) occupies a mirror plane. Atom Cl(2) occupies a crystallographic two-fold axis and two mirror planes. Carbon C(8) is on a mirror plane and is equally disordered over two positions. The solvate molecule of chloroform was refined with idealized C-Cl distances. The crystal was found to be a merohedral twin with a 52:48 component contribution ratio. The final least-squares refinement of 100 parameters against 2183 data resulted in residuals $R$ (based on $F^2$ for $I \geq 2\sigma$) and $wR$ (based on $F^2$ for $I \geq 2\sigma$) of 0.0275 and 0.0775, respectively. The final difference Fourier map contained three high peaks (1.92-1.19 e/Å$^3$) in the vicinity of atom Cl(1) in chemically unreasonable positions and were considered noise.

The ORTEP diagrams were drawn with 50% probability ellipsoids.

## REFERENCES

1. Blessing, R. H. *Acta Cryst.* 1995, A51, 33-38.
2. All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-Ray System, Madison, WI).

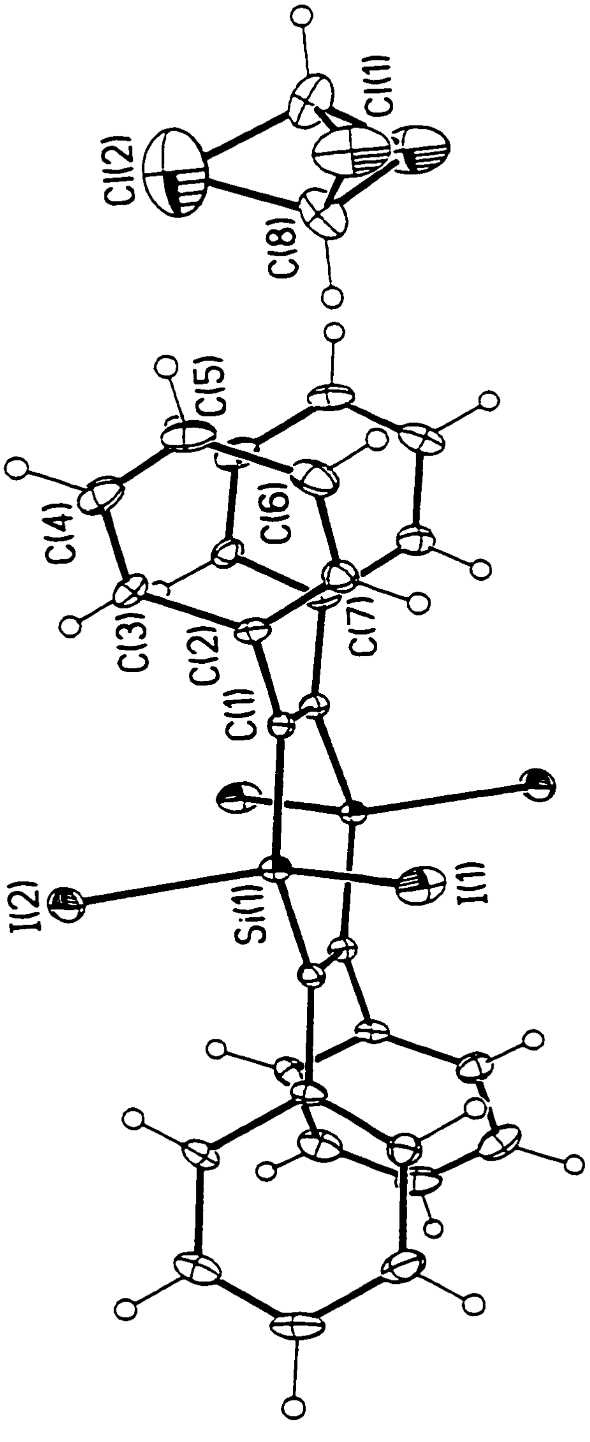


Figure 1. ORTEP drawing of **9c** with solvate $CHCl_3$ molecule.

Table 1. Crystallographic Data for **9c**

| | | |
|---|---|---|
| Empirical Formula | $C_{29}H_{21}Cl_3I_4Si_2$ | |
| Formula Weight | 1039.59 | |
| Temperature (K) | 173(2) | |
| Wavelength | MoKα (λ = 0.71073 Å) | |
| Crystal System | Tetragonal | |
| Space Group | P4(2)nm | |
| Unit Cell Dimensions | a = 11.7536(5) Å | α = 90° |
| | b = 11.7536(5) Å | β = 90° |
| | c = 12.2191(6) Å | γ = 90° |
| Volume | 1688.03(13) $Å^3$ | |
| Z | 2 | |
| Density (calc.) | 2.045 $Mg/m^3$ | |
| Absorption Coefficient | 4.019 $mm^{-1}$ | |
| F (000) | 972 | |
| Crystal Size (mm) | 0.35 x 0.35 x 0.30 | |
| θ Range | 2.40 to 28.30° | |
| Index Ranges | $-15 \leq h \leq 15$ $-15 \leq k \leq 15$ | |
| | $-16 \leq l \leq 15$ | |
| Reflections Collected | 14104 | |
| Independent Reflections | 2183 (R(int) = 0.0334) | |
| Completeness to theta = 26.37° | 99.0% | |
| Absorption Correction | Empirical with SADABS | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2183 / 3 / 100 | |
| Goodness-of-fit on $F^2$ | 1.052 | |
| Final R indices [I > 2 sigma(I)] | R1 = 0.0275, wR2 = 0.0775 | |
| R Indices (all data) | R1 = 0.0286, wR2 = 0.0782 | |
| Twin component contributions | 0.52(3) and 0.48(3) | |
| Largest diff. peak and hole | 1.920 and –0.744 e.$Å^{-3}$ | |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for **8**. Ueq is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| I(1) | 8196(1) | -1805(1) | 8586(1) | 37(1) |
| I(2) | 8079(1) | -1921(1) | 5351(1) | 34(1) |
| Cl(1) | 4129(2) | 4129(2) | 8338(3) | 81(1) |
| Cl(2) | 5000 | 5000 | 6307(5) | 139(3) |
| Si(1) | 8991(1) | -1009(1) | 6914(2) | 17(1) |
| C(1) | 8644(3) | 537(3) | 6876(4) | 17(1) |
| C(2) | 7417(3) | 854(3) | 6908(5) | 19(1) |
| C(3) | 6822(3) | 1008(4) | 5904(4) | 25(1) |
| C(4) | 5683(4) | 1321(4) | 5940(4) | 34(1) |
| C(5) | 5116(3) | 1487(4) | 6898(6) | 36(1) |
| C(6) | 5694(4) | 1331(5) | 7892(5) | 37(1) |
| C(7) | 6842(4) | 1021(4) | 7867(4) | 28(1) |
| C(8) | 5398(4) | 4602(4) | 7668(4) | 49(1) |

Table 3. **Bond lengths (Å) and bond angles (°) for 9c.**

| | | | |
|---|---|---|---|
| I(1)-Si(1) | 2.4339(19) | C(1)-C(2) | 1.491(4) |
| I(2)-Si(1) | 2.4382(18) | C(2)-C(7) | 1.367(7) |
| Cl(1)-C(8) | 1.7894(10) | C(2)-C(3) | 1.423(7) |
| Cl(2)-C(8)#1 | 1.7894(10) | C(3)-C(4) | 1.389(6) |
| Cl(2)-C(8) | 1.7896(10) | C(4)-C(5) | 1.360(8) |
| Cl(2)-C(8)#1 | 1.7896(10) | C(5)-C(6) | 1.405(8) |
| Si(1)-C(1)#2 | 1.862(3) | C(6)-C(7) | 1.397(6) |
| Si(1)-C(1) | 1.862(3) | C(8)-CL(1)#1 | 1.7894(10) |
| C(1)-C(1)#3 | 1.362(6) | | |

| | | | |
|---|---|---|---|
| C(8)-CL(1)-C(8)#1 | 43.4(5) | C(7)-C(2)-C(1) | 122.4(4) |
| C(8)-CL(2)-C(8)#1 | 43.4(5) | C(3)-C(2)-C(1) | 119.0(4) |
| C(1)#2-SI(1)-C(1) | 115.3(2) | C(4)-C(3)-C(2) | 118.7(5) |
| C(1)#2-SI(1)-I(1) | 108.14(16) | C(5)-C(4)-C(3) | 122.5(5) |
| C(1)-SI(1)-I(1) | 108.14(16) | C(4)-C(5)-C(6) | 119.2(4) |
| C(1)#2-SI(1)-I(2) | 108.27(15) | C(7)-C(6)-C(5) | 118.8(5) |
| C(1)-SI(1)-I(2) | 108.27(15) | C(2)-C(7)-C(6) | 122.2(5) |
| I(1)-SI(1)-I(2) | 108.61(5) | C(1)-C(8)-CL(1)#1 | 107.9(3) |
| C(1)#3-C(1)-C(2) | 120.51(16) | CL(1)-C(8)-CL(2) | 106.7(3) |
| C(1)#3-C(1)-SI(1) | 122.33(10) | CL(1)#1-C(8)-CL(2) | 106.7(3) |
| C(2)-C(1)-SI(1) | 117.1(2) | C(7)-C(2)-C(3) | 118.5(3) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, -y+1, z; #2 y+1, x-1, z; #3 -y+1, -x+1, z

Table 4. Anistropic displacement parameters ($Å^2 \times 10^3$) for **8**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 hka^*b^*U^{12}]$

| Atom | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| I(1) | 36(1) | 36(1) | 40(1) | 16(1) | 16(1) | 6(1) |
| I(2) | 31(1) | 31(1) | 40(1) | -13(1) | -13(1) | 4(1) |
| Cl(1) | 57(1) | 57(1) | 130(3) | 12(1) | 12(1) | 2(1) |
| Cl(2) | 166(4) | 166(4) | 86(4) | 0 | 0 | -28(6) |
| Si(1) | 14(1) | 14(1) | 23(1) | 1(1) | 1(1) | -1(1) |
| C(1) | 16(1) | 17(1) | 19(1) | -3(2) | -4(2) | 1(1) |
| C(2) | 14(1) | 13(1) | 31(2) | 0(2) | -5(2) | 0(1) |
| C(3) | 18(2) | 30(2) | 26(2) | 7(2) | -6(2) | 0(2) |
| C(4) | 22(2) | 31(2) | 50(3) | 5(2) | -11(2) | -1(2) |
| C(5) | 16(2) | 29(2) | 63(3) | 0(3) | 0(2) | 4(1) |
| C(6) | 23(2) | 39(3) | 49(3) | -14(2) | 6(2) | 2(2) |
| C(7) | 25(2) | 27(2) | 32(3) | -8(2) | -4(2) | 3(2) |
| C(8) | 49(6) | 49(6) | 50(9) | -14(5) | 14(5) | -15(7) |

Table 5. Hydrogen coordinates ( $\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **9c**.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3) | 7197 | 900 | 5223 | 30 |
| H(4) | 5284 | 1421 | 5271 | 41 |
| H(5) | 4339 | 1707 | 6893 | 43 |
| H(6) | 5312 | 1434 | 8570 | 45 |
| H(7) | 7236 | 924 | 8539 | 34 |
| H(8) | 6000 | 4000 | 7668 | 59 |

# SUPPLEMENTAL MATERIAL 4. X-RAY DATA FOR *1,1,4,4*-TETRAPHENOXY-*2,3,5,6*-TETRAPHENYL-*1,4*-DISILACYCLOHEXA*2,5*-DIENE, 9e

A colorless crystal with approximate dimensions 0.45 x 0.45 x 0.40 mm$^3$ was selected from oil under ambient conditions and was attached to the tip of a glass capillary. The crystal was mounted in a stream of cold nitrogen at 173(2) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K$\alpha$ ($\lambda$ = 0.71073 Å) radiation and the diffractometer to crystal distance of 5.08 cm.

The initial cell constants were obtained from three series of $\omega$ scans at different starting angles. Each series consisted of 20 frames at intervals of 0.3° in a 6° range about $\omega$ with the exposure time of 10 seconds per frame. A total of 60 reflections was obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 6408 strong reflections from the actual data collection.

The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of 1.9 hemisphere to a resolution of 0.80 Å. A total of 17677 data were harvested by collecting three sets of frames with 0.3° scans in $\omega$ with an exposure time 30 second per frame. These highly redundant data sets were corrected for Lorentz and polarization effects. The absorption correction was based on

fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[1]

The systematic absences in the diffraction data were uniquely consistent for the space groups $P2_1/n$ that yielded chemically reasonable and computationally stable results of refinement.[2] A successful solution by the direct methods provided the positions of most atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anistropic displacement coefficients. All hydrogen atoms were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The molecule occupies a crystallographic inversion center. The final least-squares refinement of 262 parameters against 4084 data resulted in residuals *R* (based on $F^2$ for $I \geq 2\sigma$) and *wR* (based on $F^2$ for $I \geq 2\sigma$) of 0.0338 and 0.0854, respectively. The final difference Fourier was featureless.

The ORTEP diagrams were drawn with 50% probability ellipsoids.

## REFERENCES

1. Blessing, R. H. *Acta Cryst.* 1995, A51, 33-38.
2. All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-Ray System, Madison, WI).

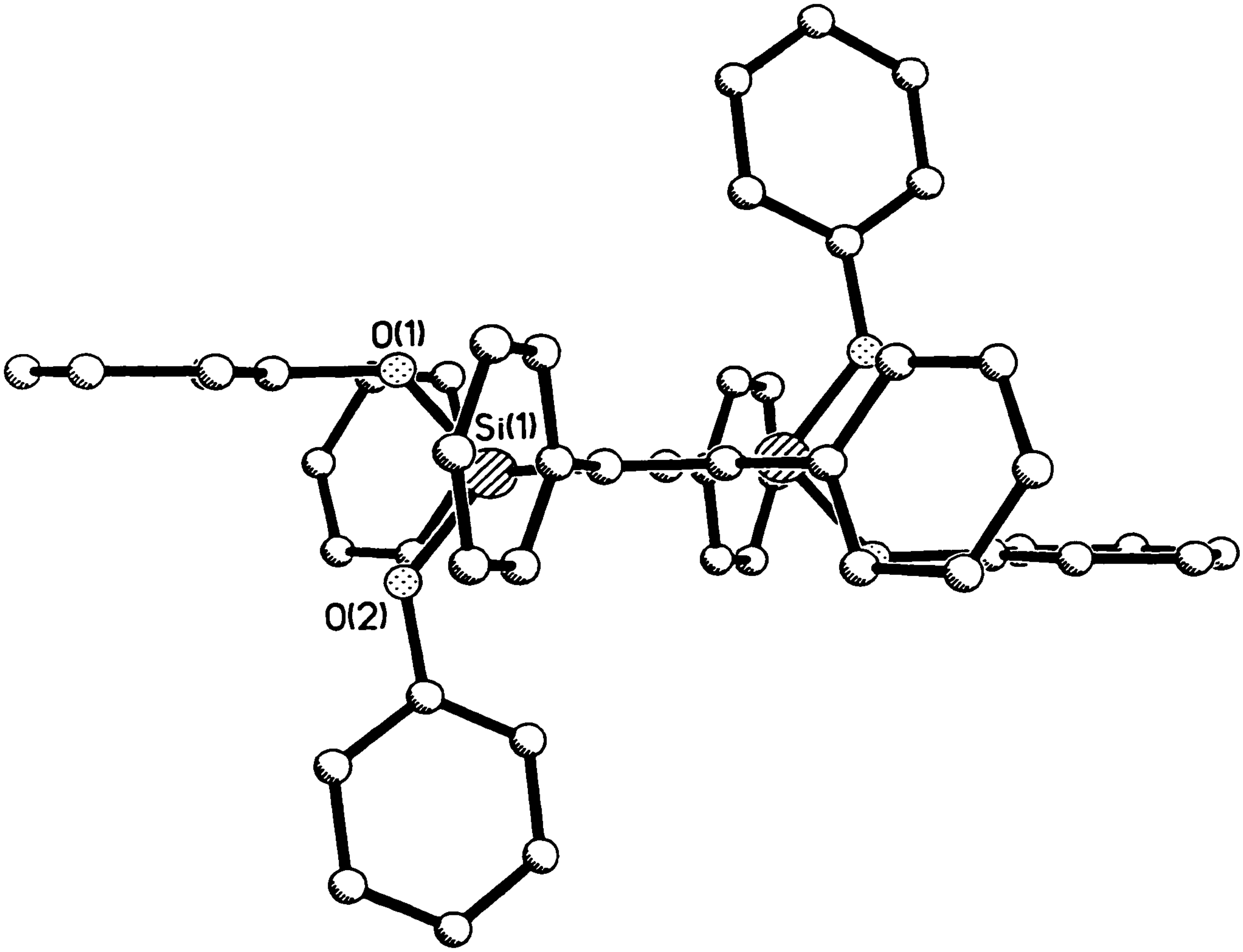


Figure 1. Side view of the ORTEP drawing of **9e**, showing two sets of phenoxy groups.

Table 1. Crystallographic Data for **9e**

| | | |
|---|---|---|
| Empirical Formula | $C_{52}H_{40}O_4Si_2$ | |
| Formula Weight | 785.02 | |
| Temperature (K) | 173(2) | |
| Wavelength | MoKα (λ = 0.71073 Å) | |
| Crystal System | Monoclinic | |
| Space Group | $P2_1/n$ | |
| Unit Cell Dimensions | a = 9.1542(5) Å | α = 90° |
| | b = 17.1747(6) Å | β = 97.649(1)° |
| | c = 15.6315(7) Å | γ = 90° |
| Volume | 2010.26(17) $Å^3$ | |
| Z | 2 | |
| Density (calc.) | 1.297 $Mg/m^3$ | |
| Absorption Coefficient | 0.137 $mm^{-1}$ | |
| F (000) | 824 | |
| Crystal Size (mm) | 0.45 x 0.45 x 0.40 | |
| θ Range | 1.95 to 26.37° | |
| Index Ranges | $-11 \leq h \leq 11$ $0 \leq k \leq 17$ | |
| | $0 \leq l \leq 19$ | |
| Reflections Collected | 17677 | |
| Independent Reflections | 4084 (R(int) = 0.0334) | |
| Completeness to theta = 26.37° | 99.5 % | |
| Absorption Correction | Empirical with SADABS | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Max. and Min. transmission | 0.9474 and 0.9411 | |
| Data / restraints / parameters | 4084 / 0 / 262 | |
| Goodness-of-fit on $F^2$ | 1.035 | |
| Final R indices [I > 2 sigma(I)] | R1 = 0.0338, wR2 = 0.0854 | |
| R Indices (all data) | R1 = 0.0451, wR2 = 0.0907 | |
| Largest diff. peak and hole | 0.325 and -0.300 e.$Å^{-3}$ | |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for **9e**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Si(1) | 1105(1) | 5802(1) | 570(1) | 26(1) |
| O(1) | 2556(1) | 6304(1) | 273(1) | 32(1) |
| O(2) | 998(1) | 6251(1) | 1522(1) | 31(1) |
| C(1) | 105(2) | 6083(1) | 2149(1) | 26(1) |
| C(2) | 625(2) | 6373(1) | 2977(1) | 33(1) |
| C(3) | -232(2) | 6249(1) | 3631(1) | 39(1) |
| C(4) | -1612(2) | 5846(1) | 3461(1) | 38(1) |
| C(5) | -2118(2) | 5560(1) | 2631(1) | 37(1) |
| C(6) | -1265(2) | 5671(1) | 1971(1) | 32(1) |
| C(7) | 3443(2) | 6995(1) | 699(1) | 28(1) |
| C(8) | 4652(2) | 6734(1) | 1266(1) | 36(1) |
| C(9) | 5556(2) | 7427(1) | 1674(1) | 42(1) |
| C(10) | 5255(2) | 8367(1) | 1510(1) | 41(1) |
| C(11) | 4044(2) | 8618(1) | 940(1) | 40(1) |
| C(12) | 3127(2) | 7932(1) | 532(1) | 35(1) |
| C(13) | -520(2) | 6130(1) | -214(1) | 28(1) |
| C(14) | -755(2) | 7172(1) | -335(1) | 29(1) |
| C(15) | -1316(2) | 7713(1) | 281(1) | 41(1) |
| C(16) | -1488(2) | 8681(1) | 167(1) | 49(1) |
| C(17) | -1089(2) | 9112(1) | -555(1) | 45(1) |
| C(18) | -526(2) | 8580(1) | -1173(1) | 44(1) |
| C(19) | -360(2) | 7613(1) | -1064(1) | 37(1) |
| C(20) | 1422(2) | 4509(1) | 653(1) | 27(1) |
| C(21) | 2774(2) | 4213(1) | 1240(1) | 28(1) |
| C(22) | 4064(2) | 4022(1) | 901(1) | 37(1) |
| C(23) | 5318(2) | 3742(1) | 1432(1) | 41(1) |
| C(24) | 5289(2) | 3651(1) | 2308(1) | 38(1) |
| C(25) | 4020(2) | 3849(1) | 2652(1) | 40(1) |
| C(26) | 2770(2) | 4137(1) | 2123(1) | 36(1) |

Table 3. Bond lengths ( Å) of **9e**.

| | | | |
|---|---|---|---|
| Si(1)-O(1) | 1.6287(10) | C(11)-C(12) | 1.383(2) |
| Si(1)-O(2) | 1.6334(10) | C(13)-C(20)#1 | 1.350(2) |
| Si(1)-C(13) | 1.8561(14) | C(13)-C(14) | 1.5009(19) |
| Si(1)-C(20) | 1.8569(14) | C(14)-C(15) | 1.383(2) |
| O(1)-C(7) | 1.3853(16) | C(14)-C(19) | 1.389(2) |
| O(2)-C(1) | 1.3773(16) | C(15)-C(16) | 1.390(2) |
| C(1)-C(6) | 1.378(2) | C(16)-C(17) | 1.375(2) |
| C(1)-C(2) | 1.3812(19) | C(17)-C(18) | 1.379(2) |
| C(2)-C(3) | 1.381(2) | C(18)-C(19) | 1.388(2) |
| C(3)-C(4) | 1.379(2) | C(20)-C(13)#1 | 1.350(2) |
| C(4)-C(5) | 1.380(2) | C(20)-C(21) | 1.4983(19) |
| C(5)-C(6) | 1.383(2) | C(21)-C(22) | 1.384(2) |
| C(7)-C(8) | 1.373(2) | C(21)-C(26) | 1.386(2) |
| C(7)-C(12) | 1.377(2) | C(22)-C(23) | 1.382(2) |
| C(8)-C(9) | 1.384(2) | C(23)-C(24) | 1.379(2) |
| C(9)-C(10) | 1.378(2) | C(24)-C(25) | 1.372(2) |
| C(10)-C(11) | 1.373(2) | C(25)-C(26) | 1.381(2) |

Table 4. Bond angles (°) for **9e**.

| | | | |
|---|---|---|---|
| O(1)-Si(1)-O(2) | 103.88(5) | C(7)-C(12)-C(11) | 119.39(14) |
| O(1)-SI(1)-C(13) | 108.30(6) | C(20)#1-C(13)-C(14) | 121.87(13) |
| O(2)-Si(1)-C(13) | 111.34(6) | C(20)#1-C(13)-Si(1) | 123.36(11) |
| O(1)-Si(1)-C(20) | 109.00(6) | C(14)-C(13)-Si(1) | 114.77(10) |
| O(2)-Si(1)-C(20) | 110.43(6) | C(15)-C(14)-C(19) | 118.88(14) |
| C(13)-Si(1)-C(20) | 113.41(6) | C(15)-C(14)-C(13) | 121.23(13) |
| C(7)-O(1)-Si(1) | 128.31(9) | C(19)-C(14)-C(13) | 119.85(13) |
| C(1)-O(2)-Si(1) | 133.93(9) | C(14)-C(15)-C(16) | 120.32(15) |
| O(2)-C(1)-C(6) | 122.70(13) | C(17)-C(16)-C(15) | 120.42(16) |
| O(2)-C(1)-C(2) | 116.88(13) | C(16)-C(17)-C(18) | 119.81(15) |
| C(6)-C(1)-C(2) | 120.40(13) | C(17)-C(18)-C(19) | 119.97(15) |
| C(3)-C(2)-C(1) | 119.83(14) | C(18)-C(19)-C(14) | 120.61(15) |
| C(4)-C(3)-C(2) | 120.41(14) | C(13)#1-C(20)-C(21) | 121.52(13) |
| C(3)-C(4)-C(5) | 119.16(14) | C(13)#1-C(20)-Si(1) | 123.16(11) |
| C(4)-C(5)-C(6) | 121.04(15) | C(21)-C(20)-Si(1) | 115.31(10) |
| C(1)-C(6)-C(5) | 119.15(14) | C(22)-C(21)-C(26) | 118.76(13) |
| C(8)-C(7)-C(12) | 120.90(13) | C(22)-C(21)-C(20) | 119.87(12) |
| C(8)-C(7)-O(1) | 119.38(13) | C(26)-C(21)-C(20) | 121.37(13) |
| C(12)-C(7)-O(1) | 119.69(13) | C(23)-C(22)-C(21) | 120.58(14) |
| C(7)-C(8)-C(9) | 119.16(14) | C(24)-C(23)-C(22) | 119.97(15) |
| C(10)-C(9)-C(8) | 120.47(15) | C(25)-C(24)-C(23) | 119.94(14) |
| C(11)-C(10)-C(9) | 119.73(14) | C(24)-C(25)-C(26) | 120.17(14) |
| C(10)-C(11)-C(12) | 120.34(15) | C(25)-C(26)-C(21) | 120.55(14) |

Symmetry transformations used to generate equivalent atoms: #1 -x, -y+1, -z

Table 4. Anistropic displacement parameters (Å$^2$ x 10$^3$) for **9e**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^*2 U^{11} + ... + 2 hka^*b^*U^{12}]$

| Atom | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Si(1) | 29(1) | 25(1) | 24(1) | -1(1) | 1(1) | -4(1) |
| O(1) | 35(1) | 33(1) | 29(1) | -5(1) | 5(1) | -10(1) |
| O(2) | 33(1) | 34(1) | 27(1) | -4(1) | 5(1) | -7(1) |
| C(1) | 29(1) | 22(1) | 28(1) | 1(1) | 4(1) | 3(1) |
| C(2) | 31(1) | 35(1) | 31(1) | -3(1) | 0(1) | -2(1) |
| C(3) | 46(1) | 42(1) | 28(1) | -3(1) | 6(1) | 1(1) |
| C(4) | 44(1) | 35(1) | 39(1) | 3(1) | 15(1) | 2(1) |
| C(5) | 31(1) | 34(1) | 46(1) | 3(1) | 7(1) | -2(1) |
| C(6) | 35(1) | 31(1) | 31(1) | -1(1) | 0(1) | -3(1) |
| C(7) | 29(1) | 29(1) | 27(1) | -3(1) | 8(1) | -6(1) |
| C(8) | 36(1) | 30(1) | 40(1) | -1(1) | 2(1) | -1(1) |
| C(9) | 34(1) | 46(1) | 43(1) | -4(1) | -3(1) | -4(1) |
| C(10) | 40(1) | 39(1) | 44(1) | -12(1) | 8(1) - | 14(1) |
| C(11) | 47(1) | 28(1) | 47(1) | -1(1) | 11(1) | -5(1) |
| C(12) | 35(1) | 34(1) | 36(1) | 4(1) | 3(1) | -3(1) |
| C(13) | 31(1) | 27(1) | 25(1) | 0(1) | 4(1) | -2(1) |
| C(14) | 27(1) | 28(1) | 31(1) | -1(1) | -4(1) | -4(1) |
| C(15) | 53(1) | 32(1) | 37(1) | -1(1) | 6(1) | 1(1) |
| C(16) | 64(1) | 32(1) | 49(1) | -8(1) | -1(1) | 7(1) |
| C(17) | 45(1) | 26(1) | 58(1) | 5(1) | -13(1) | -2(1) |
| C(18) | 37(1) | 40(1) | 51(1) | 17(1) | -3(1) | -4(1) |
| C(19) | 37(1) | 36(1) | 38(1) | 5(1) | 3(1) | 1(1) |
| C(20) | 31(1) | 28(1) | 23(1) | 0(1) | 3(1) | -2(1) |
| C(21) | 31(1) | 22(1) | 29(1) | -1(1) | 1(1) | -4(1) |
| C(22) | 39(1) | 41(1) | 30(1) | 0(1) | 5(1) | 1(1) |
| C(23) | 33(1) | 45(1) | 46(1) | 0(1) | 6(1) | 4(1) |
| C(24) | 32(1) | 36(1) | 44(1) | 3(1) | -6(1) | 1(1) |
| C(25) | 41(1) | 47(1) | 30(1) | 3(1) | -2(1) | 0(1) |
| C(26) | 34(1) | 44(1) | 30(1) | 2(1) | 4(1) | 2(1) |

Table 6. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$ x $10^3$) for **9e**.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 1571 | 6657 | 3096 | 39 |
| H(3) | 130 | 6443 | 4202 | 47 |
| H(4) | -2206 | 5767 | 3910 | 46 |
| H(5) | -3068 | 5282 | 2511 | 44 |
| H(6) | -1619 | 5466 | 1403 | 39 |
| H(8) | 4866 | 6086 | 1377 | 43 |
| H(9) | 6391 | 7253 | 2071 | 50 |
| H(10) | 5882 | 8840 | 1789 | 49 |
| H(11) | 3835 | 9265 | 825 | 48 |
| H(12) | 2287 | 8106 | 140 | 42 |
| H(15) | -1584 | 7422 | 785 | 49 |
| H(16) | -1884 | 9047 | 590 | 58 |
| H(17) | -1202 | 9775 | -628 | 54 |
| H(18) | -252 | 9775 | -628 | 52 |
| H(19) | 27 | 7249 | -1492 | 45 |
| H(22) | 4089 | 4083 | 298 | 44 |
| H(23) | 6199 | 3613 | 1194 | 49 |
| H(24) | 6146 | 3451 | 2673 | 46 |
| H(25) | 4001 | 3788 | 3256 | 48 |
| H(26) | 1901 | 4284 | 2367 | 43 |

# SUPPLEMENTAL MATERIAL 5. X-RAY DATA FOR *1,1,4,4*-TETRAHYDRO-*2,3,5,6*-TETRAPHENYL-*1,4*-DISILACYCLOHEXA-*2,5*-DIENE, 10

A colorless crystal with approximate dimensions 0.45 x 0.40 x 0.35 mm$^3$ was selected from oil under ambient conditions and was attached to the tip of a glass capillary. The crystal was mounted in a stream of cold nitrogen at 173(2) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K$\alpha$ ($\lambda$ = 0.71073 Å) radiation and the diffractometer to crystal distance of 5.08 cm.

The initial cell constants were obtained from three series of $\omega$ scans at different starting angles. Each series consisted of 20 frames at intervals of 0.3° in a 6° range about $\omega$ with the exposure time of 10 seconds per frame. A total of 61 reflections was obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 4137 strong reflections from the actual data collection.

The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of 1.9 hemisphere to a resolution of 0.80 Å. A total of 8638 data were harvested by collecting three sets of frames with 0.3° scans in $\omega$ with an exposure time 30 second per frame. These highly redundant data sets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[1]

The systematic absences in the diffraction data were uniquely consistent for the space groups $P2_1/c$ that yielded chemically reasonable and computationally stable results of refinement.[2] A successful solution by the direct methods provided the positions of most atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anistropic displacement coefficients. All hydrogen atoms except H(1) and H(2) were included in the structure factor calculation at idealized position and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Atoms H(1) and H(2) were located from the difference map and independently refined with isotropic displacement coefficients. The molecule occupies a crystallographic inversion center located in the middle of the heterocyclic six-membered ring. The final least-squares refinement of 144 parameters against 2331 data resulted in residuals $R$ (based on $F^2$ for $I \geq 2\sigma$) and $wR$ (based on $F^2$ for $I \geq 2\sigma$) of 0.0314 and 0.0841, respectively. The final difference Fourier was featureless.

The ORTEP diagrams were drawn with 30% probability ellipsoids.

## REFERENCES

1. Blessing, R. H. *Acta Cryst.* 1995, A51, 33-38.
2. All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-Ray System, Madison, WI).

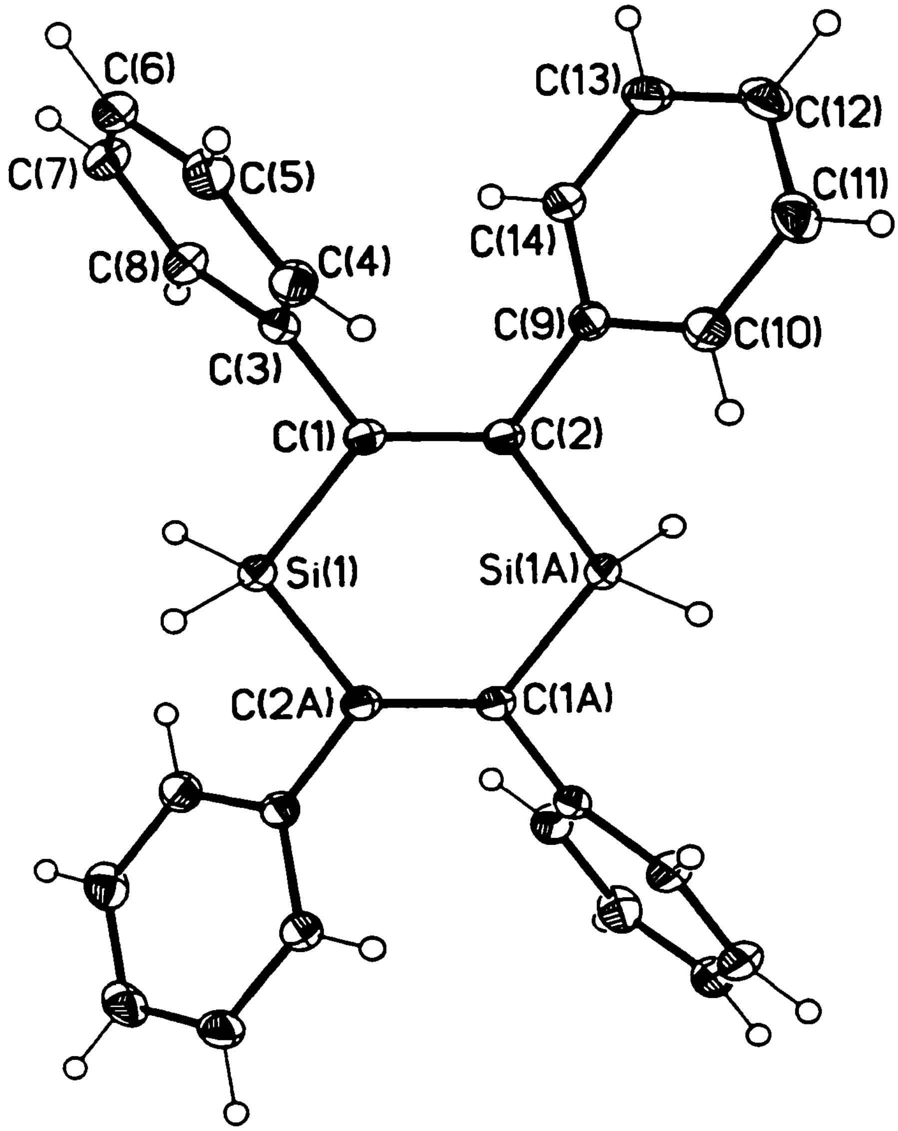


Figure 1. ORTEP drawing of **10**.

Table 1. Crystallographic Data for **10**.

| | | |
|---|---|---|
| Empirical Formula | $C_{28}H_{24}Si_2$ | |
| Formula Weight | 416.65 | |
| Temperature (K) | 173(2) | |
| Wavelength | MoKα (λ = 0.71073 Å) | |
| Crystal System | Monoclinic | |
| Space Group | $P2_1/c$ | |
| Unit Cell Dimensions | a = 7.8373(4) Å | α = 90° |
| | b = 11.9759(7) Å | β = 99.120(1)° |
| | c = 12.3495(7) Å | γ = 90° |
| Volume | 1144.46(11) $Å^3$ | |
| Z | 2 | |
| Density (calc.) | 1.209 $Mg/m^3$ | |
| Absorption Coefficient | 0.167 $mm^{-1}$ | |
| F (000) | 440 | |
| Crystal Size (mm) | 0.45 x 0.40 x 0.35 | |
| θ Range | 2.38 to 26.37° | |
| Index Ranges | $-9 \leq h \leq 9$ $0 \leq k \leq 14$ | |
| | $0 \leq l \leq 15$ | |
| Reflections Collected | 8638 | |
| Independent Reflections | 2331 (R(int) = 0.0197) | |
| Completeness to theta = 26.37° | 99.8 % | |
| Absorption Correction | Empirical with SADABS | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Max. and Min. transmission | 0.9438 and 0.9285 | |
| Data / restraints / parameters | 2331 / 0 / 144 | |
| Goodness-of-fit on $F^2$ | 1.048 | |
| Final R indices [I > 2 sigma(I)] | R1 = 0.0314, wR2 = 0.0841 | |
| R Indices (all data) | R1 = 0.0385, wR2 = 0.0879 | |
| Largest diff. peak and hole | 0.326 and −0.200 e.$Å^{-3}$ | |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for **9e**.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Si(1) | 3123(1) | -142(1) | -898(1) | 28(1) |
| C(1) | 3719(2) | 1148(1) | -72(1) | 24(1) |
| C(2) | 5194(2) | 1263(1) | 657(1) | 25(1) |
| C(3) | 2353(2) | 2034(1) | -238(1) | 25(1) |
| C(4) | 1552(2) | 2376(1) | 631(1) | 32(1) |
| C(5) | 266(2) | 3184(1) | 481(1) | 40(1) |
| C(6) | -231(2) | 3654(1) | -540(1) | 39(1) |
| C(7) | 543(2) | 3318(1) | -1412(1) | 38(1) |
| C(8) | 1825(2) | 2504(1) | -1267(1) | 31(1) |
| C(9) | 5681(2) | 2326(1) | 1269(1) | 26(1) |
| C(10) | 6201(2) | 2324(1) | 2400(1) | 34(1) |
| C(11) | 6743(2) | 3301(1) | 2957(1) | 41(1) |
| C(12) | 6787(2) | 4291(1) | 2390(1) | 41(1) |
| C(13) | 6282(2) | 4307(1) | 1263(1) | 38(1) |
| C(14) | 5740(2) | 3336(1) | 705(1) | 31(1) |

U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

Table 3. Bond lengths (Å) and angles (°) for **10**.

| | | | |
|---|---|---|---|
| Si(1)-C(1) | 1.8695(13) | C(5)-C(6) | 1.379(2) |
| Si(1)-C(2)#1 | 1.8723(13) | C(6)-C(7) | 1.377(2) |
| C(1)-C(2) | 1.3550(18) | C(7)-C(8) | 1.391(2) |
| C(1)-C(3) | 1.4978(17) | C(9)-C(10) | 1.3920(19) |
| C(2)-C(9) | 1.4988(18) | C(9)-C(14) | 1.3994(19) |
| C(2)-Si(1)#1 | 1.8723(13) | C(10)-C(11) | 1.390(2) |
| C(3)-C(4) | 1.389(2) | C(11)-C(12) | 1.381(2) |
| C(3)-C(8) | 1.3917(19) | C(12)-C(13) | 1.386(2) |
| C(4)-C(5) | 1.388(2) | C(13)-C(14) | 1.384(2) |

| | | | |
|---|---|---|---|
| C(1)-Si(1)-C(2)#1 | 113.38(6) | C(6)-C(5)-C(4) | 120.02(15) |
| C(2)-C(1)-C(3) | 122.34(11) | C(7)-C(6)-C(5) | 120.01(14) |
| C(2)-C(1)-Si(1) | 124.02(10) | C(6)-C(7)-C(8) | 120.17(14) |
| C(3)-C(1)-Si(1) | 113.54(9) | C(7)-C(8)-C(3) | 120.38(14) |
| C(1)-C(2)-C(9) | 122.92(12) | C(10)-C(9)-C(14) | 118.26(12) |
| C(1)-C(2)-Si(1)#1 | 122.58(10) | C(10)-C(9)-C(2) | 120.96(12) |
| C(9)-C(2)-Si(1)#1 | 114.32(9) | C(14)-C(9)-C(2) | 120.63(12) |
| C(4)-C(3)-C(8) | 118.75(13) | C(11)-C(10)-C(9) | 120.89(14) |
| C(4)-C(3)-C(1) | 120.26(12) | C(12)-C(11)-C(10) | 120.16(14) |
| C(8)-C(3)-C(1) | 120.96(12) | C(11)-C(12)-C(13) | 119.70(14) |
| C(5)-C(4)-C(3) | 120.67(14) | C(14)-C(13)-C(12) | 120.29(14) |
| C(13)-C(14)-C(9) | 120.70(14) | | |

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y, -z

Table 4. Anistropic displacement parameters ($Å^2 \times 10^3$) for **9e**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^*2\ U^{11} + \ldots + 2\ hka^*b^*U^{12}]$

| Atom | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Si(1) | 26(1) | 23(1) | 31(1) | -3(1) | -4(1) | 3(1) |
| C(1) | 27(1) | 22(1) | 24(1) | 1(1) | 4(1) | 2(1) |
| C(2) | 28(1) | 22(1) | 24(1) | 1(1) | 4(1) | 2(1) |
| C(3) | 24(1) | 20(1) | 29(1) | -2(1) | 2(1) | 0(1) |
| C(4) | 32(1) | 33(1) | 3191) | -3(1) | 3(1) | 3(1) |
| C(5) | 32(1) | 42(1) | 46(1) | -15(1) | 7(1) | 6(1) |
| C(6) | 28(1) | 29(1) | 58(1) | -6(1) | -3(1) | 7(1) |
| C(7) | 35(1) | 31(1) | 44(1) | 8(1) | -2(1) | 5(1) |
| C(8) | 30(1) | 32(1) | 32(1) | 3(1) | 4(1) | 5(1) |
| C(9) | 22(1) | 25(1) | 31(1) | -4(1) | 3(1) | 3(1) |
| C(10) | 37(1) | 32(1) | 32(1) | -3(1) | 3(1) | 2(1) |
| C(11) | 43(1) | 43(1) | 35(1) | -14(1) | 2(1) | 2(1) |
| C(12) | 37(1) | 32(1) | 54(1) | -19(1) | 6(1) | 0(1) |
| C(13) | 34(1) | 24(1) | 54(1) | -3(1) | 5(1) | 2(1) |
| C(14) | 29(1) | 27(1) | 35(1) | -1(1) | 1(1) | 2(1) |

Table 6. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$ x $10^3$) for **10**.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 2830 | 117 | -1992 | 38 |
| H(2) | 1570 | -568 | -628 | 43 |
| H(4A) | 1888 | 2054 | 1336 | 39 |
| H(5A) | -272 | 3413 | 1082 | 48 |
| H(6A) | -1107 | 4209 | -641 | 47 |
| H(7A) | 201 | 3644 | -2115 | 45 |
| H(8A) | 2342 | 2268 | -1874 | 38 |
| H(10A) | 6184 | 1645 | 2796 | 40 |
| H(11A) | 7084 | 3287 | 3731 | 49 |
| H(12A) | 7162 | 4959 | 2771 | 49 |
| H(13A) | 6308 | 4988 | 871 | 45 |
| H(14A) | 5403 | 3354 | -68 | 37 |

# SUPPLEMENTAL MATERIAL 6. X-RAY DATA FOR *1, 4*-DIHYDRO-*1,4*-DI-TERT-BUTYL-*2,3,5,6*-TETRAPHENYL-*1,4*-DISILACYCLOHEXA-*2,5*-DIENE, 13

A colorless crystal with approximate dimensions 0.5 x 0.4 x 0.4 mm$^3$ was selected from oil under ambient conditions and was attached to the tip of a glass capillary. The crystal was mounted in a stream of cold nitrogen at 173(2) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K$\alpha$ ($\lambda$ = 0.71073 Å) radiation and the diffractometer to crystal distance of 5.08 cm.

The initial cell constants were obtained from three series of $\omega$ scans at different starting angles. Each series consisted of 20 frames at intervals of 0.3° in a 6° range about $\omega$ with the exposure time of 10 seconds per frame. A total of 64 reflections was obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 7508 strong reflections from the actual data collection.

The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of a full hemisphere to a resolution of 0.80 Å. A total of 13896 data were harvested by collecting three sets of frames with 0.3° scans in $\omega$ with an exposure time 30 second per frame. These highly redundant data sets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[1]

The systematic absences in the diffraction data were uniquely consistent for the space groups P1 and P1.[2] The E-statistics strongly suggested the centrosymmetric space group P1 that yielded chemically reasonable and computationally stable results of refinement. A successful solution by the direct methods provided the positions of most atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anistropic displacement coefficients. All hydrogen atoms except H(1) on Si(1) and H(2) on Si(2) were included in the structure factor calculation at idealized position and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. There are two independent half molecules of **13** in the asymmetric unit. Each molecule of **13** occupies a crystallographic inversion center located. The final least-squares refinement of 357 parameters against 6397 data resulted in residuals $R$ (based on $F^2$ for $I \geq 2\sigma$) and $wR$ (based on $F^2$ for $I \geq 2\sigma$) of 0.0422 and 0.1092, respectively. The final difference Fourier was featureless.

The ORTEP diagrams were drawn with 30% probability ellipsoids.

The rings of both molecules are planar within 0.04 Å.

# REFERENCES

1. Blessing, R. H. *Acta Cryst.* 1995, A51, 33-38.
2. All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-Ray System, Madison, WI).

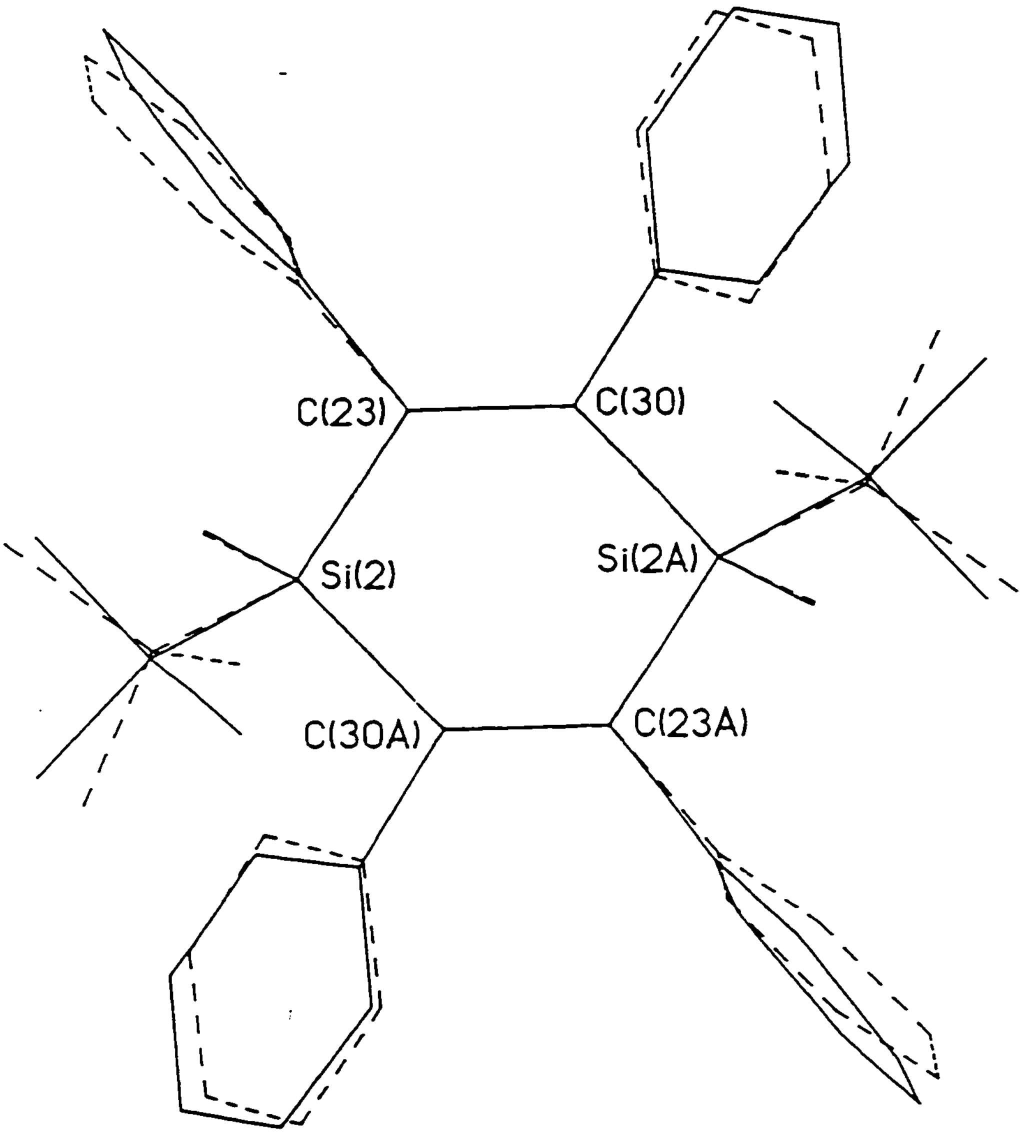


Figure 1. Structure of **13** showing the superposition of two independent molecules.

Table 1. Crystallographic Data for **13**.

| | |
|---|---|
| Empirical Formula | $C_{36}H_{40}Si_2$ |
| Formula Weight | 528.86 |
| Temperature (K) | 173(2) |
| Wavelength | MoKα (λ = 0.71073 Å) |
| Crystal System | Triclinic |
| Space Group | P1 |
| Unit Cell Dimensions | a = 12.0270(5) Å α = 69.5348(10)° |
| | b = 12.1135(5) Å β = 77.0789(10)° |
| | c = 12.9378(5) Å γ = 63.6759(10)° |
| Volume | 1577.52(11) $Å^3$ |
| Z | 2 |
| Density (calc.) | 1.113 $Mg/m^3$ |
| Absorption Coefficient | 0.134 $mm^{-1}$ |
| F (000) | 568 |
| Crystal Size (mm) | 0.50 x 0.40 x 0.40 |
| θ Range | 1.69 to 26.37° |
| Index Ranges | $-14 \leq h \leq 15$ $-13 \leq k \leq 15$ |
| | $0 \leq l \leq 16$ |
| Reflections Collected | 13896 |
| Independent Reflections | 6397 (R(int) = 0.0172) |
| Completeness to theta = 26.37° | 99.2 % |
| Absorption Correction | Empirical with SADABS |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Max. and Min. transmission | 0.9483 and 0.9359 |
| Data / restraints / parameters | 6397 / 0 / 357 |
| Goodness-of-fit on $F^2$ | 1.038 |
| Final R indices [I > 2 sigma(I)] | R1 = 0.0442, wR2 = 0.1092 |
| R Indices (all data) | R1 = 0.0494, wR2 = 0.1133 |
| Largest diff. peak and hole | 0.367 and –0.292 e.$Å^{-3}$ |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2$ x $10^3$) for **9e**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Si(1) | 6009(1) | 5663(1) | 10011(1) | 29(1) |
| Si(2) | 5267(1) | 3465(1) | 5884(1) | 30(1) |
| C(1) | 7073(2) | 6167(2) | 8776(1) | 40(1) |
| C(2) | 7140(2) | 5606(2) | 7862(2) | 59(1) |
| C(3) | 6605(2) | 7633(2) | 8321(2) | 81(1) |
| C(4) | 8395(2) | 5661(2) | 9125(2) | 57(1) |
| C(5) | 6445(1) | 3885(1) | 10351(1) | 29(1) |
| C(6) | 7774(1) | 3067(2) | 10609(1) | 31(1) |
| C(7) | 8213(2) | 3086(2) | 11513(1) | 38(1) |
| C(8) | 9451(2) | 2368(2) | 11740(2) | 47(1) |
| C(9) | 10271(2) | 1633(2) | 11064(2) | 47(1) |
| C(10) | 9853(2) | 1605(2) | 10165(2) | 42(1) |
| C(11) | 8616(2) | 2311(2) | 9939(1) | 36(1) |
| C(12) | 5683(1) | 3377(1) | 10256(1) | 29(1) |
| C(13) | 6125(1) | 1963(2) | 10409(1) | 31(1) |
| C(14) | 6657(2) | 1036(2) | 11367(1) | 38(1) |
| C(15) | 7020(2) | -263(2) | 11493(2) | 45(1) |
| C(16) | 6852(2) | -645(2) | 10673(2) | 49(1) |
| C(17) | 6340(2) | 260(2) | 9716(2) | 44(1) |
| C(18) | 5976(2) | 1555(2) | 9587(1) | 34(1) |
| C(19) | 5655(2) | 1962(2) | 5456(2) | 45(1) |
| C(20) | 6832(2) | 845(2) | 5964(2) | 73(1) |
| C(21) | 4620(3) | 1481(3) | 5900(2) | 124(2) |
| C(22) | 5884(4) | 2253(3) | 4211(2) | 97(1) |
| C(23) | 3681(1) | 4736(2) | 5481(1) | 29(1) |
| C(24) | 2615(1) | 4357(1) | 6048(1) | 30(1) |
| C(25) | 2352(2) | 4138(2) | 7190(1) | 33(1) |
| C(26) | 1360(2) | 3807(2) | 7731(2) | 42(1) |
| C(27) | 647(2) | 3639(2) | 7147(2) | 47(1) |
| C(28) | 905(2) | 3828(2) | 6020(2) | 47(1) |
| C(29) | 1871(2) | 4204(2) | 5469(2) | 40(1) |
| C(30) | 3481(1) | 5898(2) | 4728(1) | 30(1) |
| C(31) | 2198(2) | 6875(2) | 4421(1) | 33(1) |
| C(32) | 1941(2) | 7441(2) | 3310(2) | 40(1) |
| C(33) | 797(2) | 8426(2) | 3013(2) | 50(1) |
| C(34) | -102(2) | 8874(2) | 3809(2) | 55(1) |
| C(35) | 131(2) | 8312(2) | 4919(2) | 51(1) |
| C(36) | 1264(2) | 7320(2) | 5219(2) | 40(1) |

Table 3. Bond lengths (Å) for **13**.

| | | | |
|---|---|---|---|
| Si(1)-C(5) | 1.8822(16) | C(15)-C(16) | 1.380(3) |
| Si(1)-C(12)#1 | 1.8842(16) | C(16)-C(17) | 1.381(3) |
| Si(1)-C(1) | 1.9131(18) | C(17)-C(18) | 1.386(2) |
| Si(2)-C(30)#2 | 1.8857(17) | C(19)-C(22) | 1.512(3) |
| Si(2)-C(23) | 1.8865(16) | C(19)-C(21) | 1.519(3) |
| Si(2)-C(19) | 1.9172(19) | C(19)-C(20) | 1.537(3) |
| C(1)-C(2) | 1.529(3) | C(23)-C(30) | 1.354(2) |
| C(1)-C(3) | 1.532(3) | C(23)-C(24) | 1.503(2) |
| C(1)-C(4) | 1.539(3) | C(24)-C(29) | 1.393(2) |
| C(5)-C(12) | 1.356(2) | C(24)-C(25) | 1.394(2) |
| C(5)-C(6) | 1.500(2) | C(25)-C(26) | 1.389(2) |
| C(6)-C(7) | 1.396(2) | C(26)-C(27) | 1.378(3) |
| C(6)-C(11) | 1.399(2) | C(27)-C(28) | 1.379(3) |
| C(7)-C(8) | 1.389(2) | C(28)-C(29) | 1.39193) |
| C(8)-C(9) | 1.382(3) | C(30)-C(31) | 1.506(2) |
| C(9)-C(10) | 1.382(3) | C(30)-Si(2)#2 | 1.8857(16) |
| C(10)-C(11) | 1.386(2) | C(31)-C(32) | 1.397(2) |
| C(12)-C(13) | 1.502(2) | C(31)-C(36) | 1.398(2) |
| C(12)-Si(1)#1 | 1.8842(16) | C(32)-C(33) | 1.387(3) |
| C(13)-C(18) | 1.393(2) | C(33)-C(34) | 1.378(3) |
| C(13)-C(14) | 1.397(2) | C(34)-C(35) | 1.389(3) |
| C(14)-C(15) | 1.390(3) | C(35)-C(36) | 1.382(3) |

Table 4. Bond angles (°) of **13**. Symmetry transformation to generate atoms:
#1 -x+1, -y+1, -z+2; #2 -x+1, -y+1, -z+1

| | | | |
|---|---|---|---|
| C(5)-Si(1)-C(12)#1 | 111.70(7) | C(15)-C(16)-C(17) | 120.09(17) |
| C(5)-Si(1)-C(1) | 109.33(7) | C(16)-C(17)-C(18) | 119.89(18) |
| C(12)#1-Si(1)-C(1) | 111.64(7) | C(17)-C(18)-C(13) | 121.01(16) |
| C(30)#2-Si(2)-C(23) | 111.45(7) | C(22)-C(19)-C(21) | 111.9(3) |
| C(30)#2-Si(2)-C(19) | 109.96(7) | C(22)-C(19)-C(20) | 107.9(2) |
| C(23)-Si(2)-C(19) | 111.58(8) | C(21)-C(19)-C(20) | 105.5(2) |
| C(2)-C(1)-C(3) | 109.4(2) | C(22)-C(19)-Si(2) | 109.80(14) |
| C(2)-C(1)-C(4) | 108.78(16) | C(21)-C(19)-Si(2) | 110.26(15) |
| C(3)-C(1)-C(4) | 107.36(17) | C(20)-C(19)-Si(2) | 111.37(15) |
| C(2)-C(1)-Si(1) | 109.43(13) | C(30)-C(23)-C(24) | 120.94(14) |
| C(3)-C(1)-Si(1) | 111.52(13) | C(30)-C(23)-Si(2) | 124.34(12) |
| C(4)-C(1)-Si(1) | 110.28(14) | C(24)-C(23)-Si(2) | 114.71(11) |
| C(12)-C(5)-C(6) | 121.76(14) | C(29)-C(24)-C(25) | 118.04(15) |
| C(12)-C(5)-Si(1) | 123.74(12) | C(29)-C(24)-C(23) | 122.06(15) |
| C(6)-C(5)-Si(1) | 114.11(11) | C(25)-C(24)-C(23) | 119.90(14) |
| C(7)-C(6)-C(11) | 118.21(15) | C(26)-C(25)-C(24) | 121.01(16) |
| C(7)-C(6)-C(5) | 120.09(14) | C(27)-C(26)-C(25) | 120.09(17) |
| C(11)-C(6)-C(5) | 121.65(14) | C(26)-C(27)-C(28) | 119.76(17) |
| C(8)-C(7)-C(6) | 120.80(16) | C(27)-C(28)-C(29) | 120.33(17) |
| C(9)-C(8)-C(7) | 120.15(17) | C(28)-C(29)-C(24) | 120.71(17) |
| C(8)-C(9)-C(10) | 119.81(17) | C(23)-C(30)-C(31) | 122.43(14) |
| C(9)-C(10)-C(11) | 120.31(16) | C(23)-C(30)-Si(2)#2 | 123.63(12) |
| C(10)-C(11)-C(6) | 120.71(16) | C(31)-C(30)-Si(2)#2 | 113.45(11) |
| C(5)-C(12)-C(13) | 121.72(14) | C(32)-C(31)-C(36) | 118.04(16) |
| C(5)-C(12)-Si(1)#1 | 123.90(12) | C(32)-C(31)-C(30) | 120.32(15) |
| C(13)-C(12)-Si(1)#1 | 114.32(11) | C(36)-C(31)-C(30) | 121.43(15) |
| C(18)-C(13)-C(14) | 118.39(15) | C(33)-C(32)-C(31) | 120.72(18) |
| C(18)-C(13)-C(12) | 119.48(14) | C(34)-C(33)-C(32) | 120.44(18) |
| C(14)-C(13)-C(12) | 122.11(15) | C(33)-C(34)-C(35) | 119.65(18) |
| C(15)-C(14)-C(13) | 120.46(17) | C(36)-C(35)-C(34) | 120.09(19) |
| C(16)-C(15)-C(14) | 120.15(17) | C(35)-C(36)-C(31) | 121.02(17) |

Table 5. Anistropic displacement parameters ($Å^2 \times 10^3$) for **13**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 hka^*b^*U^{12}]$

| Atom | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Si(1) | 28(1) | 28(1) | 33(1) | -13(1) | -5(1) | -8(1) |
| Si(2) | 29(1) | 29(1) | 26(1) | -4(1) | -1(1) | -9(1) |
| C(1) | 35(1) | 34(1) | 50(1) | -13(1) | 4(1) | -15(1) |
| C(2) | 60(1) | 78(2) | 40(1) | -18(1) | 6(1) | -31(1) |
| C(3) | 58(1) | 38(1) | 114(2) | -7(1) | 33(1) | -20(1) |
| C(4) | 38(1) | 63(1) | 76(2) | -26(1) | 6(1) | -26(1) |
| C(5) | 30(1) | 28(1) | 26(1) | -10(1) | -3(1) | -7(1) |
| C(6) | 29(1) | 27(1) | 32(1) | -7(1) | -3(1) | -9(1) |
| C(7) | 34(1) | 43(1) | 35(1) | -13(1) | -3(1) | -11(1) |
| C(8) | 36(1) | 57(1) | 41(1) | -11(1) | -10(1) | -14(1) |
| C(9) | 29(1) | 47(1) | 52(1) | -8(1) | -6(1) | -9(1) |
| C(10) | 32(1) | 37(1) | 51(1) | -15(1) | 5(1) | -10(1) |
| C(11) | 35(1) | 33(1) | 39(1) | -13(1) | 0(1) | -12(1) |
| C(12) | 32(1) | 27(1) | 26(1) | -10(1) | -2(1) | -8(1) |
| C(13) | 26(1) | 28(1) | 35(1) | -9(1) | 1(1) | -9(1) |
| C(14) | 34(1) | 37(1) | 37(1) | -7(1) | -2(1) | -11(1) |
| C(15) | 36(1) | 33(1) | 50(1) | 1(1) | -1(1) | -9(1) |
| C(16) | 39(1) | 28(1) | 71(1) | -13(1) | 1(1) | -10(1) |
| C(17) | 39(1) | 36(1) | 59(1) | -22(1) | 1(1) | -13(1) |
| C(18) | 33(1) | 31(1) | 36(1) | -11(1) | 0(1) | -10(1) |
| C(19) | 39(1) | 32(1) | 59(1) | -14(1) | 3(1) | -14(1) |
| C(20) | 64(2) | 34(1) | 109(2) | -22(1) | -11(1) | -5(1) |
| C(21) | 61(3) | 67(2) | 266(5) | -90(2) | 50(2) | -41(1) |
| C(22) | 167(3) | 65(2) | 64(2) | -32(1) | -22(2) | -36(2) |
| C(23) | 30(1) | 32(1) | 26(1) | -10(1) | -3(1) | -10(1) |
| C(24) | 28(1) | 27(1) | 32(1) | -7(1) | -5(1) | -7(1) |
| C(25) | 30(1) | 33(1) | 33(1) | -10(1) | -3(1) | -8(1) |
| C(26) | 33(1) | 39(1) | 38(1) | -6(1) | 2(1) | -9(1) |
| C(27) | 30(1) | 43(1) | 57(1) | 1(1) | -5(1) | -15(1) |
| C(28) | 40(1) | 44(1) | 60(1) | -5(1) | -19(1) | -19(1) |
| C(29) | 42(1) | 42(1) | 37(1) | -7(1) | -11(1) | -16(1) |
| C(30) | 29(1) | 33(1) | 27(1) | -10(1) | -3(1) | -9(1) |
| C(31) | 31(1) | 29(1) | 38(1) | -8(1) | -6(1) | -10(1) |
| C(32) | 43(1) | 35(1) | 39(1) | -9(1) | -11(1) | -11(1) |
| C(33) | 53(1) | 40(1) | 53(1) | -7(1) | -25(1) | -10(1) |
| C(34) | 40(1) | 40(1) | 76(2) | -14(1) | -23(1) | -1(1) |
| C(35) | 35(1) | 45(1) | 64(1) | -20(1) | -2(1) | -5(1) |
| C(36) | 33(1) | 38(1) | 64(1) | -20(1) | -2(1) | -5(1) |

Table 6. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$ x $10^3$) for **13**.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 6244 | 5911 | 10898 | 40 |
| H(2) | 5235 | 3072 | 7039 | 37 |
| H(2A) | 7684 | 5865 | 7229 | 89 |
| H(2B) | 6303 | 5928 | 7629 | 89 |
| H(2C) | 7475 | 4666 | 8143 | 89 |
| H(3A) | 7217 | 7859 | 7746 | 122 |
| H(3B) | 6490 | 7999 | 8922 | 122 |
| H(3C) | 5810 | 7977 | 8003 | 122 |
| H(4A) | 8362 | 6006 | 9718 | 85 |
| H(4B) | 8927 | 5935 | 8488 | 85 |
| H(4C) | 8736 | 4720 | 9392 | 85 |
| H(7) | 7657 | 3595 | 11977 | 46 |
| H(8) | 9735 | 2383 | 12362 | 56 |
| H(9) | 11119 | 1149 | 11217 | 56 |
| H(10) | 10416 | 1100 | 9700 | 51 |
| H(11) | 8337 | 2280 | 9322 | 43 |
| H(14) | 6772 | 1293 | 11935 | 46 |
| H(15) | 7386 | -888 | 12145 | 54 |
| H(16) | 7088 | -1532 | 10767 | 58 |
| H(17) | 6237 | -5 | 9146 | 52 |
| H(18) | 5619 | 2172 | 8929 | 41 |
| H(20A) | 7552 | 1072 | 5662 | 110 |
| H(20B) | 6966 | 72 | 5783 | 110 |
| H(20C) | 6730 | 680 | 6769 | 110 |
| H(21A) | 4895 | 630 | 5800 | 186 |
| H(21B) | 3880 | 2081 | 5498 | 186 |
| H(21C) | 4418 | 1421 | 6690 | 186 |
| H(22A) | 5131 | 2937 | 3868 | 145 |
| H(22B) | 6098 | 1478 | 3998 | 145 |
| H(22C) | 6573 | 2535 | 3960 | 145 |
| H(25) | 2860 | 4217 | 7604 | 40 |
| H(26) | 1173 | 3696 | 8504 | 50 |
| H(27) | -20 | 3393 | 7519 | 56 |
| H(28) | 422 | 3702 | 5618 | 56 |
| H(29) | 2024 | 4358 | 4689 | 48 |
| H(32) | 2556 | 7147 | 2752 | 48 |
| H(33) | 633 | 8794 | 2255 | 60 |
| H(34) | -876 | 9563 | 3601 | 66 |
| H(35) | -491 | 8610 | 5471 | 62 |
| H(36) | 1410 | 6935 | 5981 | 48 |

# CHAPTER 5. REACTIONS OF DISILANES WITH *1,2*-QUINONES AND *p*-QUINONES VIA HYPERCOORDINATED Si INTERMEDIATES: A SPECULATION WITH EVIDENCE

A paper to be submitted to the Journal of Organometallic Chemistry

Jinchao Yang and John G. Verkade

## Abstract

Disilanes activated by multiple electron-withdrawing substituents were found to be efficient in the disilylation of *1,2*-quinones and *p*-quinones to form *bis*(siloxy)-ethylenes in excellent conversions in the absence of a transition metal catalyst. This contrasts to the reactions of non-activated disilane with *1,2*-quinone and *p*-quinone in which transition metal catalysts had to be applied. The formation of hypercoordinated silicon intermediates was proposed to explain the behavior of disilanes with quinones. The driving force of this type of disilyation reactions is possibly the formation of the stronger Si-O bonds, in addition to the aromatization for the reactions involving *p*-quinones and disilanes. Disilanes bearing multitple electron withdrawing substituents were also found to readily form adducts with DMF and diamines, supporting the idea of the formation of hypercoordination silicon intermediates. Hexachlorodisilane was also reacted with the lithium salt of *N*-methylpropionamide to give bicyclic hexacoordinated silicon product, whose structure was determined by X-ray diffraction means.

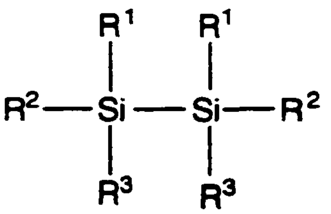
## Introduction

Increasing attention has been directed toward organosilicon compounds owing to their versatile synthetic utility and unique physical/chemical properties.[1] One of the most promising methods for their preparation is transition metal catalyzed addition of Si-Si bonds[2] to unsaturated compounds such as acetylenes,[3] olefins,[4] dienes,[5] allenes,[6] a diyne,[7] α,β-unsaturated ketones,[5a, 8] quinones,[5a, 9a, b] α-diketones,[9c] an α-keto ester,[9c] aldehydes,[10] a ketone,[10] isocyanides[11] and imines.[12] However, disilane linkages that are not activated by electron-withdrawing substitutents are in general reluctant to undergo the addition reaction even when conventional $Pd\text{-}PPh_3$ catalysts were used [3a, 7]

It was reported very recently that $Pt_2(dba)_2P(OCH_2)_3CEt$ and $PdCl_2L_2$ (L = $PEt_3$, $PMe_3$, $P^tBu_3$, $PPh_3$, etc.) systems were very efficient for the insertion of acetylenes into Si-Si bonds of hexamethyldisilane, octamethyltrisilanes and polymers with Si-Si links,[13] and that α-diketones and α-keto ester were also discovered to undergo double silylation or double reductive coupling with hexamethyldisilane in the presence of palladium or platinum catalysts.[13] Remarkably, *1,2*- and *1,4*-quinones were found to react smoothly with non-activated disilanes in the presence of Pd catalysts.

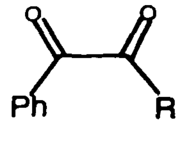
Despite that the formation of *p-bis*(fluorodimethylsiloxy)benzene from *p*-benzoquinone and $FMe_2SiSiMe_2F$ was known, it represents the only example of activated disilane involved reaction in this field. However, even this reaction was also catalyzed by $Pd(PPh_3)_2Cl_2$ or $Pd(PPh_3)_4$.[13, 14] No disilane/*p*-quinone or disilane/*1,2*-quinone reaction which is not catalyzed by a transition metal catalyst has been reported.

Here we report the aromatization reactions of *p*-quinones and double silylation reactions of disilanes [hexachlorodisilane (**1a**), *symmetric*-dichlorotetramethyldisilane (**1b**), hexamethyldisilane (**1c**), hexamethoxydislane (**1d**), of which **1a**, **1b** and **1d** are

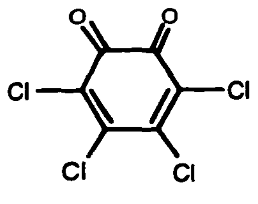


**1a**: $R^1 = R^2 = R^3 = Cl$
**1b**: $R^1 = R^2 = Cl, R^3 = Me$
**1c**: $R^1 = R^2 = R^3 = Me$
**1d**: $R^1 = R^2 = R^3 = OMe$

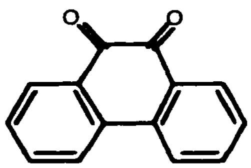
activated by halogen or alkoxy groups] with *1,2*-quinones [Benzil (**2a**), *1*-phenyl-*1,2*-propanedione (**2b**), tetrachloro-*1,2*-benzoquinone (**2c**), phenanthrenequinone (**2d**), *p*-benzoquinone (**3a**), tetrafluoro-*1,4*-benzoquinone (**3b**), tetramethyl-*1,4*-benzoquinone (duroquinone) (**3c**), *2,6*-dimethylbenzoquinone (**3d**), *2*-methyl-*1,4*-naphathoquinone (**3e**), diphenyl(*2,4,6*-trimethylbenzoyl)phsophine oxide (**4**)] can proceed in excellent conversions (yields) without the presence of a transition metal catalyst.



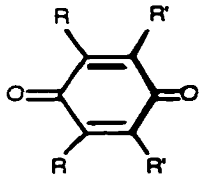
**2a**: R = Ph
**2b**: $R = CH_3$



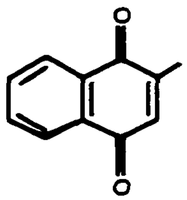
**2c**



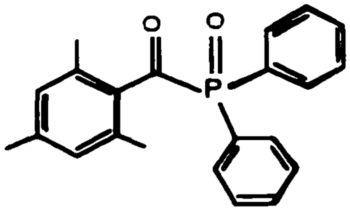
**2d**



3a: R = R' = H
3b: R = R' = F
3c: R = R' = $CH_3$
3d: R = H, R' = $CH_3$

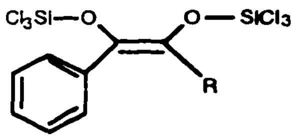


**3e**

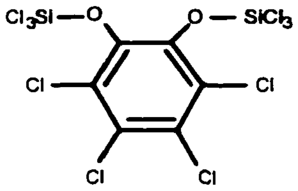


**4**

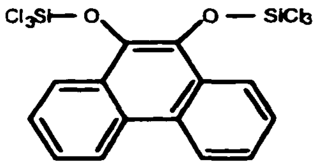
Corresponding aromatized products **5a**, **5b**, **5c**, **5d**, **6a**, **6b**, **6c**, **6d**, **6e**, **7a**, **7b**, **8a**, **8b** were obtained. Based on the observations that disilanes with electron withdrawing groups are ready to form hypercoordinated adducts (based on the solid state $^{29}$Si spectroscopy) with diamines,[15] dimethyl formamide (DMF)[15] and other similar compounds with lone pair electrons, we speculate that the formation of hypercoordinated disilane intermediates could be the initial step, and the consequent intra-molecular rearrangements, accompanied by Si-Si bond cleavage to give final products. The formation of stronger Si-O bonds (along with the aromatization of *p*-quinones) could be the driving force for these reactions.



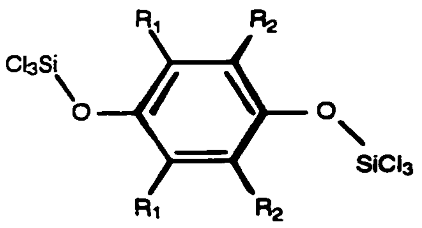
**5a**: R = Ph
**5b**: R = Me



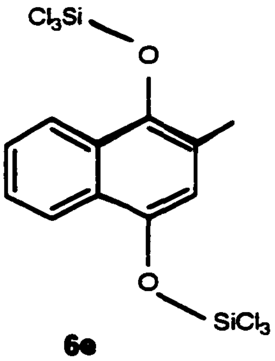
**5c**



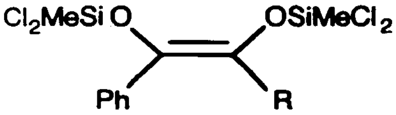
**5d**



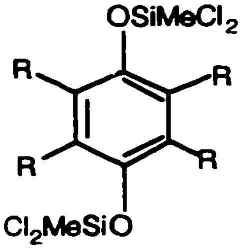
| | $R_1$ | $R_2$ |
|---|---|---|
| **6a** | H | H |
| **6b** | F | F |
| **6c** | Me | Me |
| **6d** | H | Me |



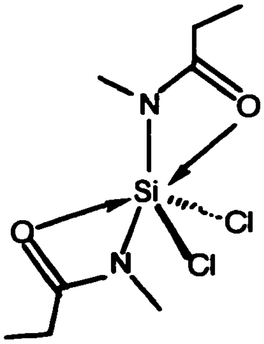
**6e**



**7a** R = Ph
**7b** R = Me



**8a** R = H
**8b** R = Me



**9**

The idea of forming hypercoordinated silicon intermediates was also supported by the recently reported synthesis of several pentacoordinated silicon compounds, in which coordination bonds between acetamide groups and the silicon atoms exist (see **12** on pp 174).[16] Further evidence was obtained from the successful synthesis of complex **9** by this research group. Compound **9** possesses two four-membered rings which show interesting coordination properties between acetamide ligands and the silicon atom.

## Experimental Section

NMR spectra were measured Bruker AC-200 ($^{29}$Si), Bruker DRX-400 ($^{1}$H and $^{13}$C), Bruker MSL-300 (solid $^{29}$Si) instruments. The NMR solvent is $CDCl_3$ unless otherwise noted. Chemical shifts are calibrated according to $CDCl_3$ (7.24 ppm) for $^{1}$H NMR, $CDCl_3$ (77.0 ppm) for $^{13}$C NMR, and $SiMe_4$ (0 ppm) for $^{29}$Si NMR spectra. Mass, high resolution mass (HRMS) spectra and elemental analysis were performed at Iowa State University by the chemistry department instrument service unit.

Solvents diethyl ether, THF were dried with sodium, DMF was distilled under nitrogen after stirred with $CaH_2$ and further dried by molecular sieves. Disilanes hexachlorodisilane (**1a**), dimethyltetrachlorodisilane (**1b**) and hexamethyldisilane (**1c**) were purchased from Aldrich Chem. Co.; hexamethoxydisilane (**1d**) was purchased from Gelest Inc. and were used as received without further treatment. Benzil (**2a**), *1*-phenyl-*1,2*-propanedione (**2b**), tetrachloro-*1,2*-benzoquinone (**2c**), phenanthrenequinone (**2d**), *p*-benzoquinone (**3a**), tetrafluoro-*1,4*-benzoquinone (**3b**), tetramethyl-*1,4*-benzoquinone (duroquinone) (**3c**), *2,6*-dimethylbenzoquinone (**3d**), *2*-methyl-*1,4*-naphathoquinone (**3e**), diphenyl(*2,4,6*-trimethylbenzoyl)phsophine oxide (**4**), *N,N,N',N'*-tetramethylethylenediamine, *N*-methylpropionamide and *N*-methyltrimethylacetamide were purchased from Aldrich Chem. Co. and were used as received unless otherwise noted.

**General description of reactions**. Reactions of hexachlorodisilane **1a** with DMF and *N,N,N',N'*-tetramethylethylenediamine were carried out at room temperature in $Et_2O$ or pentane under nitrogen. Each reaction of a disilane with a quinone was carried out in an NMR tube under nitrogen either at room temperature (with $CHCl_3$ solvent) or at 80-120 °C (without a solvent), the conversions of all the reactions were quantitative unless otherwise mentioned. Products were analyzed by $^1H$, $^{13}C$, $^{29}Si$ NMR and HRMS means, and compound **5a** and **9** was further characterized by X-ray diffraction spectroscopy. Products **5-9** are all new compounds unless otherwise noted.

**Adducts formation of 1a with *N,N,N',N'*-tetramethylethylenediamine**. In a 50 mL flask equipped with a magnetic stirrer and flushed with nitrogen, $Et_2O$ *ca.* 20 mL was added by a syringe, followed by *N,N,N',N'*-tetramethylethylenediamine (2.32 g, 20.0 mmol). **1a** (2.69 g, 10.0 mmol) was then introduced dropwise with stirring at room temperature. White precipitate was observed to form immediately with the addition of **1a**, and the flask became warm during the addition of **1a**. The reaction mixture was stirred for two hours. The precipitate was filtered off and washed by 3x10 mL $Et_2O$. Drying the precipitate under vacuum gave 4.70 g product as white powder (93% yield) assuming a 1:1 reaction pathway. The product was analyzed as hypercoordinated adduct of **1a** with

*N,N,N',N'*-tetramethylethylenediamine by $^{29}$Si NMR spectroscopy. $^{29}$Si (solid, hexamethylcyclotrisiloxane) for the adduct: δ -79.24; $^{1}$H NMR ($CDCl_3$): δ 2.87 (s, 4H), 2.61 (s, 12H); $^{13}$C NMR ($CDCl_3$): δ 55.14, 46.57. Mass spectra gave decomposed products. Efforts (recrystallization from $CHCl_3$, $CH_2Cl_2$, sublimation under vacuum) to obtain crystals from this adduct product failed. Therefore no evidence was obtained to support the speculation that the adduct has a six-membered ring structure.

**Adduct formation of 1a with DMF.** In a 50 mL flask flushed with nitrogen, $Et_2O$ *ca.* 20 mL was added by a syringe, followed by DMF (1.46 g , 20.0 mmol). **1a** (2.69 g, 10.0 mmol) was then introduced dropwise at room temperature. White precipitate was observed to form immediately with the addition of **1a**, accompanied with heat generation during addition of **1a**. The reaction mixture was stirred for three hours. The precipitate was filtered out and washed by 5x10 mL $Et_2O$. Drying the precipitate under vacuum afforded 3.10 g product (90% yield) assuming a 1:1 adduct formation pathway. The product was analyzed as hypercoordinated adduct of **1a** with DMF by $^{29}$Si NMR spectroscopy. $^{29}$Si (solid, hexamethylcyclotrisiloxane): δ -184.71, -192.10; $^{1}$H NMR ($CDCl_3$): δ 8.02 (s, 1H), 2.95 (s, 3H), 2.87 (s, 3H); $^{13}$C NMR ($CDCl_3$): δ 162.69, 36.68, 31.61. This reaction does not give pure compound, and we believe that the complication could be caused by several different adduct formation possibilities (either intermolecular or intramolecular). Mass spectra showed only decomposed species. Efforts (recrystallization from $CHCl_3$, sublimation under vacuum) to purify the product failed, and tries to obtain crystals by these methods did not succeed either.

**Reaction of 1a with 2a (Method A: at 100 °C without a solvent).** In a nitrogen flushed NMR tube, **2a** (42.0 mg, 0.200 mmol) was added, followed by the introduction of **1a** (64.0 mg, 0.240 mmol, 20% excess). The NMR tube was stoppered with a septum and the mixture was heated to 100 °C for 1 hour. After cooled to room temperature, a yellow solution was obtained which was analyzed by $^1$H, $^{13}$C, $^{29}$Si NMR and HRMS spectroscopies as product **5a**. NMR data for **5a**. $^1$H NMR (CDCl$_3$): δ 7.25 (m, 10H); $^{13}$C NMR (CDCl$_3$): δ 136.60, 133.04, 129.46, 129.01, 128.27. $^{29}$Si NMR (CDCl$_3$, SiMe$_4$): δ -21.27. HRMS (EI): Calcd. for $C_{14}H_{10}Cl_6O_2Si_2$: 475.83506, found: 475.83527. Purifying the product (to remove **1a**) by evaporation under vacuum afforded pure 5a. Elemental analysis: calcd. for $C_{14}H_{10}Cl_6O_2Si_2$: C 35.07 %, H 2.08 %, Cl 44.46 %, Si 11.69 %; found: C 35.84 %, H 2.16 %, Cl 44.19 %, Si 11.65%.

**Reaction of 1a with 2a (Method B: at r.t. with CHCl$_3$ as solvent)** In a nitrogen flushed NMR tube, **2a** (42.0 mg, 0.200 mmol) was added, followed by the introduction of **1a** (64.0 mg, 0.240 mmol, 20% excess). The NMR tube was stoppered with a septum and 0.70 mL CDCl$_3$ was added by a syringe. A light yellow solution was obtained after **2a** was dissloved. Taking the NMR spectra right after adding the CDCl$_3$ showed the absence of starting material **2a**, indicating immediate reaction between **1a** and 2a. $^1$H and $^{13}$C NMR spectroscopies confirmed that methods **A** and **B** gave identical product **5a**.

**Reaction of 1a with 2a at lower temperature (crystal formation of 5a).** In a glass tube equipped with a magnetic stirrer and cooled by an ice bath (0 °C), **2a** (0.42 g, 2.0 mmol) was added, followed by the introduction of (0.64 g, 2.4 mmol, 20% excess) **1a**. The tube was then cooled by liquid nitrogen and flame sealed under vacuum. The mixture was allowed to warm to 0 °C in an ice bath and stirred well until a homogeneous mixture was obtained. Shaking the reaction mixture occasionally was essential to ensure better mixing. The tube was then kept undisturbed for two days at 0 °C , during which time colorless crystals were observed to form. Crystals suitable for X-ray diffraction spectroscopy were obtained from the reaction tube (90 % yield) and the structure of reaction product was solved to be **5a** with $Si_2Cl_6$ as an inclusion.

**Reaction of 1a with 2b.** In a nitrogen flushed NMR tube, **2b** (30.0 mg, 0.200 mmol) was added by a syringe. The NMR tube was cooled to 0 °C by an ice bath. **1a** (64.0 mg, 0.240 mmol) was then introduced. The reaction was exothermic judging from the boiling of the mixture and the warm-up of the tube. The product was analyzed by $^1H$, $^{13}C$, $^{29}Si$ NMR and HRMS spectroscopies as **5b** (one conformer only, presumably the *cis*-isomer inferred from the reaction of **1a** and **2a**) after the reaction mixture was cooled to room temperature. $^1H$ NMR ($CDCl_3$): δ 7.40 (m, 5H), 2.07 (s, 3H); $^{13}C$ NMR ($CDCl_3$): δ 134.70, 134.15, 133.07, 129.22, 129.10, 128.41, 17.70; $^{29}Si$ NMR ($CDCl_3$, $SiMe_4$): δ -21.79, -22.74. MS (70 eV, EI): m/z (relative intensity, ion) 418.0 (8.97, $M^+$(2 $^{37}Cl$, 4 $^{35}Cl$)), 416.0 (11.13, $M^+$($^{37}Cl$, 5 $^{35}Cl$)), 265.0 (4.50, $(M-OSiCl_3)^+$). HRMS (EI): Calcd. for $C_9H_8Cl_6O_2Si_2$: 413.81941, found: 413.81935. Purification of the product by distillation, column chromatography did not succeed.

**Reaction of 1a with 2c.** In an NMR tube which is flushed by nitrogen, **2c** (49.0 mg, 0.200 mmol) was put in, and **1a** (60.0 mg, 0.220 mmol) was introduced by a syringe. The tube was then stoppered by a septum and heated to 80 °C for 2 hours, during which time a homogeneous light brown solution was obtained. The product was analyzed by $^{1}$H, $^{13}$C, $^{29}$Si NMR and HRMS as being compound **5c**. $^{13}$C NMR ($CDCl_3$): $\delta$ 140.18, 129.51, 125.97; $^{29}$Si ($CDCl_3$, $SiMe_4$): $\delta$ -20.17. MS (70eV, EI): m/z (relative intensity, ion) 518.0 (4.48, M$^{+}$(4 $^{37}$Cl, 6 $^{35}$Cl)), 516.0 (8.67, M$^{+}$(3 $^{37}$Cl, 7 $^{35}$Cl)), 514.0 (9.66, M$^{+}$(2 $^{37}$Cl, 8 $^{35}$Cl)), 344.0 (8.16, [M-($SiCl_3$+Cl)]$^{+}$). HRMS (EI): Calcd. for $C_6Cl_{10}O_2Si_2$: 509.63222, found: 509.63227. Efforts to purify the product by distillation, column chromatography did not succeed.

**Reaction of 1a with 2d.** This reaction procedure is the same as that of **1a** with **2c**, so only characterization of product is given. NMR data for **5d**. $^{1}$H NMR ($CDCl_3$): $\delta$ 8.67-8.69 (m, 2H), 8.21-8.23 (m, 2H), 7.70-7.71 (m, 4H); $^{13}$C NMR ($CDCl_3$): $\delta$ 134.88, 128.87, 127.43, 127.03, 126.66, 122.91, 122.84; $^{29}$Si NMR ($CDCl_3$, $SiMe_4$): $\delta$ -20.09. MS (70 eV, EI): m/z (relative intensity, ion) 482.0 (1.18, M$^{+}$(4 $^{37}$Cl, 2 $^{35}$Cl)), 480.0 (4.23, M$^{+}$(3 $^{37}$Cl, 3 $^{35}$Cl), 478.0 (9.55, M$^{+}$(4 $^{37}$Cl, 2$^{35}$Cl), 476.0 (12.38, M$^{+}$($^{37}$Cl, 5 $^{35}$Cl)), 474.0 (6.18, M$^{+}$(6 $^{35}$Cl), 135.0 (6.64, $SiCl_3$). HRMS (EI): Calcd. for $C_{14}H_8Cl_6O_2Si_2$: 473.81941, found: 473.81953. Purification of the product by distillation, column chromatography did not succeed.

**Reaction of 1a with 3a-e.** The typical reaction procedures of **1a** with *1,4*-benzoquinones can be illustrated by the reaction of **1a** and benzoquinone (**3a**) described as follows. **3a** (purified by recrystallization from hexane) (22.0 mg, 0.200 mmol) was put in an NMR tube under nitrogen, then **1a** (60.0 mg, 0.220 mmol) was introduced by a syringe. The NMR tube was stoppered by a septum and then was heated to 80 °C for 2 hours, during the time the reaction mixture became a clear light yellow solution. After reaction the product was analyzed by $^1H$, $^{13}C$, $^{29}Si$ NMR and HRMS spectroscopies as **6a**. $^1H$ NMR ($CDCl_3$): δ 7.04 (s, 4H); $^{13}C$ NMR ($CDCl_3$): δ 147.62, 121.00; $^{29}Si$ NMR ($CDCl_3$): δ -22.02. MS (70eV, EI): m/z (relative intensity, ion) 380.0 (5.34, $M^+(4\ ^{37}Cl, 2\ ^{35}Cl)$), 378.0 (11.75, $M^+(3\ ^{37}Cl, 3\ ^{35}Cl)$), 376.0 (17.21, $M^+(2\ ^{37}Cl, 4\ ^{35}Cl)$), 241.0 (1.01, $[M\text{-}SiCl_3]^+$). HRMS (EI): Calcd. for $C_6H_4Cl_6O_2Si_2$: 373.78811, found: 373.78780. This reaction was also carried out in $CHCl_3$ at room temperature, same product **6a** was obtained in 100% conversion immediately after mixing **1a** and **3a**. Purification of the product by removal of **1a** under vacuum afforded pure product. Elemental analysis: calcd. for $C_6H_4Cl_6O_2Si_2$: C 19.09 %, H 1.19 %, Cl 56.49%, Si 14.77 %; found C 19.31%, H 1.19 %, Cl 56.04 %, Si 14.48.

*Reaction temperature and time for **1a** and **3b**:* Due to poor solubility of **3b** in **1a** and $CDCl_3$, this reaction was carried out in $CD_3CN$. In an NMR tube, **3b** (18.0 mg, 1.00 mmol) was dissolved in 0.7 mL $CD_3CN$ to give a light yellow solution. **1a** (40.0 mg, 1.50 mmol) was added by a syringe. Two layers of liquid were formed, of which the bottom layer was **1a**. Shaking the NMR tube frequently for 10 minutes, and the tube was kept at room temperature for another 2 hours, during which time the **3b** $CD_3CN$ solution became colorless. The unreacted **1a** at the bottom was sucked out by a syringe, and the product was analyzed by NMR spectroscopies as **6b**. NMR spectra for **6b**. $^{13}$C NMR ($CD_3CN$): δ 144.09, 138.84; $^{29}$Si NMR ($CD_3CN$, $Si_2Cl_6$): δ 0.03. Purification of the product by distillation, column chromatography methods did not succeed.

*Reaction temperature and time for **1a** with **3c**:* 80 °C, 2 hours (no solvent) in an NMR tube. NMR data for **6c**. $^{1}$H NMR ($CDCl_3$): δ 2.21 (s, 12H); $^{13}$C NMR ($CDCl_3$): δ 145.84, 125.68, 14.58; $^{29}$Si NMR ($CDCl_3$, $SiMe_4$): -23.83. MS (70eV, EI): m/z (relative intensity, ion) 436.0 (2.76, $M^+$ (3 $^{37}$Cl, 3 $^{35}$Cl)), 434.0 (6.28, $M^+$ (2 $^{37}$Cl, 4 $^{35}$Cl)), 432.0 (9.73, $M^+$ ($^{37}$Cl, 5 $^{35}$Cl)), 430.0 (4.66, $M^+$ (6 $^{35}$Cl)). HRMS (EI): Calcd. for $C_{10}H_{12}Cl_6O_2Si_2$: 429.85071, found: 429.85092. Purification of the product by distillation, column chromatography did not succeed.

*Reaction temperature and time for **1a** with **3d**:* 80 °C, 1 hour (no solvent) in an NMR tube. NMR spectra for **6d**. $^{1}$H NMR ($CDCl_3$): δ 6.75 (s, 2H), 2.28 (s, 6H); $^{13}$C NMR ($CDCl_3$): δ 146.86, 146.21, 130.16, 119.66, 17.86; $^{29}$Si NMR ($CDCl_3$, $SiMe_4$): δ -18.07, -22.53. MS (70eV, EI): m/z (relative intensity, proposed ion) 410.0 (1.38, $M^+$ (4 $^{37}$Cl, 2 $^{35}$Cl)), 406.0 (9.60, $M^+$ (3 $^{37}$Cl, 3 $^{35}$Cl)), 404.0 (10.00, $M^+$ (2 $^{37}$Cl, 4 $^{35}$Cl)), 402 (7.80, $M^+$ ($^{37}$Cl, 5 $^{35}$Cl)). HRMS (EI): Calcd. for $C_8H_8Cl_6O_2Si_2$: 401.81941, found: 401.81927. Efforts to purify the product by distillation, column chromatography did not succeed.

*Reaction temperature and time for **1a** with **3e**:* 100 °C, 2 hours (no solvent) in an NMR tube. NMR data for **6e**. $^{1}$H NMR ($CDCl_3$): δ 8.05-8.07 (m, 2H), δ 7.55-7.62 (m, 2H), δ 7.05 (s, 1H), δ 2.49 (s, 3H); $^{13}$C NMR ($CDCl_3$): δ 143.64, 142.32, 127.76, 127.46, 126.20, 125.90, 123.64, 122.07, 121.86, 116.79, 17.73; $^{29}$Si NMR ($CDCl_3$, $SiMe_4$): δ -21.96, -22.53. MS (70eV, EI): m/z (relative intensity, ion) 446.0 (1.31, $M^+$ (4 $^{37}$Cl, 2 $^{35}$Cl)), 444.0 (4.93, $M^+$ (3 $^{37}$Cl, 3 $^{35}$Cl)), 442.0 (10.62, $M^+$ (2 $^{37}$Cl, 4 $^{35}$Cl)), 440.0 (13.69, $M^+$ ($^{37}$Cl, 5 $^{35}$Cl)). HRMS (EI): Calcd. for $C_{10}H_8Cl_6O_2Si_2$: 437.81942, found: 437.81946. Product purification by distillation, column chromatography methods did not succeed.

**General description of NMR reactions of 1b with 2a, 2b, 3a and 3c.** The procedures for these reactions were similar to those described for **1a** based reactions, except for the reaction temperature and time, as discussed individually below.

**Reaction of 1b with 2a**: temperature 110 °C, 2 hours. NMR data for **7a**. $^1$H NMR ($CDCl_3$): δ 7.19-7.26 (m, 10H); $^{13}$C NMR ($CDCl_3$): δ 136.29, 134.47, 129.48, 129.39, 128.06, 5.42; $^{29}$Si NMR ($CDCl_3$, $SiMe_4$): δ 9.18. HRMS (EI): Calcd. for $C_{16}H_{16}Cl_4O_2Si_2$: 435.94330, found: 435.94435. Purification of the product by distillation, column chromatography failed.

**Reaction of 1b with 2b**: temperature 110 °C, 2 hours. NMR spectra for **7b**. $^1$H NMR ($CDCl_3$): δ 7.31-7.39 (m, 4H), 2.03 (s, 3H), .096 (s, 3H), 0.74 (s, 3H); $^{13}$C NMR ($CDCl_3$): δ 134.57, 134.06, 133.81, 129.15, 128.82, 128.42, 128.18, 17.92, 5.34, 5.28; $^{29}$Si NMR ($CDCl_3$, $SiMe_4$): δ 8.48, 6.64; HRMS (EI): Calcd. for $C_{11}H_{14}Cl_4O_2Si_2$: 373.92865, found: 373.92834. Purification of the product by distillation, column chromatography methods did not succeed.

**Reaction of 1b with 3a**: temperature 120 °C, 5 hours. NMR data for **8a**. $^1H$ NMR ($CDCl_3$): δ 6.96 (s, 4H), 0.94 (s, 6H); $^{13}C$ NMR ($CDCl_3$): δ 147.71, 4.59; $^{29}Si$ NMR ($CDCl_3$, $SiMe_4$): δ 6.99; HRMS (EI): Calcd. for $C_8H_{10}Cl_4O_2Si_2$: 333.89735, found: 333.89749. Tries to purifying the product by distillation, column chromatography did not succeed.

**Reaction of 1b with 3c**: temperature 120 °C, conversion: 5 hours, 14%; 24 hours, 50%. NMR data for **8b**. $^1H$ NMR ($CDCl_3$): δ (s, 12H), 0.93 (s, 6H); $^{13}C$ NMR ($CDCl_3$): δ 145.47, 125.29, 14.55, 5.41; $^{29}Si$ NMR ($CDCl_3$, $SiMe_4$): δ 6.44.; HRMS (EI): Calcd. for $C_{12}H_{18}Cl_4O_2Si_2$: 389.95995, found: 389.96003. Purification of the product by distillation, column chromatography did not succeed.

**Reactions of 1b with 2a, 2b, 3a, 3c in $CDCl_3$ at room temperature** These reactions were performed under same conditions as for **1a/2a**, **1a/2b**, **1a/3a** and **1a/3b** reactions, products **7a**, **7b**, **8a** and **8b** were obtained in quantitative conversions by $^1H$ NMR spectroscopy. No product purification was performed.

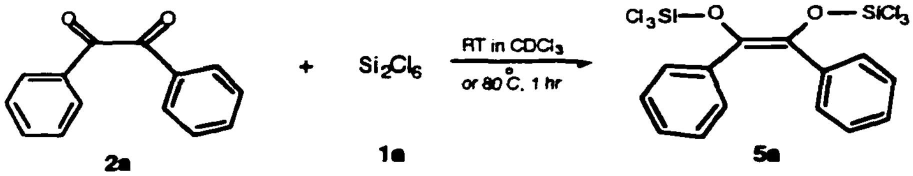
**Synthesis of hexacoordinated bicyclic silicon compound 9**. In a 250 mL flask equipped with a magnetic stirrer, $Et_2O$ 100 mL was added under nitrogen, followed by *N*-methylpropionamide (2.61 g, 30.0 mmol). The solution was cooled to 0 °C by ice, and *tert*-butyllithium (1.7 M in pentane) 18.0 mL was added dropwise under nitrogen through a syringe. White suspension was observed to form during the addition of $^tBuLi$. After the addition of $^tBuLi$ solution, the reaction mixture was stirred at 0 °C for one hour, and at room temperature for another 2 hours. Then the reaction mixture was re-cooled to 0 °C by an ice bath and $Si_2Cl_6$ (2.01 g, 7.50 mmol) or $SiCl_4$ (2.55 g, 15 mmol) was added dropwise to the suspension. The reaction mixture was allowed to warm up and was stirred for 2 hours at room temperature, followed by refluxing overnight. After reaction, the reaction mixture was filtered and crystals were observed to form during filtration. Colorless crystal material (3.13 g) was obtained and analyzed by $^1H$, $^{13}C$, $^{29}Si$ NMR and mass spectroscopies to be product **9**. Characterizations for **9**: $^1H$ NMR ($CDCl_3$): δ 2.99 (s, 3H), 2.40-2.47 (q, 2H), 1.17-1.22 (t, 3H); $^{13}C$ NMR ($CDCl_3$): δ 183.31, 29.27, 21.09, 8.02; $^{29}Si$ NMR (solid): δ -159.89. MS (EI) m/z (intensity, ion): 270.9 (19.46, $M^+$). Crystals suitable for x-ray diffraction spectroscopy were also obtained and the structure was solved to confirm the proposed structure for **9** (*cis*-conformation).

## Results and Discussion

We were investigating the possibilities of using disilanes in organic syntheses,[17,18] and we reported that at a temperature between 170 and 200 °C, hexachlorodisilane (**1a**) and hexamethoxydisilane (**1d**) were effective in cyclo-trimerizing alkynes into the corresponding aromatic products via a radical pathway. This occurs primarily because of the weak linkage of Si-Si bonds, especially when electron-withdrawing groups are attached to the Si atoms.

As an effort to detect the silyl radicals, *1,2*-quinones and *1,4*-quinones, which are commonly known as efficient radical traps,[19] were utilized in our reaction systems. When benzil (**2a**) was introduced in the reactions of **1a** with alkynes, no cyclotrimerization product was detected, however, new product *cis-1,2*-diphenyl-*1,2*-*bis*(trichlorosiloxy)ethene (**5a**) was formed as a viscous liquid. Lowering the reaction temperature to 80 °C, or simply mixing **1a** and **2a** in $CHCl_3$ (or toluene) at room temperature gave **5a** in quantitative conversion (reaction 1), as confirmed by $^1H$, $^{13}C$ and $^{29}Si$ NMR spectroscopies. Other *1,2*-quinones such as *1*-phenyl-*1,2*-propanedione (**2b**), tetrachloro-*1,2*-benzoquinone (**2c**) and phenanthrenequinone (**2d**) also readily reacted with **1a** to give corresponding products **5b-d** in quantitative conversions.

On the other hand, *1,4*-quinones *p*-benzoquinone (**3a**), tetrafluoro-*1,4*-benzoquinone (**3b**), tetramethyl-*1,4*-benzoquinone (**3c**), *2*-methyl-*1,4*-naphathoquinone (**3d**) and *2,6*-dimethylbenzoquinone (**3e**) were also tried under same reaction conditions



(1)

(either heated to 80-100 °C or just mix the reagents in $CHCl_3$ at room temperature), corresponding aromatized compounds **6a-e** were obtained in quantitative conversions. These compounds have been characterized by $^1H$, $^{13}C$, $^{29}Si$ NMR and HRMS spectroscopies.

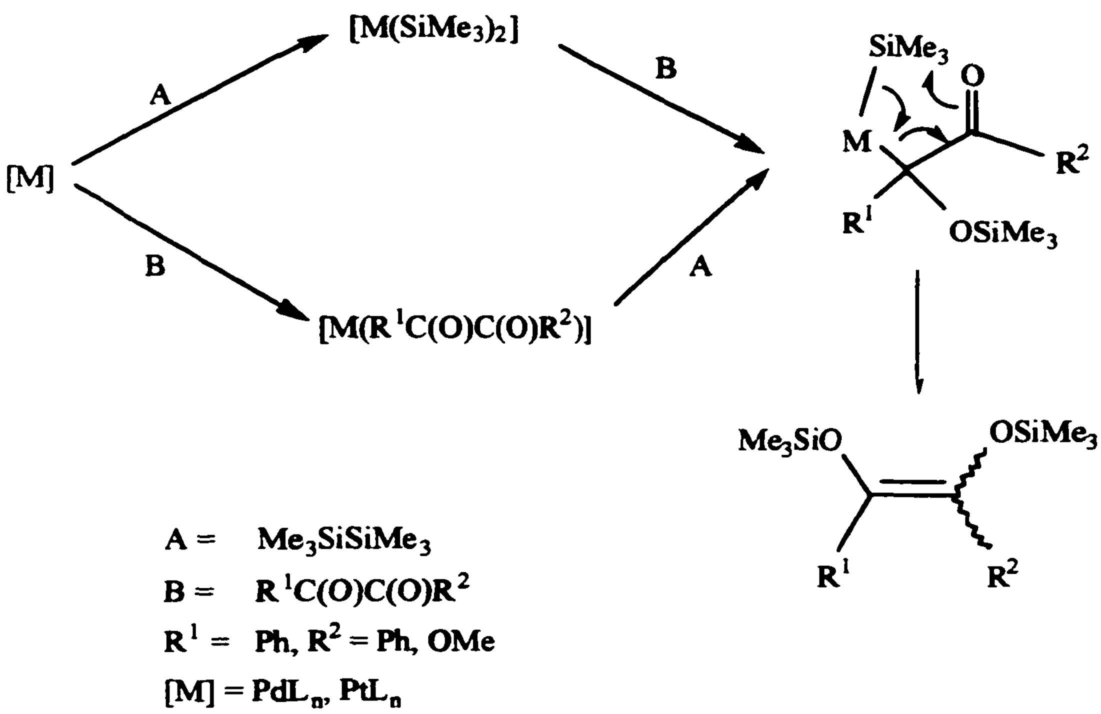
Literature search showed that non-activated disilane/quinone reactions had been carried out, however, these reactions did not occur in the absence of transition metal complexes such as $Pd(PPh_3)_2Cl_2$ and $Pt_2(dba)_3P(OCH_2)_3CEt$ (dba =

dibenzylideneacetone).[13, 20] It was reported [13 20] that non-activated disilanes such as hexamethyldisilane (**1c**), which themselves did not react with α-diketones or *p*-quinones, could be catalyzed by the transition metals to give *1,2-* or *1,4-bis*(trimethylsiloxy)ethenes possibly via a metal-disilane complex formation pathway as illustrated in Schemes 1[20] and 2[13].

Whether this pathway is true for this type of non-activated disilane-based reactions is subject to future research, however, for disilanes such as **1a**, **1b** and **1d**, which are activated by multiple halogen atoms or alkoxy groups, a different explanation would be expected.

The strength of Si-Si linkage in disilanes would be weakened when electron withdrawing groups are present, therefore $SiCl_3$ radicals could be generated when **1a** was heated.[17,18] We therefore suspected that the radical generation might account for the occurrence of reaction 1 at 100 °C. However, the following two observations excluded this possibility. First, when **1a** and **2a** were mixed in chloroform or toluene, we observed immediate formation of **5a** even under ambient conditions, at which temperature the $SiCl_3$ radicals, if any, would have too low a concentration to induce the reaction in such a short time. Second, **1b**, although efficient in this reaction, was known to be inert to the cyclotrimerization of alkynes.[17] When **1b** was introduced to react with *1,2*-quinones and *p*-quinones, we found that it worked as well in these reactions, though a higher temperature and longer time was required, as described in experimental section. Furthermore, non-activated disilane **1c**, together with mono-activated $FMe_2$ $SiSiMe_2F$,

Scheme 1



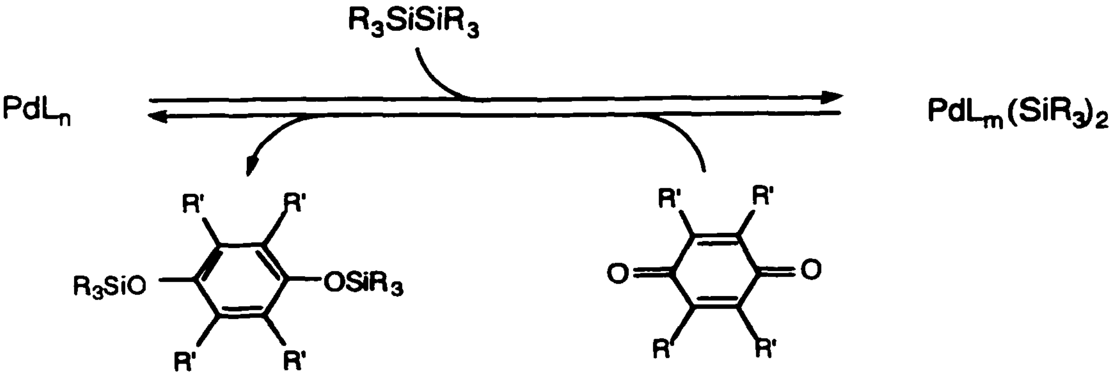
A = $Me_3SiSiMe_3$

B = $R^1C(O)C(O)R^2$

$R^1$ = Ph, $R^2$ = Ph, OMe

[M] = $PdL_n$, $PtL_n$

Scheme 2



was known to be inert in reactions with *1,2*-quinones and *p*-quinones in the absence of a transition metal complex.[5a]

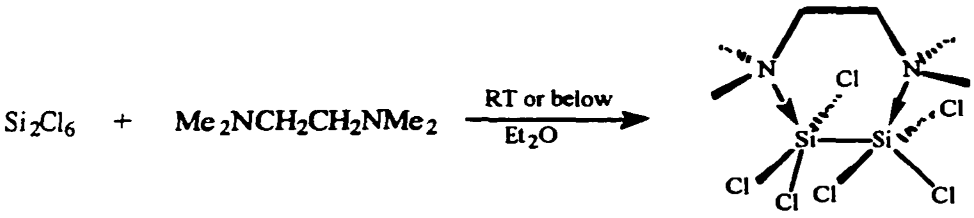
We speculate that all the disilane/*1,2*-quinone and disilane/*p*-quinones reactions were probably initiated by the formation of hypercoordinated (most possibly pentacoordinated in this case) (di)silicon species, the presence of which became more apparent when electron withdrawing groups such as halogens were attached to silicon atoms. In the following part we attempt to provide some support for this speculation.

Hypercoordinated silicon compounds have been investigated extensively, this type of complexes were known to be efficient in many reactions.[20] However, similar researches on disilanes are quite insufficient. Our previous reports[17, 18] gave a brief description of the catalytic reactions of disilanes in the temperature range of 170-200 °C, the lower temperature behavior of disilanes, especially hypercoodination adduct formation and reactivity of the adducts, remains unexplored. As an effort to discover the pathway for activated disilane/*1,2*-quinone and disilane/*p*-quinones reactions, we tried some reactions at different temperature conditions: from moderate temperature (around 100 °C), to room temperature and to a temperature close to 0 °C , and some note-worthy phenomena were observed as discussed below.

**Disilane adduct formation.** Silanes such as methyltrichlorosilane have long been known to be able to form adducts with compounds possessing lone-paired electrons (e.g. DMF),[20, 21] the formation of the adducts was detected in solution by $^{29}$Si NMR and supported by some characteristic catalytic reactions.[20, 21] For disilanes, we observed that

$Si_2Cl_6$ reacted with triethylamine to form white precipitate quantitatively when we attempted to use this amine as a solvent, this white powder material was analyzed by solid state $^{29}$Si NMR (see experimental section) to contain hypercoordination Si species, although no detailed analysis was made to this compound. Later we found that $Si_2Cl_6$ readily forms hypercoordinated adducts with many other compounds.

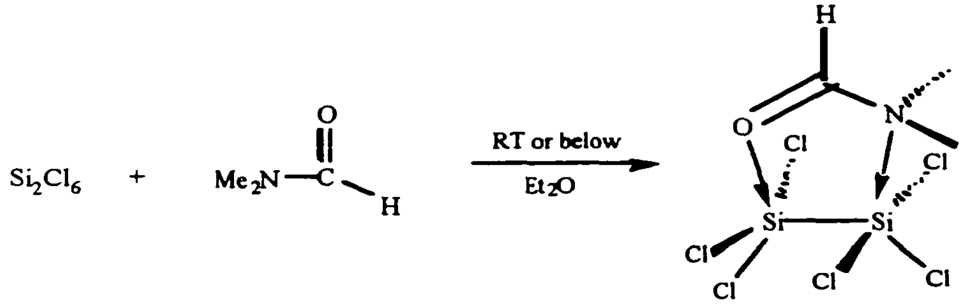
When $Si_2Cl_6$ was added to the *N,N,N',N'*-tetramethylethylenediamine solution (in $Et_2O$) at room temperature (or -78 °C), white precipitate formed immediately. Filtering off the solvent and drying the product under vacuum afforded white powder material in 93% yield. Although only a slight change in $^1$H and $^{13}$C NMR was observed with regard to the diamine starting material, the evidence for the presence of hypercoordinated silicon species was obtained from solid $^{29}$Si NMR, in which only a strong signal at δ -79.24 ppm was observed, and the lack of other $^{29}$Si peaks was in consistence with the idea of a stochiometric reaction. The proposed reaction pathway and the speculated structure of the product is shown in reaction 2.



(2)

Adduct **A**

The reaction of $Si_2Cl_6$ with DMF further supported the notion of formation of hypercoordinated disilane species. In this case, although we could not obtain pure product from the reaction, two high field signals at δ -184.71 ppm and δ -192.10 ppm, respectively, were observed in the solid $^{29}Si$ NMR spectroscopy (despite the similarity in $^{1}H$ and $^{13}C$ NMR of the adduct to DMF itself). Equation 3 shows the proposed reaction pathway and structure of the adduct. A ring structure was proposed in both reactions 2 and 3 just for the simplicity of argument. Other hypercoordinated disilane adducts can in principle be obtained similarly by reacting **1a**, **1b** or **1d** with a tertiary amine, diamine or compounds with lone-paired electrons. Although in these reactions we could not obtain crystals suitable for X-ray analysis, the experimental results suggested that disilanes with electron withdrawing groups have as strong a tendency as, if not stronger than, silanes to form hypercoordinated silicon species.



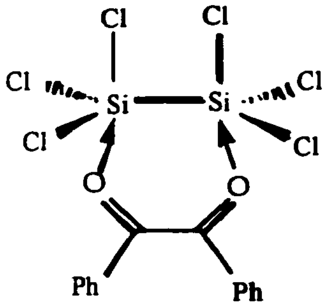
Adduct **B**

(3

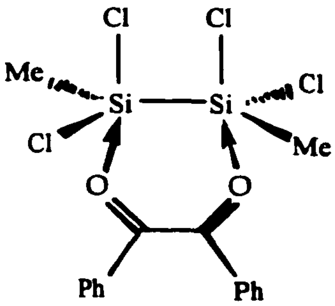
**Reactions of disilane with quinone.** As pointed out, when benzil (or other *1,2*-quinones) reacted with **1a** at moderate temperature (<120 °C), *1,2*-diphenyl-*1,2*-*bis*(trichlorosiloxy)ethene (**5a**) was obtained in quantitative conversion, similarly, products **5b**-**5d** were obtained in excellent conversions, However, when we carried out these reactions at room temperature, it was found that if the reaction was performed in a solvent such as $CHCl_3$ (or toluene), reaction 1 went to completion within a few seconds.

In the same way, **1b** also reacted with *1,2*-quinones (**2a-b**) and *p*-quinones (**3a**, **3c**) at moderate temperature to afford **7a**, **7b**, **8a** and **8c** in mild to excellent conversions, of which **1b/2a** and **1b/3c** reactions (120 °C) gave products in 14% and 83% conversions after 5 hours, and 50% and 100% conversions after 24 hours, respectively. It suggests that the steric hindrance caused by four methyl groups in **3c** might become a destructive factor. When carried out in chloroform (or toluene) at room temperature, the reactions also went to completion within a few minutes.

We hence propose that adduct formation (as an unstable intermediate) between disilane **1a** (or **1b** ) and an *1,2*-quinone be the initial step for these reactions, as shown by the following adducts (adducts **C** and **D**).



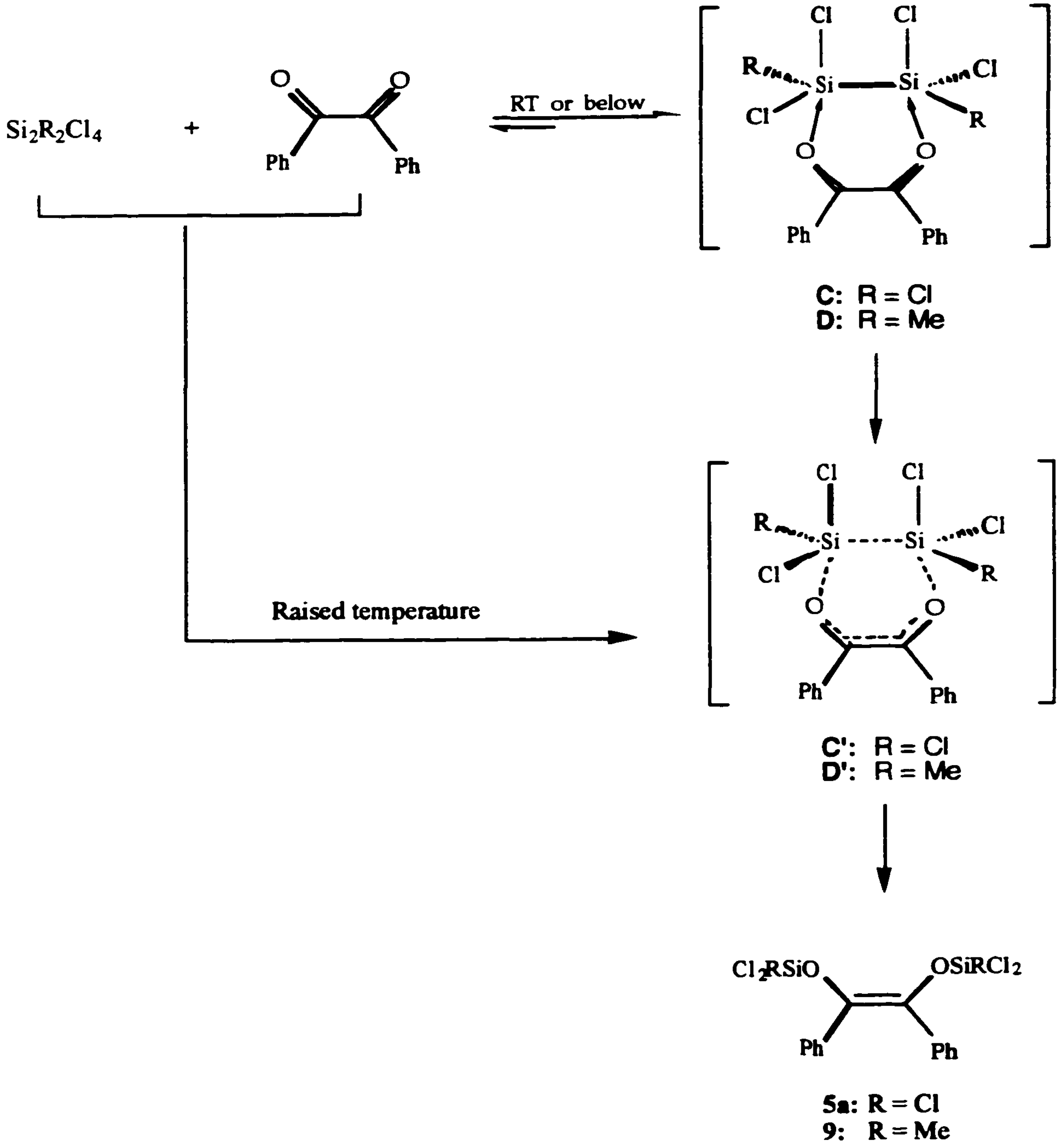
**Adduct C**



**Adduct D**

**Relationship between disilane/quinone adducts and the products.** It might be interesting to ask this question: why at higher temperature (or in reactions at room temperature with a solvent), we can obtain the products **5-8** through the cleavage of Si-Si and C=O bonds, accompanied by the formation of C=C bond, whereas in other cases, only the adducts **A** and **B** could be formed? We speculate that in all those reactions the formation of the hypercoordinated disilane adducts was the initial step, followed by intra-molecular rearrangements (true for the reactions of **1a** (or **1b**) with *1,2*-quinones (or *p*-quinones)) to give the final products. It is apparent that there is no driving force for the cleavage of Si-Si bond in adducts **A** and **B**, therefore these species are expected to be stable and no further intra-molecular rearrangements would occur. On the contrary, adducts **C** and **D** seek for the more stable forms given by products **5-8**, as shown in Scheme 3 (with **2a** as an example), where, species **C** (or **D**) forms at the beginning of the reactions, which upon heated (or dissolved in a suitable solvent) tends to have equilibrium with the resonance structure **C'** (or **D'**). Since product **5a** (or **7a**) is clearly more stable than both **C** (or **D**) and **C'**(or **D'**) , **C'** (or **D'**) undergoes Si-Si bond cleavage, accompanied by the formation of stronger Si-O bonds, leading to **5a** (or **7a**). We might as well think that Si-Si bond cleavage and Si-O bond formation occur at the same time. However, for disilanes such as **1c**, due to the lack of electron withdrawing groups, the tendency for the formation of pentacoordinated species would not be as strong, if any, and so the Si-Si bond would not be weakened as much as in the **1a**, **1b** cases. That is, the reluctancy of formation of a pentacoordinated species such as **C** (or **D**) and the

Scheme 3


Si2R2Cl4
+
O
O
Ph
Ph
RT or below
Raised temperature
Cl
Cl
R
Si
Si
Cl
Cl
R
O
O
Ph
Ph
C: R = Cl
D: R = Me
C': R = Cl
D': R = Me
Cl2RSiO
OSiRCl2
Ph
Ph
5a: R = Cl
9: R = Me

unwillingness of the Si-Si bond cleavage accounted for the inertness of **1c** in the absence of a transition metal complex. This intra-molecular pentacoordination pathway was further supported by the X-ray structure of **5a**, and the observation that in any of the *1,2*-quinone reactions involving **1a** or **1b**, only one isomer (presumably the *cis*-conformation) was obtained, which is different from non-activated disilane/quinone reactions, in which both *cis*- and *trans*- conformations were obtained in various ratios.[9c]

We were therefore motivated to investigate on the adduct **C**. Instead of carrying out the reaction in a solvent or at a raised temperature, we performed the reaction at 0 °C (in an ice bath) without using a solvent. The mixture of **1a** and **2a** (**1a** 20% in excess) was sealed in a glass tube, and was stirred vigorously until a homogeneous solution was obtained. Occasional shaking was essential to ensure good mixing. The solution was stored without disturbance at 0 °C for two days, during which time colorless crystals were seen to form. Analysis by X-ray diffraction means indicated that the crystals were *cis-1,2*-diphenyl-*1,2-bis*(trichlorosiloxy)ethylene (with **1a** as an inclusion), instead of the desired adduct product **C**. Moreover, monitoring the reaction by recording $^{29}$Si NMR spectra in toluene at −50 °C showed instant formation of the product **5a**. These results suggested that the adduct intermediates, even if formed, must be too unstable to be detected or isolated. As an extension, compound **4** was also reacted with **1a**, similar disilylation product was detected by mass spectroscopy.[22]

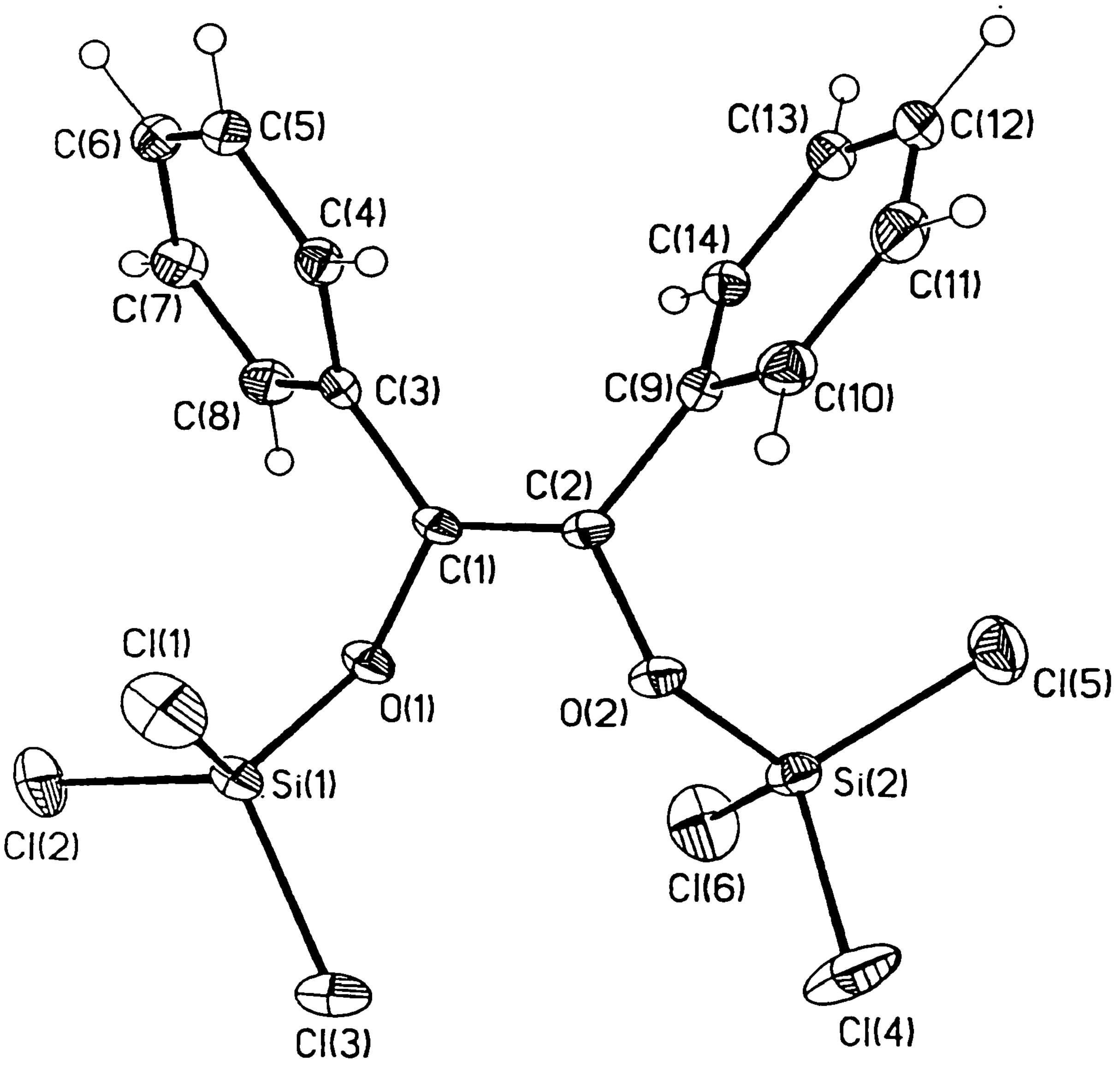
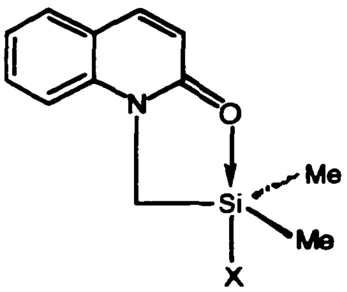


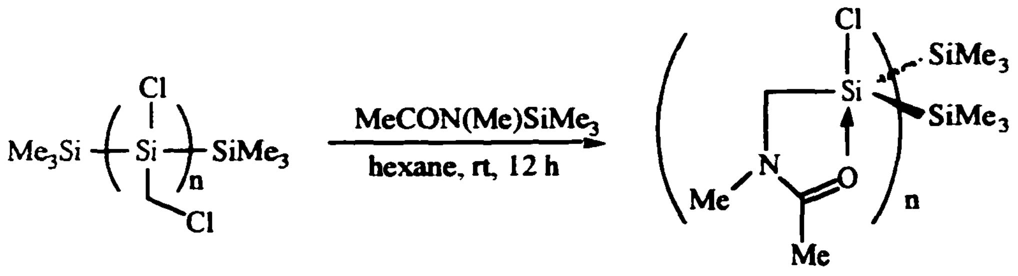
Fig. 1. ORTEP drawing of compound **5a**

**Synthesis of hexacoordinated silicon species with new ligands.** The concept of formation of a coordination bond between an acetyl group (via oxygen) and a silicon atom has been known.[23] It was reported that in the following structures, the Si-X (X= halogens, $SO_3CF_3$), as well as the Si-O bond distances, would change accordingly with different substituting X groups. The shortest Si-O bond (1.74 Å) was observed for X=$SO_3CF_3$ case, which was comparable to the Si-O formal bond in *1,2*-diphenyl-*1,2*-*bis*(trichlorosilyoxy)ethylene (1.61 Å).



| X | F | Cl | Br | $SO_3CF_3$ |
|---|---|---|---|---|
| d(Si-X)[pm] | 168 | 232 | 265 | 276 |
| d(O-Si)[pm] | 206 | 194 | 185 | 174 |

More recently it was reported[16] that trisilane **10** and tetrasilane **11** could react with *N*-methyl-*N*-trimethylsilylacetamide to afford pentacoordinated silicon compounds **12** and **13**, respectively. In both cases, the intra-molecular O→Si coordination within the five-membered rings was present.

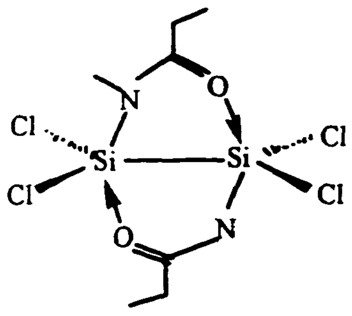


(4)

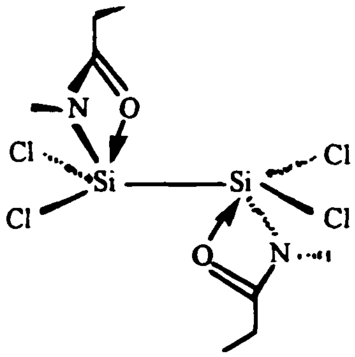
**10**: n = 1
**11**: n = 2

**12**: n = 1
**13**: n = 2

When we performed the reaction between **1a** and four equivalents of the lithium salt of *N*-methylpropionamide, which was obtained by reacting equal amount of *N*-methylpropionamide and ${}^{t}$BuLi, in $Et_2O$ (refluxed for 20 hours), we obtained interesting hexacoordinated compound **9**, instead of the expected product **14a** or **14b**.



**14a**



**14b**

Compound **9** represents the first example that a main group element has formed a four-membered ring with this type of ligand. It was also surprising to notice that in **9** the

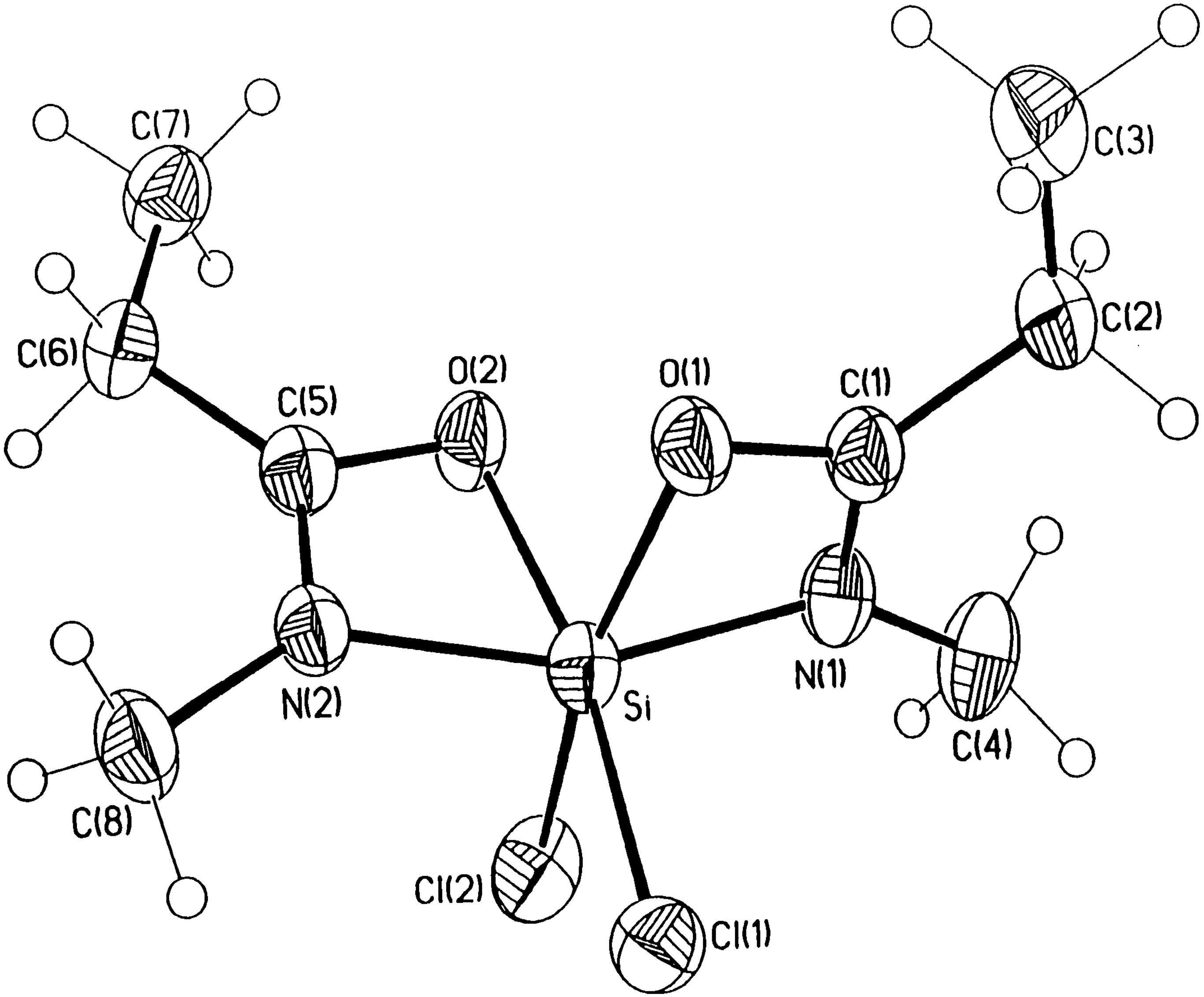


Fig. 2. ORTEP drawing of compound **9**.

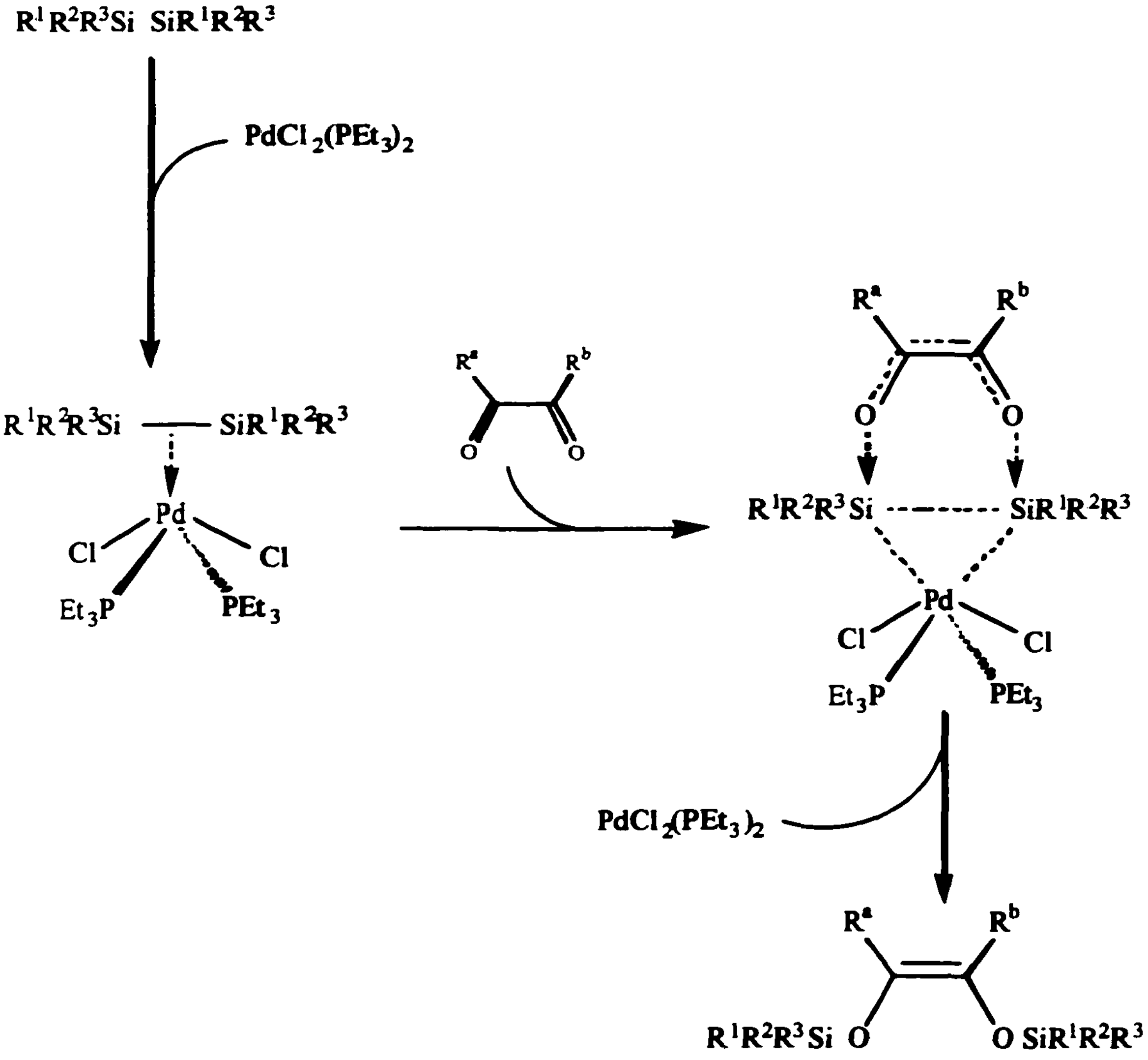
Si-N, Si-O bond lengths are very close (1.83 Å and 1.88 Å, respectively), and O-C, N-C links (on the rings) are essentially of the same length (1.30 Å), indicating complete delocalization of the electron(s) within the four-membered ring systems. It was later found that lithium salt of *N*-methyltrimethylacetamide could also react with $Si_2Cl_6$ (or $SiCl_4$) to give the corresponding bicyclic product.[22] The corresponding Ge compounds can be made in the same way.[22]

To rationalize the reaction path of non-activated disilanes with *1,2*- and *1,4*-quinones, we propose that in the reactions which were catalyzed by a transition metal complex such as $PdCl_2(PPh_3)_2$, the metal complexes could have formed intermediates with disilanes, making disilanes electronically more positive and thus have a tendency to achieve hypercoordinated Si-Si structure as shown below, where a quasi-18-electron shell configuration could be achieved for Pd or Pt complexes, against the initial 16 electron unsaturated shell in the catalysts such as $PdCl_2(PEt_3)_2$.

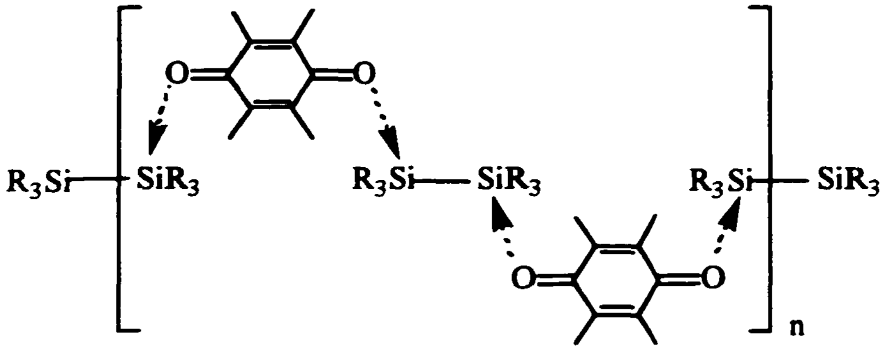
The proposed coordination of Si-Si moiety to the transition metal may be advantageous for the reactions with quinones: firstly, the Si atoms use part of their electrons to coordinate to the metal via the Si-Si bond, reducing the electron density around the Si atoms, therefore weakening the Si-Si bond; secondly, the resulting more electropositive Si atoms, weaker Si-Si bond and a longer Si-Si link favor the formation a hypercoordinated Si complex. This argument was consistent with the observation that Cl containing Pd complexes such as $PdCl_2(PPh_3)_2$ were much more efficient than

$Pd(PPh_3)_4$,[13] possibly due to the greater tendency the transition metal has to form [M-Si] complex with the presence of more electron withdrawing Cl atoms on the metal.

Scheme 4



In *p*-quinone/disilane reactions, the additional driving force of could be from the formation of aromatized products. Although these reactions were also believed to proceed via the formation of hypercoordinated silicon species, it is more reasonable to regard that this hypercoordination behavior occurred in an intermolecular way (shown below), rather than the intramolecular path proposed for *1,2*-quinone/disilane reactions.



Efforts to further clarify the reaction pathway, explore the potential applications of the new ligands in hypercoordination and hypocoordination chemistry, and evaluate the scope and limitations of this type of reactions are underway.

## Acknowledgements

The authors thank NSF and Petroleum Research Foundation for grant supports. Also thanks go to Dr. Wang Zhigang (a former postdoctor in this research group) for helpful discussion.

## References

1. For instance: (a) *Silicon Chemistry*; Corey, E. R., Corey, J. Y., Gaspar, P. P., Eds.; Ellis Horwood: Chichester, U. K., **1988**. (b) *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wilet: Chichester, U. K., **1989**. (c) *Frontiers of Organosilicon Chemistry*; Bassindale, A. R.; Gaspar, P. P., Eds.; The Royal Society of Chemistry: Cambridge, U. K., **1991**. (d) *Progress in Organosilicon Chemistry*; Marciniec, B., Chojnowski, J., Eds.; Gordon and Breach: Basel, Switzerland, **1995**.
2. For reviews on transition-metal-catalyzed reactions of Si-Si bonds: (a) Sharma, H. K.; Pannell, K. H.; *Chem. Rev.* **1995**, 95, 1351. (b) Horn, K. A. *Chem. Rev.* **1995**, 95, 1317.
3. For instance: (a) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975**, 97, 931. (b) Yamashita, H.; Catellani, M.; Tanaka, M. *Chem. Lett.* **1991**, 241. (c) Murakami, M.; Oike, H.; Sugawara, M.; Suginome, M.; Ito, Y. *Tetrahedron* **1993**, 49, 3933. (d) Murakami, M.; Suginome, M.; Fujimoto, K.; Ito,

Y. *Angew, Chem., Int. Ed. Engl.* **1993**, *32*, 1473. (e) Suginome, M.; Oike, H.; Shuff, P. H.; Ito, Y. *Organometallics* **1996**, *15*, 2170.

4. For instance: (a) Ishikawa, M.; Naka, A.; Oshita, J. *Organometallics* **1993**, *12*, 4987. (b) Suginome, M.; Matsumoto, A.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3061. and references therein.

5. (a) Tamao, K.; Okazaki, S.; Kumada, M. *J. Organomet. Chem.* **1978**, *146*, 87. (b) Obora, Y.l Tsuji, Y.; Kawamura, T. *Organometallics* **1993**, *12*, 2853. and references therein.

6. (a) Watanabe, H.; Saito, M.; Sutou, N.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1981**, 617. (b) Watanabe, H.; Saito, M.; Sutou, N.; Kishimoto, K.; Inoue, J.; Nagai, Y. *J. Organomet. Chem.* **1982**, *225*, 343.

7. Kusumoto, T.; Hiyama, T. *Tetrahedron Lett.* **1987**, *28*, 1907.

8. (a) Hayashi, T.; Matsumoto, Y. Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 4147. (b) Hayashi, T.; Matsumoto, Y. Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 5578. (c) Hayashi, T.; Matsumoto, Y. Ito, Y. *Tetrahedron Lett.* **1994**, *50*, 335.

9. (a) Reddy, N. P.; Yamashita, H.; Tanaka, M. *J. Am. Chem. Soc.* **1992**, *114*, 6596. (b) Yamashita, H.; Reddy, N. P.; Tanaka, M. *Macromolecules* **1993**, *26*, 2143. (c) Yamashita, H. Reddy, N. P.; Tanaka, M. *Chem. Lett.* **1993**, 315.

10. Uchimaru, Y.; Williams, N. A.; Tanaka, M. Presented at the 67th Annual Meeting of the Chemical Society of Japan, Tokyo, Japan, March 29-April, **1994**; Abstract 1H107.

11. (a) Ito, Y,; Nishimura, S.; Ishikawa, M. *Tetrahedron Lett.* **1987**, *28*, 1293. (b) Ito, Y.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1988**, *110*, 3692. (c) Ito, Y.; Suginome, M.; Murakami, M.; Shiro, M. *J. Chem. Soc. Chem. Commun.* **1989**, 1494. (d) Ito, Y.; Suginome, M.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1991**, *113*, 8899.

12. Williams, N. A.; Uchimaru, Y.; Tanaka, M. Presented at the 69th Annual Meeting of the Chemical Society of Japan, Tokyo, Japan, March 27-30, **1995**; Abstract 2C746.

13. Yamashita, H.; Reddy, N. P.; Tanaka, M. *Organometallics* **1997**, *16*, 5223.

14. Tamao, K.; Okazaki, S.; Kumada, M. *J. Organomet. Chem.* **1978**, *146*, 87.

15. Besson, A. C. R. *Held Seances Acad Sci.*, **1890**, *110*, 518.

16. El-Sayed, I.; Hatanaka, Y.; Muguruma, C.; Shimada, S.; Tanaka, M.; Koga, N.; Mikami, M. *J. Am. Chem. Soc.* **1999**, *121*, 5095.

17. Yang, J.; Verkade, J. G. *J. Am. Chem. Soc.* **1998**, *120*, 3855.

18. Yang, J.; Verkade, J. G. *Organometallics.***2000**, *19*, 893.

19. (a) Creber, K.; Ho, T. *Can. J. Chem.* **1982**, *60*, 1504. (b) Adeleka, B.; Wan, J. *J. Chem. Soc., Perkin Trans. 2*, **1980**, *1*, 225. (c) Roginskii, V.; Belyakov, V. *Dokl. Akad Nauk SSSR*, **1977**, *237*, 1404.

20. For review on hypercoordinated silicon chemistry, see: (a) Chuit, C.; Corriu, R. J. P.; Young, J. C. *Chem. Rev.*, **1993**, 93, 1371. (b) Holmes, R. R *Chem. Rev.*, **1996**, 96, 927.

21. Kobayashi, S.; Nishio, K. *J. Org. Chem.*, **1994**, 59, 6620.

22. Yang, J.; Verkade, J. G.; unpublished results.

23. Bassindale, A.; Borbaruah, M.; Glynn, S.; Parker, D.; Talyor, P. *J. Chem. Soc., Perkin Trans. 2*, **1999**, *110*, 2099.

# APPENDIX

## SUPPLEMENTAL MATERIAL 1. X-RAY DATA FOR *1, 2*-BIS(TRICHLOROSILOXY)-*1,2*-DIPHENYL ETHLENE, 5a

A colorless crystal with approximate dimensions 0.43 x 0.31 x 0.14 $mm^3$ was selected from oil under ambient conditions and was attached to the tip of a glass capillary. The crystal was mounted in a stream of cold nitrogen at 173(2) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K$\alpha$ ($\lambda$ = 0.71073 Å) radiation and the diffractometer to crystal distance of 5.08 cm.

The initial cell constants were obtained from three series of $\omega$ scans at different starting angles. Each series consisted of 20 frames at intervals of 0.3° in a 6° range about $\omega$ with the exposure time of 10 seconds per frame. A total of 43 reflections was obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 6921 strong reflections from the actual data collection.

The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of 1.8 hemisphere to a resolution of 0.80 Å. A total of 22002 data were harvested by collecting three sets of frames with 0.3° scans in $\omega$ with an exposure time 30 second per frame. These highly redundant data sets were corrected for Lorentz and polarization effects. The absorption correction was based on

fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[1]

The systematic absences in the diffraction data were uniquely consistent for the space groups $P2_1/c$ that yielded chemically reasonable and computationally stable results of refinement.[2] A successful solution by the direct methods provided the positions of most atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anistropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized position and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The molecule of hexachlorodisialne occupies a crystallographic inversion center. The final least-squares refinement of 253 parameters against 5077 data resulted in residuals $R$ (based on $F^2$ for $I \geq 2\sigma$) and $wR$ (based on $F^2$ for $I \geq 2\sigma$) of 0.0397 and 0.1122, respectively. The final difference Fourier was featureless.

## REFERENCES

1. Blessing, R. H. *Acta Cryst.* 1995, A51, 33-38.

1. All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-Ray System, Madison, WI).

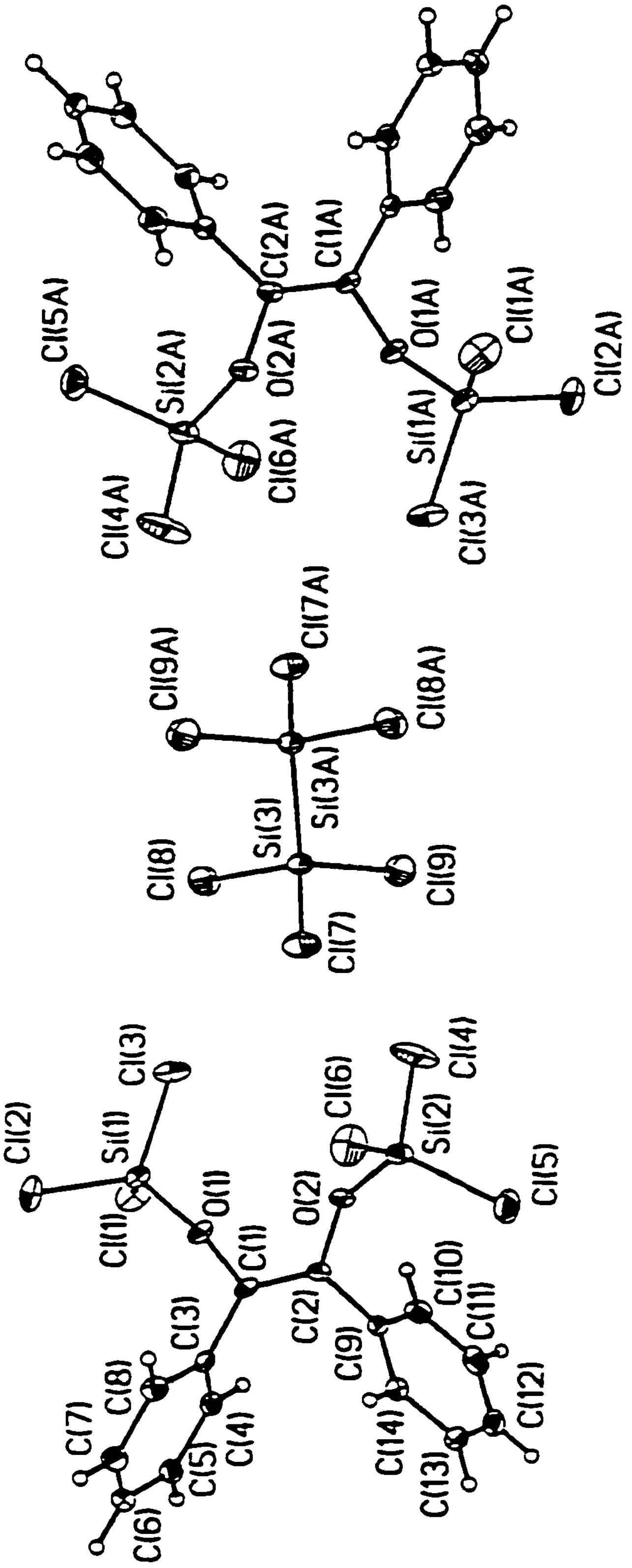


Figure 1. ORTEP drawing of **5a** showing the hexachlorodisilane inclusion

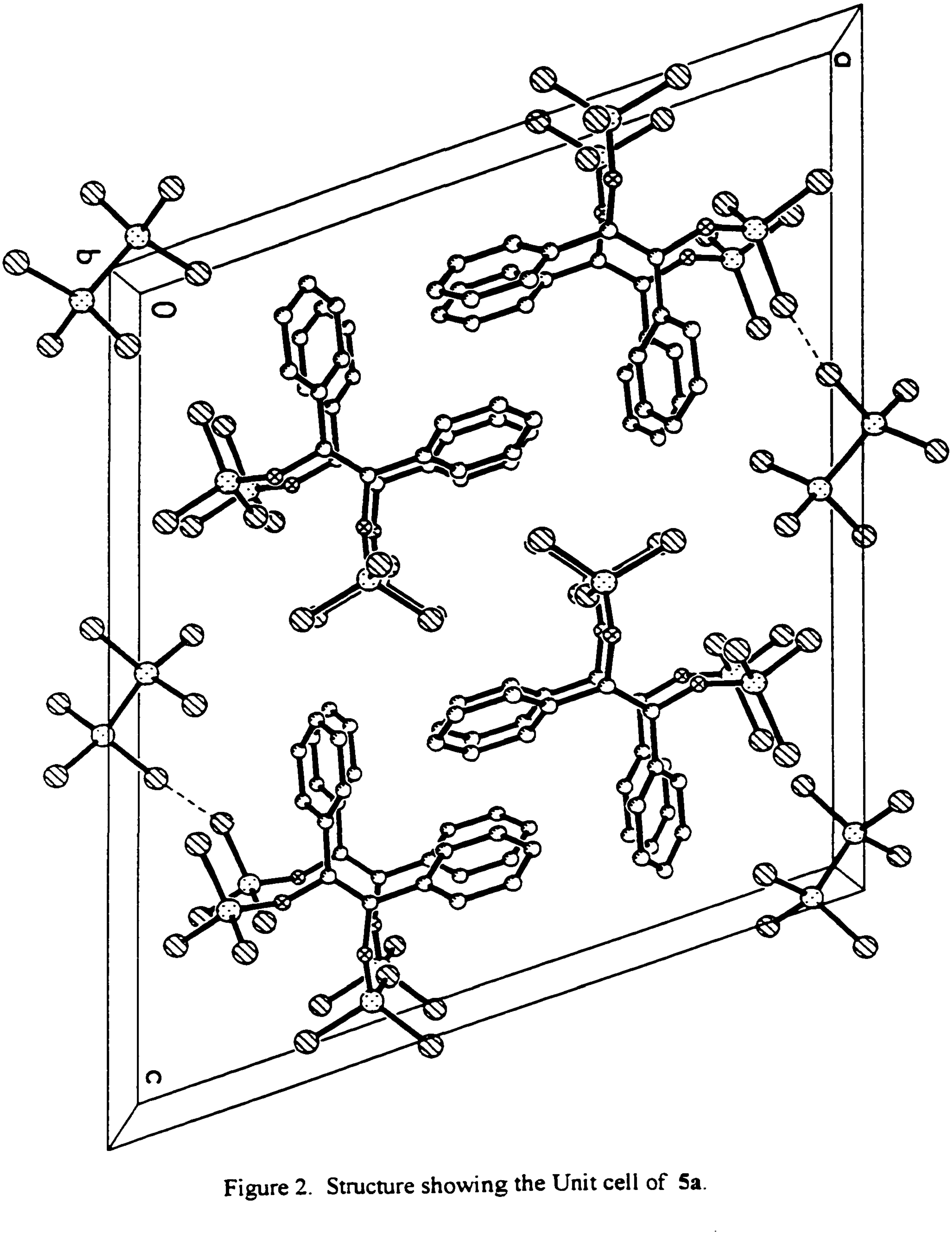


Figure 2. Structure showing the Unit cell of **5a**.

Table 1. Crystallographic Data for **5a**.

| | | |
|---|---|---|
| Empirical Formula | $C_{28}H_{20}Cl_{18}O_4Si_2$ | |
| Formula Weight | 1227.08 | |
| Temperature (K) | 173(2) | |
| Wavelength | MoKα (λ = 0.71073 Å) | |
| Crystal System | Monoclinic | |
| Space Group | $P2_1/c$ | |
| Unit Cell Dimensions | a = 19.5119(10) Å | α = 90° |
| | b = 5.9456(5) Å | β = 110.493(1)° |
| | c = 22.7893(12) Å | γ = 90° |
| Volume | 2476.5(3) $Å^3$ | |
| Z | 2 | |
| Density (calc.) | 1.646 $Mg/m^3$ | |
| Absorption Coefficient | 1.173 $mm^{-1}$ | |
| F (000) | 1220 | |
| Crystal Size (mm) | 0.43 x 0.31 x 0.14 | |
| θ Range | 1.11 to 26.37° | |
| Index Ranges | $-24 \leq h \leq 22$ $0 \leq k \leq 7$ | |
| | $0 \leq l \leq 28$ | |
| Reflections Collected | 22002 | |
| Independent Reflections | 5077 (R(int) = 0.0385) | |
| Completeness to theta = 26.37° | 99.8 % | |
| Absorption Correction | Empirical with SADABS | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Max. and Min. transmission | 0.8530 and 0.6324 | |
| Data / restraints / parameters | 5077 / 0 / 253 | |
| Goodness-of-fit on $F^2$ | 1.081 | |
| Final R indices [I > 2 sigma(I)] | R1 = 0.0397, wR2 = 0.1122 | |
| R Indices (all data) | R1 = 0.0574, wR2 = 0.1247 | |
| Largest diff. peak and hole | 0.694 and –0.543 e.$Å^{-3}$ | |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for **5a**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Cl(1) | 3640(1) | 2182(2) | 9421(1) | 54(1) |
| Cl(2) | 4284(1) | 6757(2) | 10242(1) | 48(1) |
| Cl(3) | 2531(1) | 5782(2) | 9720(1) | 56(1) |
| Cl(4) | 740(1) | 5432(2) | 8070(1) | 75(1) |
| Cl(5) | 1112(1) | 7801(2) | 6915(1) | 53(1) |
| Cl(6) | 1803(1) | 9911(2) | 8300(1) | 62(1) |
| Cl(7) | 874(1) | 11626(2) | 9440(1) | 49(1) |
| Cl(8) | 1067(1) | 7030(2) | 10287(1) | 46(1) |
| Cl(9) | -342(1) | 7554(2) | 8972(1) | 49(1) |
| Si(1) | 3454(1) | 5450(1) | 9526(1) | 27(1) |
| Si(2) | 1503(1) | 7007(2) | 7830(1) | 30(1) |
| Si(3) | 336(1) | 9207(1) | 9723(1) | 28(1) |
| O(1) | 3371(1) | 6847(2) | 8903(1) | 28(1) |
| O(2) | 2183(1) | 5281(2) | 7991(1) | 26(1) |
| C(1) | 3437(2) | 6154(5) | 8339(1) | 23(1) |
| C(2) | 2833(2) | 5564(5) | 7870(1) | 23(1) |
| C(3) | 4195(2) | 6219(5) | 8337(1) | 23(1) |
| C(4) | 4463(2) | 4472(5) | 8070(1) | 28(1) |
| C(5) | 5176(2) | 4536(6) | 8076(1) | 30(1) |
| C(6) | 5628(2) | 6336(6) | 8351(2) | 32(1) |
| C(7) | 5367(2) | 8047(6) | 8623(2) | 35(1) |
| C(8) | 4656(2) | 7991(5) | 8619(2) | 31(1) |
| C(9) | 2776(2) | 5101(5) | 7214(1) | 24(1) |
| C(10) | 2418(2) | 3195(6) | 6909(2) | 33(1) |
| C(11) | 2349(2) | 2789(6) | 6288(2) | 42(1) |
| C(12) | 2633(2) | 4307(7) | 5977(2) | 41(1) |
| C(13) | 2984(2) | 6214(6) | 6274(2) | 37(1) |
| C(14) | 3055(2) | 6629(5) | 6893(1) | 28(1) |

Table 3. Bond lengths (Å) for **5a**.

| | | | |
|---|---|---|---|
| Cl(1)-Si(1) | 2.0061(12) | C(1)-C(3) | 1.482(4) |
| Cl(2)-Si(1) | 2.0096(12) | C(2)-C(9) | 1.484(4) |
| Cl(3)-Si(1) | 2.0086(12) | C(3)-C(8) | 1.388(4) |
| Cl(4)-Si(2) | 1.9914(13) | C(3)-C(4) | 1.395(4) |
| Cl(5)-Si(2) | 2.0107(13) | C(4)-C(5) | 1.386(4) |
| Cl(6)-Si(2) | 2.0085(14) | C(5)-C(6) | 1.389(5) |
| Cl(7)-Si(3) | 2.0150(12) | C(6)-C(7) | 1.379(5) |
| Cl(8)-Si(3) | 2.0193(12) | C(7)-C(8) | 1.384(4) |
| Cl(9)-Si(3) | 2.0153(12) | C(9)-C(10) | 1.385(4) |
| Si(1)-O(1) | 1.603(2) | C(9)-C(14) | 1.392(4) |
| Si(2)-O(2) | 1.614(2) | C(10)-C(11) | 1.393(5) |
| Si(3)-Si(3)#1 | 2.3158(16) | C(11)-C(12) | 1.378(5) |
| O(1)-C(1) | 1.397(3) | C(12)-C(13) | 1.375(5) |
| O(2)-C(2) | 1.400(3) | C(13)-C(14) | 1.388(4) |
| C(1)-C(2) | 1.332(4) | | |

Table 3. Bond angles (°) for **5a**. (Symmetry transformations used to generate equivalent atoms: #1 -x, -y+2, -z+2)

| | | | |
|---|---|---|---|
| O(1)-Si(1)-Cl(1) | 111.27(9) | C(2)-C(1)-C(3) | 127.4(3) |
| O(1)-Si(1)-Cl(3) | 108.92(9) | O(1)-C(1)-C(3) | 114.1(2) |
| Cl(1)-Si(1)-Cl(3) | 109.59(6) | C(1)-C(2)-O(2) | 118.7(2) |
| O(1)-Si(1)-Cl(2) | 108.72(9) | C91)-C(2)-C(9) | 126.3(3) |
| Cl(1)-Si(1)-Cl(2) | 110.08(6) | O(2)-C(2)-C(9) | 115.0(2) |
| Cl(3)-Si(1)-Cl(2) | 108.20(6) | C(8)-C(3)-C(4) | 119.0(3) |
| O(2)-Si(2)-Cl(4) | 105.82(9) | C(8)-C(3)-C(1) | 120.3(3) |
| O(2)-Si(2)-Cl(6) | 111.26(9) | C(4)-C(3)-C(1) | 120.7(3) |
| Cl(4)-Si(2)-Cl(6) | 111.34(7) | C(5)-C(4)-C(3) | 120.4(3) |
| O(2)-Si(2)-Cl(5) | 111.63(9) | C(4)-C(5)-C(6) | 120.5(3) |
| Cl(4)-Si(2)-Cl(5) | 110.29(7) | C(7)-C(6)-C(5) | 119.4(3) |
| Cl(6)-Si(2)-Cl(5) | 106.58(6) | C(6)-C(7)-C(8) | 120.4(3) |
| Cl(7)-Si(3)-Cl(9) | 109.72(6) | C(7)-C(8)-C(3) | 120.5(3) |
| Cl(7)-Si(3)-Cl(8) | 109.25(6) | C(10)-C(9)-C(14) | 119.4(3) |
| Cl(9)-Si(3)-Cl(8) | 109.58(6) | C(10)-C(9)-C(2) | 120.3(3) |
| Cl(7)-Si(3)-Si(3)#1 | 110.02(6) | C(14)-C(9)-C(2) | 120.3(3) |
| Cl(9)-Si(3)-Si(3)#1 | 109.44(6) | C(9)-C(10)-C(11) | 120.3(3) |
| Cl(8)-Si(3)-Si(3)#1 | 108.81(6) | C(12)-C(11)-C(10) | 119.7(3) |
| C(1)-O(1)-Si(1) | 130.39(18) | C(13)-C(12)-C(11) | 120.5(3) |
| C(2)-O(2)-Si(2) | 127.41(18) | C(12)-C(13)-C(14) | 120.1(3) |
| C(2)-C(1)-O(1) | 118.5(3) | C(13)-C(14)-C(9) | 120.0(3) |

Table 5. Anistropic displacement parameters (Å$^2$ x 10$^3$) for **13**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 hka^*b^*U^{12}]$

| Atom | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Cl(1) | 86(1) | 24(1) | 54(1) | 0(1) | 29(1) | 2(1) |
| Cl(2) | 56(1) | 47(1) | 28(1) | -4(1) | -1(1) | 0(1) |
| Cl(3) | 53(1) | 82(1) | 49(1) | 2(1) | 37(1) | 1(1) |
| Cl(4) | 48(1) | 71(1) | 128(1) | 39(1) | 59(1) | 15(1) |
| Cl(5) | 54(1) | 62(1) | 35(1) | 8(1) | 6(1) | 18(1) |
| Cl(6) | 81(1) | 38(1) | 60(1) | -13(1) | 16(1) | 16(1) |
| Cl(7) | 58(1) | 42(1) | 60(1) | 2(1) | 37(1) | -10(1) |
| Cl(8) | 44(1) | 42(1) | 54(1) | 7(1) | 17(1) | 15(1) |
| Cl(9) | 51(1) | 51(1) | 43(1) | -18(1) | 15(1) | -8(1) |
| Si(1) | 36(1) | 26(1) | 23(1) | 0(1) | 13(1) | 0(1) |
| Si(2) | 29(1) | 28(1) | 36(1) | 5(1) | 17(1) | 5(1) |
| Si(3) | 30(1) | 25(1) | 33(1) | -3(1) | 16(1) | 0(1) |
| O(1) | 39(1) | 28(1) | 28(1) | -1(1) | 15(1) | 4(1) |
| O(2) | 27(1) | 24(1) | 33(1) | 3(1) | 17(1) | 1(1) |
| C(1) | 32(2) | 22(1) | 19(1) | -1(1) | 13(1) | 2(1) |
| C(2) | 24(1) | 23(2) | 27(2) | 2(1) | 14(1) | 2(1) |
| C(3) | 26(1) | 27(2) | 16(1) | 2(1) | 6(1) | 1(1) |
| C(4) | 29(2) | 28(2) | 25(2) | -5(1) | 7(1) | 0(1) |
| C(5) | 28(2) | 38(2) | 25(2) | -4(1) | 9(1) | 5(1) |
| C(6) | 24(2) | 42(2) | 31(2) | 1(1) | 9(1) | -2(1) |
| C(7) | 35(2) | 36(2) | 35(2) | -5(1) | 13(2) | -10(1) |
| C(8) | 36(2) | 27(2) | 31(2) | -5(1) | 15(1) | -3(1) |
| C(9) | 21(1) | 29(2) | 22(1) | 0(1) | 7(1) | 3(1) |
| C(10) | 30(2) | 35(2) | 36(2) | -5(1) | 13(1) | -4(1) |
| C(11) | 31(2) | 47(2) | 41(2) | -20(2) | 5(2) | 0(2) |
| C(12) | 32(2) | 66(3) | 22(2) | -6(2) | 6(1) | 12(2) |
| C(13) | 32(2) | 52(2) | 26(2) | 7(2) | 11(1) | 6(2) |
| C(14) | 25(1) | 33(2) | 25(2) | 0(1) | 8(1) | -2(1) |

Table 6. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$ x $10^3$) for **13**.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(4) | 4157 | 3235 | 7883 | 33 |
| H(5) | 5355 | 3347 | 7891 | 36 |
| H(6) | 6115 | 6387 | 8352 | 39 |
| H(7) | 5677 | 9272 | 8815 | 42 |
| H(8) | 4483 | 9174 | 8810 | 37 |
| H(10) | 2218 | 2158 | 7123 | 40 |
| H(11) | 2107 | 1473 | 6081 | 50 |
| H(12) | 2585 | 4033 | 5554 | 49 |
| H(13) | 3179 | 7250 | 6057 | 44 |
| H(14) | 3294 | 7955 | 7096 | 34 |

# SUPPLEMENTAL MATERIAL 2. X-RAY DATA FOR HEXACOORDINATED Si COMPLEX 9

A colorless crystal with approximate dimensions 0.45 x 0.45 x 0.45 $mm^3$ was selected from oil under ambient conditions and was attached to the tip of a glass capillary. The crystal was mounted in a stream of cold nitrogen at 173(2) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo Kα (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 5.08 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames at intervals of 0.3° in a 6° range about ω with the exposure time of 10 seconds per frame. A total of 125 reflections was obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 6921 strong reflections from the actual data collection.

The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of 1.9 hemisphere to a resolution of 0.80 Å. A total of 11557 data were harvested by collecting three sets of frames with 0.3° scans in ω with an exposure time 20 second per frame. These highly redundant data sets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[1]

The systematic absences in the diffraction data were uniquely consistent for the space groups $P2_1/n$ that yielded chemically reasonable and computationally stable results of refinement.[2] A successful solution by the direct methods provided the positions of most atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anistropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized position and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The final least-squares refinement of 140 parameters against 2669 data resulted in residuals *R* (based on $F^2$ for $I \geq 2\sigma$) and *wR* (based on $F^2$ for $I \geq 2\sigma$) of 0.0250 and 0.0914, respectively. The final difference Fourier was featureless.

The ORTEP diagrams were drawn with 50% probability ellipsoids.

## REFERENCES

1. Blessing, R. H. *Acta Cryst.* 1995, A51, 33-38.

1. All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-Ray System, Madison, WI).

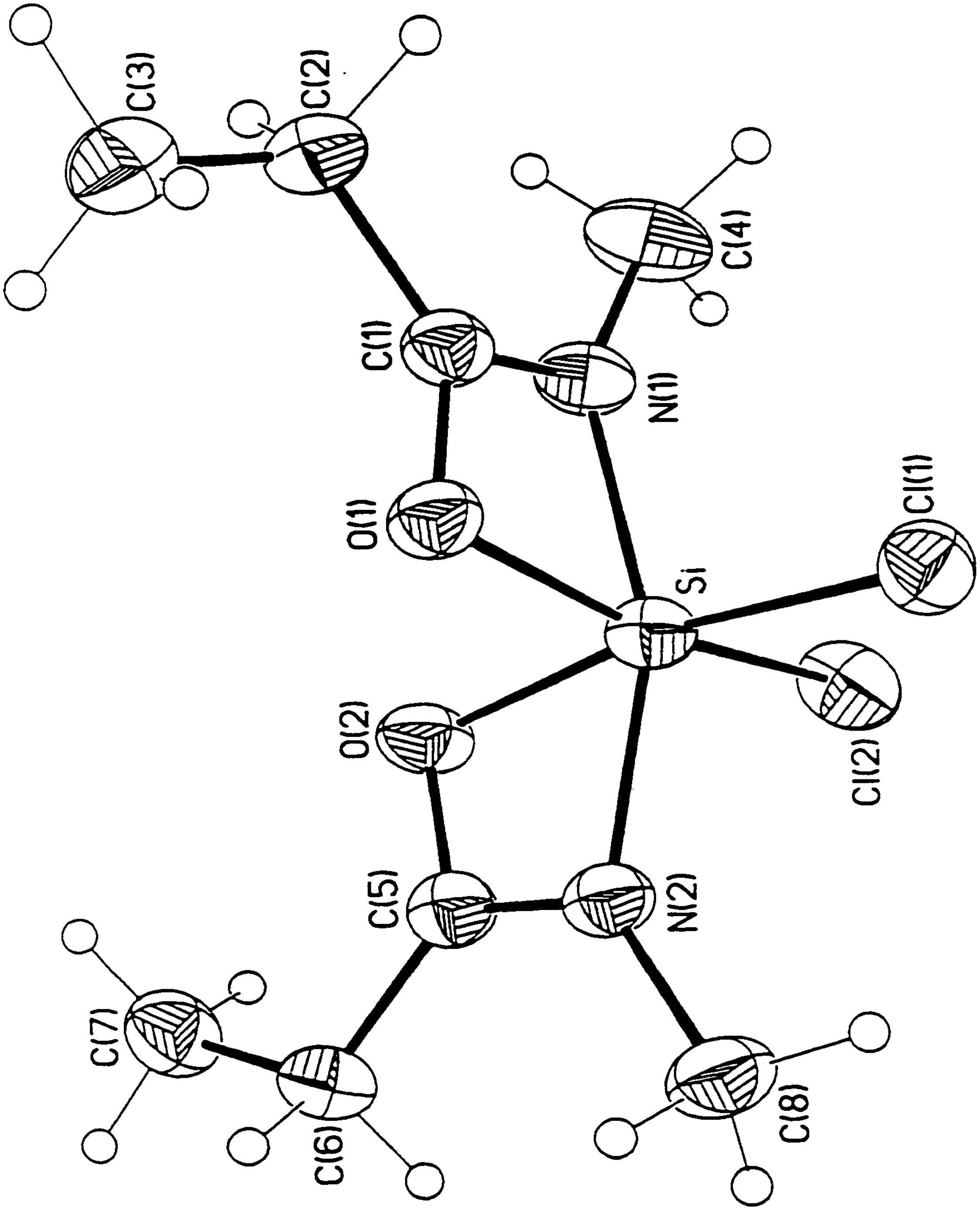


Figure 1. ORTEP drawing of **9**.

Table 1. Crystallographic Data for **5a**.

| | |
|---|---|
| Empirical Formula | $C_8H_{16}Cl_2N_2O_2Si_2$ |
| Formula Weight | 271.22 |
| Temperature (K) | 173(2) |
| Wavelength | MoKα (λ = 0.71073 Å) |
| Crystal System | Monoclinic |
| Space Group | $P2_1/n$ |
| Unit Cell Dimensions | a = 10.3238(5) Å α = 90°<br>b = 9.0982(5) Å β = 103.822(1)°<br>c = 14.3632(7) Å γ = 90° |
| Volume | 1310.04(12) $Å^3$ |
| Z | 4 |
| Density (calc.) | 1.375 $Mg/m^3$ |
| Absorption Coefficient | 0.572 $mm^{-1}$ |
| F (000) | 568 |
| Crystal Size (mm) | 0.45 x 0.45 x 0.45 |
| θ Range | 2.67 to 26.36° |
| Index Ranges | $-12 \leq h \leq 12$ $0 \leq k \leq 11$<br>$0 \leq l \leq 17$ |
| Reflections Collected | 11557 |
| Independent Reflections | 2669 (R(int) = 0.0170) |
| Completeness to theta = 26.36° | 99.9 % |
| Absorption Correction | Empirical with SADABS |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Max. and Min. transmission | 0.7830 and 0.7830 |
| Data / restraints / parameters | 2669 / 0 / 140 |
| Goodness-of-fit on $F^2$ | 1.006 |
| Final R indices [I > 2 sigma(I)] | R1 = 0.0250, wR2 = 0.0914 |
| R Indices (all data) | R1 = 0.0288, wR2 = 0.0948 |
| Largest diff. peak and hole | 0.239 and -0.219 e.$Å^{-3}$ |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for **5a**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Si | 4846(1) | 4217(1) | 2325(1) | 29(1) |
| Cl(1) | 6057(1) | 4942(1) | 3675(1) | 36(1) |
| Cl(2) | 5289(1) | 1916(1) | 2575(1) | 44(1) |
| O(1) | 4707(1) | 6160(1) | 1856(1) | 31(1) |
| O(2) | 3429(1) | 3755(1) | 1270(1) | 34(1) |
| N(1) | 6050(1) | 4538(1) | 1596(1) | 33(1) |
| N(2) | 3247(1) | 4229(1) | 2672(1) | 31(1) |
| C(1) | 5678(1) | 5902(2) | 1436(1) | 31(1) |
| C(2) | 6232(2) | 7024(2) | 893(1) | 40(1) |
| C(3) | 5480(2) | 8447(2) | 729(2) | 61(1) |
| C(4) | 7152(2) | 3814(2) | 1308(1) | 46(1) |
| C(5) | 2593(1) | 3859(1) | 1815(1) | 31(1) |
| C(6) | 1138(1) | 3578(2) | 1464(1) | 36(1) |
| C(7) | 715(2) | 3185(2) | 410(1) | 43(1) |
| C(8) | 2727(2) | 4331(2) | 3529(1) | 38(1) |

Table 3. Bond lengths (Å) for **9**.

| | | | |
|---|---|---|---|
| Si-N(1) | 1.8303(11) | O(2)-C(5) | 1.2989(15) |
| Si-N(2) | 1.8345(11) | N(1)-C(1) | 1.3033(18) |
| Si-O(2) | 1.8850(10) | N(1)-C(4) | 1.4577(16) |
| Si-O(1) | 1.8859(10) | N(2)-C(5) | 1.2995(18) |
| Si-Cl(1) | 2.1447(5) | N(2)-C(8) | 1.4586(16) |
| Si-Cl(2) | 2.1542(5) | C(1)-C(2) | 1.4806(18) |
| Si-C(5) | 2.2886(14) | C(2)-C(3) | 1.499(2) |
| Si-C(1) | 2.2896(14) | C(5)-C(6) | 1.4881(18) |
| O(1)-C(1) | 1.3076(15) | C(6)-C(7) | 1.514(2) |

Table 4. Bond angles (°) for **9**.

| | | | |
|---|---|---|---|
| N(1)-Si-N(2) | 158.86(6) | Cl(1)-Si-C(1) | 94.75(4) |
| N(1)-Si-O(2) | 94.50(5) | Cl(2)-Si-C(1) | 130.57(4) |
| N(2)-Si-O(2) | 69.14(5) | C(5)-Si-C(1) | 113.84(5) |
| N(1)-Si-O(1) | 69.48(5) | C(1)-O(1)-Si | 89.72(8) |
| N(2)-Si-O(1) | 95.47(5) | C(5)-O(2)-Si | 89.96(8) |
| O(2)-Si-O(1) | 86.76(4) | C(1)-N(1)-C(4) | 126.69(12) |
| N(1)-Si-Cl(1) | 98.00(4) | C(1)-N(1)-Si | 92.233(8) |
| N(2)-Si-Cl(1) | 96.92(4) | C(4)-N(1)-Si | 140.68(11) |
| O(2)-Si-Cl(1) | 165.49(3) | C(5)-N(2)-C(8) | 127.13(12) |
| O(1)-Si-Cl(1) | 90.74(3) | C(5)-N(2)-Si | 92.21(9) |
| N(1)-Si-Cl(2) | 95.97(4) | C(8)-N(2)-Si | 140.00(9) |
| N(2)-Si-Cl(2) | 97.45(4) | N(1)-C(1)-O(1) | 108.44(11) |
| O(2)-Si-Cl(2) | 90.58(4) | N(1)-C(1)-C(2) | 127.93(12) |
| O(1)-Si-Cl(2) | 164.92(4) | O(1)-C(1)-C(2) | 123.62(12) |
| Cl(1)-Si-Cl(2) | 95.40(2) | N(1)-C(1)-Si | 53.01(7) |
| N(1)-Si-C(5) | 128.07(5) | O(1)-C(1)-Si | 55.45(6) |
| N(2)-Si-C(5) | 34.57(5) | C(2)-C(1)-Si | 177.92(10) |
| O(2)-Si-C(5) | 34.58(4) | C(1)-C(2)-C(3) | 115.33(12) |
| O(1)-Si-C(5) | 91.95(4) | O(2)-C(5)-N(2) | 108.66(12) |
| Cl(1)-Si-C(5) | 131.43(4) | O(2)-C(5)-C(6) | 123.07(12) |
| Cl(2)-Si-C(5) | 94.26(4) | N(2)-C(5)-C(6) | 128.27(12) |
| N(1)-Si-C(1) | 34.67(5) | O(1)-C(5)-Si | 55.45(6) |
| N(2)-Si-C(1) | 128.99(5) | N(2)-C(5)-Si | 53.23(7) |
| O(2)-Si-C(1) | 91.34(5) | C(6)-C(5)-Si | 177.91(10) |
| O(1)-Si-C(1) | 34.83(4) | C(5)-C(6)-C(7) | 113.94(11) |

Table 5. Anistropic displacement parameters ($Å^2$ x $10^3$) for **9**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + \ldots + 2 hka^*b^*U^{12}]$

| Atom | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Si | 27(1) | 29(1) | 32(1) | -1(1) | 11(1) | -1(1) |
| Cl(1) | 36(1) | 37(1) | 34(1) | 1(1) | 5(1) | -4(1) |
| Cl(2) | 39(1) | 27(1) | 64(1) | 0(1) | 10(1) | -2(1) |
| O(1) | 31(1) | 33(1) | 34(1) | 3(1) | 15(1) | 2(1) |
| O(2) | 28(1) | 44(1) | 33(1) | -6(1) | 13(1) | -3(1) |
| N(1) | 29(1) | 35(1) | 40(1) | -6(1) | 16(1) | -1(1) |
| N(2) | 29(1) | 35(1) | 30(1) | 1(1) | 12(1) | -1(1) |
| C(1) | 28(1) | 38(1) | 28(1) | -3(1) | 9(1) | -3(1) |
| C(2) | 35(1) | 51(1) | 38(1) | 8(1) | 15(1) | -5(1) |
| C(3) | 43(1) | 57(1) | 83(1) | 34(1) | 17(1) | -1(1) |
| C(4) | 33(1) | 47(1) | 66(1) | -16(1) | 25(1) | 1(1) |
| C(5) | 32(1) | 29(1) | 33(1) | 0(1) | 11(1) | 0(1) |
| C(6) | 27(1) | 40(1) | 41(1) | -3(1) | 11(1) | -3(1) |
| C(7) | 35(1) | 49(1) | 43(1) | -4(1) | 6(1) | -2(1) |
| C(8) | 39(1) | 47(1) | 32(1) | 0(1) | 17(1) | -4(1) |

Table 6. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($\AA^2$ x $10^3$) for **9**.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | 6260 | 6605 | 262 | 48 |
| H(2B) | 7162 | 7233 | 1242 | 48 |
| H(3A) | 4544 | 8254 | 415 | 91 |
| H(3B) | 5872 | 9086 | 320 | 91 |
| H(3C) | 5533 | 8934 | 1346 | 91 |
| H(4A) | 7143 | 4088 | 646 | 69 |
| H(4B) | 7055 | 2746 | 1348 | 69 |
| H(4C) | 7998 | 4120 | 1734 | 69 |
| H(6A) | 644 | 4466 | 1579 | 43 |
| H(6B) | 883 | 2765 | 1842 | 43 |
| H(7A) | 974 | 3977 | 29 | 64 |
| H(7B) | -255 | 3056 | 224 | 64 |
| H(7C) | 1152 | 2269 | 296 | 64 |
| H(8A) | 2157 | 5201 | 3485 | 57 |
| H(8B) | 3471 | 4410 | 4097 | 57 |
| H(8C) | 2204 | 3449 | 3582 | 57 |

# CHAPTER 6. PROPOSED FUTURE RESEARCH ON DISILANES, DISILACYCLOHEXA-*2,5*-DIENES AND RELATED FIELDS

## Introduction

The four papers presented in this dissertation represent the three discoveries in disilane chemistry: (a) silyl radical generation that catalyzes cyclo-trimerization of alkynes by disilanes bearing electron-withdrawing substituents (methoxy, chlorine), (b) *1,4*-disilacyclohexa-*2,5*-diene formation from reactions of alkynes with disialnes bearing multiple dimethylamino groups, and (c) formation of hypercoorde products from disilanes bearing electron-withdrawing groups with substrates possessing unpaired electrons (O, N). These reactions represent some general features of disilane chemistry.

Although this dissertation covers disilane reactions under a variety of temperature conditions, the research in this area and the related fields still leaves much to be accomplished. The following three section give some suggestions to the future exploration in dislane chemistry.

## Part One. Proposed Research on Disilanes

In the first two papers of this dissertation we reported that electron withdrawing substituents (halogens, alkoxy) attached to the silicon atoms can weaken the Si-Si linkage of disilanes, allowing silyl radicals to be generated when these disilanes are heated to *ca.* 200 °C. The radicals $SiCl_3$ and $Si(OMe)_3$ were found to be effective in cyclo-trimerizing alkynes into corresponding benzene derivatives. However, other possibilities exist in this field including: (a) applying such silyl radicals to systems other than those cyclo-trimerization of alkynes. Many examples of radical induced reactions below 100 °C are known to be useful in organic/inorganic synthesis.[1] A drawback of the aforementioned silyl radical induced reactions is that the temperature required to generate the radicals is much too high for most applications. Although UV-irradiation of $Si_2Cl_6$ at ambient temperature is also able to generate $SiCl_3$ radicals (judging from the detection of cyclo-trimerization products, as reported in the second paper in this dissertations) the yield of this reaction (5% after 40 h) is much too low to be practical. This brings up the second possibility: (b) synthesis of new disilanes or related compounds which upon heating (or irradiation by a UV light source), can generate silyl radicals more efficiently at much lower temperatures. Some general features can be envisioned for the systems that can meet this requirement. First of all, more electron withdrawing substituents than chlorine should be present on the silicon atoms to further weaken the Si-Si link. Although $Si_2F_6$ would seem to be a suitable candidate, a theoretical study in the literature and experiments performed in our laboratory exclude this possibility (see second paper in this dissertation). In fact $Si_2F_6$ was found ineffective in cyclo-trimerization reactions. Compounds such as $Si_2(CF_3)_6$ could be a suitable system in view of the electron-withdrawing $CF_3$ groups and the stability of $Si\text{-}CF_3$ bonds. Another factor that influences the reactivity of a (silyl) radical is the electron density distribution on the radical species, since it probably determines the nature of the radical induced reaction. Thus if the reactive center of the radical species is electron deficient, it possibly faciliates a nucleophilic attack from other reactive species, on the other hand, an electrophilic attack would be expected. A reasonable extension can be made to $Ge_2(CF_3)_6$[2] and $Ge_2Cl_6$, considering the fact that Ge-Ge bonds are weaker than Si-Si links. Similarly $Si_2(C_6F_5)_6$ and $Ge_2(C_6F_5)_6$ are also worthwhile to try. The synthetic routes to these compounds are generally one of the following approaches: (a) coupling between two silane molecules; (b) substituting the groups on the silicon atoms by the desired fluorinated substituents. For example, $Ge_2(CF_3)_6$ was synthesized by reaction 1.

$$ClGe(CF_3)_3 \xrightarrow[\text{- NaCl/KCl}]{\text{Na/K}} (CF_3)_3GeGe(CF_3)_3 \qquad (1)$$

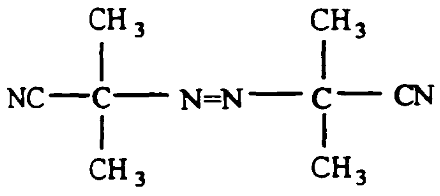
On the other hand, $Si_2(C_6F_5)_6$ can be obtained by reactions 2 and 3.

$$C_6F_5Br + Li \xrightarrow[\text{- LiBr}]{Et_2O} LiC_6F_5 \qquad (2)$$

$$Si_2Cl_6 + LiC_6F_5 \xrightarrow{\text{- LiCl}} Si_2(C_6F_5)_6 \qquad (3)$$

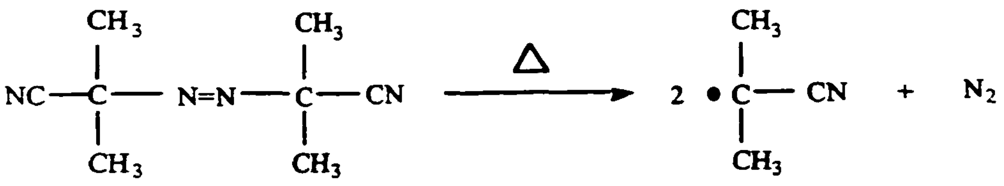
We would expect the most suitable disilanes to have the following three properties: (i) easy to synthesize and stable; (ii) readily generate silyl radicals; and (iii) the radicals generated should be both sufficiently reactive while having lifetime long enough to attack the target substrates before being quenched.

Disilanes analogous to widely used radical sources such as *2,2'*-azo*bis*isobutyronitrile (AIBN) and other related compounds are also suggested for investigation. The latter compounds have in common a $R^1R^2R^3$-C-N=N-C-$R^3R^2R^1$ core structure to facilitate radical generation by $N_2$ extrusion upon warming (reaction 4[3]).



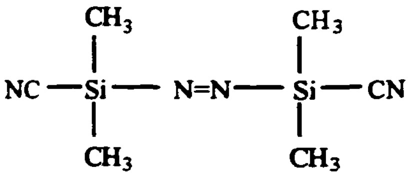
$$\mathrm{NC-\underset{CH_3}{\overset{CH_3}{C}}-N{=}N-\underset{CH_3}{\overset{CH_3}{C}}-CN}$$

Structure of AIBN



$$\mathrm{NC-\underset{CH_3}{\overset{CH_3}{C}}-N{=}N-\underset{CH_3}{\overset{CH_3}{C}}-CN} \xrightarrow{\Delta} 2\ \bullet\mathrm{\underset{CH_3}{\overset{CH_3}{C}}-CN} + N_2 \qquad (4)$$

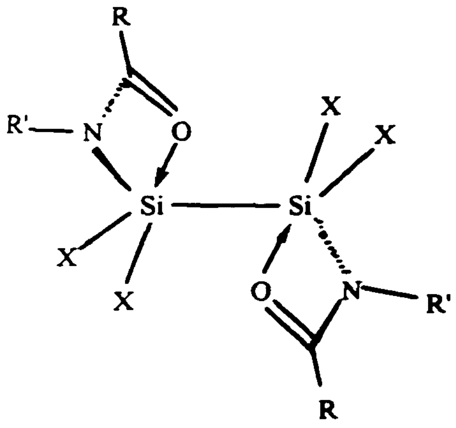
If we apply this idea to the silicon systems, we would expect the following series of compounds $R^1R^2R^3Si\text{-}N\text{=}N\text{-}SiR^1R^2R^3$, where $R^i$ can be Cl, OMe, $CF_3$, $C_6F_5$, etc. Although no detailed synthetic approaches will be presented here for any of these compounds, one example has already been reported ($Me_3Si\text{-}N\text{=}N\text{-}SiMe_3$[4]). We would expect that if further examples of these compounds can be successfully synthesized, the generation of the silyl radical $SiR_3$ would occur at much lower temperatures compared with the conditions described in Chapters 2 and 3. In fact it is reasonable to believe that the silicon analogue of AIBN can generate radicals more efficiently than AIBN itself owing to the weakness of the Si-N bond. Therefore, it might be practical to apply these radical initiators to a wider range of chemical reactions.



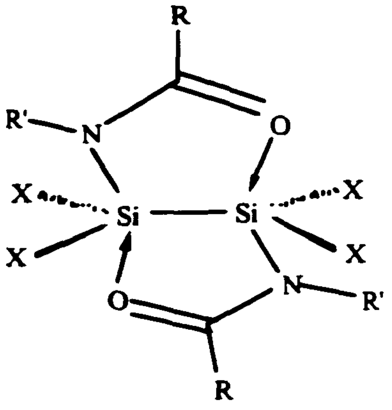
$NC\text{-}Si(CH_3)_2\text{-}N\text{=}N\text{-}Si(CH_3)_2\text{-}CN$

Si analogue of AIBN

Disilanes bearing multiple electron withdrawing groups are also known to have enhanced hypercoordination properties as explored in the fourth paper in this dissertation. Although compound **9** in paper 4 was formed by homolytic cleavage of Si-Si when $Si_2Cl_6$ was reacted with the lithium salt of an acetamide, this structure demonstrated



**A**

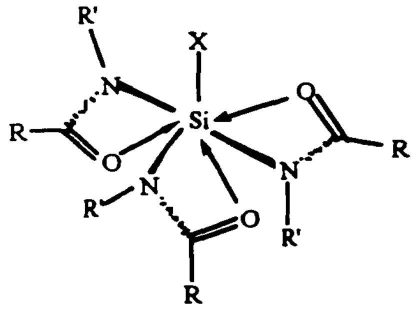


**B**

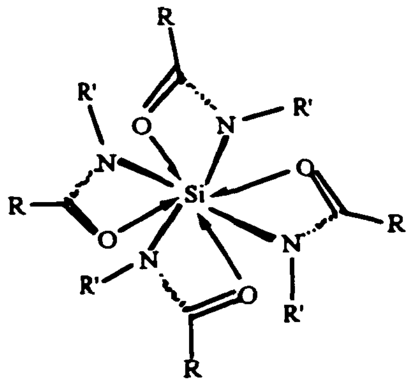
that two four-membered rings are formed, leading to a hexacoordinated Si species. The X-ray structure also showed that this compound is not severely encumbered by the steric hindrance, in contrast to the case for most of other hypercoordinated systems. Two possibilities for exploration present themselves: first, in the synthesis of **9**, if the homolytic cleavage of Si-Si bond of $Si_2Cl_6$ was caused by the weakness of this bond due to the presence of the six polar Si-Cl links, we might substitute one or more of the chlorine atoms by other less electron-withdrawing groups such as alkyl, alkoxy groups to prevent this cleavage. This possibility in fact had been tried in an earlier publication (reference 16 in paper 4 of this dissertation) in which disilanes and trisilanes bearing multiple methyl groups were utilized to make five-membered pentacoordinated ring silicon compounds. In addition, the steric hindrance caused by the substituted groups should be minimized to accommodate the atoms coordinated to Si atoms. Therefore if the

Si-Si bond in the desired disilanes (e.g. dimethyltetrachlorodisilane) is strong enough to withstand the attack of the anion of the acetamide salt, it is possible that we can synthesize compounds of type **A**, in which both Si atoms of the disilane become hypercoordinated in a system with two four-membered rings. Hypercoordination between the Si atoms is also possible provided that the Si-Si bond distance matches that of the N→O distance (in N...C(O)) to form a stable five-membered ring, a structure analogous to **B**.

A second possibility is to synthesize heptacordinated or even octacoordinated silicon species based on the synthesis of **9** (in paper 4). Compounds of type **C** and **D** (where R, R' = alkyl, alkoxy; X = H, alkyl, $CF_3$, $C_6F_5$) could possibly be synthesized in an analogous manner to the synthesis of **9**. Synthesis of the caged compound **E** is also possible according to Scheme 1.

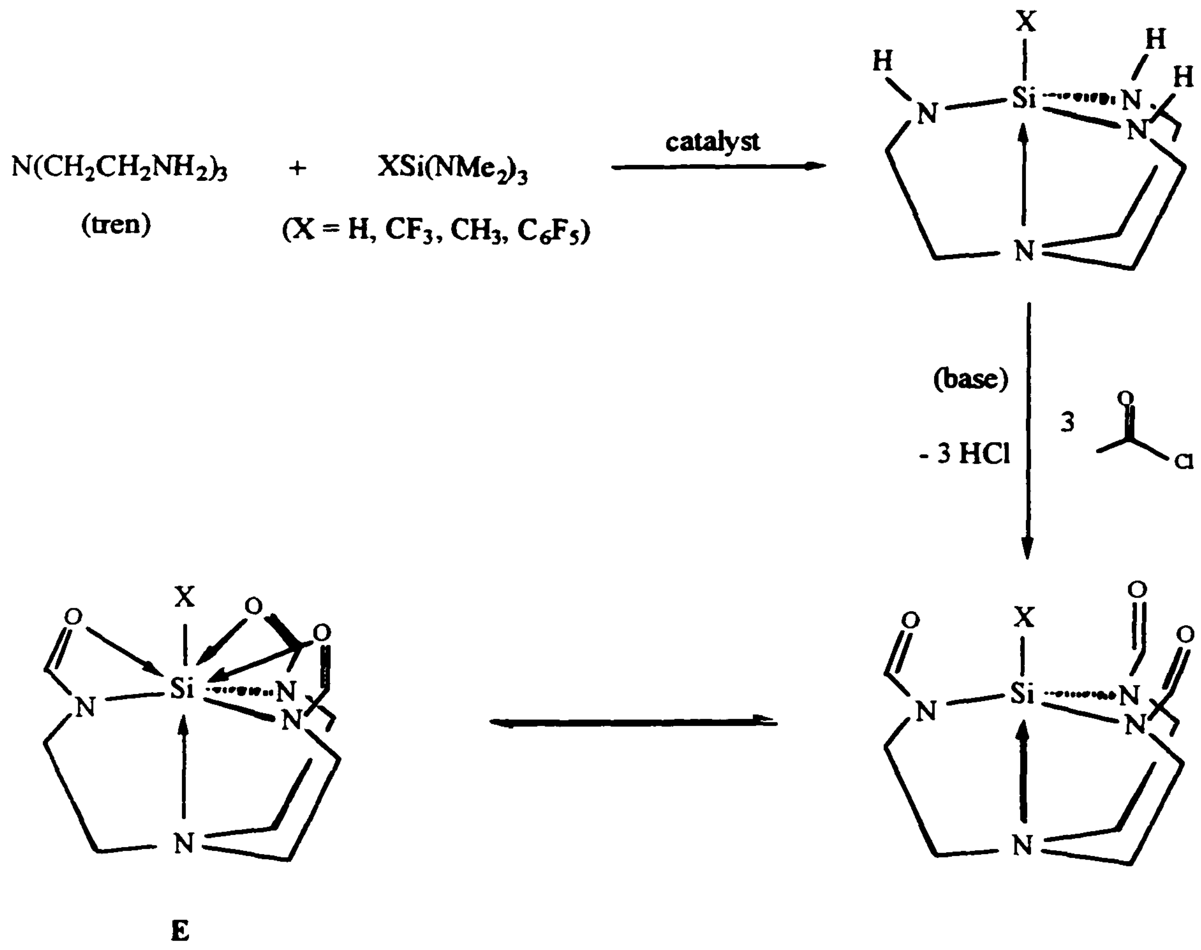


**C**



**D**

Scheme 1

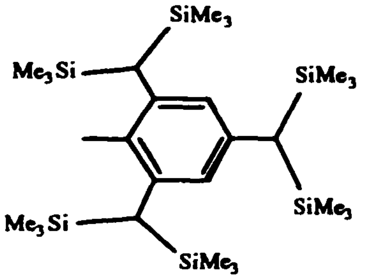


## Part Two. Proposed Research on *1,4*-Disilacyclohexa-*2,5*-dienes

The initial goal of the research reported in the previous papers of this thesis was to synthesize stable *1,4*-disilabenzenes from the corresponding *1,4*-disilacyclohexa-*2,5*-

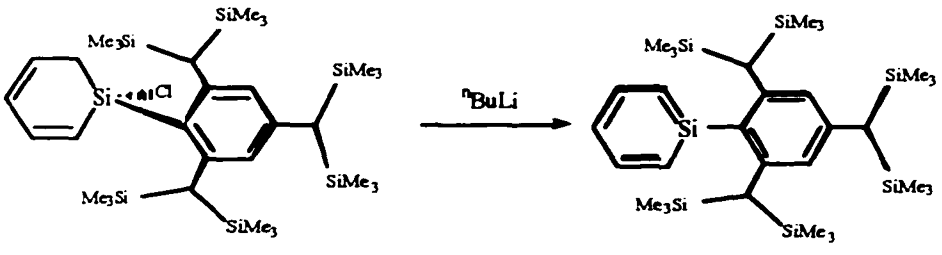
dienes. In fact much attention has been directed to research on disilabenzenes.[5] 1,4-Disilabenzenes have only been detected and trapped as unstable intermediates at very low temperature. Recently a *1,4*-disila(Dewar-benzene) was isolated.[6] No *1,4*-disilabenzene stable at room temperature has been synthesized or isolated.

The most suitable *1,4*-disilacyclohexa-*2,5*-diene precusors synthesized for this purpose are compounds **8** , **9a** and **10** mentioned in paper 3 in this dissertation since they possess halogen atoms as functional groups that can be removed.



Structure of Tbt

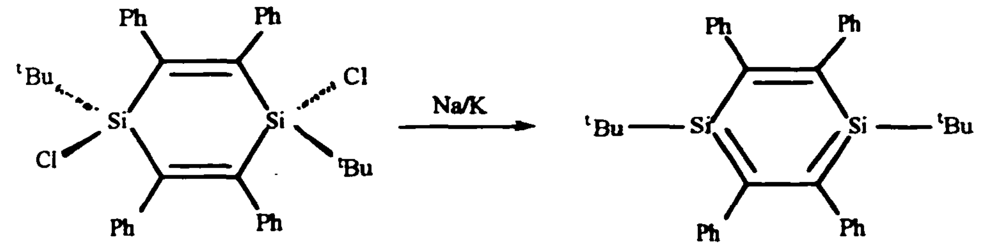
Silabenzenes that are stable enough to be isolated and characterized are known. These compounds are stabilized by very bulky groups such as Tbt shown above. In fact a good example of a stable silabenzene was obtained by reacting compound **F** with *tert*-butyllithium at low temperature via a deprotonation and coupling pathway (reaction 5).[7]



**F**

(5)

Similarly, in order to obtain *1,4*-disilabenzene, we could utilize *1,4*-disilacyclohexa-*2,5*-dienes **8**, **9a** and **13** (in paper three) as starting materials. Alkali metals Na, K and Na/K alloy are commonly used to remove halogen atoms from a Si-X bond (X = halogen). Therefore *1,4*-disilabenzene **G** could possibly be synthesized according to the following path (reaction 6).

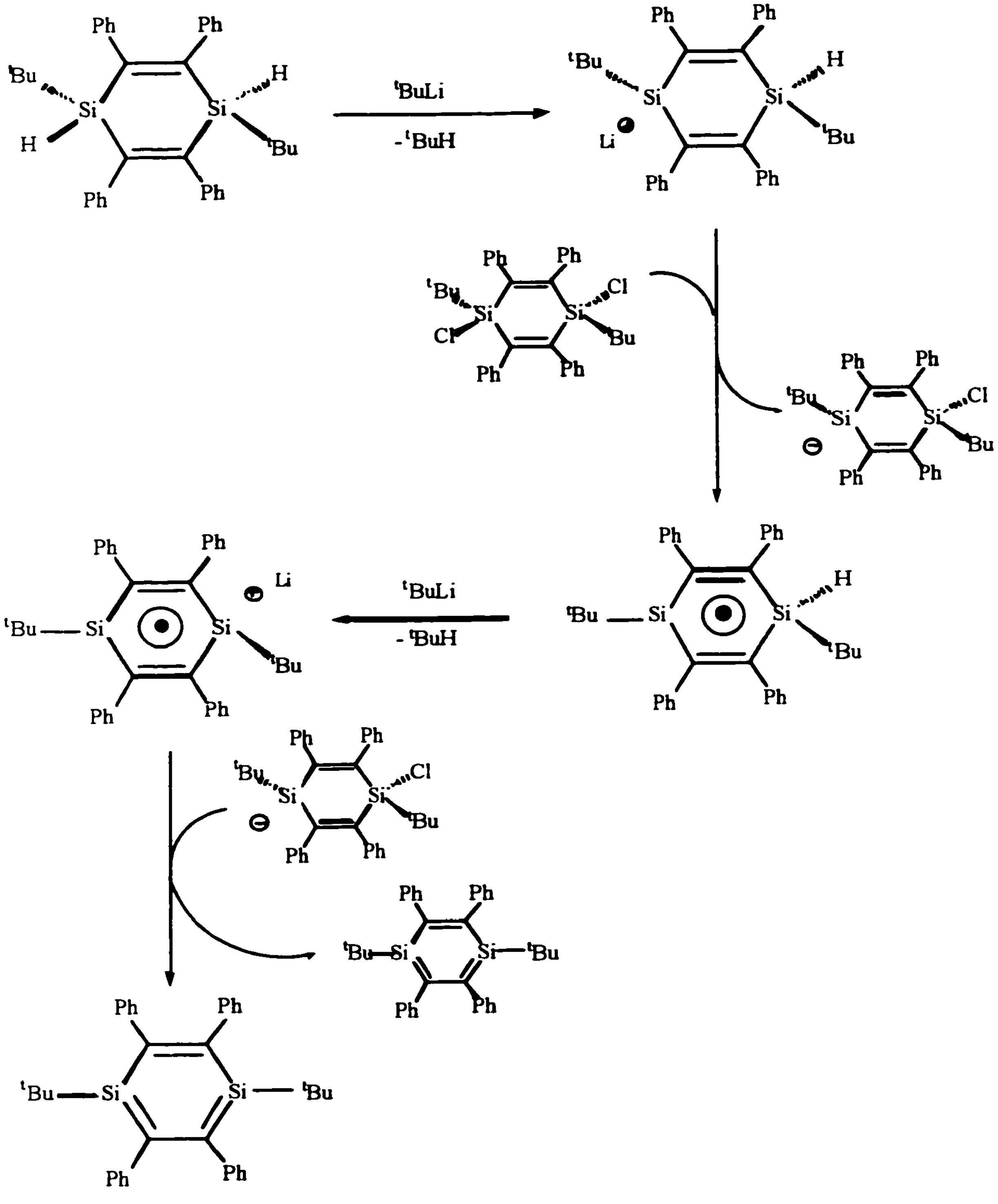


(6)

This type of reactions require strict exclusion of moisture and oxygen, both of which readily react with the *1,4*-disilabenzene, therefore the solvents and the reaction vessels should be carefully pre-treated. The most suitable solvent for this type of reactions are tetrahydrofuran (THF), diethyl ether ($Et_2O$) for their suitable solubility of the starting materials and the products. Although halogenated solvents such as $CH_2Cl_2$ and $CHCl_3$ should be avoided, hydrocarbons such as hexanes and benzene may also be tried due to the stability of these solvents and the ease of product separation.

Another approach invloving **8** (in paper 3) can be attempted by an intermolecular coupling reaction using *tert*-butyllithium as a strong ionic base and coupling reagent. As mentioned in paper 3, compound **13** was prepared by the reduction of **8** with $LiAlH_4$. This compound is also of considerable stability and solubility in THF. If an equimolar mixture of **8** and **13** are reacted with *tert*-butyllithium, a *1,4*-disilabenzene can possibly be synthesized via an intermolecular deprotonation and coupling pathway, as depicted in Scheme 2. In order to avoid possible thermal decomposition of the *1,4*-disilabenzene formed, a low temperature (e.g. –30 °C) may be required. Product isolation can be achieved by evaporating the solvent (THF), followed by redissolving the reaction mixture in a solvent which hopefully only dissolves the product. On the other hand, if $Et_2O$ or hydrocarbons are used as a solvent, a simple filtration may be sufficient for product separation since the by-product has only negligible solubility in these solvents. Product purification can be accomplished by either sublimation or recrystallization from a suitable solvent.

Scheme 2



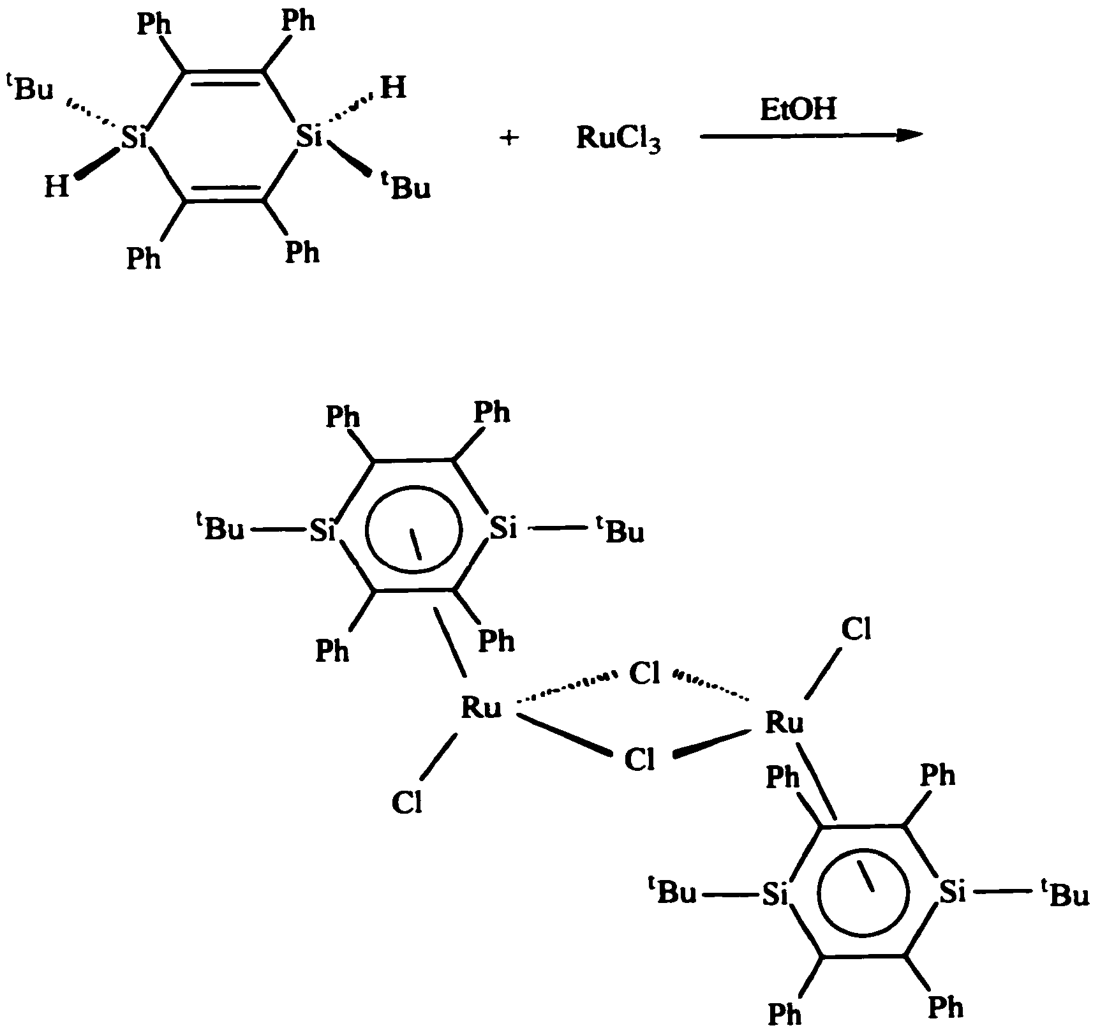
An extension of the aforementioned approaches to synthesize *1,4*-disilabenzene, organometallic methods can also beconsidered. Transition metal complexes of Pd, Ru are known to be efficient in removing the carbon hydrogen from cyclohexa-*1,3*-diene and cyclohexa-*1,4*-diene to produce the aromatized product benzene in coordinated form.[8] The same possibility exists if **13** (in paper 3) is treated with a Pd or Ru complex. The Si-H bond is weaker than the C-H link and therefore removal of a hydrogen from a Si-H bond could be easier than from a C-H bond. Detaching the transition metal moiety from the *1,4*-disilabenzene with a ligand with stronger complex formation affinity may afford *1,4*-disilabenzene in its free form. This possibility is depicted in Scheme 3.

Polymers commonly have greater stability than the corresponding monomers due to depressed reactivity. Polymers of *1,4*-disilabenzene, namely, poly-*1,4*-disilabenzene, may be more stable than a monomeric form. This provides another choice for the synthesis of the aromatized *1,4*-disilabenzene system if *1,4*-disilabenzene itself is not stable enough to be isolated. The possible synthesis of polymeric 1,4-disilabenzene is shown in reaction 7.

## Part Three. Synthesis of *1,2*-Disilacyclohexa-*3,5*-dienes and the Corresponding *1,2*-Disilabenzenes

When diphenylacetylene is reacted with lithium in $Et_2O$ at ambient temperature, *1,4*-dilithium-*1,2,3,4*-tetraphenyl-*1,3*-butadiene salt is formed as a precipitate. This salt

Scheme 3


Ph
Ph
ᵗBu
H
Si
Si
H
ᵗBu
Ph
Ph
+
RuCl3
EtOH
Ph
Ph
ᵗBu
Si
Si
ᵗBu
Ph
Ph
Cl
Ru
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Ru
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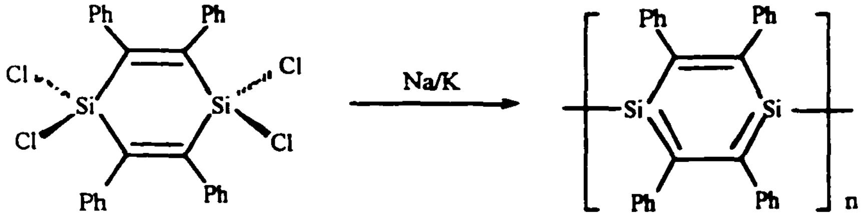
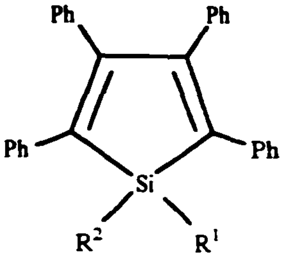


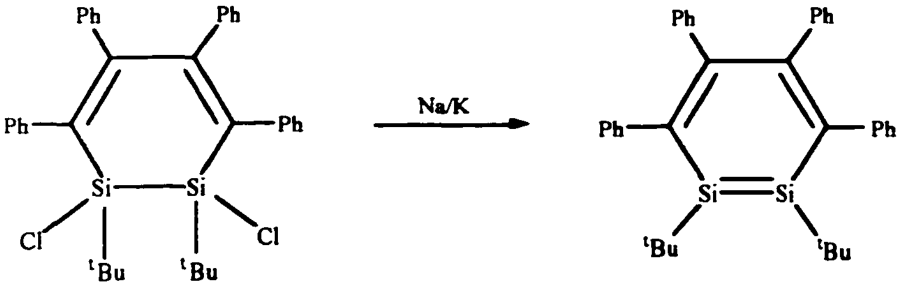
(7)



A silole

has been applied to reactions with chloro silanes to afford five-membered silole[9] whose structure is shown below.

When *symmetric*-dichlorotetramethyldisilane was reacted with the dilithium salt, *1,2*-disilacyclohexa-*3,5*-diene was formed as an air-sensitive compound.[10] If bulkier groups other than methyl groups are introduced, we can possibly synthesize compound **H** if the Si-Si is strong enough and the steric hindrance from the *tert*-butyl groups does not prevent product formation. More importantly, if chlorine atoms are present on each of the two silicon atoms of the *1,2*-disilacyclohexa-*3,5*-diene, it becomes a suitable precursor for the subsequent synthesis of the *1,2*-disilabenzene **I**, shown in reaction 8.



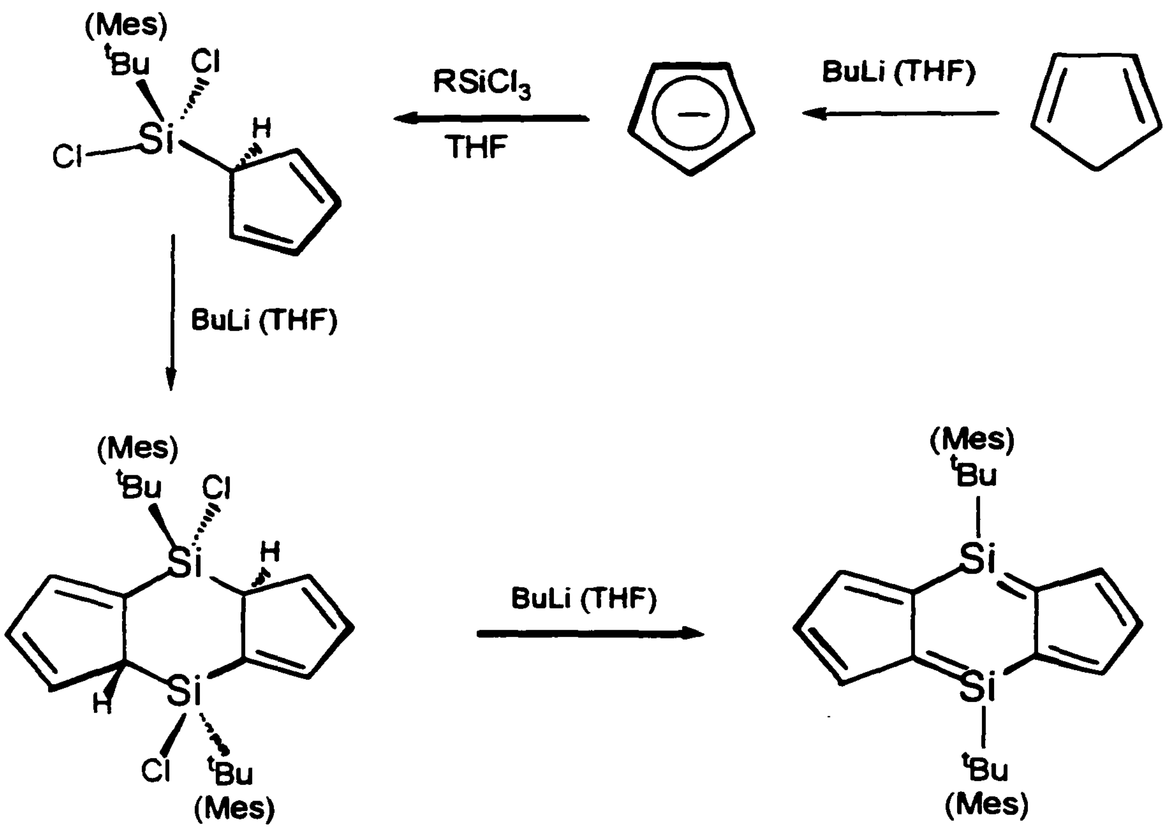
**H** **I**

(8)

Formation of a Si=Si bond by intermolecular coupling of two bulky moieties containing the Si-Cl bonds is well known. In fact the first stable compound possessing a Si=Si bond was synthesized by reacting $Mes_2SiCl_2$ with Na or K in THF.[11] It seems that in the presence of sufficiently bulky groups on the Si atoms, a *1,2*-disilabenzene such as **I** can possibly be stabilized. If a tert-butyl group is not suitable,a mesityl group can be considered.

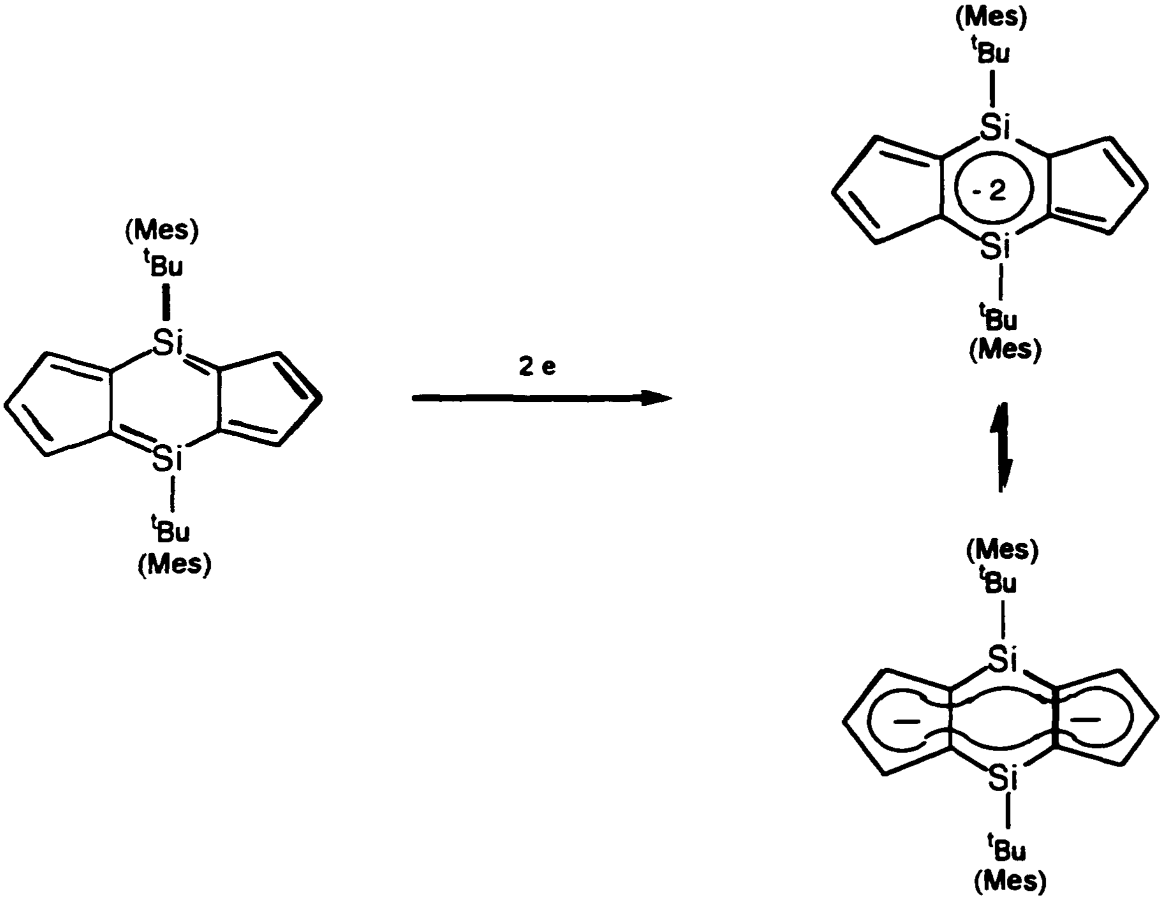
Systems bearing the cyclopentadienes (Cp's) could be another possibility to be investigated to achieve *1,4*-disilabenzenes. The starting materials can be synthesized in an analogous manner as reported earlier.[12, 13] The proposed reaction path is shown in Scheme 4.

Scheme 4



The obtained conjugated product can be further treated with an electron donor to give aromatic product 1,4-disilabenzene, as shown in Scheme 5.

Scheme 5



## References

1. For examples of radical reactions, see reviews: (a) Chatgilialoglu, C.; Crich, D.; Komatsu, M.; Ryu, I. *Chem. Rev.* **1999**, 99, 1991. (b) Stubbe, J.; van der Donk, W. A. *Chem. Rev.* **1998**, 98, 705. (c) Easton, C. J. *Chem. Rev.* **1997**, 97, 53. (d) Parsons, P. J.; Penkett, C. S.; Shell, A. J. *Chem. Rev.* **1996**, 96, 195.

2. Lagow, R. J.; Eujen, R.; Gerchman, L. L.; Morrison, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 1722.

3. (a) Tabka, M. T.; Chenal, J.; Widmaier, J.. Polym. Int. 2000, 494, 412. (b) Hageman, H. J. Eur. Polym. J. 1999, 36, 345. and references therein.

4. Wiberg, N.; Vasisht, S. K.; Fischer, G. *Angew. Chem.* **1976**, *88*, 257. and reference therein.

5. For recent examples, see: (a) Baldridge, Kim K.; Uzan, O.; Martin, J. *Organometallics* **2000**, *19*, 1477. (b) Ando, W.; Shiba, T.; Hidaka, T.; Morihashi, K.; Kikuchi, O. *J. Am. Chem. Soc.* **1997**, *119*, 3629. (c) Koo, K.; Marks, T. J. J. *Am. Chem. Soc.* **1998**, *120*, 4019.

6. Kabe, Y.; Ohkubo, K.; Ishikawa, H.; Ando, W. *J. Am. Chem. Soc.* **2000**, *122*, 3775.

7. Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 634.

8. Pertici, P.; Vitulli, G.; Paci, M.; Porri, L. *J.Chem. Soc., Dalton Trans.* **1980**, 1961.

9. For recent instances, see: (a) Yamaguchi, S.; Jin, R.; Itami, Y.; Goto, T.; Tamao, K. *J. Am. Chem. Soc.* 1999, *121*, 10420. (b) Kanno, K.; Kira, M. *Chem. Lett.* **1999**, *1127*. (c) rackmeyer, B.; Kehr, G.; Subb, J.; Molla, E. *J. Organomet. Chem.* **1999**, *577*, 82.

10. Kako, M.; Takada, H.; Nakadaira, Y. *Tetrahedron Lett.* **1997**, *38*, 3525.

11. West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343.

12. Hiermeier, J.; Kohler, F.; Muller, G. *Organometallics* **1991**, 10, 1787.

13. Siemeling, U.; Jutzi, P.; Neumann, B.; Stammler, H. *Organometallics* **1992**, 11, 1328.

# CHAPTER 7. GENERAL CONCLUSION

The four papers in this thesis present new radical reactions for alkyne trimerization, alkyne silylene reactions to give *1,4*-disilacyclohexa-*2,5*-dienes and disilyated product formation via hypercoordination silicon species between disilanes (bearing electron-withdrawing groups) and *1,2*-quinones and *p*-quinones.

$Si_2Cl_6$ and $Si(OMe)_6$ were found to be efficient in cyclo-trimerizing alkynes into the corresponding aromatic products. A proposed silyl radical pathway is supported by the addition of radical quenchers to the reaction system, by the observation of catalytic trimerization properties of hexachlorodisilane and hexamethyoxydisilane toward alkynes, and by UV-visible irradiation which afforded cyclo-trimerization products. The temperature, Si-Si bond energy and the driving force of forming stable aromatic products are apparently critical to this type of reactions.

A radical process is also involved in the thermal dimerization of alkynes. It was discovered that only terminal, conjugated alkynes are capable of this sort of reaction, and the existence of ring structures is helpful to the stabilization of the thermally generated radicals.

*1,4*-Disilacyclohexa-*2,5*-dienes can be synthesized either by reacting disilanes bearing multiple dimethylamino groups, or by reacting a *1,4*-disilacyclohexa-*2,5*-diene bearing $NMe_2$ groups with a phosphine or a halogenated silane, or by the reduction of a *1,4*-dislacyclohexa-*2,5*-diene possessing multiple halogen atoms with $LiAlH_4$. *1,4*-

disilacyclo-hexa-*2,5*-dienes are potential precursors to disilabenzenes and polydisilabenzenes. This approach provides an convenient and efficient approach to synthesize *1,4*-disilacyclohexa-*2,5*-diene with functional groups accessible to further modification. A proposed silylene pathway is supported by the identification of the by-products from the reactions, and by trapping an intermediate the reaction product after addition of *1,4*-diphenyl-*1,3*-butadiene to the *pentakis*(dimethylamino)-disilane/diphenylacetylene reaction system.

Disilanes with electron-withdrawing groups react readily with *1,2*-quinones and *p*-quinones to afford disilylated products in the absence of a transition metal catalyst in contrast to earlier reports. A proposed pathway invloving the formation of hypercoordinated silicon species was supported by adduct formation reactions between $Si_2Cl_6$ and diamines and DMF, and the reaction between acetamide salts and $Si_2Cl_6$, a hexacoordinated silicon complex was synthesized in one of these experiments.

The observations reported in the papers of this thesis are related by the following properties of disilanes: relative weakness of the Si-Si bonds, especially when electron-withdrawing substituents are present on the silicon atoms; relatively easy disproportionation of disilanes bearing multiple dimethylamino to afford silylene species due to the weakness of Si-Si and Si-N bonds; enhanced hypercoordination tendencies of disilanes bearing electron-withdrawing groups.

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