STUDIES ON PREPARATIONS, STRUCTURES AND REACTIVITIES OF 9, 10-DISILAANTHRACENE DERIVATIVES

1997

KEN HATANO

STUDIES ON PREPARATIONS, STRUCTURES AND REACTIVITIES

①

STUDIES ON PREPARATIONS, STRUCTURES AND REACTIVITIES OF 9,10-DISILAANTHRACENE DERIVATIVES

KEN HATANO

A dissertation submitted to the Doctoral Program in Chemistry, the University of Tsukuba in partial fulfillment of the requirements for the degree of Doctor of Philosophy(Science)

January, 1997

Contents

Chapter 1.	General Introduction	1
Chapter 2.	Preparation of 9,10-Dimethyl -9,10-Disilaanthracene Dimer	48
Chapter 3.	Preparation and Reactivity of 9,10-Disilaanthracene Dianion	87
Chapter 4.	Structural Characterization of 9,10-Disilaanthracene Dianion in Solution	124
Chapter 5.	Photochemical Reaction of Silyl bridged 9,10-Disilaanthracene	141
List of Publication		156
Acknowledgment		159

To my parents

CHAPTER 1

GENERAL INTORODUCTION

1-1 INTORODUCTION

Preparation of silaaromatic compound, silicon containing cyclic conjugated π system, is a great challenge for the organosilicon chemists for last few decaies, whereas these compounds have not yet been isolated around at ambient temperature. Numerous syntheses and studies of silaaromatic compounds, some spectroscopic investigation have been effected by the use of low temperature techniques. Today, there is a general acceptance of their existence, reactivity and characterization in many reactions. Their synthetic strategy for silabenzene and disilabenzene derivatives will been classified into three categories. Thermal generation is the simplest approach for the generation of silaaromatics. On the other hand, photochemical procedure is also popular method for this purpose. And Barton pioneered base induced generation of silatoluene has been the first successful approach in this area. These procedures and results will be shown in next section (Chapter 1-3)

While, Cho has been reported that an efficient and convenient general method of aromatization, utilizing the anthracene dilithium and cadmium dichloride as an electron accepter. The author has been stimulated to prepare a

silaaromatics by use of electron-transfer reaction from the dianion compound as new type approach for preparation of silaaromatics.

Silyl anion, represented silyllithium, has been easily prepared from corresponding organosilicon halide or disilane with alkali metal, however only few molecule containing two silyl anions, bis (silyl anion), have been prepared. It is difficult to prepare the molecule having two silyl anions which is highly reactive species.

A silyl anion containing π systems have much attention in recent years. Boudjouk has been suggested that the negative charge upon silicon atom is delocalized into butadiene moiety in silacyclopentadienide anion. Actually, 1,1-dilithio-1-silacyclopentadiene is prepared and chraracterization by X ray analysis which show one lithium atom diffused on silacyclopentadiene skeleton.

Allowing for these area, dianion compound of disilabenzene or disilaanthracene are important and interesting compounds for delocalization of silyl anion charge into π systems, and for possibility of silaaromatics precursor.

1-2 THORETICAL STUDIES OF SILABENZENS AND DISILABENZENES

There have a number of calculation at various levels of sophistication of silabenzenes[1)] and disilabenzenes.[1f,2)] Representative results are shown as follows, respectively.

1-2-1 SILABENZENE

A calculated by Schleyer,[1f)] with the 3-21G(*) basis set ab intio calculation, were carried out on silabenzene (1), Dewar silabenzene (2), 1-silacyclohexadienylidene (3), 2-silacyclohexadienylidene (4) and 4-silacyclohexadienylidene (5).[3)]

1	2	3	4	5
0	38.4	18.0	23.5	singlet 72.5 triplet 37.2

Planar (1) is most stable isomer with aromatic stabilization of ca. 20 kcal/mol; estimated to be only two-thirds of that in benzene. The isomer (3) and (4) are estimated to be only 20-25 kcal/mol higher in energy and may be suitable precursors for the synthesis of 1. The

calculated relative energy of 38 kcal/mol for 2 represents on upper bound. The last stable structure considered, 5, is only structure indicated to have a ground state.

Schleyer suggested that the stability of 1 relative to 3 and 4 can be attributed to aromaticity in silabenzene and some π delocalization is possible in silylenes 3 and 4 by interaction of diene fragment with the empty pπ orbital on silicon, the resulting stabilization is far less effective than the aromaticity of 1.

C_{2v}

bond length / Å

SiC_1 = 1.722 (1.715)	C_1C_2 = 1.381 (1.395)
C_2C_3 = 1.395 (1.407)	SiH = 1.419 (1.435)

bond angles / deg.

SiC_1C_2 = 117.4 (117.1)	$C_1C_2C_3$ = 125.1 (124.7)
$C_2C_3C_4$ = 124.6 (124.9)	C_2C_1H = 118.2 (118.0)
C_1C_2H = 118.4 (119.5)	

Figure 1. STO-3G and MNDO Optimized Geometries of Silabenzene.

1-2-2 DISILABENZENES

Calculation show that all isomer of disilabenzene are stable structures in the planar geometries with positive force constant matrices as the STO-2G level of theory.[2b)]

6

7

8

The geometries of 6-8 reveals that the bond lengths, including the bond to silicon, are intermediated to single and double bond lengths, reflecting electron delocalization and aromaticity. The three disilabenzenes are within 10 kcal/mol of each other, the order of stability; 7 > 8 > 6. The using appropriate bond-separation reaction, aromatic stabilization for three isomers are found to be 22.5, 47.2 and 36.4 kcal/mol, respectively, compared to 47 kcal/mol for silabenzene.

Chandrasekhar[2c)] studied the system using the 3-21G(*)//STO-3G level of theory. In addition to Dewar isomer (9), isomeric silylene (10) and 11 also studied. At 3-21G(*)//STO-3G the Dewar structure is only 5.9 kcal/mol higher in energy than 8. Furthermore, the silylene structure (10) is found to be more stable than 8 by 9.9 kcal/mol. It is expected that higher levels of theory would be stabilized 9 relative to 10.

9

10

11

The 8-9 energy difference is considerably smaller than the difference between Dewar silabenzene and silabenzene and it is much smaller than the (Dewar benzene)-(benzene) energy difference. Two factors are mainly responsible for the observed energy differences;

1) The ring strain is expected to decrease in order: Dewar benzene > Dewar silabenzene > Dewar disilabenzene, because silicon is more capable of accommodating the smaller valence angle.

2) Successive replacement of unsaturated carbon centers by silicon destabilized the planar aromatic due to the lower stabilizing of C=Si bonds relative to C=C bonds.

The remarkable stability of silylene isomer 10 relative to 8 can be understood as resulting mainly from the fact that C=C bonds are by at least 25 kcal/mol stronger than Si=C bonds.

1-3 EXPERIMENTAL STUDIES OF SILABENZENS AND DISILABENZENES

1-3-1 BASE-PROMOTED GENERATION

The first evidence for a silabenzenes has been reported by Barton in 1977.[3] Dehydrochlorination of 1-chloro-1-methyl-1-silacyclohexa-2,4-diene with N-lithiodisilazane in presence of excess perfluoro-2-butyne gave silatoluene.

Scheme 1

However, a possible mechanism involving carbanionic attack on the acetylene followed by intramolecular displacement of chloride was not able to finally rule out.

1-3-2 THERMAL GENERATION

The simplest apparently the best precursor for silaaromatics are corresponding dihydro derivatives, which have been successful in production of matrix-isolated silabenzene and disilabenzene.[4)]

The retro-ene reaction is well established as a pyrolitic source of silaaromatics.[5)]

Scheme 2

Pyrolysis of 1-allyl-1-sila-3,5-cyclohexabutadiene, gives [2+4] dimer and trapping products by methanol and acetylene, respectively (Scheme 2).

Similar 1,2-elimination of neutral compound have been successful in the pyrolysis of 1-methoxy-2-trimethylsilyl-1-sila-3,5-cyclohexadiene[6] or 1-acetoxy-1-sila-3,5-cyclohexadiene[7] gave silabenzene, respectively. The silabenzene were trapped by methanol and acetylene. In the absence of trapping reagents [2+4] dimer was isolated.

Alternative rout to generation of silabenzene by ring expansion of cyclic silylcarbene have been reported (Scheme 3).[8]

Scheme 3

This is believed that pyrolysis of diazirine rearranged to silabenzene by 1,2-migration of methyl group.

West[9] was reported that disilabenzene was thermally generated *via* retro Diels-Alder reaction (Scheme 4). Trapping adduct was obtained in the thermolysis of 12 using a hexafluoro-2-butyne as a trapping reagent. Co-pyrolysis of 12 with methanol at 600 °C in a nitrogen flow reaction gave a 1-methoxy-4-hydro-1,4-disila-2,5-cyclohexadiene as a *cis*:*trans* = 1:1 mixture. But in this reaction 1,2-methanol adduct was not yielded.

Scheme 4

1-3-3 PHOTOCHEMICAL GENERATION

Photochemical approaches[13] are known as well. Trapping with alcohols, oxygen or acetylenes shows evidence of the existence of silaaromatic. In many cases, photolysis of the precursor agree with that of pyrolysis. Photolysis of 12 at 254 nm in the presence of hexafluoro-2-butyne obtained anthracene and disilabarrelene derivative (88 % yield) as shown in Scheme 4.[9] The compound have been explained as arising from a Diels-Alder reaction of 1,4-disilabenzene and hexafluoro-2-butyne . The paper was the first evidence for the presence of disilabenzene.

As shown in Scheme 3, Irradiation of diazo compound and diazirine in the presence of alcohol gave the alcohol adducts of silatoluene and the isomeric silafuluvene.[8] These intermediate silatoluene and silafuluvene presumably formed by rearrangement of the silylcarbene as well as thermally generation of these intermediate.

Along similar lines, first stable silabenzene derivative in solution at -100 °C was obtained by the irradiation of diazo compound.[10] Methanol adduct have been isolated when the irradiation was underwent in the presence of methanol as a trapping reagent of silabenzene.

13

Scheme 5

On the irradiation of 13 under pure nitrogen in sealed NMR tube at -110~-120 °C the ^{29}SI NMR signals of disappeared and new signals at -18.7 and +26.8 ppm observed. The authors have been assigned to δ = +26.8 ppm trivet from sp^2 ring silicon atom of silabenzenes (Scheme 5).

Silabenzene and 9-phenyl-silabenzene can be produced by UV irradiation of their Dewar isomer.[11] This has little practical significance at the moment since the only known way to produce the Dewar isomer is photoisomerization of two silaaromatics.

Scheme 6

1-3-4 GENERATION OF 9-SILAANNTHRACENES

Flash pyrolysis of 14, 15 and 16 may be generated, corresponding 9-silaanthracenes and these characteristic UV spectra were measured in argon matrix at 15 K.[12] Neutralization-regionization mass spectrometry of silaanthracene radical cation, which are generated from the 9,10-dihydro-9-silaanthracene under electron-inpuct conditions, reported by Bicklhaupt (Scheme 7). However, trapping products of 9-silaanthracenes have not isolated which lead to their polymerization. Bicklhaupt have reported that indirect evidence for the presence of 9-silaanthracene was obtained: expected by-product, 1,2-diphenylethane, was formed in considerable yield.

Scheme 7

Attempt to generate 9-silaanthracene *via* base-promoted procedure has been failed (Scheme 8).[13] The reaction of 17 with *t*-butyllithium afford the corresponding 10-position

lithiated compound at -78 °C. The lithium compound converted to their polymer at room temperature. No evidence for the presence of 9-silaanthracene was attained with the base-promoted 1,4-elimination of LiCl from 18.

Scheme 8

The formation of 9-silaanthracene from dibenzosilacyclohexadienylidene *via* 1,4-methyl migration, which is not so familiar, was attempted (Scheme 9).[8] The pyrolysis of 19 in the presence of methanol produce 20 and 21. No evidence for the intermediary of 9-silaanthracene was observed.

Scheme 9

In recent years, Hirastuka[14] reported that UV photolysis of 9,10-dihydro-9-silaanthracenes at 77 K resulted in the formation of 9-silaanthracenes and diphenylmethyl-type radicals (Scheme 10). It was confirmed that these were produced *via* the lowest triplet state.

Scheme 10

1-3-5 SPECTROSCOPIC DATA OF SILAAROMATICS

PES, UV, IR and NMR spectra of silaaromatics, which have been reported, are summarized as followed. All spectra measurements for silaaromatics, exceptional of NMR measurement, were carried out in argon or 3-methylpentane matrix.

PES 8.0, 9.3, 11.3 eV

UV 212, 272, 305, 313, 320 nm

IR 418, 566, 598, 886, 1259, 1353, 1500 1526, 2217 (Si-H stretch) cm^{-1}

PES 7.7, 9.2 eV

UV 263, 301, 307, 314, 322 nm

IR 563, 655, 697, 770, 842, 883, 890, 900 965, 980, 1268, 1360, 1410, 1500, 1530 cm^{-1}

UV 222, 287, 316, 328, 332, 338 nm

IR 840, 982, 1006, 1213, 1312, 1350, 1523 cm^{-1}

UV 227, 285, 320, 331, 341 nm

IR 840, 1010, 1209, 1312, 1350, 1398, 1523 cm^{-1}

^{13}C NMR 126, 139.5 (C-2, 6 / C-4), 166.8 ppm

^{29}SiNMR -17.8 (-$SiMe_3$), +26.8 (sp^2-ring Si-atom)

UV 275, 340, 385, 396, 408 nm

UV 326, 380, 400, 420, 444, 468, 494 nm

absorption 20200, 25000 cm^{-1}

fluorescent 400, 494 nm

UV 364, 384, 404, 420, 444, 470, 502 nm

absorption 19500, 24600, 35100 cm^{-1}

fluorescent 285, 407, 513 nm

UV 362, 388, 408, 424, 450, 480, 512 nm

absorption 19500, 24600 cm^{-1}

fluorescent 406, 513 nm

1-4 SILYLANIONS[15)]

Numerous investigations have been supported that silylanions are synthetically useful tools not only in organosilicon chemistry but also in organic synthesis. Many kind of approaches for the generation of silyl anions were studied.

1-4-1 PREPARATION OF SILYLLITIUMs

Silyllithiums are prepared from the reduction of related halo-silanes or disilanes with lithium metal, normally in an ethereal solutions.[16)]

$$Ph_3Si\text{-}SiPh_3 \xrightarrow{Li} Ph_3SiLi$$

$$Ph_3SiCl \xrightarrow{Li} Ph_3SiLi + LiCl$$

Scheme 11

In former case, it is believed that this procedure includes three steps (Scheme 12).

$$Ph_3SiLi + 2Li \longrightarrow Ph_3SiLi$$

$$Ph_3SiLi + Ph_3SiCl \longrightarrow Ph_3Si\text{-}SiPh_3 + LiCl$$

$$Ph_3Si\text{-}SiPh_3 + 2Li \longrightarrow 2\ Ph_3SiLi$$

Scheme 12

The first step is initial formation of Ph_3SiLi. The resulting silyllithium reacts with the Ph_3SiCl to afford $Ph_3SiSiPh_3$ in the second step. The third step is a symmetrical cleavage of the disilane with lithium metal. The final step much slower than the initial formation of silyllithium and is effected only by electropositive alkali metals. Thus, the reaction of Ph_3SiCl with less electropositive Mg compared with lithium give only $Ph_3SiSiPh_3$.

However, these procedure for the preparation of silyllithium dose not applied to the generation of trialkylsilyllithium. Trimethylsilyllithium[17] is prepared from the treatment of hexamethyldisilane with methyllithium in aprotic solvents like a hexamethylphosphoric triamide (HMPA).

$$Me_3Si\text{-}SiMe_3 \xrightarrow[\text{HMPA}]{\text{MeLi}} SiMe_4 + MeSiLi$$

Scheme 13

Highly substituted tris(trimethylsilyl)silyllithium[18] also obtained by the reaction of tetrakis(trimethylsilyl)silane with MeLi.

$Ar_2(alkyl)SiLi$ and $Ar(alkyl)_2SiLi$ are prepared by the methods the cleavage of arylsilanes in extraordinarily sensitive to the nature of the aromatic ring (Scheme 14).[19] When the anisyldimethylchlorosilane is treated with lithium, disilane is obtained in low yield.

$$Ar_n(alkyl)_{3-n}SiCl \xrightarrow{Li} Ar_n(alkyl)_{3-n}SiLi$$

$$Ar_n(alkyl)_{3-n}Si\text{-}Si(alkyl)_{3-n}Ar_n \xrightarrow{Li} Ar_n(alkyl)_{3-n}SiLi$$

Scheme 14

Other arylsilylchloride (Ar = p-tolyl and 2-furyl) give disilanes, respectively. Most surpassingly, the bis(p-tolyl)tetramethyldisilane do not cleavage at 0 °C, even with lithium powder in THF (Scheme 15). When this mixture is refluxed, cleavage apparently occur, but the only identifiable product is the 4-hydroxybutylsilane, produced presumably form the fugitive silyllithium reagent opening the THF ring (Scheme 16).

Ar = *p*-anisyl, *p*-tolyl and 2-furyl

Scheme 15

Scheme 16

Recently, preparation of functionalized silyllithium have been reported by Tamao.[20] Reduction of alkoxy-, amino-, and hydrochlorosilane with lithium 1-(dimethylamino)

naphthalenide gives the corresponding (alkoxysilyl)-, (aminosilyl)-, and (hydrosilyl)lithiums, respectively (Scheme 17).

X	^{t}BuO	^{i}PrO	MeO	^{t}BuO	Et_2N	H
n	1	1	1	2	1	1

Scheme 17

The method can avoid the use of polar solvents, so the reagents undergo coupling reaction with chlorosilanes, without undesirable Si-Si bond cleavage, to afford various oligosilanes.

Sekiguchi and Sakurai[21] reported the first preparation and full characterization of (pentamethyldisilanyl)- and two isomeric (heptamethyltrisilanyl)lithium compounds (Scheme 18). Similarly, obtained polysilanyllithium containing phenyl groups, are used building block for polysilanyl dendrimer.

Scheme 18

1-4-2 PREPARATION OF SILYLSODIUMS AND SILYLPOTASSIUMS

Silylsodiums[22] and silylpotassiums[23] are generated from the reaction of related disilanes with sodium methoxide or potassium methoxide.

HMPA or crown ether are usually used as solvent and/or co-solvent. Trimethylsilylsodium in HMPA is excellent as an electron-transfer reagent especially to produced radical anion from a variety of compound (Scheme 19).

Scheme 19

However, the value of the silylsodium for synthetic purpose is somewhat limited. Since such facile electron-transfer reaction offer gives a mixture of Me_3SiNa with alkylhalide (RX ; X = Cl, Br and I) resulted in the formation of $RSiMe_3$ and R-R. The ratio of R-R / $RSiMe_3$

increasing in order X = I ≈ Br > Cl.[22b] The problem is resolved by use of 1,3-dimethyl-2-imidazolidone (DMI) as solvent instead of HMPA.[22a]

The reaction of Me_3SiNa formed in DMI with primary alkyl chloride give the alkyltrimethylsilane in high yield (Scheme 20).

Scheme 20

However, alkyl bromides and iodides give expected product in poor yield. Apparently, electron-transfer reactions occur dominantly in these cases.

Hexamethyldisilane can be also cleaved KOMe in aprotic solvents as THF, benzene and ether in the presence of crown ether. The reaction of Me_3SiK with octyl chloride gave octyltrimethylsilane in 88 % yield. Me_3SiK also gave a electron to benzophenone and naphthalene, to afford these radical anion.

Another procedure for the preparation of silylsodium and silylpottasium are achieved by the reaction of hydrosilanes or disilanes with sodium hydride or potassium hydride in HMPA, DME, or THF / crown ether.[24]

Scheme 21

Treatment of (+)-(1-Np)-PhMeSi*H with KH and subsequent addition of n-butyl bromide give racemic (±)-(1-Np)-PhMeSi-n-Bu, via the formation of corresponding silylpotassium with loss of optical activity.[25] These results clearly rule out a mechanism in which the silyl anion is formed by proton abstraction from the hydrosilane, because of the retention of the configuration would be expected. A possible mechanism involves a pentacoordinate dihydrosilyl anion with loss of molecular hydrogen as shown in Scheme 22.

Scheme 22

Triphenylsilylpotassium is prepared from the reaction of phenylisopropyltriphenylsilane with sodium - potassium alloy (1 : 5). in ether.[26]

Scheme 23

1-4-3 METAL-FREE SILYL ANIONS

Generation of the silyl anion includes of Si-X or Si-Si bond alkali metal or nucleophilic substitution of one of disilane silicon atom with metal alkoxide or methyllithium at the sacrifice of half the molecule. The chemical behavior of the silyl anion thus produce should be understood in association with the metal counter ion. The Si-Si bond is cleaved by tetrabutylammonium fluoride (TBAF) to give metal-free triorganosilyl anion.[27]

$$Me_3Si\text{-}SiMe_3 + Bu_4N^+F^- \rightleftharpoons Bu_4N^+[Me_3SiSiMe_3F^-]$$

$$\rightleftharpoons Bu_4N^+SiMe_3^- + Me_3SiF$$

Scheme 23

On addition to unsaturated functional group A=B, trimethylsilyl anion gives $Me_3SiA\text{-}B^-$ which is converted into $Me_3SiA\text{-}BSiMe_3$ by silylation with Me_3SiF. The characteristic feature of the disilane / TBAF reagent system is observed in the transformation of 1,3-diene into 1,4-disilyl-2-butenes (Scheme 24).

Scheme 24

E isomer of the reaction products are obtained with high selectivity. 1,2-Disilylation product is not produced.

1-4-4 NMR STUDIES OF SILYL ANIONS[28]

^{13}C NMR studies provide much information on electronic structure of phenylsilyl anion. The main interest is the charge delocalization of lone pair electrons from silicon to the phenyl groups.

The ^{13}C NMR chemical shift changes on phenyl-rings on going from chlorosilane to the corresponding silyl anion give the major tend; The *ipso*-carbon is strongly deshielded, and the para-carbon is shielded.[29] As shown in Fig. 2, the charge distribution pattern is typical for π-polarization effect and quite different from the pattern of a resonance effect. Thus, a large amount of negative charge remain on silicon atom.

Figure 2 ^{13}C NMR chemical sift changes

Configurational stability of Ph(*i*-Pr)$_2$SiLi has been estimated by means of ^{1}H NMR.[30] The two methyl groups in

each isopropyl group are diastereopic and anisochronous at room temperature in a wide range of solvents.

Scheme 25

The nonequivalence is observed up to 185 °C. Since rotation around the Si-C bonds appears to be fast on the NMR time scale, the nonequivalence of the isopropyl methyl groups in the anion is evidence for slow inversion about silicon. This result indicates that unimolecular atomic inversion about silicon must be slow on the NMR time scale, and a lower limit to inversion about the trivalent silicon can be set at about 24 kcal/mol, which is consistent with theoretical studies.

1-5 STRUCTURES OF DIANION COMPOUNDS

A remarkable number of dianion compounds have been investigated. Interests for dianion compound focused on their structure, reactivity and electron distribution. For carbon dianion, a series of aromatic hydrocarbon dianion were well studied for alternation anti-aromatic or non-aromatic compound by means of X ray analysis and some spectroscopic analysis.

Type I Type II Type III Type IV

single contact double bridging single bridging difusion E = C or Si

In dianion compound, the relationship between organic compound and metal atoms can be classified into four categories.

1-5-1 BIS(CARBANION)S

The author has been proposed that dianion compound should be clearly distinguished between *geminal* and *vicinal* dianion. In this dissertation, the author defined bis(silyl anion) as *vicinal* dianion compound. Bis(anion) compound is more interesting for the structure compared with that of *geminal* dianion.

TYPE I - single contact structure

The structures of lithium compounds seldom follow classical bonding consideration. Lithium bonds have a high degree of ionic character; this lead to large energies of association. Dimer, tetramer, and other oligomeric structures are common. Similarly, two or more lithium atoms often bridge the set of atoms simultaneously; this is the intramolecular aggregation.

For dianion which the negative charge is concentrated on remote positions in the molecule (e.g., shown as follows) this information mat be extrapolated from the monomers.

However, for, dianion, in which the negative charge is concentrated with in one π-electron framework such extrapolation is unreliable.

TYPE II - lithium doubly bridged structure

The crystal structure of 2,2'-dilithio-biphenylene and 1,5-dilithio-heteroatom linked diaryl system with sulfur, oxygen, and nitrogen are well known. All are monomer in crystals. Each lithium bridges both deprotonated ortho carbons symmetrically. The coordination sphere of the metal is completed by the bidentate ligand TMEDA.

Scheme 26

Figure 3 ORTEP drawing of 1,1'-dilitio-biphenyl

Figure 4 ORTEP drawing of *o,o'*-dilithio-diphenylether

A series of ethylene dianions (M = Li, Na, K, Rb and Cs) have been recognized to have two cationic metal were bonded to two anionic carbons to give a this category. The case of 1,1,2,2-tetrakis(trimethylsilyl)ethylene bis[(tetrahydrofurane)lithium] is in shown Scheme 27 as a representation of this series.

Scheme 27

Both lithium atoms symmetrically bridged to anionic carbon atoms and can be considered as tight ion pair species.

Figure 5 ORTEP drawing of ethylene dilithium

TYPE III - lithium singly bridged structure

Tetrakis(trimethylsilyl)ethylene bis[(tetrahydrofurane) lithium] has structurally unique character. It is observed from several NMR spectra of the compound found in crystals is remained in toluene-d_8 however the structure changed to singly-bridged type by exchange of solvent to THF-d_8.

Scheme 28

Anther lithium atom free from ethylene framework and found a solvent-separated lithium ion, $Li^+(THF)_4$; the signal is observed at -0.39 ppm in ^{6}LiNMR spectrum.

TYPE IV - metal atom diffused on π-system structure

Dianion of aromatic hydrocarbon compounds have been studied as well as its radical anion species.

Scheme 29

Stucky has obtained the crystal structure of bis(carbaion): $Naph^{2-}(Li^{+}\ TMEDA)_2$ and $Anth^{2-}(Li^{+}\ TMEDA)_2$. These compounds can be considered as extremely complexed tight ion pair species.

Figure 6 ORTEP drawing of naphthalene dilithium

In $Naph^{2-}(Li^{+}\ TMEDA)_2$, prepared as shown in Scheme 29, each TMEDA chelated lithium is located over a six-membered rind and this can form multicenter bond involving the lithium-2p orbital and a combination of carbon-2p orbitals. The anionic unit is nonplaner geometry in keeping with substantial anti-aromatic character.

The complex $Anth^{2-}(Li^{+}\ TMEDA)_2$ similarly contains a non-planer dianion fragment; the two $(Li^{+}\ TMEDA)$ unit are located over the central six-membered ring and one of the outer six-membered ring.

Figure 7 ORTEP drawing of anthracene dilithium

Bis[(dimethoxyethane)lithium] 1,2,4,5-tetrakis(trimethylsilyl)benzene has been prepared as first anti-aromatic benzene dianion by reduction of the neutral compound in DME.

Scheme 30

The lithium atoms are perfectly located on above and below the center of benzene ring, and each lithium atoms is coordinated by DME.

Figure 8 ORTEP drawing of benzene dilithium

The 7Li NMR showed one signal at 10.7 ppm. The appreciable downfied shift is considered by the strong deshielding effect on lithium atoms by the paratropic ring current.

1-5-2 BIS(SILYL ANION)S

For bis(silyl anion), the interest focused on the structure and reactivity like as bis(carbanion). Nevertheless, only a few bis(silyl anion) derivatives has been reported. Among these bis(silyl anion), only four molecules can be characterized. However, all of these structurally characterized bis(silyl anion)s favoured type I bond style.

1,3-Dilithio-trisilane and 1,2-dilithio-disilane were prepared by the reaction of the cyclo-trisilane with lithium in 1,4-dioxane.[39] These structures were determined by X ray analysis, respectively. Each lithium atom attached to a terminal silicon atoms, respectively.

Scheme 31

Figure 9 ORTEP drawing of 1,2-dilihio-disilane

Figure 10 ORTEP drawing of 1,3-dilithio-trisilane

Reduction of octaphenyl-cyclo-tetrasilane with lithium in THF afford the 1,4-dilitio-octaphenyltetrasilane.[40] An X ray structure determination showed the existence of Li-Si4-Li; either lithium atom is bonded to silicon atom and to the oxygen atoms of three molecules of THF.

Scheme 32

Figure 11 ORTEP drawing of 1,4-dilithiotetrasilane

Masamune[41] has been reported the preparation of bicyclo[1,1,1]pentasilane. 1,3-Dilithio-cyclo-tetrasilane which was generated from the reaction of trichlorosilane (22) with lithium naphthalenide was used as the precursor of bicyclo[1,1,1]pentasilane. However, the bond style of the dianion (23) was not reported.

Scheme 33

Sonication of 24 with 3 equiv. of Li gave two products. The 13C NMR spectrum showed two sets of ten peaks; the large was assigned to the bis(silyl anion) (25) and smaller group was attributed to *gem*-dilithiosilane.[42]

Scheme 34

Although, Boudjouk discussed on the electronic structure of the bis(silyl anion), the bond style between silicon and lithium atoms was not determined.

N-Alkyl-1,3-dilithio-1,3-disilaisoindoline[43] was generated by the reduction of related dichloro derivative with lithium naphthalenide at -78 °C. On treatment of the bis(silyl anion) with chlorosilane, expected dimethylsilylated product was obtained as a mixture of *cis* and *trans* isomer. Although, the bond type between Si and Li of the bis(silyl anion) was not characterized.

Scheme 35

Reaction of 1,2-dichloro-1,2-disilaacenaphthene[44] with excess of lithium resulted in the formation of corresponding bis(silyl anion).

Scheme 36

NMR spectroscopic analysis and theoretical investigation strongly supered the *trans*-structure in which the negative charge is localized on the silicon atom and lithium atom interactes with one silicon atom, respectively. The measurement of the Si-Li coupling at low temperature showed that a Si-Li bond has a covalency.

1-6 REFERENCES

1) (a) H. B. Schlegel, B. Coleman, and M. Jones, Jr., *J.Am. Chem. Soc.*, 100, 6499 (1978).

(b) M. J. S. Dewar, D. H. Lo, and C. A. Ramsden, *J, Am, Chem, Soc*, 97, 1311 (1975).

(c) K. K. Balldridge and M. S. Gordon, *J. Am. Chem. Soc.*, 110, 4204 (1988).

(d) K. K. Baldridge and M. S. Gordon, *Organometallics*, 144 (1988).

(e) P. H. Blustin, *J. Organomet. Chem.*, 166, 21 (1979).

(f) J. Chandrasekhar, P. R. Schlyer, R. O. W. Baumgärtner, and M. T. Reetz., *J. Org. Chem.*, 48, 3453 (1983).

2) (a) . Chandrasekhar and P. R. Schleyer, *J. Organomet. Chem.*, 289, 51 (1985).

(b) K. K. Baldridge and M. S. Gordon, *J. Organomet. Chem.*, 271, 369 (1984).

(c) J. Chandrasekhar, P. R. Schlyer, R. O. W. Baumgärtner, and M. T. Reetz., *J. Org. Chem.*, 48, 3453 (1983).

3) (a) T. J. Barton and D. S. Banasiak, *J. Am. Chem. Soc.*, 99, 5199 (1977).

(b) G. Märkle and P. Hofmeister, *Angew. Chem., Int. Ed. Engl.*, 18, 789 (1979).

4) (a) G. Maier, G. Mihm and G. Maier, *Chem. Ber.*, 115, 801 (1982).

(b) . Maier, K. Schöttler, and P. Reisenauer, *Terahedron Lett.*, 26 (34), 4079 (1985).

5) (a) T. J. Barton and G. T. Burns, *J. Am. Chem. Soc.*, 100, 246 (1978).

(b) C. L. Kreil, O. L. Chapman. G. T. Burns, and T. J. Barton, *J. Am. Chem. Soc.*, 102, 841 (1980).

(c) H. Bock. P. Rosmus, and B. Solouki, *J. Orgamomet. Chem.*, 271, 145 (1984).

(d) H. Bock, A. A. Bowling, B. Solouki, T. J. Barton, and G. T. Burns, *J. Am. Chem. Soc.*, 102, 429 (1980).

(e) B. Solouki, P. Rosmuus, H. Bock, and G. Maier, *Angew. Chem., Int. Ed. Engl.*, 19, 51 (1980).

6) (a) T. J. Barton, M. Vuper, *J. Am. Chem. Soc.*, 103, 6788 (1981).

(b) P. Jutzi, M. Maier, H. P. Reinauer, and G. Maier, *Chem. Ber.*, 122, 1227 (1989).

7) G. Maier, G. Mihm, R. Otto, W. Baumgärtner, and H. P. Reisenauer, *Chem. Ber.*, 117, 2337 (1984).

8) A. Sekiguchi, H. Tanikawa, and W. Ando, *Organometallics*, 4, 584 (1985).

9) (a) J. D. Rich. R. West, *J. Am. Chem. Soc.*, 104, 6884 (1982).

(b) K. M. Welsh, J. D. Rich, R. West, *J. Organomet. Chem.*, 325, 105 (1987).

10) G. Märkl and W. Schlosser, *Angew. Chem., Int. Ed. Eng.*, 27, 963 (1988).

11) G. Maier, G. Mihm, R. Otto, W. Baumgärtner, and H. P. Reisenauer, *Chem. Ber.*, 117, 2337 (1984).

12) Y. van den Winkel, B. L. M. Baar, F. Bickelhaupt, W. Kulik, C. Sierakowski, and G. Maier, *Chem. Ber.*, 124, 185 (1991).

13) (a) Y. van den Winkel, B. M. van Baar, H. M. M. Bastiaans., and F, Bickelhaupt, *Tetrahedron*, 46, 1009 (1990).

(b) P. Jutzi, *Angew. Chem., Int. Edit.*, 14, 232 (1975).

(c) P. Jutzi and H. Fetz, *Chem. Ber.*, 104, 1455 (1971).

(d) P. Jutzi, *Chem. Ber.*, 104, 1455 (1971).

14) H. Hiratsuka, M. Tanaka, T. Okutsu, M. Oba, and K. Nishiyama, J. Chem. Soc., *Chem. Commun.*, 215 (1995).

15) (a) K. Tamao, A. Kawachi, *Adov. in Organometallic Chemistry*, 38, 1 (1995).

(a) E. Wiberg, O. Stecher, H. J. Andrascheck, L. Kreuzbichler, and E. Staude, *Angew. Chem., Int. Ed.*, 2, 507 (1963).

(c) M. Fujita, T. Hiyama, *Yugoka*, 42, 293 (1984).

16) (a) J. B. Lambert, W. J. Schulz, Jr., In *The Chemictry of Organic Silicon Compounds*; S. Patai, Z. Rappoport, Eds.; Wiley: Chichester, U. K., 1007 (1989).

(b) I. Fleming, In *Comprehensive Organic Chemistry*; D. Barton, W. D. Ollis, Eds.; Pergmon Press: Oxford, U. K., Vol 3, 664 (1979).

17) W. C. Still, *J. Org. Chem.*, 41, 3063 (1976).

18) G. Gutekunst, A. G. Brook, *J. Organomet. Chem.*, 225, 13 (1982).

19) N. A. Rahman, I. Fleming, and A. B. Zwicky, *J. Chem. Reserch (s)*, 292 (1992).

20) (a) K. Tamao, A. Kawachi, *Organometallics*, 14, 3108 (1995).

(b) K, Tamao, G. Sun, and A. Kawachi, J. Chem. Soc., Chem. Commun., 2079 (1995).

21) (a) A. Sekiguchi, M. Nanjo, C. Kabuto, and H. Sakurai, *Organometallics*, 14, 2630 (1995).

(b) A. Sekiguchi, M. Nanjo, C. Kabuto, and H. Sakurai, *J. Am. Chem. Soc.*, 117, 4195 (1995).

22) (a) H. Sakurai and F. Kondo, *J. Organomet. Chem.*, C46-C48, 92 (1975).

(b) H. Sakurai, A. Okada, M. Kira, and K. Yonezawa, *Tetrahedron Lett.*, 19, 1511 (1971).

23) H. Sakurai, M. Kira, and H. Umino, *Chem. Lett.*, 1265 (1977).

24) R. J. P. Corriu and C. Guerin, *J. Chem. Soc., Chem. Commun.*, 168 (1980).

25) J. L. Brefort, R. J. P. Corriu, C. Guérin, and B. Henner, *J. Organomet. Chem.*, 370, 9 (1989).

26) R. A. Benkeser and R. G. Severson, *J. Am. Chem. Soc.*, 73, 1424 (1951).

27) T. Hiyama, M. Obayashi, I. Mori, and H. Nozaki, *J. Org. Chem.*, 48, 912 (1983).

28) U. Edlund and E. Buncel, In *Progress in Physical Organic Chemistry*; R, W. Talf, Ed.: Wiley: New york, 19, 254 (1993).

29) (a) E. Buncel, T. K. Venkatachalam, U. Edlund, and B. Eliasson, *J. Chem. Soc., Chem. Commun.*, 1476 (1984).

(b) G. A. Olah and R. J. Hunadi, *J. Am Chem. Soc.*, 102, 6989 (1980).

(c) E. Buncel, R. D. Gordon, T. K. Venkatachalam, *J. Organomet. Chem.*, 508, 81 (1996).

(d) E. Buncel, T. K. Venkatachalam, B. Eliasson, and U. Edlund, *J. Am. Chem. Soc.*, 107, 303 (1985).

30) J. B. Lambert and M. Urdaneta-Pérez, *J. Am. Chem. Soc.*, 100, 157 (1978).

31) (a) J. L. Wardell, In *Comprehensive Organometallic Chemistry*, St.G. Wilkinson, F. G. A. Stone, and E. W. Abel, Eds.: Pergamon press: UK, vol 1, 43 (1981).

(b) W. N. Setzer and P. von R. Schleyer, *Adv. in Organometallic Chemistry*, 24, 355 (1995).

32) (a) M. F. Lappert, C. L. Raston, B. W. Skelton, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 14 (1982).

(b) P. von R. Schleyer, *Pure Appl. Chem.*, 55, 355 (1983).

33) U. Schubert, W. Neugebaeer, and P. von R. Schleyer, *J. Chem. Soc., Chem. Commun.*, 1184 (1982).

34) P. von R. Schleyer et al, *J. Am. Chem. Soc.*, 115, 4698 (1993).

35) (a) A. Sekiguchi, M. Ichinohe, C. Kabuto, and H. Sakurai, *Organometallics*, 14, 1092 (1995).

(b) A. Sekiguchi, M. Ichinohe, C. Kabuto, and H. Sakurai,*Bull. Chem. Soc. Jpn.*, 68, 2981 (1995).

(c) A. Sekiguchi, T. Nakanishi, C. Kabuto, and H. Sakurai, *J. Am. Chem. Soc.*, 111, 3748 (1989).

36) A. Sekiguchi, M. Ichinohe, T. Nakanishi, and H. Sakurai, *Chem. Lett.*, 267 (1993).

37) (a) M. Nir, R. E. Hoffman, I. O. Shapiro, and M. Rabinovitz, *J. Chem Sos., Perkin Trans.* 2, 1433 (1995).

(b) M. Nir, R. E. Hoffman, I. O. Shapiro, and M. Rabinovitz, *J. Chem Sos., Perkin Trans.* 2, 1607 (1996).

(c) M. C. Cassani, Y. K. Gun'ko, P. B. Hitchcock, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1987 (1996).

(d) P. W. Rabideau, Tetrahedron, 46, 1579 (1989).

(e) H. Cho and R. G. Harvey, *J. Org. Chem.*, 40, 3097 (1975).

(f) R. G. Harvey, L. Nazareno, and H. Cho, *J. Am. Che. Soc.*, 95, 2376 (1973).

(g) W. E. Rhine, J. Davis, and G. Stucky, *J. Am. Chem. Soc.*, 97, 2079 (975).

(h) A. Minsky, A. Y. Meyer, and M. Rabinovitz, *Angew. Chem., Int. Ed. Engl.*, 22, 45 (1983).

(i) G. R. Stevenson and R. T. Hashim, *J. Phys. Chem.*, 90, 1896 (1986).

(j) A. Sygula, K. Lipkowitz, and P. W. Rabideau., *J. Am. Chem. Soc.*, 109, 6602 (1987).

(k) A. Minsky. A. Y. Meyer, and M. Rabinovitz, *Tetrahedron Lett.*, 23, 5351 (1982).

38) A. Sekiguchi, K. Ebata, C. Kabuto, and H. Sakurai, *J. Am. Chem. Soc.*, 113, 7081 (1991).

39) J. Belzner, U. Dehnert, and D. Stalke, *Angew. Chem., Int. Ed. Engl.*, 33, 2450 (1994).

40) G. Becker, H. -M. Hartmann, E. Hengge, and F. Schrank, *Z. anorg. allg. Chem.*, 572, 63 (1989).

41) Y. Kabe, T. Kawase, J. Okada, O. Yamashita, M. Goto, S. Masamune, *Angew. Chem., Int. Ed. Engl.*,29, 794 (1990).

42) J. H. Hong, P. Boudjouk, and S. Castellino, *Organometallics*, 13, 3387 (1994).

43) K. Tamao, G. Sun, and A. Kawachi, *J. Chem. Soc., Chem. Commun.*, 2079 (1995).

44) W. Ando, T. Wakahara, and T. Akasaka, *Organometallics*, 13, 4683 (1994).

CHAPTER 2

PREPARATION OF 9,10-DIMETHYL-9,10-DISILAANTHRACENE DIMER

ABSTRUCT

Title compound is synthesized by Wurtz coupling reaction of 9,10-dichloro-9,10-dimethyl-9,10-disilaanthracene (2b) with sodium in low yield. Increasing yield of dimer was achieved by direct reaction of 9,10-dihydro-9,10-dimethyl-9,10-disilaanthracene (2a) with lithium. The structure of 9,10-dimethyl-9,10-disilaanthracene dimer 1 was characterized by means of X ray analysis. Si-Si and Si-C bond lengths and bond angles around silicon atoms fall in normal values. Dimer (1) was photochemically and thermally stable .

2-1 INTORODUCTION

The chemistry of 9,10-dihydroanthracene[1)] with the silicon in position 9 and/or 10 has been considerably developed for some time by Jutzi, Bickelhaupt and modified by Corey; in particularly their purpose of silicon analogues of carbocyclic aromatic framework. The 9-silaanthracene head to tail dimer was synthesized by Jutzi (Chapter-1-3-4). However, the anthracene dimer analogs with all bridgehead atoms exchanged to silicon atoms has not yet been prepared. 9,10-Disilaanthracene dimer 1 has been considered that good precursor for the preparation of 9,10-disilaanthracene, because of the compound in 1 connected by only Si-Si bond.

Most popular reaction for silicon-silicon single bond formation is reaction of halosilanes with alkali metals by Wurtz type coupling reaction. Dehydrogenative silicon-silicon bond formation from hydrosilanes[2)] has much interest in omitting of the reaction steps and in avoidance of unstable compounds, as halosilanes. However, there are few reports for the development of these reactions. Corey has been reported the dehydrogenative coupling reaction of 9,9,10-trihydro-10-methyl-9,10-disilaanthracene with transition metal complex to afford its polymer. In this reaction, the silylene complex has been proposed for the reaction intermediate. Thus, a starting material of this reaction has been restricted to di- or trihydrosilane.

2-2 RESULTS AND DISCUSSION

2-2-1 PREPARATION OF DIMER (1) FROM THE REACTION OF CHLOROSILANE (2b) WITH SODIUM

Wurtz coupling reaction of halosilane with alkali metal is the simplest approach for silicon-silicon bond formation. At first, we tried to prepare 9,10-disilaanthracene dimer (1) by Wurtz coupling reaction of 9,10-dichloro-9,10-dimethyl-9,10-disilaanthracene (2b) with sodium.

Scheme 1 Reagents : i) 2Mg / $MeSiHCl_2$; ii) Rieke's Mg*, $MeSiHCl_2$

9,10-Dihydro-9,10-dimethyl-9,10-disilaanthracene (2a) was prepared by Corey's procedure.[1e,f] 9,10-Dichloro-9,10-disilaanthracene (2b) was obtained by chlorination of 2a with palladium dichloride in carbon tetrachloride. The treatment of *cis/trans* mixture of 2b with sodium in refluxing toluene to afford expected bridged dimer (1) in only 7 % yield and polymeric product. Formation of large amount of undesired polymeric products reveals that this reaction is not efficiently to prepare the dimer (1).

One is less possibility of the intermolecular Si-Si coupling reaction between the two molecules.

Scheme 2 Reagents and Conditions: i) cat. $PdCl_2$, CCl_4, reflux, 18 h; ii) Na (x 2), toluene, reflux, 12 h

The other is intramolecular coupling reaction onto 9 and 10 positions to afford Dewar-9,10-disilaanthracene which is unstable in such a condition, to result the formation of polymer.

2-2-2 PREPARATION OF DIMER (1) FROM THE REACTION OF HYDROSILANE (2a) WITH LITHIUM.

Recently, the author has developed the dehydrolithiation of hydrosilane with lithium metal in THF containing TMEDA to afford corresponding silyllithium.[3)]

Scheme 3 Reagents and Conditions i) Li (x2), TMEDA (x2), THF, r. t., 48 h; ii) TMSCl (excess), -78 °C to r. t.; iii) $Ph_2Si(H)Me$ (x1.2)

Reaction of diphenymethylsilane with lithium, followed by quenching with trimethylchlorosilane produced 1,1-diphenyl-1,2,2,2-tetramethyldisilane in 44 % yield. It is possible from the result that diphenylsilyllithium was generated in this reaction. On treatment of the silyllithium with diphenylmethylsilane, 1,1,2,2-tetraphenyl-1,2-dimethyldisilane was obtained in 38 % yield.

It is thought that silicon-silicon bond can be made by the reaction of hydrosilane with lithium via the silyllithium. Gilman[4)] has been reported that silyllithium

react with hydrosilane to afford corresponding disilane and lithium hydride.

Scheme 4

Table 1 Preparation of 9,10-disilaanthracene dimer (1)

entry	TMEDA[i)]	reaction temp. / time	yield
1	-	r.t. / 48 hr	29
2	-	r.t. / 48 hr	61
3	+	reflux / 24 hr	0
4	+	reflux / 24 hr	10

i) + : presence of 2 eq. of TMEDA for 2a.
- : absence of TMEDA

Reaction of *cis/trans* mixture (=45/55) of 9,10-dihydro-9,10-dimethyl-9,10-disilaanthracene (2a) with two equivalents of lithium in THF containing TMEDA at room temperature for 48 hours produced an expected bridged dimer (1) in 61 % yield. The role of TMEDA is important for the reaction of 2a with lithium. In the absence of TMEDA, yield of dimer (1) decreased in 29 % yield (Table 1). Presumably, electron-transfer reaction of hydrosilane from lithium metal is accelerated by addition of TMEDA.

Selected bond lengths and bond angles are shown in Fig. 1. Si-Si and Si-C bond lengths and bond angles around silicon atoms are settle in standard values. Fig. 2 is shown ORTEP drawing of 1

Figure 1 Selected bond angles and lengths for 1

Figure 2. ORTEP drawing of 9,10-disilaanthracene dimer (1)

2-2-3 POSSIBLE MECHANISM FOR THE FORMATION OF 1 FROM HYDROSILAN (2a).

Three mechanisms are considered from the formation of dimer (1). One is a head to tail coupling reaction of 9,-lithio-10-hydro-9,10-dimethyl-9,10-disilaanthracene (4) yielded from the reduction of 2a with lithium (path A in Scheme 5).

Scheme 5

Next is dimerization of Dewar-9,10-disilaanthracene (5) generated from intramolecular coupling reaction of 4 (path B). The other is coupling reaction of 9,10-dilithio-9,10-

disilaanthracene (6) with hydrosilane (2a) as path C. However, the intermediate could not clear because formation of dimer (1) from the intermediate is fast. In order to shed light on the structure of the intermediate, reaction of 9,10-di(*tert*-butyl)-9,10-dihydro-9,10-disilaanthracene (7) with lithium was made; it was expected that the dimerization of intermediate was interrupted by repulsion of bulky *tert*-butyl froup.

7 8 9

Scheme 6 Reagents and Conditions i) Li (x2), TMEDA (x2), THF r. t., 1week; ii) MeI (excess), -78 °C to r. t.

The reaction of *trans*-9,10-dihydro-9,10-di-*tert*-butyl-9,10-disilaanthracene (7) with lithium in THF-TMEDA produced a yellow suspension. After removal unreacted lithium, the yellow suspension was treated with methyl iodide afford 9,10-di(*tert*-butyl)-9-methyl-10-hydro-9,10-disilaanthracene (9) as a mixture of *cis/trans* mixture in 35 % yield. No 9,10-di(tert-butyl)-9,10-disilaanthracene dimer was obtained because the dimerization was restricted by repulsion of crowded *tert*-butyl groups; a head to tail coupling reaction of silyllithium (8) could not occur It is considered from the result that *cis/trans*-9-lithium-9,10-di(*tert*-butyl)-10-

hydro-9,10-disilaanthracene (8) is formed in the reaction of 7 with lithium.

In the view of these results and silicon-silicon bond formation from the reaction of hydrosilane with silyllithium, we proposed that dimer (1) has been produced by the intermolecular head to tail coupling of 9-lithio-10-hydro-9,10-dimethyl-9,10-disilaanthracene (7), shown in Scheme 5 (path A).

2-2-4 PHOTOREACTION AND PYROLYSIS OF DIMER (1)

9,10-Disilaanthracene dimer (1) is photochemically and thermally stable. When 1 was irradiated at 254 nm in the presence of acetylenes, 1 was recovered in quantitatively. No reaction was observed in co-pyrolysis of 1 and acetylenes at 600 °C in a argon flow reaction.

Scheme 7

Thus the author abandoned the synthesis of 9,10-disilaanthracene from the dimer (1) by photolysis or pyrolysis at this point.

2-3 EXPERIMENTAL SECTION

General method.

^{1}H, ^{13}C and, ^{29}Si NMR spectra were obtained with Brucker AC-400PS(100 and, 80 MHz), AC-300P(75 and, 60MHz) spectrometer chloroform-*d* or benzene-d_6 using tetramethylsilane (TMS) was used as an internal or external standard. Mass spectra were obtained on a Shimadzu QP 2000 and QP 5000 spectrometers. IR spectra were measured on a JEOL FT/IR-5000 spectrometer. UV-vis spectra were recorded on a JEOL Ubest-50 spectrometer. Elemental Analyses were carried out by the Chemical Analytical Center of the University of Tsukuba.

Gel permission chromatographic separation was performed on a model LC-908 recycling preparative HPLC (Japan Analytical Industry Co., Ltd.) with a series of Jaigel 1H and 2H columns using toluene as a eluant. For thin-layer chromatography Kieselgel(Merck, Art. 7747) was used.

Solvent were dried over sodium benzophenone ketyl or molten sodium prior to use.

Preparation of *o*-chlorobromobenzene.

A mixture of 127.5 g (1.0 mol) of *o*-chloroaniline and 300 mL (2.5 mol) of 47 % hydrobromic acid in a 2-L flask set in an cooling bath at cooled to 0 °C by addition of dry-ice.

A solution of 70 g (1.0 mol) of sodium nitrite in 125 mL of water was added rapidly, with stirring, the temperature being kept below -20 °C by addition of small pieces of dry-ice. A mixture of 79 g (0.55 mol) of cuprouse bromide and 80 mL of 47 % hydrobromic acid was heated to boiling in a 3-L round bottomed two necked flask, equiped with condenser set for distillation and provided with 2-L receiving flask, and a separately funnel. The diazonium solution was transferred to the separately funnel, without filtration, and immediately run into the curprous bromide-hydrobromic acid solution, which is kept boiling over at such a free flame, at such a rate that boiling is continuous. All the diazonium solution was added in this way over a period of about 30 min. When the addition was complet, the stopcock in separately funnel was closed, about 1~1.5 L of distillate was collect. Organic compounds were extracted with dichloromethane. The combined organic fraction was concentrated by use of rotary evaporator. The product was dried over a about 3 g of calcium chloride and distilled to afford title compound.

Yield	143.5 g (75 %)
colorless oil	m.p. 87~91 °C/ 25 mmHg
^{1}H NMR(90MHz,$CDCl_3$)δ	7.27(4H,m)
^{13}C NMR(23MHz,$CDCl_3$)δ	122.4, 127.8, 128.3, 130.3, 133.7, 134.4

A solution of 70 g (1.0 mol) of sodium nitrite in 125 mL of water was added rapidly, with stirring, the temperature being kept below -20 °C by addition of small pieces of dry-ice. A mixture of 79 g (0.55 mol) of cuprouse bromide and 80 mL of 47 % hydrobromic acid was heated to boiling in a 3-L round bottomed two necked flask, equiped with condenser set for distillation and provided with 2-L receiving flask, and a separately funnel. The diazonium solution was transferred to the separately funnel, without filtration, and immediately run into the curprous bromide-hydrobromic acid solution, which is kept boiling over at such a free flame, at such a rate that boiling is continuous. All the diazonium solution was added in this way over a period of about 30 min. When the addition was complet, the stopcock in separately funnel was closed, about 1~1.5 L of distillate was collect. Organic compounds were extracted with dichloromethane. The combined organic fraction was concentrated by use of rotary evaporator. The product was dried over a about 3 g of calcium chloride and distilled to afford title compound.

Yield	143.5 g (75 %)
colorless oil	m.p. 87~91 °C/ 25 mmHg
^{1}H NMR(90MHz,$CDCl_3$)δ	7.27(4H,m)
^{13}C NMR(23MHz,$CDCl_3$)δ	122.4, 127.8, 128.3, 130.3, 133.7, 134.4

Preparation of bis(o-chlorophenyl)methylsilane.

A mixture of o-chlorobromobenzene (57.4 g, 0.3 mol) and methyldichlorosilane (1.54 mL, 0.15 mol) in THF (150 mL) was added to 7.36 g (0.3 mol) of magnesium shaving in THF (20 mL) at room temperature, and the reaction mixture was stirred overnight. The slurry was filtered, hexane was used as eluant, and extracted with ether. The combined organic fractions were concentrated with rotary evaporator to produce an oil. The oil was purified by Kugelrohr distillation to give impure title compound. The oil was purified by further distillation to produce pure title compound.

Yield	19.5 g (49 %)
colorless oil	m.p. 94~104 °C/0.05 mmHg
^{1}H NMR(300MHz,$CDCl_3$)δ	0.75(3H,d *J*=3.6Hz), 5.17(1H,q *J*=3.6Hz), 7.33(8H,m)
^{13}C NMR(75MHz,$CDCl_3$)δ	-5.02, 126.1, 129.0, 131.4, 134.0, 137.3, 141.2

Preparation of 9,10-dihydro-9,10-dimethyl-9,10-disilaanthracene (2a)

A mixture of magnesium chloride (28.56 g, 0.3 mol), potassium iodide (24.9 g, 0.15 mol), and potassium (22.67 g,

0.58 mol) which were heated at reflux in THF (200 mL) for 3 hours with stirring under argon atmosphere. After dropwise addition of bis(*o*-chloropheny)methylsilane (26.7 g, 0.1 mol) in THF (200 mL) to magnesium slurry, the mixture was heated at reflux for 3 hours after which methyldichlorosilane (10.3 mL, 0.1 mol) in THF (200 mL) was added at room temperature. The resultant mixture was stirred overnight. Hydrolysis with sat. NH_4Cl aq. was followed by ether extraction, drying of combined organic layers over $MgSO_4$, and evaporation of the solvent to give crude products mixture. The crude products was purified by Kugelrohr distillation to produce pure title compound. *Cis/trans* ratio was determined by integral of the ^1H NMR spectrum based on Corey's report.

Yield	15.56 g (65 %)
white waxy oil	m.p. ~205 °C/5 mmHg
^1H NMR(300MHz,$CDCl_3$)δ	0.58(3H,d *J*=3.9Hz), 0.64(3H,d *J*=3.9Hz), 4.91(1H,q *J*=3.9Hz), 4.95(1H,q *J*=3.9Hz), 7.42(4H,m), 7.72(4H,m)
^{13}C NMR(75MHz,$CDCl_3$)δ	-4.3, -4.1, 127.9, 128.6, 134.1, 134.2, 141.8, 141.9
^{29}Si NMR(60MHz,$CDCl_3$)δ	-36.8, -35.1
Mass m/z(%)	240(M^+,30), 225(M^+-CH_3,60)
IR (nujol) cm^{-1}	2124(Si-H), 1263(Si-CH_3), 1253(Si-CH_3)
UV-vis(c-hexane)λ_{max}(ε)	264(470), 269(490), 276(380)

Preparation of 9,10-dichloro-9,10-dimethyl-9,10-disilaanthracene (2b)

A mixture of 2a (1.0 g, 4.16 mmol) and palladium dichloride (76 mg) in carbon tetrachloride (8 mL) was refluxed for 18 hours under argon atmosphere. The solvent was slowly evaporated from the reaction mixture *in vacuo* and crude products was purified by distillation .

Yield	1.14 g (87 %)
colorless solid	120~200 °C/0.05 mmHg
Mass m/z (%)	308(M^+,65), 293(100)

Reaction of 2b with molten sodium

A mixture of 2b (1.20 g, 3.9 mol) and sodium (430 mg, 18,7 mmol) in toluene (4 mL) was refluxed for 36 hours under argon atmosphere. After removal unreacted sodium, the resultant suspension was quenched, extracted with ether. The combined organic fractions was dried over about 10 g of anhydrous magnesium sulfate, was concentrated by evaporation. The crude products were purified by preparative TLC, hexane was used as solvent, 70 mg of dimer (1) was obtained.

Yield	70 mg (7 %)
colorless crystals	b.p. >300°C

^{1}H NMR(300MHz,$CDCl_3$)δ	0.84(12H,s), 7.03(8H,AA'BB' m *J*=3.1, 5.1Hz), 7.33(8H,AA'BB' m *J*=3.1, 5.1Hz)
^{13}C NMR(75MHz,$CDCl_3$)δ	-7.18, 127.08, 131.89, 143.47
^{29}Si NMR(60MHz,$CDCl_3$)δ	-27.9
Mass m/z(%)	476(M^+,100), 461(M^+-CH_3,56), 471(67)
IR (nujol) cm^{-1}	1263(Si-CH_3)
UV-vis(c-hexane)λ_{max}(ε)	243(54200), 276(6900), 284(5400)
Anal (for $C_{28}H_{28}Si_4$)	Calc.: C,70.58 %; H, 5.8 % Found: C, 69.29 %; H, 5.90 %

Preparation of diphenylmethylsilyllithium (3)

Lithium dispersion (325 mg, 30 wt%, 5 mmol) was washed with dry hexane under argon atmosphere prior to use. To a flask placed the lithium dispersion was added diphenylmethylsilane (495 mg, 2.5 mmol) dissolved in 7 mL of THF with syringe, followed by addition of TMEDA (0.75 mL). The mixture was deggassed by use of freeze-pump-thraw cycles, equiped with dry argon, then sonicated for 3 hours to produce brown solution. After removal unreacted lithium dispersion, the brown solution was treated with 405 mg of trimethylchlorosilane (3.75 mmol) which was poured into dil. HCl aq., followed by extraction with ether, drying of combined organic layers over $MgSO_4$, and evaporation of solvent to give crude products mixture. Separation of the

reaction mixture by preparative TLC to produced 1,1-diphenyl-1,2,2,2-tetramethyldisilane.

Yield	160.3 mg (44 %)
^{1}H NMR(300MHz,$CDCl_3$)δ	0.14(9H,s), 0.59(3H,S), 7.33(6H,m), 7.47(4H,m)
^{13}C NMR(75MHz,$CDCl_3$)δ	-4.92, -1.70, 127.81, 128.67, 134.81, 137.44.
^{29}Si NMR(60MHz,$CDCl_3$)δ	-21.96, -18.91.
Mass m/z	270(M^+), 197(M^+-TMS)

Preparation of 1,1,2,2-tetraphenyl-1,2-dimethyldisilane

To a THF solution of diphenylmethylsilane (594 mg, 2.75 mmol) was added the diphenylmethylsilyllithium solution at -78 °C. The mixture was stirred for 30 min at same temperature, then the bath was removed and further stirred overnight. The mixture was hydrolyzed and extracted with ether. The organic layers were combined , dried over MgSO4, then concentrated by evaporation to give crude product mixture. Purification and separation of the mixture produced title compound and 330 mg of diphenylmethylsilane.

Yield	374 mg (38 %)
^{1}H NMR(300MHz,$CDCl_3$)δ	0.65(6H,s), 7.23-7.38(20H,m)
^{13}C NMR(75MHz,$CDCl_3$)δ	-4.12, 127.78, 128.90, 135.17, 136.53.
^{29}Si NMR(60MHz,$CDCl_3$)δ	-23.26.
Mass m/z	394(M^+), 197(M^+-$SiPh_2Me$)

Preparation of 9,10-dimethyl-9,10-disilaanthracene dimer (1)

A mixture of 9,10-dihydro-9,10-dimethyl-9,10-disilaanthracene (2a, 4.80 g, 20.0 mol) dissolved in 35 mL of THF, lithium wire (0.28 g, 40.0 mmol), and N,N,N',N'-tetramethylethylene diamine (TMEDA, 6 mL, 40.0mmol) in 500 mL round bottle two necked flask was degassed by freeze-pump-thraw cycles and was sonicated for 1 hours *in vacuo*. The resultant mixture changed to yellow suspension from browm solution in dry argon equiped glove box during about 2 days. Further reaction of the mixture to afford pale-yellow suspension which ca.50 mL of benzene was added. The suspension was filtered, benzene was used as eluant solvent, and extracted with benzene. The combined organic fractions was washed with water, dried over 10 g of anhydrous magnesium sulfate, and concentrated with rotary evaporator to afford white solid and colorless oil mixture. The crude products were purified by filtration, by using ethanol, to produce pure title compound (2.917 g, 61 %) as a white powder. For the measurement of X ray analysis, the sample was recrystallized from *cyclo*-hexane.

Reaction of 2a with lithium in the absence of TMEDA

A mixture of 2a (721 mg, 3.0 mmol) and large excess of lithium in 5 mL of THF was degassed by freeze-pump-thraw cycles, and sonicated for 1 hour *in vacuo*. The resultant mixture was stirred in argon glove box for tree days at room temperature. After removal unreacted lithium, the filtrate was allowed to pour into water, extracted with benzene. The combined organic fractions was dried over ca. 3 g of anhydrous magnesium chloride, was concentrated by evaporation to afford colorless solid and oil mixture. The crude product was purified by filtration , ethanol was use as solvent, to produce 206 mg of 1 (yield 29 %)

Reaction of 9,10-di(*tert*-butyl)-9,10-dihydro-9,10-disila-anthracene with lithium (7)

A mixture of 4 (162 mg, 0.5 mmol), lithium wire (15 mg, 1.44 mmol), and TMEDA (0.3 mL, 2.1 mmol) in THF (5 mL) was degassed by use of freeze-pump-thraw cycles and sonicated for 1 hour *in vacuo*. The resultant reaction mixture was stirred during 1 week to afford yellow suspension. After removal unreacted lithium, the residue was treated with 0.5 mL of methyl iodide (8 mL), was added to dil.HCl aq., which was extracted with ether. The combined organic fractions was dried over ca.3 g of $MgSO_4$, concentrated by evaporation. The crude products were purified by preparative TLC to afford 9-hydro-10-methyl-9,10-di(tert-butyl)-9,10-disilaanthracene (8) as a mixture of *cis/trans* mixture.

Yield	59 mg (34 %)
^{1}H NMR(300MHz,$CDCl_3$)δ	0.61(s), 0.66(s), 0.71(s), 1.02(s), 1.07(s), 1.10(s), 4.69(s), 4.74(s), 7.39(m), 7.68(m)
Mass m/z (%)	281(M^+-Bu, 74 %)

Photoreaction of 9,10-disilaanthracene dimer (1)

A mixture of 1 (33 mg, 0.07 mmol), diphenylacetylene (124 mg, 0.7 mmol), and cyclo-hexane (10 mL) was placed in a quartz tube under argon atmosphere. The mixture was irradiated with a low pressure mercury lamp for 3 hours. Separation and purification of the mixture by preparative TLC gave 14 mg of 1 (42 % recovered), diphenyl acetylene, and unidentifiable polymeric products.

Pyrolysis of 9,10-disilaanthracene dimer (1)

Reaction of 1 (100 mg, 0.21 mmol) was performed in gas phase at ca.600 °C in vertical flow pyrolysis apparatus. The tetrahydrofurane solution of 1 was introduced by syringe through a septum with argon/acetylene mixing gas into the heated quartz tube equiped its chips. ^{1}H NMR spectrum analysis of the product revealed that dimer (1) was recovered even at 600 °C.

Crystallographic data of 2

fw 476.88, monoclinic, a = 14.157(1) Å, b = 10.765(1) Å, c = 18.469(2) Å, β = 110.25(1) °, V = 2640.6 Å^3, space group $P2_1/a$, Z = 4, μ(Mo Kα) = 2.3 cm^{-1}, ρ(calcd) = 1.20 g/cm^3, R = 0.036 (R_w = 0.036). The 3954 independent reflections ($2\theta \leq 52.6°$; $|Fo^2| \geq 3\sigma|Fo^2|$) were measured on an Enraf-Nonius CAD4 diffrectometer using Mo Kα irradiation and an ω-θ scan. An empirical absorption correction based on a series of Ψ scans were applied to the data 0.925/0.999. The structure was solved by direct methods, and hydrogen atoms were located and added to the structure factor calculations but their positions were not refined.

Crystallographic data for dimer (1)

Table of Bond Distances in Angstroms of 1

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
SI1	SI4	2.3710(9)	C11	C16	1.401(4)
SI1	C1	1.867(3)	C12	C13	1.372(4)
SI1	C16	1.884(2)	C12	H12	0.93(3)
SI1	C46	1.879(3)	C13	C14	1.367(4)
SI2	SI3	2.377(1)	C13	H13	0.89(4)
SI2	C2	1.870(3)	C14	C15	1.384(4)
SI2	C21	1.882(2)	C14	H14	0.84(4)
SI2	C36	1.878(2)	C15	C16	1.401(4)
SI3	C3	1.875(3)	C15	H15	0.88(3)
SI3	C26	1.877(2)	C21	C22	1.393(3)
SI3	C31	1.881(2)	C21	C26	1.410(4)
SI4	C4	1.873(3)	C22	C23	1.381(4)
SI4	C11	1.872(2)	C22	H22	0.88(3)
SI4	C41	1.877(3)	C23	C24	1.367(5)
C1	H111	0.977(4)	C23	H23	0.94(3)
C1	H112	0.908(3)	C24	C25	1.376(4)
C1	H113	0.888(3)	C24	H24	0.93(3)
C2	H211	1.03(3)	C25	C26	1.397(4)
C2	H212	0.98(2)	C25	H25	0.90(3)
C2	H213	0.91(2)	C31	C32	1.397(3)
C3	H311	0.96(3)	C31	C36	1.407(4)
C3	H312	0.93(2)	C32	C33	1.385(3)
C3	H313	0.96(2)	C32	H32	0.93(3)
C4	H411	0.88(2)	C33	C34	1.366(4)
C4	H412	0.98(3)	C33	H33	0.94(2)

C4	H413	0.93(3)	C34	C35	1.378(4)
C11	C12	1.405(3)	C34	H34	0.91(2)

Bond Distances (cont.)

Atom 1	Atom 2	Distance
C35	C36	1.399(4)
C35	H35	0.93(3)
C41	C42	1.401(4)
C41	C46	1.400(3)
C42	C43	1.377(4)
C42	H42	0.93(2)
C43	C44	1.359(4)
C43	H43	0.98(3)
C44	C45	1.385(4)
C44	H44	0.89(3)
C45	C46	1.405(4)
C45	H45	0.92(3)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Angles in Degrees of **1**

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
SI4	SI1	C1	110.9(1)	H111	C1	H112	93.2(3)
SI4	SI1	C16	106.40(8)	H111	C1	H113	113.0(3)
SI4	SI1	C46	108.8(2)	H112	C1	H113	113.3(4)
C1	SI1	C16	111.8(1)	SI2	C2	H211	110.1(1)
C1	SI1	C46	110.9(2)	SI2	C2	H212	110.8(1)
C16	SI1	C46	107.9(2)	SI2	C2	H213	112.3(2)
SI3	SI2	C2	111.7(1)	H211	C2	H212	98.4(2)
SI3	SI2	C21	106.29(7)	H211	C2	H213	108.5(2)
SI3	SI2	C36	108.29(8)	H212	C2	H213	115.8(2)
C2	SI2	C21	111.7(1)	SI3	C3	H311	105.3(2)
C2	SI2	C36	110.5(1)	SI3	C3	H312	110.6(2)
C21	SI2	C36	108.1(1)	SI3	C3	H313	110.4(2)
SI2	SI3	C3	111.2(1)	H311	C3	H312	108.1(2)
SI2	SI3	C26	107.35(8)	H311	C3	H313	108.7(2)
SI2	SI3	C31	107.99(8)	H312	C3	H313	113.3(2)
C3	SI3	C26	111.6(1)	SI4	C4	H411	107.0(1)
C3	SI3	C31	110.5(1)	SI4	C4	H412	110.5(1)
C26	SI3	C31	108.2(1)	SI4	C4	H413	112.3(1)
SI1	SI4	C4	109.9(1)	H411	C4	H412	115.5(1)
SI1	SI4	C11	107.78(8)	H411	C4	H413	110.5(2)
SI1	SI4	C41	107.69(7)	H412	C4	H413	101.1(2)
C4	SI4	C11	112.0(1)	SI4	C11	C12	120.6(2)
C4	SI4	C41	111.3(1)	SI4	C11	C16	120.9(2)

C11	SI4	C41	107.9(1)	C12	C11	C16	118.4(2)
SI1	C1	H111	112.8(3)	C11	C12	C13	121.5(2)
SI1	C1	H112	110.1(2)	C11	C12	H12	117.4(2)
SI1	C1	H113	112.9(3)	C13	C12	H12	120.9(2)

Bond Angles (cont.)

C12	C13	C14	120.0(3)	SI3	C26	C25	120.6(2)
C12	C13	H13	122.6(3)	C21	C26	C25	118.3(3)
C14	C13	H13	117.4(3)	SI3	C31	C32	120.9(2)
C13	C14	C15	120.3(3)	SI3	C31	C36	120.2(4)
C13	C14	H14	125.8(2)	C32	C31	C36	118.9(2)
C15	C14	H14	113.5(3)	C31	C32	C33	121.0(3)
C14	C15	C16	120.6(2)	C31	C32	H32	118.7(1)
C14	C15	H15	120.0(2)	C33	C32	H32	120.1(1)
C16	C15	H15	119.1(2)	C32	C33	C34	120.1(2)
SI1	C16	C11	119.6(3)	C32	C33	H33	116.4(1)
SI1	C16	C15	121.2(3)	C34	C33	H33	123.5(1)
C11	C16	C15	119.2(3)	C33	C34	C35	120.1(2)
SI2	C21	C22	121.5(2)	C33	C34	H34	122.6(2)
SI2	C21	C26	119.5(3)	C35	C34	H34	117.3(2)
C22	C21	C26	118.8(3)	C34	C35	C36	121.4(3)
C21	C22	C23	121.4(3)	C34	C35	H35	121.4(2)
C21	C22	H22	120.5(2)	C36	C35	H35	117.1(2)
C23	C22	H22	118.1(2)	SI2	C36	C31	120.3(3)
C22	C23	C24	119.8(3)	SI2	C36	C35	120.9(1)
C22	C23	H23	118.9(2)	C31	C36	C35	118.6(2)
C24	C23	H23	121.2(2)	SI4	C41	C42	121.0(2)
C23	C24	C25	120.1(2)	SI4	C41	C46	120.0(2)

C23	C24	H24	120.8(2)	C42	C41	C46	119.0(2)
C25	C24	H24	118.9(2)	C41	C42	C43	121.4(2)
C24	C25	C26	121.6(3)	C41	C42	H42	119.5(2)
C24	C25	H25	119.3(2)	C43	C42	H42	118.9(2)
C26	C25	H25	119.0(2)	C42	C43	C44	119.7(3)
SI3	C26	C21	120.9(2)	C42	C43	H43	118.8(2)

Bond Angles (cont.)

C44	C43	H43	121.5(2)
C43	C44	C45	120.8(2)
C43	C44	H44	124.6(2)
C45	C44	H44	114.6(2)
C44	C45	C46	120.6(2)
C44	C45	H45	121.3(2)
C46	C45	H45	118.0(2)
SI1	C46	C41	120.5(3)
SI1	C46	C45	120.8(2)
C41	C46	C45	118.5(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Torsion Angles in Degrees

Atom1	Atom2	Atom3	Atom4	Angle	
C1	SI1	SI4	C4	0.42	(0.17)
C1	SI1	SI4	C11	-121.90	(0.14)
C1	SI1	SI4	C41	121.88	(0.14)
C16	SI1	SI4	C4	-121.35	(0.13)
C16	SI1	SI4	C11	116.33	(0.11)
C16	SI1	SI4	C41	0.11	(0.13)
C2	SI2	SI3	C3	0.86	(0.14)
C2	SI2	SI3	C26	-121.39	(0.13)
C2	SI2	SI3	C31	122.18	(0.13)
C21	SI2	SI3	C3	-121.20	(0.12)
C21	SI2	SI3	C26	116.55	(0.11)
C21	SI2	SI3	C31	0.12	(0.16)
C36	SI2	SI3	C3	122.81	(0.12)
C36	SI2	SI3	C26	0.56	(0.11)
C36	SI2	SI3	C31	-115.87	(0.11)
SI3	SI2	C21	C22	94.99	(0.20)
C2	SI2	C21	C22	-27.12	(0.25)
C36	SI2	C21	C22	-148.92	(0.20)
SI2	SI3	C31	C32	-95.96	(0.20)
C3	SI3	C31	C32	25.79	(0.24)
C26	SI3	C31	C32	148.16	(0.20)
SI1	SI4	C11	C12	97.72	(0.20)
C4	SI4	C11	C12	-23.32	(0.25)
C41	SI4	C11	C12	-146.23	(0.20)
SI1	SI4	C41	C42	-95.88	(0.20)
SI1	SI4	C41	C46	81.52	(0.19)

C4	SI4	C41	C42	24.69 (0.25)

Table of Torsion Angles in Degrees (cont.)

Atom1	Atom2	Atom3	Atom4	Angle
C4	SI4	C41	C46	-157.91 (0.20)
C11	SI4	C41	C42	148.01 (0.20)
C11	SI4	C41	C46	-34.59 (0.22)
SI4	C11	C12	C13	-173.89 (0.23)
C11	C12	C13	C14	0.41 (0.45)
C12	C13	C14	C15	-1.49 (0.47)
SI2	C21	C22	C23	-175.04 (0.21)
C21	C22	C23	C24	-0.33 (0.43)
C22	C23	C24	C25	0.14 (0.45)
SI3	C31	C32	C33	177.74 (0.21)
C31	C32	C33	C34	1.06 (0.42)
C32	C33	C34	C35	-1.48 (0.44)
SI4	C41	C42	C43	176.93 (0.23)
C46	C41	C42	C43	-0.50 (0.40)
SI4	C41	C46	C45	-178.40 (0.19)
C42	C41	C46	C45	-0.94 (0.35)
C41	C42	C43	C44	1.96 (0.46)
C42	C43	C44	C45	-1.93 (0.48)
C43	C44	C45	C46	0.48 (0.46)
C44	C45	C46	C41	0.97 (0.40)

Table of Positional Parameters and Their Estimated Standard Deviations (cont.)

Atom	x	y	z	B(A2)
H32	1.274	0.113	0.995	5.3*
H33	1.403	0.092	1.109	4.5*
H34	1.383	-0.047	1.203	5.3*
H35	1.238	-0.157	1.178	5.8*
H42	0.779	0.379	0.510	5.3*
H43	0.811	0.394	0.397	7.1*
H44	0.706	0.533	0.303	8.0*
H45	0.582	0.642	0.322	6.5*
H111	0.601	0.154	0.617	9.5*
H112	0.503	0.144	0.613	9.5*
H113	0.567	0.227	0.676	9.5*
H211	0.898	0.368	0.890	8.9*
H212	1.005	0.349	0.889	8.9*
H213	0.913	0.280	0.826	8.9*
H311	1.167	0.004	0.843	7.4*
H312	1.068	0.068	0.797	7.4*
H313	1.154	0.145	0.858	7.4*
H411	0.802	0.488	0.666	6.1*
H412	0.773	0.347	0.649	6.1*
H413	0.743	0.419	0.706	6.1*

Starred atoms were refined isotropically.
Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Table of Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
SI1	0.50830(5)	0.33878(6)	0.55904(4)	3.33(1)
SI2	0.95891(4)	0.16490(6)	0.94249(4)	3.23(1)
SI3	1.07034(4)	0.01502(6)	0.92193(3)	3.14(1)
SI4	0.63989(4)	0.48573(6)	0.58018(3)	3.18(1)
C1	0.5499(2)	0.2050(3)	0.6270(2)	6.30(8)
C2	0.9421(2)	0.3013(3)	0.8765(2)	5.62(8)
C3	1.1194(2)	0.0668(3)	0.8447(1)	5.04(7)
C4	0.7550(2)	0.4313(3)	0.6600(2)	5.45(8)
C11	0.5934(2)	0.6384(2)	0.6031(1)	3.36(5)
C12	0.6174(2)	0.6771(3)	0.6800(1)	4.65(6)
C13	0.5766(2)	0.7829(3)	0.6985(2)	6.04(7)
C14	0.5106(2)	0.8528(3)	0.6414(2)	6.17(7)
C15	0.4864(2)	0.8190(3)	0.5648(2)	4.92(6)
C16	0.4722(2)	0.2880(2)	0.4554(1)	3.50(5)
C21	1.0146(2)	0.2121(2)	1.0469(1)	3.36(5)
C22	1.0759(2)	0.3166(3)	1.0695(2)	4.29(6)
C23	1.1228(2)	0.3458(3)	1.1465(2)	5.12(7)
C24	1.1091(2)	0.2716(3)	1.2021(2)	5.03(7)
C25	1.0488(2)	0.1680(3)	1.1815(1)	4.14(6)
C26	0.9991(2)	-0.1351(2)	0.8958(1)	3.21(5)

Table of Positional Parameters and Their Estimated Standard Deviations (cont.)

Atom	x	y	z	B(A2)
C31	1.1771(2)	-0.0081(2)	1.0158(1)	3.18(5)
C32	1.2678(2)	0.0561(3)	1.0316(1)	4.13(6)
C33	1.3453(2)	0.0425(3)	1.1017(2)	4.96(7)
C34	1.3344(2)	-0.0362(3)	1.1563(2)	4.70(6)
C35	1.2455(2)	-0.1001(3)	1.1425(1)	3.93(6)
C36	0.8347(2)	0.0874(2)	0.9273(1)	3.14(5)
C41	0.6648(2)	0.5037(2)	0.4873(1)	3.26(5)
C42	0.7417(2)	0.4363(3)	0.4737(2)	4.69(6)
C43	0.7575(2)	0.4446(3)	0.4044(2)	5.75(7)
C44	0.6995(2)	0.5221(3)	0.3485(1)	5.69(7)
C45	0.6228(2)	0.5903(3)	0.3596(1)	4.55(6)
C46	0.6036(2)	0.5815(2)	0.4292(1)	3.33(5)
H12	0.658	0.625	0.718	8.3*
H13	0.589	0.807	0.747	13.7*
H14	0.487	0.922	0.647	12.2*
H15	0.449	0.869	0.528	7.3*
H22	1.086	0.365	1.035	5.8*
H23	1.162	0.419	1.160	6.0*
H24	1.143	0.287	1.254	6.5*
H25	1.041	0.119	1.219	5.8*

Table of General Displacement Parameter Expressions - B's

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	Beqv
SI1	3.14(2)	2.85(2)	3.91(2)	0.13(2)	1.11(2)	0.38(2)	3.33(1)
SI2	3.22(2)	2.93(2)	3.73(2)	-0.03(2)	1.45(2)	0.31(2)	3.23(1)
SI3	3.07(2)	3.42(3)	3.29(2)	-0.24(2)	1.55(1)	-0.07(2)	3.14(1)
SI4	2.71(2)	3.39(3)	3.27(2)	0.04(2)	0.82(2)	-0.04(2)	3.18(1)
C1	6.4(1)	4.5(1)	7.6(2)	0.7(1)	1.9(1)	2.4(1)	6.30(8)
C2	6.1(1)	4.1(1)	6.5(1)	-0.1(1)	1.9(1)	-1.8(1)	5.62(8)
C3	5.0(1)	6.7(2)	4.26(9)	-0.8(1)	2.62(7)	0.1(1)	5.04(7)
C4	4.0(1)	6.4(2)	4.9(1)	-0.3(1)	0.2(1)	-0.5(1)	5.45(8)
C11	3.35(7)	3.25(9)	3.89(8)	0.92(7)	1.77(6)	0.72(8)	3.36(5)
C12	5.6(1)	4.8(1)	4.31(9)	1.9(1)	2.67(7)	1.13(9)	4.65(6)
C13	8.6(1)	5.2(1)	6.3(1)	-2.6(1)	5.10(8)	-2.4(1)	6.04(7)
C14	7.8(1)	4.1(1)	9.1(1)	-1.2(1)	5.99(8)	-2.4(1)	6.17(7)
C15	4.9(1)	3.2(1)	7.6(1)	-0.21(9)	3.37(8)	-0.7(1)	4.92(6)
C16	3.11(7)	2.87(9)	4.87(9)	0.52(7)	1.84(6)	0.79(8)	3.50(5)
C21	2.81(7)	3.12(9)	4.34(9)	0.12(7)	1.47(6)	-0.44(8)	3.36(5)
C22	3.81(9)	3.7(1)	5.5(1)	0.50(9)	1.80(8)	0.3(1)	4.29(6)
C23	3.9(1)	4.2(1)	6.6(1)	1.0(1)	1.0(1)	1.5(1)	5.12(7)
C24	4.3(1)	5.6(1)	4.6(1)	0.6(1)	0.76(9)	1.5(1)	5.03(7)
C25	3.78(9)	4.6(1)	3.95(9)	0.12(9)	1.27(7)	-0.44(9)	4.14(6)
C26	2.75(7)	3.3(1)	3.78(8)	0.20(7)	1.38(6)	-0.54(8)	3.21(5)

Table of General Anisotropic Displacment Parameter Expressions - B's (Continued)

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	Beqv
C31	2.73(7)	3.27(9)	3.74(8)	0.00(7)	1.38(6)	-0.44(8)	3.18(5)
C32	3.43(8)	4.5(1)	4.9(1)	-0.63(8)	1.93(7)	-0.42(9)	4.13(6)
C33	2.96(9)	5.8(1)	5.9(1)	-1.0(1)	1.26(8)	-1.2(1)	4.96(7)
C34	3.5(1)	5.5(1)	4.3(1)	0.3(1)	0.38(8)	-0.6(1)	4.70(6)
C35	3.75(9)	4.0(1)	3.95(9)	0.35(9)	1.24(7)	-0.04(9)	3.93(6)
C36	2.88(7)	3.10(9)	3.59(8)	0.31(7)	1.32(6)	-0.29(8)	3.14(5)
C41	2.74(7)	3.4(1)	3.91(8)	0.31(7)	1.47(6)	0.53(8)	3.26(5)
C42	3.50(9)	5.1(1)	5.8(1)	-0.47(9)	2.02(8)	0.4(1)	4.69(6)
C43	4.7(1)	7.2(2)	6.5(1)	-0.2(1)	3.40(7)	1.3(1)	5.75(7)
C44	5.18(9)	8.1(2)	5.04(9)	1.5(1)	3.41(7)	1.4(1)	5.69(7)
C45	4.3(1)	5.6(1)	3.98(9)	1.0(1)	1.74(7)	0.1(1)	4.55(6)
C46	2.93(7)	3.6(1)	3.55(8)	0.77(7)	1.27(6)	0.50(8)	3.33(5)

The form of the anisotropic displacement parameter is:
exp[-0.25{h2a2B(1,1) + k2b2B(2,2) + l2c2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3)}] where a,b, and c are reciprocal lattice constants.

Table of General Displacement Parameter Expressions - U's

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
SI1	0.0398(3)	0.0361(3)	0.0495(3)	0.0017(3)	0.0141(2)	0.0048(3)
SI2	0.0408(3)	0.0372(3)	0.0472(3)	-0.0004(3)	0.0184(2)	0.0039(3)
SI3	0.0388(2)	0.0433(3)	0.0417(3)	-0.0031(3)	0.0196(2)	-0.0008(3)
SI4	0.0343(3)	0.0430(3)	0.0414(3)	0.0005(3)	0.0103(2)	-0.0005(3)
C1	0.081(2)	0.057(2)	0.097(2)	0.009(2)	0.024(2)	0.030(2)
C2	0.077(2)	0.052(2)	0.082(2)	-0.001(1)	0.024(1)	-0.023(1)
C3	0.063(1)	0.084(2)	0.054(1)	-0.010(1)	0.0331(9)	0.001(1)
C4	0.050(1)	0.081(2)	0.062(2)	-0.004(1)	0.003(1)	-0.006(2)
C11	0.0424(9)	0.041(1)	0.049(1)	0.0116(9)	0.0225(7)	0.009(1)
C12	0.071(1)	0.061(2)	0.055(1)	0.024(1)	0.0339(9)	0.014(1)
C13	0.109(2)	0.066(2)	0.079(1)	-0.033(1)	0.065(1)	-0.030(1)
C14	0.099(1)	0.051(2)	0.115(2)	-0.016(1)	0.076(1)	-0.030(1)
C15	0.062(1)	0.041(1)	0.096(2)	-0.003(1)	0.043(1)	-0.009(1)
C16	0.0393(9)	0.036(1)	0.062(1)	0.0066(9)	0.0233(8)	0.010(1)
C21	0.0356(9)	0.040(1)	0.055(1)	0.0015(9)	0.0186(8)	-0.006(1)
C22	0.048(1)	0.047(1)	0.070(1)	0.006(1)	0.023(1)	0.003(1)
C23	0.050(1)	0.053(2)	0.083(2)	0.012(1)	0.013(1)	0.019(1)
C24	0.055(1)	0.071(2)	0.058(1)	0.008(1)	0.010(1)	0.018(1)
C25	0.048(1)	0.059(2)	0.050(1)	0.001(1)	0.0161(9)	-0.006(1)
C26	0.0348(9)	0.042(1)	0.048(1)	0.0025(9)	0.0175(7)	-0.007(1)

Table of General Anisotropic Displacement Parameter Expressions - U's (Continued)

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
C31	0.0346(9)	0.041(1)	0.047(1)	0.0000(9)	0.0174(7)	-0.006(1)
C32	0.043(1)	0.057(1)	0.062(1)	-0.008(1)	0.0245(9)	-0.005(1)
C33	0.038(1)	0.074(2)	0.075(2)	-0.013(1)	0.016(1)	-0.015(1)
C34	0.045(1)	0.069(2)	0.055(1)	0.003(1)	0.005(1)	-0.008(1)
C35	0.047(1)	0.051(1)	0.050(1)	0.004(1)	0.0157(9)	-0.001(1)
C36	0.0365(9)	0.039(1)	0.045(1)	0.0039(9)	0.0167(7)	-0.004(1)
C41	0.0347(9)	0.043(1)	0.050(1)	0.0039(9)	0.0186(7)	0.007(1)
C42	0.044(1)	0.064(2)	0.073(1)	-0.006(1)	0.026(1)	0.005(1)
C43	0.059(1)	0.091(2)	0.083(1)	-0.003(1)	0.0431(9)	0.017(2)
C44	0.066(1)	0.103(2)	0.064(1)	0.019(2)	0.0432(8)	0.017(2)
C45	0.055(1)	0.071(2)	0.050(1)	0.013(1)	0.0220(9)	0.001(1)
C46	0.0371(9)	0.046(1)	0.045(1)	0.010(1)	0.0160(8)	0.006(1)

The form of the anisotropic displacement parameter is:
exp[-2PI2{h2a2U(1,1) + k2b2U(2,2) + l2c2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)}] where a,b, and c are reciprocal lattice constants.

2-4 REFERENCES

1) (a) H. Gilman and E. A. Zuech, *J. Am. Chem. Soc.*, 82, 3605 (1960).

(b) H. Gilman, E. A. Zuech, and W. Steudel, *J. Org. Chem.*, 27, 1836 (1962).

(c) T. Gimisis, M. Ballestri, C. Ferreri, C. Chatgilialoglu, R. Boukherroub, and G. Manuel, *Tetrahedron Lett.*, 36, 3897 (1995).

(d) F. Bickelhaupt, C. Jongsma, P. de Koe. R. Lourens, N. R. Mast, G. L. van Mourik, H. Vermeer, and R. J. M. Weustink, *Tetrahedron*, 32, 1921 (1976).

(e) J. Y. Corey and W. Z. McCarthy, *J. Organomet. Chem.*, 271, 319 (1984).

(f) W. Z. McCarthy, J. Y. Corey, and E. R. Corey, *Organometallics*, 3, 255 (1984).

(g) P. Jutzi, *Chem. Ber.*, 104, 1455 (1971).

2) J. Y. Corey, In *Advances in Silicon Chemistry*; G. L. Larson, Ed.; JAI PRESS INC.: London, vol 1, 327 (1991).

3) (a) H. Gilman and G. E. Dunn, *J. Am. Chem. Soc.*, 73, 5077 (1951).

(b) R. A. Benkeser, H. Landesman, and D. J. Foster, *J. Am. Che. Soc.*, 74, 648 (1952).

4) A. G. Brook and H. Gilman, *J. Am. Chem Soc.*, 76, 2333 (1954).

CHAPTER 3

PREPARATION AND REACTIVITY OF 9,10-DISILAANTHRACENE DIANIONS

ABSTRACT

The reaction of 9,10-disilaanthracene dimer (3) with excess of lithium or potassium resulted in formation of 9,10-disilaanthracene dilithium or dipotassium (1, 2) via opened dianion (5) in which one Si-Si bond has been cleaved. These NMR spectra of 1 and 2 show the presence of only one species which have C_{2v} symmetry. On the treatment of 7 with trimethylchlorosilane, bis(9,10-dimethyl-10-(trimethylsilyl)-9,10-disilaanthracene-9-yl) was obtained. On treatment α,ω-dichloropolysilane, 2 was converted into the corresponding cyclic compounds(8-12), respectively. Dipotassium compound (2) revealed *cis*-reactivity for these electrophiles. When the dianion was allowed to react with dibromoethane as an electron accepter, dimer (3), polymer and ethylene were yielded. It is considered that Dewar-9,10-disilaanthracene or its diradical isomer are yielded in this reaction.

3-1 INTRODUCTION

In general, reduction of Si-Si bond with lithium metal produced the corresponding silyllithium with Si-Si bond dissociation. However, silylpotassium could not prepare *via* Si-Si bond cleavage with potassium. If 9,10-disilaanthracene dianion is possible to generate from the reduction of dimer (3), the dianion will be useful intermediate for the synthesis a great variety of 9,10-disilaanthracene derivatives.

At different point of view, there is an interest in the reactivity of a cyclic bis(silyl anion) compound, two silyllithium containing in a molecular; *cis* and/or *trans* products are obtained.

Sakurai[1)] has been reported that trimethylsilylsodium was converted into the silyl radical by treatment with electron accepter.

If two electrons can be abstracted from silicon atoms in dianion (1 or 2), 9,10-disilaanthracene or its valence isomers should be obtained.

The approach for the synthesis of silaaromatics by oxidative electron-transfer reaction is the first attempt,

although, anthracene dianion into the anthracene with two electron abstraction are well known.[2)]

3-2 RESULTS AND DISCUSSION

3-2-1 GENERATION OF 9,10-DISILAANTHRACENE DIANION

Several reactions of 9,10-dimethyl-9,10-disilaanthracene dimer (3) with alkali metals were made (Table 1). Reduction of the dimer (3) with an excess of lithium in a dry argon atmosphere, yielded green solution.

Scheme 1

Table 1. Reactions of **1**and **2** with iodomethane.

entry	M	solv.	yield of **4** %
1	Li	THF	13
2	Na	THF	0[2)]
3	K	THF	80
4	K	Et_2O	0[3)]
5	K	DME	23

1) Isolation yield.
2) 9,9,10-Trimethyl-9,10-disilaanthracene was obtained in 12% yield.
3) 9,10-Disilaanthrcene dimer was recovered in 97% yield.

After removal unreacted lithium followed by treatment with an excess of methyl iodide, 9,10-dihydro-9,9,10,10-tetramethyl-9,10-disilaanthracene (4) and 9,10-dihydro-

9,9,10-trimethyl-9,10-disilaanthracene (5) were obtained in 13 % and 32 % yield, respectively. The green solution probably contains the 10-lithio-9,10-dimethyl-9,10-disilaanthracene-9-yl (9,10-disilaanthracene anion radical).

Whose existence is supported by the isolation of 5. Similar reduction of dimer (3) with sodium, the 9,10-disilaanthracene dianion was not generated (entry 2). The most dramatic change was observed, reaction of 9,10-dimethyl-9,10-disilaanthracene dimer (3) with an excess of potassium in THF at room temperature gave an *orange suspension* of 9,10-disilaanthracene dipotassium (2) within 24 h. Treatment with methyl iodide followed; 4 was produced as sole detectable product in 80 % yield entry 3). The formation of these dianions (1, 2) is strongly dependent upon the solvent; it it increased in THF and was suppressed in diethyl ether and dimethoxyethane (DME). ^{1}H, ^{13}C and ^{29}Si NMR spectra for the dipotassium compound(2) showed the presence of only one species at 298 K (Table 2). The ^{13}C NMR spectrum of 2 showed four signals, consistent with C_{2v} symmetry, and ^{29}Si NMR spectrum had only one resonance at -42.8 ppm, considerably upfield shifted in comparison the chemical shift of -17.9 ppm observed for 9,9,10,10-tetramethyl-9,10-disilaanthracenes(4)

.

Table 2. Chemical shifts for disilaanthracene dianion(**1, 2**) and **4** at 298 K.

	1 (M = Li)[1)]	**2** (M = K)[1)]	**4**[2)]
^{1}H NMR shifs	7.19(4H, AA'BB' m, J = 3.3, 5.0 Hz)	7.21(4H, AA'BB' m, J = 3.3, 4.9 Hz)	7.68(4H, AA'BB' m J = 3.3, 5.5 Hz)
	6.59(4H, AA'BB' m, J = 3.3, 5.0 Hz)	6.66(4H,AA'BB' m, J = 3.3, 4.9 Hz)	7.41(4H, AA'BB' m J = 3.3, 5.5 Hz)
	0.58(6H, s)	0.54(6H, s)	047(12H, s)
^{13}C NMR shifts	161.1, 128.2, 121.1, -0.9	161.2, 128.5, 122.0, 4.12	144.5, 133.4, 128.3, 0.0
^{29}Si NMR shifts	-45.4	-42.8	-17.9
^{7}Li NMR shift	3.8		

1) In THF-d_8, external Me_4Si as standard. 2) In $CDCl_3$, internal Me_4Si as standard.

Typically, such upfield shifts are observed for ^{29}Si nuclei when neutral organosilanes are converted to the respective silyl anions.[3)]

In constrast to the formation of the 9,10-disilaanthracene anion radical in the reaction of the dimer(3) with lithium under the conditions described, *vide supra*, quantitative preparation of the dilithium compound(1) for NMR measurement was achieved by a direct reaction of the dimer(3) with lithium in a sealed NMR tube. ^{1}H, ^{13}C and ^{29}Si NMR data for 9,10-disilaanthracene dilithium(1) indicate that its structure is similar to that found for the dipotassium compound (2).

3-2-2 MECHANISM FOR THE GENERATION OF 9,10-DISILAANTHRACENE DIANION

On account of further comprehension for this reduction, we tried to trap the reaction intermediate. Reduction of 3 with lithium in THF for 3 hours gave a yellow suspension. After removal unreacted lithium followed by treatment with trimethylchlorosilane, a bis(9,10-dimethyl-10-(trimethylsilyl)-9,10-disilaanthracene-9-yl) (6) was obtained in 67 % yield (Scheme 2).

Scheme 2

Fig. 1 ORTEP drawing of 6.

Molecular structure of the opened dimer (6) is shown in Fig. 1. Two methyl groups on the disilaanthracene unit in 5 are substituted *cis*-configuration, respectively. Thus the Si-Si bond cleavage of bridged dimer (3) with alkali metal proceed with the retention of configuration around the silicon atom.

Sommer and Mason[4)] also have been reported that configuration stability of silyllithium during the preparation from the reduction of the disilane and during the reaction with electrophile.

It is logical from these results that these dianion (1) and 2 are generated *via* Si-Si bond cleaved dianion (7). Thus configuration of cleaved silicon atoms in dianion (7) have been cosidered same configuration with dimer (3) and opened dimer (6). If another Si-Si bond dissociation in dianion (7) proceed to retain by the further reduction with alkali metals, *cis*-9,10-disilaanthracene dianion should be obtained exclusively in this reaction.

3-2-3 REACTION OF 2 WITH ELECTROPHILES

The configurational stability of the silyl anion was investigated by Lambert and Urdareta-Përez by examination of ^{1}H NMR spectrum for diisopropylphenylsilyllithium (Chapter-1-4-4). We now focussed on the elucidation of configuration of 9,10-disilaanthracene dianion.

However, in view of the generation of the anion radical from the lithium reduction of the dimer (3), the dipotassium compound (2) is suitable for the further study of the reactivity of 9,10-disilaanthracene dianion.

The reaction of the dipotassium compound (2) with trimethylchlorosilane affords the expected adduct (8); the results are consistent with the NMR studies of 1 and 2 in which these signals mean a presence of only one species having C_{2v} symmetry. The dipotassium (2) was also treated with α,ω-dichloropolysilanes as shown in Scheme 3. The products were identified by means of ^{1}H, ^{13}C and ^{29}Si NMR and mass spectra. The reaction of 2 with dimethydichlorosilane gave an expected dimethylsilyl adduct (9a) onto 9 and 10 positions of the disilaanthracene and a dimeric compound (10a) in 12 % and 18 % yields, respectively. On treatment with di(*tert*-butyl)dichlorosilane, silicon-bridged compound (9b) was obtained in 59 % yield; avoid a generation of 10b. The corresponding 9 and 10 positions adducts were obtained in good yield when the dipotassium (2) reacted with 1,2-dichlorotetramethyldisilane and 1,3-dichlorohexamethyltrisilane, respectively, without dimeric products.

Scheme 3

The formation of 9, 10, 11 and 12 clearly reveals that the generated disilaanthracene dipotassium (2) is *cis* -configuration. Conclusively speaking, 9,10-dimethyl-9,10-disilaanthracene dipotassium (2) can be a valuable intermediate for the synthesis of a great variety of *cis*-9,10-disilaanthracene derivatives.

3-2-4 ELECTRON-TRANSFER REACTION OF 2

Sakurai has been reported to oxidative electron-transfer reaction of trimethylsilylsodium which resulted in the generation of the silyl radical.[1] Similar electron-transfer reaction of bis(silyl anion) have not yet been reported, although, the attractive electron-transfer reaction of 1 or 2 is expected for the generation of the 9,10-disilaanthracene or its valence isomers.

Scheme 4

On treatment of dipotassium (2) with dibromoethane[5] under argon, dimer (3) was obtained in 34 % yield along with a polymer. It is clear from the absence of ethylene bridged 9,10-disilaanthracene that nucleophilic substitution reaction of 2 with dibromoethane does not occured. The polymer structure can be determined a co-polymer which has a oxygen atom between 9,10-disilaanthracene units. The Mw, Mn and Mw/Mn of the co-polymer (13) are shown in scheme 5.

2 13 Mn = 1497
Mw = 4681
Mw/Mn = 3.126

Scheme 5

In order to obtain further information for the reaction, similar reaction was made *in vacuo* by use of Schlenk techniques. The existences of dimer (3) and ethylene gas were confirmed from these NMR spectra and another polymer was obtained instead of the co-polymer (13). However, the structure of the polymer was not identified because of low solubility of the polymer in THF.

Scheme 6

In view of the generation of the co-polymer (13), it is probable that the polymer (14) might has been high molecular weight and does not contain oxygen atom; molecular oxygen has been interrupting the course of polymerization process. In order to shed light on the intermediate in the electron-transfer reaction, trapping experiments of 9,10-disilaanthracene were attempted.

The dipotassium (2) was added to a mixture of diphenylacetylene and dibromoethane, however dimer (3) and co-polymer were produced instead of the formation of expected diphenylacetylene adduct. Similar reaction with other trapping reagents utilizing anthracene, bis(trimethylsilyl)acetylene and benzoisofurane resulted in

the generation of same products in the case of no trapping reagent (Scheme 7).

Scheme 7

These results reveal that at least 9,10-disilaanthracene will be not generated by electron-transfer reaction of 2; 9,10-disilaanthracene probably reacts with these trapping reagents to afford corresponding adduct. It is considered from the view of generation of dimer and polymer that Dewar-9,10-disilaanthracene or its valence isomer is yielded in this reaction. However, the intermediates could not trap because of the intermolecular coupling reaction of the intermediate rather had priority over the reaction with trapping reagent (*vide supra*).

3-3 EXPERIMENTAL SECTION

General procedure.

^{1}H, ^{7}Li, ^{13}C and ^{29}Si NMR spectra were obtained with Brucker AC-400PS(156, 100 and 80 MHz) and AC-300P(117, 75 and 60MHz) instruments chloroform-*d*, benzene-d_6, or THF-d_8 using tetramethyl-silane (TMS) was used as an internal or external standard. ^{7}Li NMR is refereed to lithium in $MeOH/C_6D_6$. Mass spectra were obtained on a Shimadzu QP 2000 spectrometer. IR spectra were measured on a JEOL FT/IR-5000 spectrometer. UV-vis spectra were recorded on a JEOL Ubest-50 spectrometer. Elemental Analyses were carried out by the Chemical Analytical Center of the University of Tsukuba.

Tetrahydrofuran(THF) was dried and distilled from sodium benzophenone ketyl. THF-*d8* was dried over lithium aluminum hydride, and then transferred into a tube covered with potassium mirror and distilled prior to use.

Gel permission chromatographic separation was performed on a model LC-908 recycling preparative HPLC(Japan Analytical Industry Co., Ltd.) with a series of Jaigel 1H and 2H columns using toluene as a eluant. For thin-layer chromatography Kieselgel(Merck, Art. 7747) was used.

Reaction of 9,10-Disilaanthracene dilithium(1) with Methyl iodide.

A mixture of 3 (240 mg, 0.5 mmol) and excess of lithium in 7 mL of dry THF was allowed to stir for 24 h under an argon atmosphere; a green solution was obtained. After removal of the unreacted lithium, the green solution was treated with 0.62 mL of methyl iodide dissolved in 9 mL of THF over a period 30 min at -78 °C under argon atmosphere. After completion of the addition the resulting solution was further stirred at same temperature for 30 min; then the bath was gradually warmed to room temperature. The reaction mixture was hydrolyzed and extracted with ca. 30 mL portion of diethyl ether. The organic layers were combined and dried with copious amounts of anhydrous magnesium sulfate, filtrated and concentrated by rotary evaporation to give an oil. The crude product was chromatographed by HPLC to afford 9,9,10,10-tetramethyl-9,10-disilaanthracene (4) and 10-hydro-9,10,10-trimethyl-9,10-disilaanthracene (5) as colorless oil, respectively.

9,9,10,10-tetramethyl-9,10-disilaanthracene (4)

Yield	354 mg (13 %)
^{1}H NMR(300MHz,$CDCl_3$)δ	0.47(s, 12H), 7.47(4H,AA'BB'm J=3.3, 5.5Hz), 7.68(4H,AA'BB' m J=3.3, 5.5Hz)
^{13}C NMR(75MHz,$CDCl_3$)δ	0.01, 128.3, 133.4, 145.5
^{29}Si NMR(60MHz,$CDCl_3$)δ	-17.9
MS m/z(%)	268(M^+),253(M^+-CH_3)
UV(*c*-hexane) λ_{max} nm(ε)	257(285), 267(380), 270(389), 257(343), 283(239)
IR (nujol) cm^{-1}	1249(Si-CH_3).

10-hydro-9,10,10-trimethyl-9,10-disilaanthracene (5)

Yield	82 mg (32 %)
^{1}H NMR(300MHz,$CDCl_3$)δ	0.45(3H,s), 0.53(3H,s), 0.61(3H,d J=3.9Hz), 4.95(1H,q J=3.9Hz), 7.41(4H,m), 7.69(4H,m)
^{13}C NMR(75MHz,$CDCl_3$)δ	-4.0, -0.9, -0.6, 128.3, 128.6, 133.3, 134.1, 141.3, 145.2
^{29}Si NMR(60MHz,$CDCl_3$)δ	-17.0, -32.7
MS m/e(%)	254(M^+), 239(M^+-CH_3)
IR (nujol) cm^{-1}	2112(Si-H), 1263(Si-CH_3), 1249(Si-CH_3), 882(Si-H), 832(Si-H).

Reaction of 9,10-disilaanthracene dipotassium (2) with methyl iodide.

A mixture of 3 (240 mg, 0.5 mmol) and an excess of potassium in 7 mL of dry THF was stirred together for 24 h to afford an orange suspension. To dianion suspension, obtained after removal of unreacted potassium, was added a solution of methyl iodide (1.3 mL) dissolved in 9 mL of THF, dropwise, over a period of 30 min at -78 °C. After the completion of addition the resulting solution was further stirred at same temperature for 30 min; then the bath was gradually warmed to room temperature. The reaction mixture was hydrolyzed and extracted with ca. 30 mL portions of diethyl ether. The organic layers were combined, dried

($MgSO_4$), filtered and concentrated by rotary evaporation to give an oil. The crude product was chromatographed by PTLC to afford 4 (215 mg) as colorless oil(80%).

Reduction of dimer (3) with sodium in THF

A mixture of 3 (240 mg, 0.5 mmol), excess of sodium, and 7 mL of THF was placed in 20 mL-two necked round bottomed flask and stirred at room temperature for 24 hours under argon atmosphere. After removal unreacted sodium, the residue was added dropwise to methyl iodide (0.62 mL, 0.01 mol) dissolved in 9 mL of THF at -78 °C which was poured into dil.HCl aq., followed by extraction with ether, drying of combined organic fractions over about 3 g of $MgSO_4$, and evaporation of solvent to give crude products mixture. Separation and purification of the reaction mixture by preparative TLC to produce 15.6 mg of 10-hydro-9,10,10-trimethyl-9,10-disilaanthracene (5) in 12 % yield.

Reduction of dimer (3) with potassium in ether

A mixture of 3 (240 mg, 0.5 mmol), excess of potassium, and 7 mL of ether was placed in 20 mL-two necked round bottomed flask and stirred at room temperature for 24 hours under argon atmosphere. After removal unreacted potassium, the residue was added dropwise to methyl iodide (0.62 mL,

0.01 mol) dissolved in 9 mL of THF at -78 °C which was poured into dil.HCl aq., followed by extraction with ether, drying of combined organic fractions over about 3 g of $MgSO_4$, and evaporation of solvent to give 233 mg of dimer (3) in 97 %recovered yield.

Reduction of dimer (3) with potassium in DME

A mixture of 3 (240 mg, 0.5 mmol), excess of potassium, and 7 mL of DME was placed in 20 mL-two necked round bottomed flask and stirred at room temperature for 24 hours under argon atmosphere. After removal unreacted potassium, the residue was added dropwise to methyl iodide (0.62 mL, 0.01 mol) dissolved in 9 mL of THF at -78 °C which was poured into dil.HCl aq., followed by extraction with ether, drying of combined organic fractions over about 3 g of $MgSO_4$, and evaporation of solvent to give crude products mixture. Separation and purification of the reaction mixture by preparative TLC to produce 62.3 mg of 4 (23 % yield).

Preparation of bis(10-trimethylsilyl-9,10-dimethyl-9,10-disilaanthracene-9-yl) (6)

A mixture of 3 (334 mg, 0.7 mmol), excess of lithium wire, and 7 mL of THF was placed in 20 mL-two necked round

bottomed flask, degassed by freeze-pump-thraw cycles, filled with argon, sonicated for 10 min. The resultant mixture was stirred for 3 hours. After removal unreacted lithium, the residue was added to a THF solution of trimethylchlorosilane (0.62 mL, 4.9 mmol) at 0 °C which was poured into dil.HCl aq., followed by ether extraction, drying of combined organic layers over $MgSO_4$, and evaporation of solvent to give crude products mixture. Separation and purification of the mixture by HPLC (toluene: eluant),and PTLC to afford pure title compound (6). For the measurement of X ray analysis, 5 was recrystallized from hexane/c-hexane.

Yield	292 mg (67 %)
^{1}H NMR(300MHz,$CDCl_3$)δ	0.02(18H,s), 0.51(6H,s), 0.53(6H,s), 7.20-7.39(12H,m), 7.50(4H,d J=7.35Hz)
^{13}C NMMR(75MHz,$CDCl_3$)δ	-1.40, -0.71, -0.53, 127.55, 134.60, 135.17, 142.22, 143.54
^{29}Si NMR(60MHz,$CDCl_3$)δ	-33.70, -33.55, -18.50
Mass m/z (%)	622(M^+,26), 550(37)
Anal.($C_{18}H_{18}Si_4$)	Calcd.: C, 65.52; H, 7.44
	Found: C, 65.49; H, 7.48

Preparation of 9,10-Dimethyl-9,10-bis(trimethylsilyl)-9,10-disilaanthracene (8).

To 1.3 mL of trimethylchlorosilane in 9 mL of THF was added dropwise the dipotassium compound (2) over 30 min at -78 °C under an argon atmosphere. After the completion of the addition the resulting solution was further stirred at same temperature for 30 min; then the bath was gradually warmed to room temperature. The reaction mixture was hydrolyzed and extracted with ca. 30 mL portion of diethylether. The organic layers were combined dried ($MgSO_4$), filtrated and concentrated by rotary evaporation to give an oil. The crude product was chromatographed by PTLC to afford a title compounds colorless oil.

Yield	279 mg (73%)
^1H NMR(300MHz,$CDCl_3$)δ	0.02(18H,s), 0.57(6H,s), 7.35(4H,AA'BB' m J=3.3, 5.5Hz), 7.51(4H,AA'BB' m J=3.3, 5.5Hz);
^{13}C NMR(75MHz,$CDCl_3$)δ	-1.6, -1.5, 127.6, 134.5, 143.2
^{29}Si NMR(60MHz,$CDCl_3$)δ	-33.3, -18.3
Mass m/e (%)	384(M^+), 369(M^+-CH_3), 311(M^+-$SiCH_3$)
UV(*c*-hexane) λ_{max} nm(ε)	246(21400), 273(13200)
IR(nujol) ν cm^{-1}	1245(Si-CH_3).

Preparation of 2,3,5,6-Dibenzo-1,4,7,7-tetramethyl-1,4,7-trisilanorbornadiene (9a) and its dimeric product(10a)

To 0.13 mL of dimethyldichlorosilane dissolved in 9 mL of THF was added dropwise the potassium compound(2) over 30

min at -78 °C under argon an atmosphere. After completion of the addition the resulting solution was further stirred at same temperature for 30 min; then the bath was gradually warmed to room temperature. The reaction mixture was hydrolyzed and extracted with ca. 30 mL portion of diethylether. The organic layers were combined, dried ($MgSO_4$), filtrated and concentrated by rotary evaporation to give an oil. The crude product was chromatographed by HPLC to afford 9a and 10a.

9a;

^{1}H NMR(300MHz,C_6D_6)δ	0.04(6H, s), 0.79(6H, s), 7.17(4H, AA'BB' m J=3.2, 5.3Hz), 7.61(4H, AA'BB' m J=3.2, 5.3Hz);
^{13}C NMR(75MHz,C_6D_6)δ	-11.8, -7.1, 127.1, 131.6, 147.9
^{29}Si NMR(60MHz,C_6D_6)δ	-25.7, 15.9
Mass m/z (%)	296(M^+).

10a;

^{1}H NMR(300MHz,$CDCl_3$)δ	0.44(12H, s), 0.53(12H, s), 7.00(8H, AA'BB' m J=3.3, 5.5 Hz), 7.56(dd, J = 3.3, 5.5 Hz, 8H)
^{13}C NMR(75MHz,$CDCl_3$)δ	-5.1, -1.7, 127.4, 134.2, 142.3
^{29}Si NMR(60MHz,$CDCl_3$)δ	-50.0, -33.6
Mass m/z (%)	592(M^+)

Preparation of 9,10,11,11,12,12-hexamethyl-9,10-disilano-9,10-disilaanthracene(11).

To 250 mg of 1,1,2,2-tetramethyl-1,2-dichlorodisilane dissolved in 1.5 mL of THF was added dropwise dipotassium compound(2) over 30 min at -78 °C under an argon atmosphere. After completion of the addition the resulting solution was further stirred at same temperature for 30 min; then the bath was gradually warmed to room temperature. The reaction mixture was hydrolyzed and extracted with ca. 30 mL portion of diethylether. The organic layers were combined, dried ($MgSO_4$), filtrated and concentrated by rotary evaporation to give an oil. The crude product was chromatographed by HPLC to afford 11 .

Yield	183 mg (58% yield)
colorless solid	m.p. 148-149 °C
^1H NMR(300MHz,$CDCl_3$)δ	0.56(12H, s), 0.80(6H, s), 7.28(4H, AA'BB' m J=3.2, 5.4Hz), 7.56(4H, AA'BB' m J=3.2, 5.4Hz)
^{13}C NMR(75MHz,$CDCl_3$)δ	-10.2, -7.3, 127.9, 132.3, 144.7
^{29}Si NMR(60MHz,$CDCl_3$)δ	-58.3, -32.9
Mass m/e (%)	354(M^+), 339(M^+-CH_3)
Anal. (for $C_{18}H_{18}Si_4$)	Calc.: C, 62.36; H, 5.23 Found: C, 62.31; H, 5.28.

Preparation of 9,10,11,11,12,12,13,13-octamethyl-9,10-trisilano-9,10-disilaanthracene(12)

To 270 mg of 1,1,2,2,3,3-hexamethyl-1,3-dichlorotrisilane in 5 mL of THF was added dropwise the dipotassium compound (2) over 30 min at -78 °C under an argon atmosphere. After the completion of the addition the resulting solution was further stirred at same temperature for 30 min; then the bath was gradually warmed to room temperature. The reaction mixture was quenched and extracted with ca. 30 mL portion of diethylether. The organic layers were combined, dried ($MgSO_4$), filtrated and concentrated by rotary evaporation to give an oil. The crude product was chromatographed by w.c.c. to afford 12.

Yield	208 mg (50 %)
^{1}H NMR(300MHz,$CDCl_3$)δ	0.01(12H, s), 0.39(6H, s), 0.75(6H, s), 7.32(4H, AA'BB' m J=3.3, 5.4Hz), 7.57(4H, AA'BB' m J=3.3, 5.4Hz)
^{13}C NMR(75MHz,$CDCl_3$)δ	-7.2, -6.7, -6.6, 127.7, 133.0, 143.9
^{29}Si NMR(60MHz,$CDCl_3$)δ	-46.4, -39.6, -31.0
Mass m/z (%)	412(M^+)

Preparation of 9,10-di(*tert*-butyl)silano-9,10-dimethyl-9,10-disilaanthracene (9b)

A mixture of 9,10-dimethyl-9,10-disilaanthracene dimer (476 mg, 1.0 mmol) and excess of potassium in 15 mL of THF was stirred for 24 hours to afford an yellow suspension. After removal unreacted potassium, the dianion suspension was added di(tert-butyl)dichlorosilane (496 mg, 2.2 mmol) dissolved in 7 mL of THF over a period of 30 min at -78 °C. After completion of the addition, the resultant solution was further stirred at the same temperature for 30 min, then cooling bath was gradually warmed up to room temperature.

The reaction mixture was hydrolyzed in water, then extracted with ether. The organic layers were combined, dried over MGSO4, followed by evaporation to afford crude products mixture. Separation and purification of the mixture by HPLC (toluene eluant) to produce pure title compound (9b).

Yield	452 mg (59 %)
colorless crystals	m.p. 156~158 °C
^{1}H NMR(300MHz,C_6D_6)δ	0.82(6H,s), 0.88(18H,s), 7.13(4H,AA'BB' m *J*=3.2,5.2Hz), 7.52(4H,AA'BB' m *J*=3.2,5.2Hz)
13C NMR(75MHz,C6D6)δ	-10.9, 24.2, 32.8, 127.2, 130.9, 150.36
Mass m/z	380(M^+), 323(M^+-Bu)
UV (CH_2Cl_2) λmax nm(ε)	225(31700), 240(sh, 17900), 290(4200)

Reaction of dipotassium compound (2) with dibromoethane

To the hexane suspension of the 9,10-disilaanthracene dipotassium (2) which prepared from the reduction of 120 mg of 3 (0.25 mmol) with potassium, was added dibromoethane (87 μl, 1 mmol) dissolved in 3 mL of hexane at -78 °C. The resultant mixture was stirred for 3 days, quenched by addition of dil.HCl aq., followed by ether extraction. The combined organic fractions was dried over $MgSO_4$, concentrated by evaporation to afford crude product mixture. Separation and purification of the mixture by HPLC (toluene: eluant) to produce 10 mg of 3 (10 %) and 69 mg of co-polymer (13).

co-polymer (13)

^{1}H NMR(300MHz,$CDCl_3$)δ	0.03(br), 0.09(s), 0.14(s), 0.42(s), 0.46(s), 7.32(br), 7.44(br), 7.68(br), 7.80(br)
^{13}C NMMR(75MHz,$CDCl_3$)δ	1.22(br), 2.80(br), 128.70(br), 133.18(br), 143.48(br)
^{29}Si NMR(60MHz,$CDCl_3$)δ	-22.6, -21.8, -20.3
IR (KBr) cm^{-1}	1000~1100(Si-O), 3360(Si-OH)
GPC	Mn=1497, Mz=12269, Mw=4681, Mw/Mn=3.1264, Mz/Mn=8.19353

Crystallographic data of 5

fw = 623.26, orthohombic, space group, a = 13.051(1) Å, b = 13.911(1) Å, c = 20.697(4) Å, V = 3757.4 $Å^3$, space group Pbca, Z = 4, μ(Mo Kα) = 2.4 cm^{-1}, ρ(calcd) = 1.10 g/cm^3, R =

0.065 (R_w = 0.067). The 1287 independent reflections ($2\theta \leq 21.7°$; $|Fo^2| \geq 3\sigma|Fo^2|$) were measured on an Enraf-Nonius CAD4 diffractometer using Mo Kα irradiation and an ω-θ scan. The structure was solved by direct methods, and hydrogen atoms were located and their positions and isotropic thermal parameters were refined.

Crystallographic data for 5

Table of Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
SI1	0.1606(2)	0.1586(2)	0.6423(1)	4.69(6)
SI2	0.0560(2)	0.0671(2)	0.4972(1)	4.27(6)
SI3	0.1357(3)	0.0908(2)	0.7445(2)	6.35(8)
C11	0.2444(8)	0.2696(8)	0.6509(6)	7.4(3)
C21	0.0698(9)	0.1059(8)	0.4106(5)	7.3(3)
C31	0.052(1)	-0.0170(8)	0.7405(6)	9.1(4)
C32	0.068(1)	0.180(1)	0.7989(6)	11.6(5)
C33	0.260(1)	0.055(1)	0.7827(6)	12.4(5)
C111	0.0365(7)	0.1991(6)	0.6041(5)	4.4(2)
C112	-0.0003(6)	0.1670(6)	0.5457(5)	4.2(2)
C113	-0.0865(7)	0.2129(7)	0.5191(5)	6.0(3)
C114	-0.1382(8)	0.2835(7)	0.5518(6)	7.4(3)
C115	-0.1052(8)	0.3119(7)	0.6096(6)	7.9(3)
C116	-0.0185(7)	0.2707(7)	0.6377(6)	6.5(3)
C211	0.2273(6)	0.0728(6)	0.5864(4)	4.2(2)
C212	0.1863(6)	0.0348(6)	0.5299(4)	4.1(2)
C213	0.7490(8)	0.5256(6)	0.5086(5)	5.4(2)
C214	0.3454(7)	0.5485(7)	0.0089(6)	7.5(3)
C215	0.3861(8)	-0.0130(8)	0.5659(6)	7.0(3)
C216	0.3261(7)	0.0459(7)	0.6033(5)	6.1

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Table of General Displacement Parameter Expressions - B's

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	Beqv
SI1	4.1(1)	4.3(1)	5.6(1)	0.0(1)	-0.5(1)	-0.2(1)	4.69(6)
SI2	4.3(1)	3.9(1)	4.6(1)	-0.5(1)	-0.4(1)	0.1(1)	4.27(6)
SI3	6.3(2)	7.3(2)	5.4(1)	-0.2(2)	-0.6(1)	-0.2(2)	6.35(8)
C11	5.7(5)	6.7(6)	9.7(7)	-1.3(5)	-2.8(6)	-2.5(6)	7.4(3)
C21	7.7(6)	8.7(7)	5.5(6)	-1.2(6)	-0.2(5)	1.9(5)	7.3(3)
C31	10.3(8)	8.3(6)	8.6(7)	-3.5(7)	0.1(7)	1.1(7)	9.1(4)
C32	18(1)	10.0(8)	7.0(7)	-0.2(9)	4.8(8)	-2.6(6)	11.6(5)
C33	6.7(6)	20(1)	10.1(8)	-0.4(9)	-3.0(7)	6.2(8)	12.4(5)
C111	3.6(4)	3.4(4)	6.3(5)	0.4(4)	-0.3(4)	0.1(4)	4.4(2)
C112	3.2(4)	3.2(4)	6.3(5)	-0.2(4)	-1.4(4)	0.7(4)	4.2(2)
C113	5.7(5)	3.7(4)	8.7(7)	0.3(4)	-2.1(5)	0.1(5)	6.0(3)
C114	5.8(6)	4.6(5)	11.9(8)	1.0(5)	-2.9(6)	-0.8(6)	7.4(3)
C115	5.7(5)	4.6(5)	13.4(9)	2.1(5)	-0.4(6)	-2.7(6)	7.9(3)
C116	4.8(5)	5.2(5)	9.5(7)	1.2(5)	-1.3(5)	-2.2(5)	6.5(3)
C211	2.7(4)	4.4(4)	5.5(5)	0.2(4)	-0.5(4)	0.8(4)	4.2(2)
C212	3.6(4)	3.4(4)	5.2(5)	-0.3(4)	0.5(4)	0.7(4)	4.1(2)
C213	5.4(5)	4.3(5)	6.5(5)	0.9(4)	-1.6(5)	-0.3(5)	5.4(2)
C214	4.5(5)	5.4(5)	12.6(8)	-1.5(5)	2.3(6)	-0.9(6)	7.5(3)
C215	4.0(5)	7.1(6)	10.0(7)	0.8(5)	-0.5(5)	0.8(6)	7.0(3)
C216	0	0	0	0	0	0	6.1(3)

The form of the anisotropic displacement parameter is:
exp[-0.25{h2a2B(1,1) + k2b2B(2,2) + l2c2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3)}] where a,b, and c are reciprocal lattice constants.

Table of Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
SI1	SI3	2.339(4)	C111	C112	1.38(1)
SI1	C11	1.90(1)	C111	C116	1.41(1)
SI1	C111	1.888(9)	C112	C113	1.41(1)
SI1	C211	1.876(9)	C113	C114	1.37(1)
SI2	C21	1.88(1)	C114	C115	1.33(2)
SI2	C112	1.866(9)	C115	C116	1.39(1)
SI2	C212	1.884(9)	C211	C212	1.39(1)
SI3	C31	1.85(1)	C211	C216	1.39(1)
SI3	C32	1.89(1)	C215	C216	1.37(1)
SI3	C33	1.87(1)			

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
SI3	SI1	C11	108.8(4)	SI1	C111	C112	124.8(7)
SI3	SI1	C111	112.3(3)	SI1	C111	C116	116.2(7)
SI3	SI1	C211	111.5(3)	C112	C111	C116	119.0(8)
C11	SI1	C111	106.9(4)	SI2	C112	C111	125.2(6)
C11	SI1	C211	107.9(4)	SI2	C112	C113	116.3(7)
C111	SI1	C211	109.3(4)	C111	C112	C113	118.5(8)
C21	SI2	C112	109.6(5)	C112	C113	C114	122(1)
C21	SI2	C212	108.9(4)	C113	C114	C115	120.(1)
C112	SI2	C212	109.9(3)	C114	C115	C116	121.(1)
SI1	SI3	C31	111.5(4)	C111	C116	C115	120.(1)
SI1	SI3	C32	109.9(5)	SI1	C211	C212	125.6(6)
SI1	SI3	C33	111.7(4)	SI1	C211	C216	116.5(7)
C31	SI3	C32	106.2(6)	C212	C211	C216	117.9(8)
C31	SI3	C33	108.2(7)	SI2	C212	C211	124.0(6)
C32	SI3	C33	109.2(7)	C211	C216	C215	123(1)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Torsion Angles in Degrees

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C11	SI1	SI3	C31	178.86 (0.55)
C11	SI1	SI3	C32	61.37 (0.65)
C11	SI1	SI3	C33	-59.97 (0.68)
C111	SI1	SI3	C31	60.75 (0.54)
C111	SI1	SI3	C32	-56.74 (0.62)
C111	SI1	SI3	C33	-178.08 (0.63)
C211	SI1	SI3	C31	-62.24 (0.53)
C211	SI1	SI3	C32	-179.73 (0.61)
C211	SI1	SI3	C33	58.93 (0.64)
SI3	SI1	C111	C112	-121.69 (0.73)
SI3	SI1	C111	C116	61.31 (0.75)
C11	SI1	C111	C112	119.03 (0.81)
C11	SI1	C111	C116	-57.97 (0.83)
C211	SI1	C111	C112	2.52 (0.89)
C211	SI1	C111	C116	-174.48 (0.69)
SI3	SI1	C211	C212	116.80 (0.74)
SI3	SI1	C211	C216	-63.52 (0.76)
C11	SI1	C211	C212	-123.74 (0.80)
C11	SI1	C211	C216	55.94 (0.85)
C111	SI1	C211	C212	-7.89 (0.89)
C111	SI1	C211	C216	171.79 (0.71)
C21	SI2	C112	C111	-132.25 (0.81)
C21	SI2	C112	C113	46.86 (0.82)
C212	SI2	C112	C111	-12.54 (0.89)
C212	SI2	C112	C113	166.58 (0.67)
C21	SI2	C212	C211	127.22 (0.79)
C112	SI2	C212	C211	7.08 (0.87)
SI1	C111	C112	SI2	7.71 (1.16)
SI1	C111	C112	C113	-171.39 (0.69)
C116	C111	C112	SI2	-175.37 (0.70)
C116	C111	C112	C113	5.53 (1.29)
SI1	C111	C116	C115	173.25 (0.77)
C112	C111	C116	C115	-3.94 (1.39)
SI2	C112	C113	C114	176.16 (0.78)
C111	C112	C113	C114	-4.66 (1.39)
C112	C113	C114	C115	1.92 (1.57)
C113	C114	C115	C116	-0.17 (1.64)
C114	C115	C116	C111	1.19 (1.58)
SI1	C211	C212	SI2	2.47 (1.14)
C216	C211	C212	SI2	-177.20 (0.70)
SI1	C211	C216	C215	-177.16 (0.84)
C212	C211	C216	C215	2.54 (1.47)

3-4 REFERENCES

1) (a) H. Sakurai, A. Okada, M. Kira, and K. Yonezawa, *Tetrahedron Lett.*, 19, 1511 (1971).

(b) H. Sakurai, M. Kira, and H. Umino, *Chem. Lett.*, 1265 (1977).

2) (a) G. Harvey, L. Nazareno, and H. Cho, *J. Am. Chem. Soc.*, 95, 2376 (1973).

(b) H. Cho and R. Harvey, *J. Org. Chem.*, 40, 3097 (1975).

(c) P. P. Fu and R. G. Harvey, *Chem. Rev.*, 78, 317 (1978).

3) (a) U. Edlund and E. Buncel, In *Progress in Physical Organic Chemistry*; R, W. Talf, Ed.: Wiley: New york, 19, 254 (1993).

(b) E. Buncel, T. K. Venkatachalam, U. Edlund, and B. Eliasson, *J. Chem. Soc., Chem. Commun.*, 1476 (1984).

(c) G. A. Olah and R. J. Hunadi, *J. Am Chem. Soc.*, 102, 6989 (1980).

(d) E. Buncel, R. D. Gordon, T. K. Venkatachalam, *J. Organomet. Chem.*, 508, 81 (1996).

(e) E. Buncel, T. K. Venkatachalam, B. Eliasson, and U. Edlund, *J. Am. Chem. Soc.*, 107, 303 (1985).

4) L. H. Sommer and R. Mason, *J. Am. Chem. Soc.*, 87, 1619 (1965).

4) (a) H. Gilman and R. L. Harrell, *J. Organomet. Chem.*, 9, 67 (1967).

(b) H. Bock, J. Meuret, and K. Ruppert, *J. Organomet. Chem.*, 445, 19 (1993).

CHAPTER 4

STRUCTURAL CHARACTERIZATION OF 9,10-DISILAANTHRASEN DIANION IN SOLUTION

ABSTRUCT

NMR spectra of 9,10-dilithio-9,10-disilaanthracene(1), prepared by treatment of 9,10-disilaanthracene dimer(3) with excess lithium, revealed the presence of only one species. In the low temperature ^{29}Si NMR spectrum measurement of 1 ^{29}Si-^{7}Li scalar coupling was observed. And the ^{7}Li NMR spectrum showed the two different environments for these two lithium atoms in 1 at 168K. These spectral analyses and our theoretical investigation strongly suggest a structure which has singly bridged lithium for two silicon atoms(1c).

4-1 INTRODUCTION

Numerous investigations have supported that silyl anions are synthetically useful tools not only in organosilicon chemistry but also in organic synthesis.[1] There is current interest in the synthesis, structural characterization and chemical reactivity of molecules containing two or more silyl anions. Nevertheless, only a few bis(silyl anion) derivatives have been reported. Among those bis(silyl anion) derivatives, a limited number of molecules can be characterized. Belzner[1)] and Becker[2)] accomplished the preparations of α,β-dilithiooligosilanes, and those structures were determined by X ray diffraction. Recently, synthesis and structural characterization of *trans*-1,2-dilithio-1,2-disilaacenaphthenes[3)] in a solution have been reported in this laboratory. These bis(silyl anion) derivatives favored single contact between lithium and silicon atom (Type I).

Figure 1. Bonding styles of dianion compounds.

In the cases of carbon dianions, double bridging structures (Type II) and single bridging type (Type III) are well known

of experimental studies. However, an example of a lithium atom bridging two silicon atoms has not yet been observed.

4-2 RESULTS AND DISCUSSION

4-2-1 THEORETICAL STUDY OF 9,10-DISILAANTHRACENE DILITHIUM

As shown in Chapter 3-2-1, ^{1}H, ^{13}C and ^{29}Si NMR spectra for 9,10-disilaanthracene dilithium (1) and dipotassium (2) showed similar chemical shifts which mean presence of only one species bearing C_{2v} symmetry, respectively, and dipotassium compound (2) reveals the exclusive *cis*-reactivity for electrophiles.

1a; M = Li
2a; M = K

1b; M = Li
2b; M = K

Fig. 2

In view of these results, 1 and 2 have *cis*-9,10-dimetalo-9,10-disilaanthracene structure might be considered. However, we have been an imagination that *cis*-di(metalo) structure (1a, 2a) are more unstable than its trans-structure owing to the repulsion of each negative charges.

A theoretical study[4)] on 9,10-dihydro-9,10-disilaanthracene dilithium reveals that the most stable structure is singly bridged structure (3c); the 3-21G(*) optimized results showed that cis-dilithium (3a, 3a') and trans-

dilithium compound (3b) and double bridged (3d) are 34.2, 36.6, 25.7 and 2.7 kcal/mol higher in energy than 3c.

Fig. 3

Important feature of optimized structure for 3c is summarized in Table 1. In 3c, one of lithium atom is bridging to silicon atoms with a possible overlap between the lithium *p*-orbital and silicon lone pairs; another lithium atom is located on opposite side of the bridging lithium and is coordinated to four carbon atoms in the central six-membered ring.

3c

Table 1. Important distances(left) and angles(right) for calculated structure 3c.

	distances / Å		angles / deg
Si - Li(1)	2.620	Si - C(11) - C(12)	116.8
Si - (2)	2.944	C(11) - C(1) - C(12)	121.3
Si - C(11)	1.942	C(1) - C(2) - C(3)	120.0
C(11) - Li(2)	2.241	Si - Li(1) - Si	74.7
C(1) - C(2)	1.385	C(11) - Li(2) - C(12)	37.1
C(2) - C(3)	1.386	C(12) - Li(2) - C(13)	81.3
C(11) - C(12)	1.428	C(11) - Si - Si - C(13)	114.7 = α
Si - - -Si	3.177		

4-2-2 STRUCTURE OF 9,10-DISILAANTHRACENE DILITHIUM IN SOLUTION

Next our efforts were focussed on the elucidation of structures for 1 and 2. NMR studies have been the most informative of the structures in solution, and particularly important evidence has recently been obtained from a low-temperature measurement of ^{29}Si-^{7}Li scalar coupling.[5] In the ^{29}Si NMR spectrum of dilithio derivatives (1) at 168 K in THF-*d8*, a quartet with ^{1}J [^{29}Si-^{7}Li]=34Hz was observed (Fig. 2).

Figure 4. ^{29}Si NMR (left) and ^{7}Li NMR (right) spectra of 9,10-disilaanthracene dilithium(1) in THF-*d8* at 168K.

This implies that two silicon atoms in the molecule are magnetically equivalent and one lithium atom binds to the silicon atom at low temperature

The coupling constant, 34 Hz, between ^{29}Si and ^{7}Li was a little bit smaller, compared with 51 and 43.5 Hz for Ph_3SiLi[5a] and 1,2-dilithio-1,2-disilaacenaphthenes[3] both at 173 K in THF-*d8*, respectively. It is presumed from the observation of small coupling constant between ^{29}Si and ^{7}Li for 1 that a part of a lithium interacted to two silicon atoms, Si-Li-Si, was present in the molecule. The ^{7}Li NMR signal appears at 3.7 ppm as a singlet at 298 K. Dramatic change was observed for the low temperature NMR measurements which yielded two different singlets at 2.8 and 5.2 ppm; unfortunately no satellite signals due to ^{29}Si scalar coupling were observed. However, it is clear from ^{29}Si NMR spectrum that 1 has a partial covalence between ^{29}Si and ^{7}Li at low temperature.

1a

1b

1c

1d

The result of ^{7}Li NMR studies would be compatible with different environments for the two lithium atoms in the molecular at a low temperature.

cis-9,10-Dilithio-9,10-disilaanthracene(1a), *trans*-dilithio derivative(1b) and the single bridging structure(1c) and double bridged structure (1d) are the possible structure to be considered for 1. However, 1d is easily excluded from the candidates by the observation of a qualtet in low temperature ^{29}Si NMR spectrum measurement. 1a and 1b (with smooth conformational change) should contain magnetically equivalent lithiums and can be rule out from the result of ^{7}Li NMR studies. Thus, the observed NMR data are compatible with the structure that two silicon atoms bridged by a lithium (1c). Although, the second lithium for calculated the most stable structure (1c) coordinated to four carbon in pheny groups, unfortunately, ^{13}C-^{7}Li scalar coupling was not observed in low temperature ^{13}C NMR spectrum for 1 (Fig. 5).

Figure 5. 13C NMR spectrum of 1 at 168 K.

Thus, the author could not determined the unambiguous position of second lithium atom from the present data. However, it is supported that ^{7}Li NMR chemical shift of 1 that the second lithium atom is somewhat attracted to disilaanthracene skeleton; ^{7}Li NMR chemical shift of $^{7}Li^{+}(THF)_4$ should be appear around at 0 ppm.[6] Thus, the author proposed that 1c' is the best representation for 9,10-disilaanthracene dilithium (1).

1c'

4-2-3 COMPARIZON OF ELECTRONIC STRUCTURE BETWEEN 1 AND ANTHRACENE DILITHIUM

Stucky[7] has been reported the crystal structure of anthracene dilithium (4). One lithium atom is located over the central six-membered ring and the other is positioned on opposite side of the molecule over one of the outer six-membered rings. Anthracene skeleton take a *zigzag* structure (Chapter-1-5-1).

^{1}H NMR spectrum of anthracene dilithium (4) in THF has investigated that two AA'BB' multiplets (at 2.81 and 3.84 ppm) and a singlet (at 1.41 ppm) were observed.[8] Appreciable upfield shift of AA'BB' multiplet compared with neutral anthracene (at 7.46 and 7.97 ppm) drived from paramagnetic ring-current effect in anthracene skeleton. In other words, negative charges delocalized into outer six-membered rings; anthracene dilithium has *anti*-aromatic character in solution.

Fig. 6

While, the ^1H NMR signals of 1c were observed for two AA'BB' multiplets at 6.59 and 7.19 ppm and for a singlet at 0.58 ppm at 298 K. The AA'BB' signals appear at standard region for phenylen-proton; consequently the anion charge of 9,10-disilaanthracene dilithium is fixed upon silicon atoms. 3-21G(*) optimized singly lithium bridged structure 3c is shown in Table 1. Dihedral angle a is 114.7 ° which the value is similar to sp^3 bond angle. In the view of the NMR studies and theoretical studies, it is reasonable that 9,10-disilaanthracene dianion takes a *non*-aromatic character which has been defined not planer skeleton.

Interestingly, difference of electron densities between anthracene dilithium and 9,10-disilaanthracene dianions affect to these reactivites for the electrophiles. The reaction of 9,10-disilaanthracene dipotassium (2) with trimethylchlorosilane afforded exclusively *cis*-9,10-bis(trimethylsilyl)-9,10-dimethyl-9,10-disilaanthracene as shown in Scheme 7.

Scheme 7

However, Harvey[9] has been reported that three products (*cis*-5, *trans*-5, 6) were obtained by treatment of anthracene dilithium with trimethylchlorosilane; the molar ratio of these products *cis*-5: *trans*-5: 6 = 10 : 1 : 5. It is considered that the outer six-menbered rings of 4 having a substantial electron density reacted with trimethylchlorosilane resulted in the formation of 6. On the other hand, disilaanthracene analogue of 6 was not obtained in the reaction of 2 with trimethylchlorosilane because almost negative charges located on silicon atoms. It is predicted that the molar ratio of products related to the difference of electron density on anthracenes skeleton.

4-3 EXPERIMENTAL SECTION

^{1}H, ^{7}Li, ^{13}C, and ^{29}Si NMR spectra were recorded on a Brucker AC-400PS and AC-300P spectrometer in THF-d_8.

As alkali metal anion react with trimethylsilane (TMS), the chemical shifts were referenced to the most downfield solvent peaks. The solvent chemical shifts were determined for pure THF-d_8 containing TMS. The chemical shift of the 1-H of THF-d_7 in THF-d_8 was found to be 3.57 ppm and the chemical shift of C-1 of THF-d8 was found to be 67.39 ppm at 298 K. ^{29}Si NMR chemical shift was referenced to TMS in pure THF-d_8 as external standard. ^{7}Li NMR was referenced to lithium chloride in methanol; benzene-d6 sealed in capillary was used for *d*-lock signal. The temperature was determined using a standard NMR thermometer.

9,10-Dimethyl-9,10-disilaanthracene dimer (3) was prepared from the already reported manner (Chapter-2-3).

Alkali metals were of commercial origin.

Lithium	Merck, wire in paraffin oil
potassium	Aldrich, chunks in mineral oil

THF-d_8 was dried over lithium aluminium hydride, and then transferred into a tube covered with potassium mirror and distilled prior to use. THF was dried and distilled from sodium benzophenone ketyl.

Preparation of 1 for the measurement of NMR spectrum

A mixture of about 20 mg of dimer (3) and excess of freshly cut lithium wire was placed in a NMR tube equiped with vacuum screw-cock set for vacuum line, then degassed. THF-d8 dried from potassium mirror was vacuum transferred into the NMR tube, then degassed in several freeze-pump-thraw cycles. The NMR tube was sealed, then sonication was continued until 9,10-disilaanthracene dilithium was generated quantitatively. The course of the reaction, was checked by analysis of the ^{1}H NMR spectrum.

Preparation of dipotassium compound (2) for measurement of NMR spectrum

A mixture of ca.20 mg of dimer (3), excess of potassium, and about 1 mL of THF was placed in 10 mL-round bottomed flask, then stirred for 24 hours in vacuo; orange suspension was obtained. After removal unreacted potassium, slow evaporation of the solvent from the suspension to afford orange powder, which is placed in a NMR tube equiped vacuum screw-cock under argon atmosphere. THF-d8 dried from potassium mirror was vacuum transferred into the NMR tube, then degassed in several freeze-pump-thraw cycles. The NMR tube was sealed

4-4 REFERENCES

1) J. Belzner, U. Dehnert, and D. Stalke, *Angew. Chem., Int. Ed. Engl.*, 33, 2450 (1994).

2) G. Becker, H. -M. Hartmann, E. Hengge, and F. Schrank, *Z. anorg. allg. Chem.*, 572, 63 (1989).

3) W. Ando, T. Wakahara, and T. Akasaka, *Organometallics*, 13, 4683 (1994).

4) Spartan version 3.1.6, W. J. Hehre, Wave-function. Inc., Irvine, CA, 1994.

5) (a) U. Edlund and T. Lejon, *J. Am. Chem. Soc.*, 107, 6408 (1985).

(b) A. Heine, R. Herbst-Irmer, G. M. Sheldrick, and D. Stalke, *Inorg. Chem.*, 32, 2694 (1993).

(c) H. V. R. Dias, M. M. Olmstead, K. Ruhlandt-Senge, and P. P. Power, *J. Organomet. Chem.*, 1, 462 (1993).

6) A. Sekiguchi, M. Ichinohe, T. Nakanishi, H. Sakurai, *Chem. Lett.*, 267 (1993).

7) W. E. Rhine, J. Davis, and G. Stucky, *J. Am. Chem. Soc.*, 97, 2079 (1975).

8) (a) M. Nir, I. O. Shapiro, R. E. Hoffman, and M. Rabinovitz, *J. Chem. Soc., Perkin Trans. 2*, 1607 (1996).

(b) M. Nir, I. R. E. Hoffman, I. S. Shapiro, and M. Rabinovitz, *J. Chem. Soc., Perkin Trans. 2*, 1443 (1995).

(c) A. Minsky, A. Y. Meyer, and M. Rabinovitz, *Angew. Chem., Int. Ed. Engl.*, 22, 45 (1983).

9) H. Cho and R. G. Harvey, *J. Org. Chem.*, 40, 3097 (1975).

CHAPTER 5

PHOTOCHEMICAL REACTION OF SILYL-BRRIDGED 9,10-DISILAANTHRACENE

ABSTRUCT

Di(*tert*-butyl)silyl bridged 9,10-disilaanthracene (1) was prepared from the reaction of the 9,10-disilaanthracene dipotassium with di(*tert*-butyl)-dichlorosilane. Photolysis of 1 at room temperature proved unexpected product, *tert*-butylsilyl-bridged 9,10-disilaanthracene (2), and isobutene in quantitative yields. The ring-opened dichloro derivative 5 was formed by photoreaction of 1 in the presence of carbon tetrachloride as a trapping reagent for silyl radical. The formation of 5 has been suggested that corresponding biradical species was generated by irradiation of 1.

5-1 INTRODUCTION

Dodecamethylhexasilacyclohexane, $(Me_2Si)_6$, is particularly valuable source of dimethylsilylene, $(Me_2Si:)$, since the silylene is cleanly formed during photolysis at 254 nm. The other product of extrusion reaction are the smaller permethylcyclosilane down to the cyclotetrasilane, $(Me_2Si)_4$. On further photoreaction, this does not appear to extrude silylene, undergoing silicon-silicon bond fission instead to diradical which abstracts hydrogen to give a linear tetrasilane.

Scheme 1

On the other hand, the dimethylsilyl-bridged tetraphenylbenzocyclohexane has been propertied a useful alternate to $(Me_2Si)_6$ as a photochemical source of dimethylsilylene. Photolysis of di(*tert*-butyl)silyl-bridged 9,10-disilaanthracene (1) attracts whether the silylene and long-sought disilaanthracene are produced or not.

Scheme 2

5-2 RESULTS AND DISCUSSION

5-2-1 PHOTOREACTION OF 1

Di(*tert*-butyl)silyl-9,10-disilaanthracene (1) was prepared from the reaction of 9,10-disilaanthracene dipotassium with di(*tert*-butyl)dichlorosilane in 59 % yield. UV-vis absorption for 1 was observed at 255 (ε=31700), 240 (sh, 17900) and 290 (4200) nm.

A mixture of 1 and large excess of triethylsilane as a trapping reagent of silylene dissolving in THF was irradiated in sealed NMR tube. Although, the photolysis of 1 did not occured even for 12 hours using low pressure mercury lamp (254 nm), the reaction proceeded by exchange of light source to a high presser mercury lamp. The reaction process was checked by the measurement of ^{1}H NMR spectrum.

The time course of the ^{1}H NMR signals for the photoreaction of 1 is shown in Fig. 1.

0 h
5 h
10 h
14 h
29 h
THF
THF
○ :
t-Bu
t-Bu
Si
Me
Si
Si
Me
1
△ :
t-Bu
H
Si
Me
Si
Si
Me
2
◇ :
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm

Figure 1.

It is clear from these ^1H NMR spectra, the signals of 1 disappeared and some new peaks appeared by the irradiation of the mixture. After irradiation for 29 hours, a novel disilaanthracene derivative, having ^1H NMR chemical shift at 1.5 (s, 6H), 0.85 (s, 9H), 7.21 (AA'BB' m, 2H), 7.22 (AA'BB' m, 2H), 7.65 (AA'BB' m, 2H), was formed along with another product, bearing ^1H chemical shift 1.73 (t, 2H) and 4.67 (sep, 6H).

In absence of trapping reagent, similar product were obtained. In order to obtain the further information on the structure of the product, some spectroscopic measurements were carried out after removal volatile compounds. In the IR spectrum, observed a band at 2096 cm^{-1} could be easily attributed to sp^3 Si-H stretching vibrations. The EI mass spectroscopy reveals a peak at m/z 324, in agreement with that calculated for $C_{18}H_{24}Si_3$. In view of these results, the structure was identified to *tert*-butylsilyl-bridged 9,10-disilaanthracene (2). By-product of the photoreaction could be assigned to isobutene from the ^1H and ^{13}C NMR spectrum and formation of 2.

Scheme 2

Thus, isobutene has been excluded from 1 during the photoreaction using high presser mercury lamp. *tert*-Butylsilyl-bridged compound (2) is relatively unstable toward air and moisture compared with 1. *tert*-Butylsilyl-bridged compound (2) was gradually decomposed into the crresponding siloxane (3) by allowing to expose in air for a few days.

Scheme 4

At this point, some questions remain

1) why disilaanthracene and di(tert-butyl)silylene were generated by the photolysis of 1.

2) and why extrusion of isobutene occured in this reaction.

In order to shed light on these questions, photoreaction of 1 was carried out in the presence of carbon tetrachloride as a silyl radical trapping reagent. Irradiation of dissolved in THF/CCl_4 in sealed NMR tube gave a mixture of 9-chloro-10-di(*tert*-butyl)chlorosilyl-9,10-dimethyl-9,10-disilaanthracene (5), 9,10-dichloro-9,10-dimethyl-9,10-disilaanthracene (6) and di(*tert*-butyl)dichlorosilane.

Scheme 5

Compound (5) and (6) are the evident products of the formation of bis(silyl radical) (7) and silyl radical compound (8) formed by silicon-silicon bond dissociation in 1 and 5, respectively. Thus, it is though that irradiation of 1 at least led to an initial silicon-silicon bond dissociation to afford bis(silyl radical) (7) as shown in Scheme 6. Nevertheless, further photochemical induced silicon-silicon bond dissociation of 7 did not occur. Presumably driving force for silaanthracene generation from intermediate 7 (path A in Scheme 6), is more weak compared

with the case of photoreaction of 7-silanorbornadiene derivative in which stable naphthalenes is excluded (Scheme 2). The mechanism for formation of 2 is considered as follows (path B).

Scheme 6

The silyl radical in 7 abstracted the *tert*-butyl hydrogen to afford related hydrosilane 8 followed by isobutene extrusion to give the silylene 9. The silylene 9 was scavenged by intramolecular Si-H insertion reaction rather than by intermolecular reaction with triethylsilane.

5-3 EXPERIMENTAL SECTION

General procedure.

^{1}H, ^{13}C and ^{29}Si NMR spectra were obtained with Brucker AC-400PS(156 and 80 MHz) and AC-300P(117 and 60MHz) instruments chloroform-*d*, benzene-d_6, or THF-d_8 using tetramethylsilane (TMS) was used as an internal or external standard. Mass spectra were obtained on Shimadzu QP 2000 and QP 5000 spectrometers. IR spectra were measured on a JEOL FT/IR-5000 spectrometer. UV-vis spectra were recorded on a JEOL Ubest-50 spectrometer.

Tetrahydrofuran(THF) was dried and distilled from sodium benzophenone ketyl. THF-d_8 was dried over lithium aluminum hydride, and then transferred into a tube covered with potassium mirror and distilled prior to use.

Gel permission chromatographic separation was performed on a model LC-908 recycling preparative HPLC(Japan Analytical Industry Co., Ltd.) with a series of Jaigel 1H and 2H columns using toluene as a eluant. For thin-layer chromatography Kieselgel(Merck, Art. 7747) was used.

Preparation of 9,10-di(*tert*-butyl)silano-9,10-dimethyl-9,10-disilaanthracene (1)

A mixture of 9,10-dimethyl-9,10-disilaanthracene dimer (476 mg, 1.0 mmol) and excess of potassium in 15 mL of THF

was stirred for 24 hours to afford an yellow suspension. After removal unreacted potassium, the dianion suspension was added di(tert-butyl)dichlorosilane (496 mg, 2.2 mmol) dissolved in 7 mL of THF over a period of 30 min at -78 °C. After completion of the addition, the resultant solution was further stirred at the same temperature for 30 min, then cooling bath was gradually warmed up to room temperature.

The reaction mixture was hydrolyzed in water, then extracted with ether. The organic layers were combined, dried over MGSO4, followed by evaporation to afford crude products mixture. Separation and purification of the mixture by HPLC (toluene eluant) to produce pure title compound (1).

Yield	452 mg (59 %)
colorless crystals	m.p. 156~158 °C
^{1}H NMR(300MHz,C_6D_6)δ	0.82(6H,s), 0.88(18H,s), 7.13(4H,AA'BB' m *J*=3.2,5.2Hz), 7.52(4H,AA'BB' m *J*=3.2,5.2Hz)
13C NMR(75MHz,C6D6)δ	-10.9, 24.2, 32.8, 127.2, 130.9, 150.36
Mass m/z	380(M^+), 323(M^+-Bu)
UV (CH_2Cl_2) λmax nm(ε)	225(31700), 240(sh, 17900), 290(4200)

Photoreaction of Preparation of 9,10-di(*tert*-butyl)silano-9,10-dimethyl-9,10-disilaanthracene (1)

A mixture of 1 (30 mg, 0.08 mmol), and triethylsilane (100 μl) was placed in quartz NMR tube equiped vacuum screw-cock set for vacuum line. THF-d8 dried over potassium mirror was transfered into the NMR tube, degassed by freeze-pump-thraw cycles, then sealed. Irradiation of the mixture with a high pressure mercury lamp for 10 hours, The NMR spectra revealed that 9,10-(tert-butyl)silano-9,10-dimethyl-9,10-disilaanthracene (2) and isobutene were quantitatively generated. After removal volatile compound, IR spectrum and mass spectroscopy were made.

^{1}H NMR(300MHz,THF-d_8)δ	3.62(1H,s), 0.85(9H,s), 1.50(6H,s), 7.21(2H,AA'BB' m *J*=3.2,5.3 Hz), 7.22(2H,AA'BB' m *J*=3.2,5.3 Hz), 7.60(2H,AA'BB' m *J*=3.2,5.3 Hz), 7.65(2H,AA'BB' m *J*=3.2,5.3 Hz)
^{13}C NMR(75MHz,THF-d_8)δ	-11.2, 20.9, 24.2, 127.7, 127.8, 131.5, 131.7, 148.4, 149.2
29Si NMR(60MHz,THF-d_8)δ	-25.9, 7.6
Mass m/z	380(M^+), 323(M^+-Bu)
IR (KBr) ν cm^{-1}	2096

Photoreaction of 1 in the absence of triethylsilane to afford 2 and isobutene in quantitatively (see Figure 1).

Photoreaction of 1 in the presence of carbon tetrachloride

A mixture of 1 (30 mg, 0.08 mmol), 80 mL of carbon tetrachloride and THF-d8 in sealed NMR tube was irradiated with high pressure mercury lamp for 30 hours. The formation of 5, 6 and di(tert-butyl)dichlorosilane were confirmed with G.C. and G.C. Mass spectroscopy.

5-4 REFERENCES

1) M. Ishikawa. M. Kumada, *Adv. Organomet. Chem.*, 19, 51 (1981).

2) (a) J. A. Hawari and D. Griller, *Organometallics*, 3, 1123 (1984).

(b) H. Sakurai, Y. Nakadaira, and H. Sakaba, *Organometallics*, 2, 1484 (1983).

3) Thermal reaction for a series of silanorbornadiene. see follows.

(a) B. Mayer and W. P. Neumann, *Tetrahedron Lett.*, 21, 4887 (1980).

(b) H. Sakurai, H. Sakaba, and Y. Nakadaira, *J. Am. Chem. Soc.*, 104, 6156 (1982).

(c) H. Sakurai, Y. Kobayashi, R. Sato, and Y. Nakadaira, *Chem. Lett.*, 1197 (1983).

LIST OF PUBLICATIONS

1. "Synthesis and Reaction of the 9,19-Disilaanthracene Dimer"
   Wataru Ando, Ken Hatano, and Rie Urisaka.
   Organometallics, 14, 3625-3627 (1995).

2. "Lithium-Bridged Bis(silyl anion) of 9,19-Dimethyl-9,10-disilaanthracene"
   Ken Hatano, Kenji Morihashi, Osamu Kikuchi, and Wataru Ando.
   Chem. Lett., Submitted for Publication.

3. "Structure of 9,10-Dimethyl-9,10-disilaanthracene Dilithium in Solution: First Lithium Bridged Bis(silyl anion) derivative"
   Ken Hatano, Kenji Morihashi, Osamu Kikuchi, and Wataru Ando.
   Organometallics., submitted for publication.

4. "Electron-transfer Reaction of 9,10-Disilaanthracene Dianion"
   Ken Hatano, Kenji Morihashi, Osamu Kikuchi, and Wataru Ando. in preparation.

5. "Photoreaction of 9,10-Silano-9,10-disilaanthracenes"
   Ken Hatano, Rena Suzuki, and Wataru Ando. in preparation.

OTHERS

1. "Dissolving Metal Reduction with Crown Ether - Reductive Demethylation of Mono-, Di- and Trimethoxybenzene Derivatives with Toluene Radical Anion"
   Tomihiko Osawa, Ken Hatano, Katsukiko Kayoh, Jun Kotabe, and Takeshi Oishi.
   Tetrahedron Lett., 33, 5555-5558 (1992).

2. "Synthesis and Crystal Structure of 9,10-Disilatriptycenes"
   Masaki Takahashi, Ken Hatano, Yuzo Kawada, Gen Koga, Norihiro Tokitoh, and Renji Okazaki.
   J. Chem. Soc., Chem. Commun., 1850-1852 (1993).

3. "o-Trimethylsilylphenyllithium as a Synthetic Equivalent of o-Halophenyllithium"
   Masaki Takahashi, Ken Hatano, Mikio Kimura, Toshinari Watanabe, Takeshi Oriyama, and Gen Koga.
   Tetrahedron Lett., 35, 579-582 (1994).

Acknowledgment

The author wishes to express his sincere gratitude to Professor Wataru Ando of Department of Chemistry, University of Tsukuba for his continuing interest, valuable discussions, and helpful suggestions throughout this study.

Grateful acknowledgment is made to Professor Takeshi Akasaka, Graduate School of Science and Technology, Niigata University, for his valuable suggestions and discussions.

The author wishes to thank Dr. Yoshio Kabe, Dr. Xiang Chen and Dr. Nami Choi for thier helpful discussions.

The author also wishes to thank Ms. Rie Urisaka and Ms. Rena Suzuki for their valuable discussions and experimental assistance in completing this work.

The author gratefully thanks the member of Professor Ando's group.

Finally, the author gratefully thanks his family for constant encouragement and support during this research.

December, 1996

Ken Hatano

inches
1 2 3 4 5 6 7 8
cm
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
Kodak Color Control Patches
© Kodak, 2007 TM: Kodak
Blue
Cyan
Green
Yellow
Red
Magenta
White
3/Color
Black
Kodak Gray Scale
C
Y
M
© Kodak, 2007 TM: Kodak
A 1 2 3 4 5 6 M 8 9 10 11 12 13 14 15 B 17 18 19