

Highly reactive small and medium carbacyclic silanes and germanes

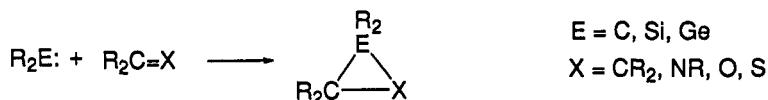
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Abstract: Reactions of silylenes and germylenes, divalent group 14 element derivatives, with various olefins were investigated. Also, reactions of these species, as well as of disila- and digermacyclobutanes with Buckminsterfullerene are described. Studies on the generation and reactivity of dilithio 1,2-disilaacenaphthene and dilithio-9,10-disilaanthracene have also been performed.

INTRODUCTION

In recent years the chemistry of small ring and cage compounds with incorporated group 14 elements has progressed rapidly with the use of divalent ($R_2E:$) and double bond ($R_2E=CR_2$, $R_2E=ER_2$, $E=Si, Ge$) species as building blocks. Especially additions of divalent species ($R_2E:$) towards a variety of unsaturated compounds have been used as a facile method for the synthesis of three-membered heterocycles.^{1,2}



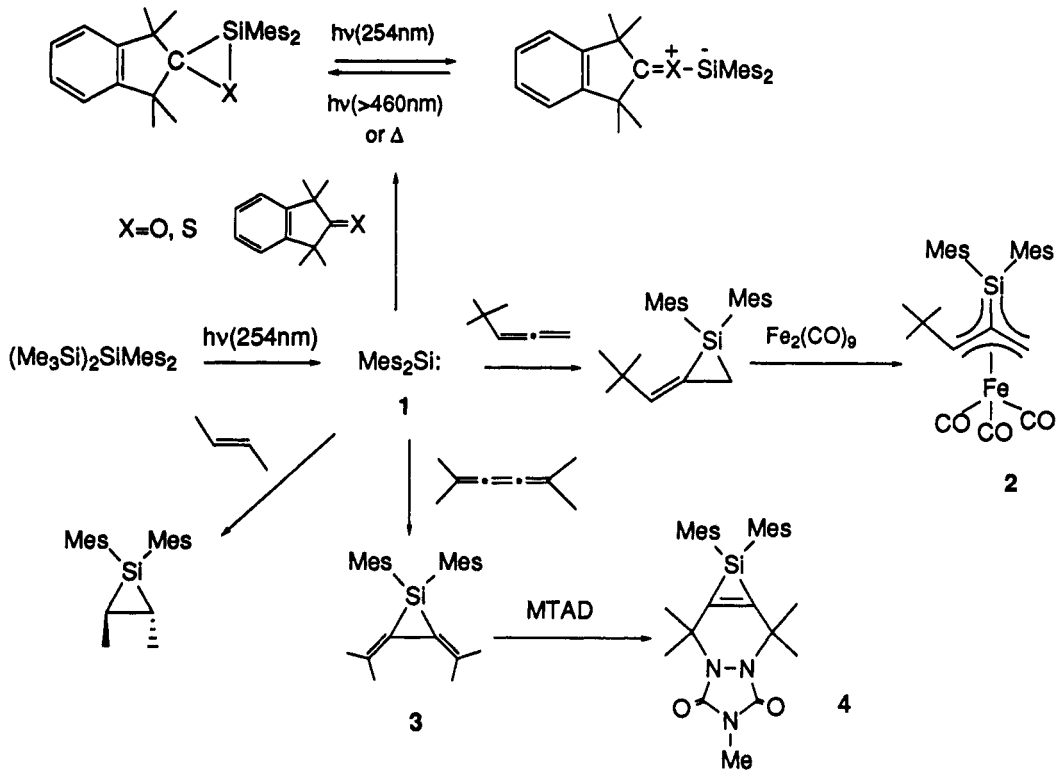
These, as well as four membered ring compounds represent a class of key reagents for the synthesis of a variety of other heterocyclic derivatives. Herewith we wish to report on 1) reactions of silylenes and germylenes with various types of olefins, 2) additions of silylene, disilirane, disilacyclobutane and digermacyclobutanes derivative to C_{60} , and 3) properties of dilithio-1,2-disilaacenaphthene and dilithio-9,10-disilaanthracene.

REACTIONS OF SILYLENES AND GERMYLENES WITH OLEFINS

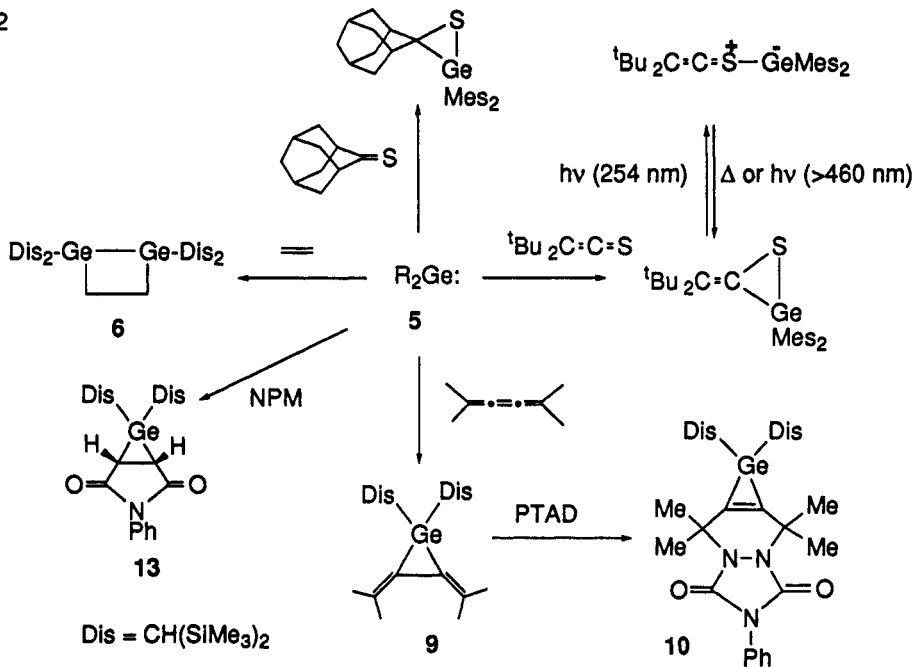
Dimesitylsilylene (1), conveniently generated photochemically, undergoes additions to alkenes, allenes and trienes as well as to ketones and thioketones to afford the corresponding three membered heterocycles. The latter, highly strained compounds, react with a variety of reagents, e.g. conversion of alkylidenesilirane with $Fe_2(CO)_9$ results in the formation of η^4 -silatrimethylenemethane iron complex 2,³ or bis(alkylidene)silirane 3 reacts with 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) in Diels-Alder manner to yield a ring-fused silirene 4 (Scheme 1).^{4,5}

Compared to silylene, the corresponding germylenes are less reactive. Cycloadditions with thioketones and thioketenes provide thiagermiranes, thiadigermetanes and alkylidene thiagermiranes, respectively (Scheme 2). These new ring systems also merit further elaboration. Upon irradiation the latter rearranges into a germathio-carbonyl ylide that was isolated by matrix techniques. Additions of germylenes to olefins are disfavored, e.g. while silylenes easily give adducts with propylene and 2-butene, bis(disyl)germylene (5) fails to react. Only ethylene reacted with 5 to give 1,2-digermacyclobutane 6 as sole product. Although it might be anticipated that initially a germacyclopropane is formed, the precursor for 6, no such compounds

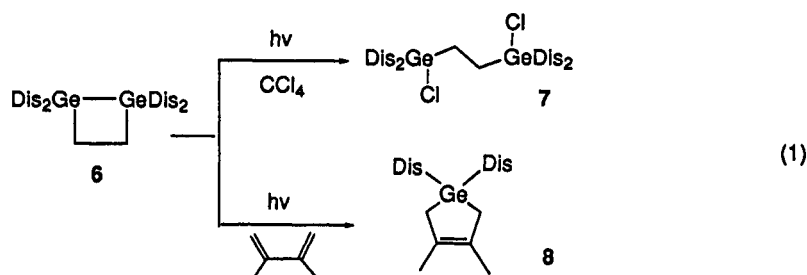
Scheme 1



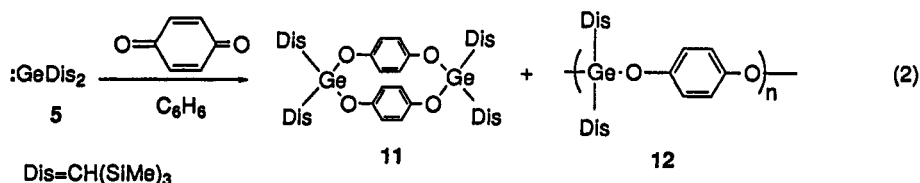
Scheme 2



could be detected. Photolysis of **6** in the presence of CCl_4 affords 1,4-dichloro-1,4-digermaputane (**7**) as a result of the Ge-Ge cleavage, while the photochemical reaction with 2,3-dimethyl-2,3-butadiene afforded adduct **8** (Eq. 1)⁶.

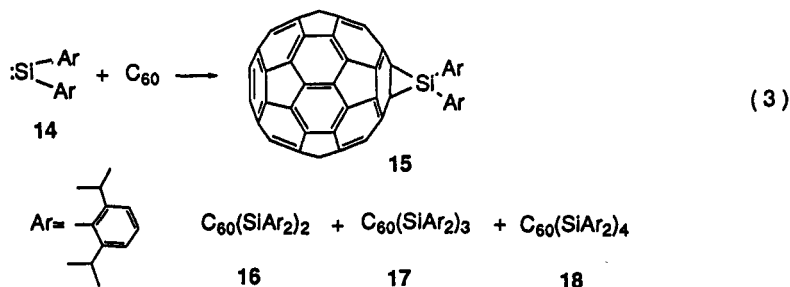


Similar to the silicon analogue **1**, germylene **5** reacts with tetramethylbutatriene to yield bisalkylidene germirane **9**, which can undergo a [4+2] cycloaddition with PTAD to afford ring-fused germirene **10** (Scheme 2). After treatment of **5** with *N*-phenylmaleimide (NPM), germirane (**13**) was obtained in 78% yield.⁷ On the other hand, conversion of **5** with *p*-benzoquinone resulted in the formation of compound **11** in 10% yield besides 67% of polymer **12** (MW=14000).

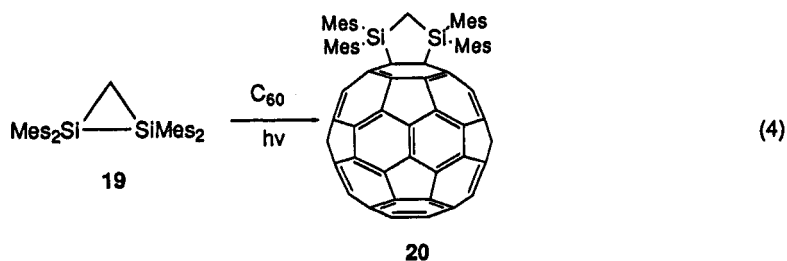


SILICON AND GERMANIUM DERIVATIVES OF FULLERENE

In spite of their potential use as new materials, silano- and germanofullerene derivatives have been investigated thoroughly. Bis(2,6-diisopropyl phenyl)silylene **14** adds to C_{60} to give thermally stable **15** and **16** in 58% and 27% yields besides small amounts of **17** and **18**.⁸ On the other hand, the conversion of dimesitylgermylene **1** or bis(disiyl)germylene **5** with C_{60} only afforded complex mixtures of insoluble products.

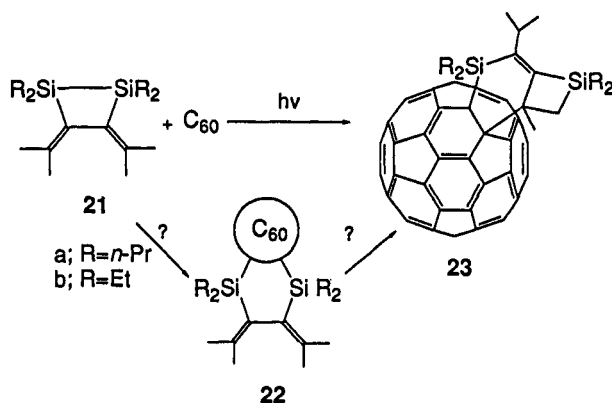


Irradiation of a toluene solution of disilirane (**19**) in the presence of an equimolar amount of C_{60} with a high pressure mercury lamp resulted in the formation of 1,1,3,3-tetramesityl-1,3-disilolane **20** in 82% yield. Most likely, since the reaction is completely inhibited by addition of rubrene, a well established triplet quencher, C_{60} in its triplet excited state seems to be involved in the course of the reaction.⁹



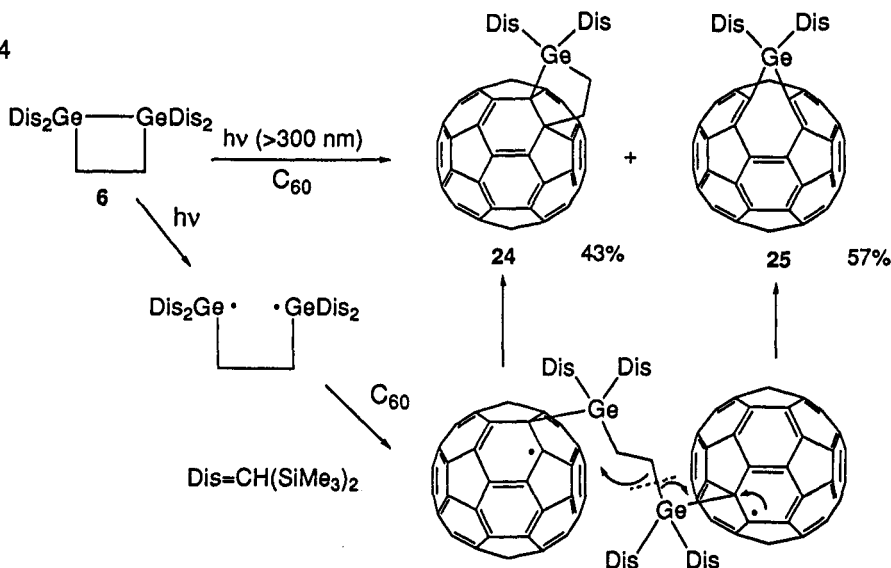
On the basis of this result one might expect, that the conversion of bis(alkylidene)disilacyclobutanes (**21**) should yield the corresponding C₆₀ annulated disilacyclohexane derivatives **22**.¹⁰ Instead adduct **23** resulting from an unexpected rearrangement of the disilacyclobutane moiety is obtained (Scheme 3). Again, triplet excited C₆₀ seems to be involved, since the presence of rubrene inhibits the reaction, and the disilacyclobutane **21** is stable under the reaction conditions. Alternatively, initially formed **22** might be photo labile and rearrange to **23**.

Scheme 3



Photolysis of a solution of 1,2-digermacyclobutane **6** and C₆₀ gave two fullerene adducts in almost equivalent amounts, i.e. **24** and **25** in 43 and 57% yield. Their structures are quite unique and probably formed by stepwise radical reaction. A plausible mechanism is depicted in Scheme 4.⁶

Scheme 4



DILITHIO 1,2-DISILAACENAPHTHENE AND DILITHIO 9,10-DISILAANTHRACENE

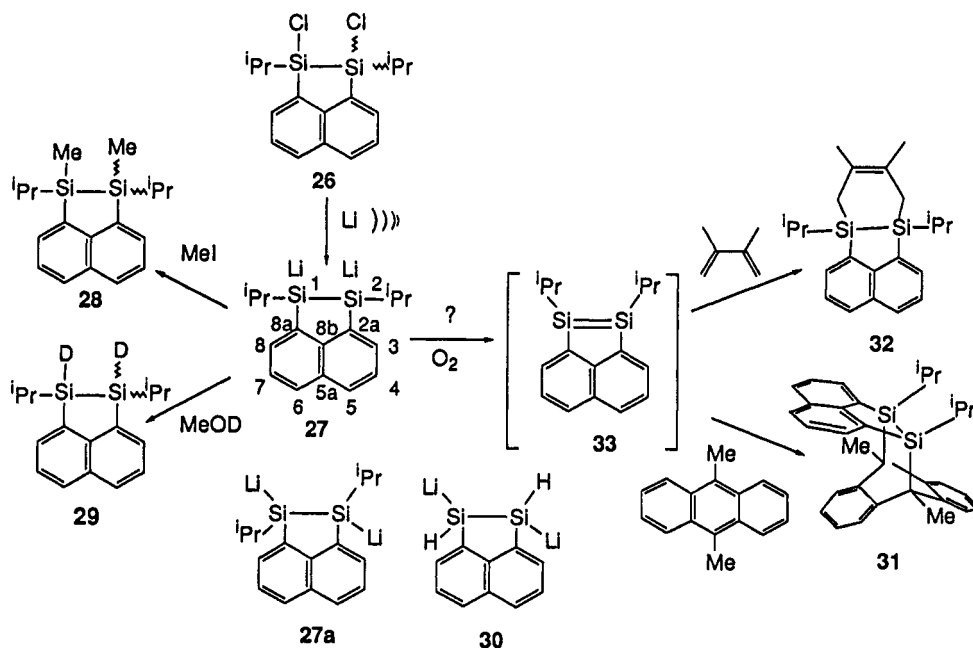
The reactivity, structure and properties of organolithium compounds have attracted much interest over the last years.¹¹⁻¹³ In this connection, studies about 1,2-dilithio-1,2-disilaacenaphthene (**27**) and 9,10-dilithio-9,10-disilaanthracene (**36**) were carried out.

Dilithio disilaacenaphthene **27** (half lifetime in THF at 30°C: 13.5h) was generated by sonicating a mixture of dichlorodisilane **26** and excess lithium in THF. As expected, addition of CH₃I and CH₃OD afforded the dimethyl- and dideuterio-trapping products **28** and **29** (Scheme 5).¹⁴ Compared to the

corresponding disilanes **26**, **28** and **29**, the ^1H -NMR resonances of the aromatic protons of **27** are shifted upfield about 0.85–1.55ppm, which is attributed to the presence of a negative charge on the silicon atoms. The ^{13}C resonance of the C-2a and C-8a ipso carbon of **27** is shifted drastically to lower field, while the C-5, C-6 carbon resonance moves slightly upfield; polarization of the aromatic rings resulting in decreased electron density at the ipso carbon seems to be respective for this behavior. The ^{29}Si NMR chemical shift of **27** was observed at 4.32 ppm, a large downfield shift compared to other silyl anions. In the ^7Li NMR spectrum of **27**, a broad signal was also observed at 5.95 ppm. The experimental finding for **27** was confirmed by the theoretical calculations at the HF/3-21G* level.¹⁵

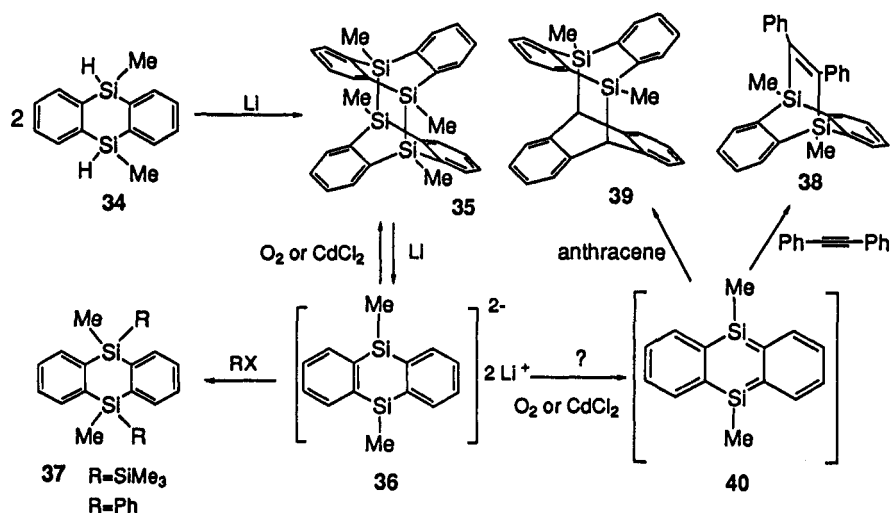
30, in the several dilithium 1,2-dihydro-1,2-disilaacenaphthendiides corresponding to energy minima, is the most stable. The good correlation between the relative charge densities based on the natural population analysis of **30** and $\Delta\delta^{27}\text{Si}(\text{SiLi}-\text{SiCl})$ and $\Delta\delta^{13}\text{C}(\text{SiLi}-\text{SiCl})$ in **27** reveals that **27a** might be considered. The spectral analysis and theoretical investigation support that the structure **27a** best represents the structure for dilithium 1,2-disilaacenaphthendiide **27**. When **27** was oxidized by molecular oxygen in the presence of 9,10-dimethylantracene, adduct **31** was obtained. Repeating this experiment with 2,3-dimethyl-2,3-butadiene as trapping reagents afforded adduct **32**. Most likely, these adducts are formed by [4+2] cycloaddition with disilene **33**, which is formed by oxidation of **27**.

Scheme 5



Similarly, when disilaanthracene dimer **35**, easily accessible from 9,10-dimethyl-9,10-disilaanthracene (**34**), was treated with excess lithium in THF, dilithio-9,10-dimethyl-9,10-disilaanthracene (**36**) was formed.¹⁶ Trapping with trimethylchlorosilane or bromobenzene yielded the corresponding 9,10-disubstituted 9,10-dimethyl-9,10-disilaanthracenes **37**. Oxidation of **36** in THF with molecular oxygen or CdCl_2 afforded dimer **35** in quantitative yield; interestingly no oxygen containing products were detected. When the oxidation of **36** was performed in the presence of toluene, adduct **38** was formed; similarly, **39** was obtained when anthracene was employed as trapping reagent. These results indicate that 9,10-disilaanthracene **40** is formed as intermediate (Scheme 6).

Scheme 6



ACKNOWLEDGMENT

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