Organometallics 1992, 11, 2494–2499

Silaheterocycles. 15.[1] Cycloaddition Behavior of 1,1-Dichloro-2-neopentyl-2-(trimethylsilyl)silene

Wolfgang Ziche, Norbert Auner,* and Joachim Behm

Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstrasse 4, D-8046 Garching, Germany

Received September 11, 1991

1,1-Dichloro-2-neopentyl-2-(trimethylsilyl)silene was prepared in situ and reacted with trapping reagents. The types of cycloaddition products with dienes give evidence regarding the electronic and steric properties of the silene whereas the reactivity of the cycloadducts suggests the intermediacy of zwitterionic or diradical species. The solid-state structure of the anthracene adduct ($C_{23}H_{30}Cl_2Si_2$) has been determined by single-crystal X-ray diffractometry. 7 is monoclinic, space group C/c, a = 11.356 (3) Å, b = 15.083 (1) Å, c = 13.387 (2) Å, Z = 4.

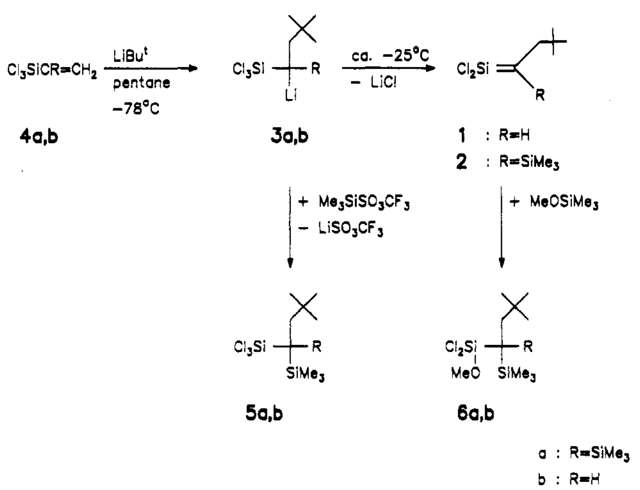
Introduction

The reactivity of dichloroneopentylsilene (1) has been studied intensively.[1-3] Its tendency to preferentially form [2 + 2] as well as [4 + 2] cycloadducts in the presence of dienes—even with some of low reactivity—has aroused interest concerning its electronic structure. In order to enlarge the experimental basis needed for discussion of its extraordinary behavior we have carried out a series of cycloaddition reactions with 1,1-dichloro-2-neopentyl-2-(trimethylsilyl)silene (2).

The additional trimethylsilyl group was expected to have two effects: (1) The steric influence of the bulky substituent should prohibit the formation of some of the possible stereo- and regioisomers. The stability and thus the lifetime of the resulting silene 2 is expected to be greater than in the case of 1. (2) The polarity of the silene will be changed in comparison to 1. Which of the known effects (inductive, hyperconjugative[4]) of changing substituents will be most effective cannot be predicted. Theoretical work shows a silyl substituent at the carbon in silene ($H(SiH_3)C{=}SiH_2$) to lengthen the Si=C bond and to slightly increase its polarity in comparison to the parent $H_2C{=}SiH_2$.[4] The most significant effect is the decrease in LUMO energy of 2 as compared to 1. We expect that this leads to prefered formation of [4 + 2] cycloadducts—1 reacts predominantly in [2 + 2] cycloadditions with dienes.

Neopentylsilenes are formed in the reaction of chloro(vinyl)silanes with *tert*-butyllithium in nonpolar solvents. The first step is the addition of *t*-BuLi to the vinyl group. How easily the α-lithiated species 3 is formed is determined by the neighboring silicon substituents which stabilize carbanions in the α-position. The magnitude of this silicon α-effect is dictated by the nature of these groups. In the case of 3a the trimethylsilyl group should exert an additional stabilization effect.[5] The addition of the organolithium reagent is followed by intramolecular LiCl elimination to form the silenes. These will readily participate in cycloaddition reactions with dienes[3,6-9] (Scheme I).

Scheme I



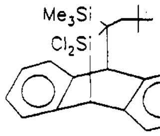
Results

Trapping of the α-lithiated species 3 and the silene is performed as shown in Scheme I.

Compound 3 may be intercepted by adding trimethylsilyl triflate to a mixture of 4a/Li-*t*-Bu that has been allowed to react for 2 h at −78 °C. The corresponding trapping product 5a is, however, only formed in less than 1% yield and can only be identified by GC–MS. This result indicates a short lifetime for 3 when R = $SiMe_3$. If R = H (reaction of trichlorovinylsilane 4b and Li-*t*-Bu), then the desired product 5b is obtained almost quantitatively.[10]

When *tert*-butyllithium is added to 4a at −78 °C and the mixture is allowed to warm to −25 °C before adding the efficient silene trap methoxytrimethylsilane, the intermediate silene 2 is transformed into the product 6a in 100% yield. In the case of 1 the reaction temperature must be higher (−15 °C) and the overall yield of 6b is lower (80%).[1]

Cycloaddition Reactions with Anthracene, Pentamethylcyclopentadiene (C_5Me_5H), and Cyclohexa-1,3-diene. 2 reacts with anthracene in toluene at 60 °C to form the crystalline [4 + 2] cycloadduct 7 exclusively.



7

---

(1) Part 14: Auner, N.; Seidenschwarz, C.; Sewald, N. *Organometallics* 1992, *11*, 1137.

(2) Auner, N. *J. Organomet. Chem.* 1988, *353*, 275.

(3) Auner, N.; Seidenschwarz, C.; Herdtweck, E.; Sewald, N. *Angew. Chem.* 1991, *103*, 425; *Angew. Chem., Int. Ed. Engl.* 1991, *30*, 444.

(4) Apeloig, Y. Theoretical aspects of organosilicon compounds. In *The chemistry of organic silicon compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, England, 1989.

(5) Brook, M. A.; Dallaire, C. *Organometallics* 1990, *9*, 2873.

(6) Jones, P. R.; Lim, T. F. O. *J. Am. Chem. Soc.* 1977, *99*, 2013.

(7) Jones, P. R.; Lim, T. F. O. *J. Am. Chem. Soc.* 1977, *99*, 8447.

(8) Jones, P. R.; Lim, T. F. O.; Pierce, R. A. *J. Am. Chem. Soc.* 1980, *102*, 4970.

(9) Jones, P. R.; Bates, T. F. *J. Am. Chem. Soc.* 1987, *109*, 913.

(10) Auner, N.; Wolff, A. To be published.

0276-7333/92/2311-2494$03.00/0

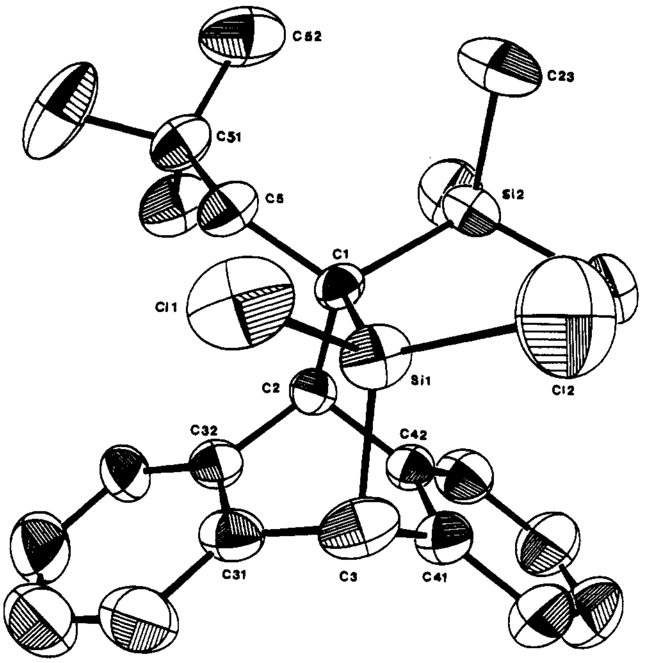
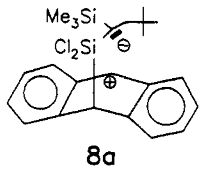
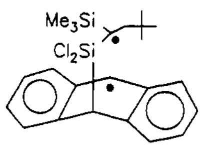


Figure 1.

In contrast to the corresponding product formed by the reaction of 1 with anthracene, 7 decomposes during GC analysis (the all-glass split injector appears to act as micro reaction vessel; see Experimental Section). We attribute this to electronic factors that determine the thermal stability of 7 and propose the formation of a zwitterionic intermediate **8a** or a diradical **8b** as the first step to decomposition. Intermediates of the type **8a** are also discussed in rearrangements of [2 + 2] cycloadducts (synthesized from dichloroneopentylsilene 1 and dienes) during thermolysis.[1,3]

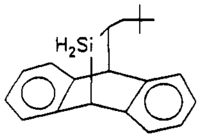


8a



8b

The anion of the above mentioned intermediate **8a** is stabilized by two silyl substituents in the α-position. The charge of the cation is delocalized by the two annelated benzo rings. Analogous reasoning holds for **8b**. In the current case the zwitterion **8a** cannot be trapped or its formation influenced by change of solvent, nor is there any evidence for the retro Diels Alder reaction as the then newly formed silene 2 cannot be intercepted in any way by the addition of trapping reagents (methoxytrimethylsilane, dienes). Another factor to be considered is the steric strain of the molecule. This can be proved by comparing the X-ray structural data of 7 (Figure 1) with compound **9** (synthesis;[2] X-ray structure[11a]). There is not much change in bond lengths or intrabond angles, which vary by 3.6% and 3.8%, respectively.[11b] The most marked changes are observed for the bond angles Si1–C1–C5



9

Table I. Summary of Crystal Data and Details of Intensity Collection for Compound 7

formula	$C_{23}H_{30}Cl_2Si_2$
fw	433.6
cryst syst	monoclinic
space group	C/c (IT No. 9)
conditions	hkl ($h + k = 2n$), $h0l$ ($l = 2n$)
cryst habit	irregular shape
temp, K	296
a, pm	1135.6 (3)
b, pm	1508.3 (1)
c, pm	1338.7 (2)
β, deg	92.31 (1)
V, pm^3	2291 × 10^6
Z	4
d_{calc}, g cm^{-3}	1.257
μ (Cu Kα), cm^{-1}	36.5
scan type	$\theta/2\theta$
scan time, s	max 60
scan width, deg	1.20 + 0.25 tan θ
θ_{max}, deg/octants	65/$\pm h$,$+k$,$\pm l$
background	25% additional scan at each end of scan
corrns	LP
no. of rflns collcd	4049
no. of unique data	3826
no. of rflns included (NV)	3816; $I > 0.0\sigma(I)$
no. of variables (NO)	243
no. of std rflns	3/h for intensity 3 for orientation every 200 reflectns
data:variable ratio	15.7
R^a	0.046
R_w^b	0.045
goodness of fit,^{c} p =	4.26/0.00
enantiomorph	
R^a	0.055
R_w	0.057
GOF	5.55
weighting scheme, w	$1/\sigma^2(F_o)$
largest shift/err	<0.01
max/min, e Å^{-3}	+0.31/−0.29

$^a R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ $^c \mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$.

Table II. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B, Å^2
Cl1	−0.046	0.64874 (6)	1.114	5.94 (2)
Cl2	0.1764 (1)	0.56896 (7)	1.0090 (1)	8.92 (3)
Si1	0.05442 (9)	0.66611 (5)	0.99131 (7)	3.63 (2)
Si2	0.28283 (9)	0.77894 (6)	0.96727 (7)	4.02 (2)
C1	0.1122 (3)	0.7829 (2)	0.9743 (2)	2.78 (6)
C2	0.0504 (3)	0.8118 (2)	0.8698 (2)	2.77 (5)
C3	−0.0385 (3)	0.6476 (2)	0.8752 (2)	4.12 (7)
C5	0.0640 (3)	0.8394 (2)	1.0640 (2)	3.59 (6)
C21	0.3442 (3)	0.6962 (3)	0.8799 (3)	6.3 (1)
C22	0.3431 (3)	0.8861 (3)	0.9180 (3)	6.5
C23	0.3446 (4)	0.7527 (3)	1.0959 (3)	6.6 (1)
C31	−0.1281 (3)	0.7216 (2)	0.8742 (2)	3.66 (7)
C32	−0.0830 (3)	0.8057 (2)	0.8702 92)	3.24 (6)
C33	−0.3216 (3)	0.7794 (3)	0.8627 (3)	7.1 (1)
C34	−0.2794 (3)	0.8626 (3)	0.8550 (3)	6.5 (1)
C35	−0.1581 (3)	0.8768 (2)	0.8588 (2)	4.71 (8)
C36	−0.2495 (3)	0.7085 (3)	0.8726 (3)	5.53 (9)
C41	0.0446 (3)	0.6646 (2)	0.7909 (2)	3.65 (7)
C42	0.0874 (2)	0.7507 (2)	0.7871 (2)	2.88 (6)
C43	0.1569 (3)	0.7757 (2)	0.7093 (2)	4.25 (7)
C44	0.1866 (3)	0.7158 (3)	0.6366 (3)	5.62 (9)
C45	0.1479 (4)	0.6311 (3)	0.6431 (3)	6.6 (1)
C46	0.0761 (3)	0.6034 (2)	0.7194 (3)	5.44 (9)
C51	0.0908 (3)	0.9375 (2)	1.0886 (2)	4.21 (7)
C52	0.2122 (4)	0.9511 (2)	1.1413 (3)	6.6 (1)
C53	0.0784 (4)	1.0000 (2)	0.9997 (3)	5.78 (9)
C54	−0.0031 (4)	0.9637 (3)	1.1631 (3)	7.8 (1)

---

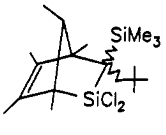
[11] (a) Auner, N.; Henkel, G. Unpublished Results. (b) Further data for comparison is available from similar compounds: the corresponding values for the [4 + 2] cycloadducts of 1/naphthalene[22] and $Ph_2Si{=}CHCH_2$-t-Bu/cyclohexadiene[13] show that there is little deviation in the bond lengths and angles in the bicyclic systems.

Table III. Selected Bond Lengths (pm) and Angles (deg) in 7 and 9

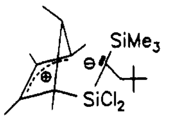
bond lengths			bond angles		
	7	9		7	9
Si–C1	189.6 (2)	190.8 (3)	C1–Si1–C3	103.14 (7)	99.9 (1)
Si1–C3	186.4 (2)	190.2 (3)	C2–C1–Si1	102.67 (9)	106.3 (2)
C1–C2	160.4 (2)	157.2 (3)	Si1–C1–C5	105.95 (11)	117.1 (2)
C1–C5	158.4 (2)	153.2 (4)	C32–C2–C42	105.56 (13)	108.7 (2)
C1–Si2	194.3 (2)		C31–C3–C41	107.60 (14)	109.6 (2)
C31–C32	137.0 (2)	139.9 (3)	Si1–C1–Si2	109.18 (8)	
C41–C42	138.6 (2)	140.8 (3)	C5–C1–Si2	115.36 (11)	
			C11–Si1–C12	102.50 (4)	
			H1–Si1–H2		110 (1)

(106.0° vs 117.1° for 9) and Cl1–Si1–Cl2 (102.5° compared to 110° for H1–Si1–H2). Important values comparing 7 and 9 are listed in Table III.

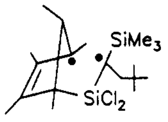
The [4 + 2] cycloadducts 10 obtained by reaction of 2 with C_5Me_5H as a viscous liquid show an exo/endo ratio of 6/1 as determined by NMR spectroscopy. The ratio of isomers of 10 will change in the gas phase but does not show overall decomposition. A ratio of exo/endo isomers is observed by gas chromatography that is significantly higher than that determined by NMR spectroscopy (3.4/1 vs 6/1). Again, we propose a zwitterionic intermediate **11a** or a diradical **11b** that is also too short-lived for trapping reactions to occur.



10



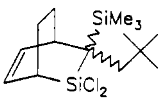
11a



11b

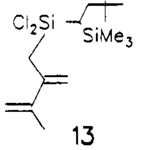
In contrast to the analogous compound formed by $1/C_5Me_5H^2$ 10 cannot be stored indefinitely at ambient temperatures because it slowly deteriorates to a dark resin, a fact that confirms the formation of an open-chain intermediate. In this case it is probably the steric strain of the molecule that leads to this behavior. We deduced this from the X-ray structure of the cycloadduct $1/C_5Me_5H$,[12] which clearly shows the strain imposed on the molecule by the five methyl groups and the neopentyl group.

The cycloadducts 12 obtained by the [4 + 2] reaction of 2 with the sterically much less demanding cyclohexa-1,3-diene are stable. The exo/endo ratio of isomers was determined as 3/4 by GC as well as by NMR spectral data. This is in accordance with the ratio obtained by the reaction of cyclohexadiene with dichloroneopentylsilene (1)[1,3] (37/63).

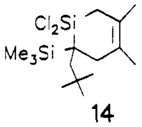


12

Cycloaddition Reactions with 2,3-Dimethylbutadiene and Butadiene. Changing the geometry from the fixed s-cis conformation of cyclohexadiene and the substitution pattern of the diene leads to different reaction pathways. When using 2,3-dimethylbutadiene to trap 2, the main product is 13, which is formed by an ene reaction. A small amount (15%) of the [4 + 2] cycloadduct 14 is also observed.



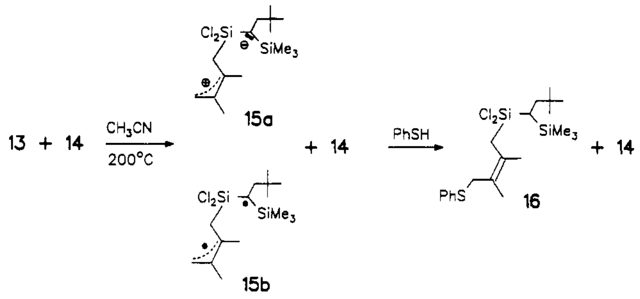
13



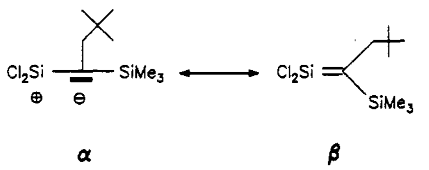
14

NMR spectral data as well as GC data, the latter obtained from a solution of 13/14 in hexane, show a ratio of products 13/14 = 85/15. However, if acetone or acetonitrile is used as solvent for gas chromatography, the ratio is determined as 73/27 or even 9/91. We believe that is the result of a solvent-aided partial retro-ene reaction that forms a zwitterionic intermediate **15a** or a diradical **15b** which then polymerizes. Apparently, the collapse of 15 to yield a [4 + 2] cycloadduct does not occur. An approximate quantitation shows that the amount of 14 does not increase (Scheme II). We assume that the solvent assists not only in the hydrogen transfer but also in the stabilization of 15. Polar retro-ene and radical reactions may not be ruled out because they would also be affected by a change in solvent properties.[14a] An efficient trap for zwitterions is thiophenol.[14b] Adding this to a mixture of 13/14 in acetonitrile gives a novel major product in the gas chromatogram. By GC–MS this compound is identified as the desired trapping product 16. It can also be obtained in preparative amounts by storing 13/14 in a 2/1 mixture of acetonitrile/thiophenol in a sealed tube for 2 months, a treatment that also results in the disappearance

Scheme II



Scheme III



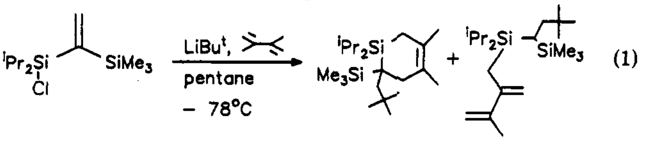
---

(12) Auner, N.; Ziche, W.; Müller, G. To be published.

(13) Auner, N.; Ziche, W.; Herdtweck, E. *J. Organomet. Chem.* **1992**, *426*, 1.

(14) (a) Sauer, J.; Sustmann, R. *Angew. Chem.* **1980**, *92*, 773; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779. (b) Kataoka, F.; Shimizu, N.; Nishida, S. *J. Am. Chem. Soc.* **1980**, *102*, 711. (c) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209.

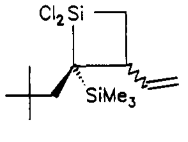
of the [4 + 2] cycloadduct **14**. No such behavior was observed for the mixture of adducts (**18** and **19** prepared from **17**) when isopropyl groups replace the chlorine atoms at silicon (eq 1). Analogous trapping reactions with thiophenol have been carried out for the compounds **7** and **10**, but no evidence for the postulated structures **8a** or **11a** could be obtained.[30] These findings lead us to assume zwitterions (or at least strongly polar species) as intermediates when discussing the reactivity of cycloadducts obtained from dichloroneopentylsilenes. The formation of [4 + 2] products from **2** with 2,3-dimethylbutadiene suggests that its electron density is higher than **1**, which forms [2 + 2] cycloadducts with all butadienes.[15] These results are due to the diminished $LUMO_{dienophile}-HOMO_{diene}$ gap—consequently, allowed "concerted" (not synchronous[14c]) reactions are more probable.[14a]



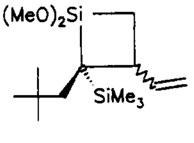
(1)

17 18 19

Butadiene possesses a lower electron density in the diene system than 2,3-dimethylbutadiene; i.e. its donor ability is much lower. Using it as a trapping reagent for **2** results in lower yields of cycloadducts and the sole formation of the [2 + 2] products **20** (cis/trans = 50/50). The products are quite stable: no decomposition occurs when **20** is heated to 200 °C for 5 days in a sealed tube, a fact that is attributable to the low steric demand of the diene moiety.



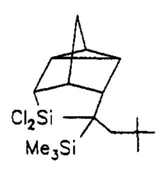
20



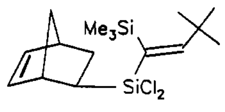
21

It is shown by ^{29}Si satellites in ^{13}C NMR spectroscopy of the dimethoxy derivative **21** (synthesized from **20** with methanol/triethylamine) that the two isomers synthesized are stereoisomers and not regioisomers. As calculations show, polarity plays a more important role than the energies of the frontier orbitals in controlling the reactivity of silenes.[16] We propose a mode of addition in which butadiene is attacked by the electrophilic silicon at the terminal carbon C1 to give a transition state in which rotation of the butadiene's central C2–C3 bond is still possible. Although unsymmetrical transition states in silene reactions have been calculated, transition states for cycloadditions with dienes have unfortunately not yet been calculated.[17] 2-Methylbutadiene shows intermediate behavior and yields a complicated mixture of products when reacted with **2**. ^{13}C NMR spectroscopy shows the presence of terminal $=CH_2$ groups and suggests that [2 + 2] as well as [4 + 2] and/or ene products are formed. This is consistent with predictions of increasing formation of [2 + 2] adducts in polar cycloaddition reactions of carbon systems when the donor ability of the diene decreases.[18] This, however, implies that the relative energies of the frontier orbitals also play a dominant role; the sole consideration of the silene polarity does not suffice to describe the cycloaddition reactions in this case.

Cycloaddition Reactions with Norbornadiene, Quadricyclane, and Norbornene. **1** yields two [2 + 2 + 2] cycloadducts, two [2 + 2] cycloadducts and one exocyclic component (ene product) in about equal amounts in the reaction with the nonconjugated diene norbornadiene. Just one [2 + 2 + 2] cycloadduct **22** (along with minor amounts of ene product **23**) is formed in the reaction of **2** with norbornadiene. Characteristic spectroscopic features are the cyclopropane ring in **22** (three resonances in the ^{13}C NMR spectrum at 12–14 ppm) and the exocyclic double bond in **23** (a quaternary ^{13}C resonance at 177 ppm, and a singlet in the proton NMR spectrum at 6.83 ppm). The stereochemistry at this double bond is not known.

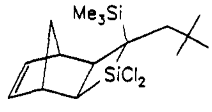


22



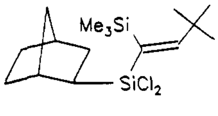
23

Formally, analogous to a [2 + 2] cycloadduct of **2**/norbornadiene is the compound obtained by trapping **2** with quadricyclane. This reaction does not proceed as cleanly and it was not possible to isolate a pure compound, but **24** constitutes the bulk of the product (80%), as determined by NMR spectroscopy.



24

The reactions of **2** with dienes show that ene reactions occur, and thus an attempt was made to intercept **2** with alkenes. Unstrained olefins, such as cyclohexene, do not react, but norbornene does intercept **2** to produce **25**, as well as a small amount of an unidentified compound.



25

Reaction of 2 without Trapping Reagents. Normally, silenes undergo head-to-tail dimerization in the absence of dienes or other traps. Generating silenes from vinylchlorosilanes gives a larger scope of possible reactions, as a lithiated intermediate is involved. The examination of the reaction of **1**/*t*-BuLi revealed a multitude of com-

---

(15) Wolff, A. Dissertation, TU München, 1991.

(16) Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* **1984**, *106*, 6676.

(17) Gordon, M. S.; Truong, T. N. *Chem. Phys. Lett.* **1987**, *142*, 110.

(18) Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361.

(19) Auner, N. *Z. Anorg. Allg. Chem.* **1988**, *558*, 55.

(20) Auner, N.; Gleixner, R. *J. Organomet. Chem.* **1990**, *393*, 33.

(21) Ziche, W. Dissertation, TU München, 1992.

(22) Auner, N.; Seidenschwarz, C.; Herdtweck, E. *Angew. Chem.* **1991**, *103*, 1172; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1151.

(23) Smith, C. D. *J. Am. Chem. Soc.* **1966**, *88*, 4273.

(24) Kaupp, G.; Prinzbach, H. *Chem. Ber.* **1971**, *104*, 182.

(25) This discussion is based on experimental facts only. We plan to do calculations so that the significant effects may be quantitatively named. We thank Prof. Y. Apeloig for helpful discussions.

(26) Boeckmann, R. K.; Blum, D. M.; Ganem, B.; Halvey, N.; Baker, W. R.; Coates, R. M. *Org. Synth.* **1978**, *58*, 152.

(27) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2 B.

(28) Cromer, D. T.; *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(29) Schmidt, R. E.; Birkhahn, M.; Massa, W.; Kiprof, P.; Herdtweck, E. STRUX-III, ein Programmsystem zur Verarbeitung von Röntgendaten, Universität Marburg (1980), and TU München (1985–1989), Germany.

(30) In response to a reviewers suggestion to trap the biradicals **8b**/**11b** with n-Bu_3SnH, we only found minor amounts of reduced compounds in GC analysis.

pounds, amongst which the disilacyclobutane was only present in small amounts.[19] Because silenes are stabilized by Lewis bases, the yield of the disilacyclobutane can be enhanced dramatically by adding triethylamine to the reaction mixture.[20]

2 does not yield the expected dimer when generated at low temperatures either with or without the addition of triethylamine. GC–MS data suggest that the product mixture contains only catenated compounds. Steric factors probably do not play a role in this case because disilacyclobutanes are formed from neopentylsilenes with much larger substituents.[21]

Discussion

1,1-Dichloro-2-neopentyl-2-(trimethylsilyl)silene (**2**) is considered to take an intermediate position between 1,1-dichloro-2-neopentylsilene (**1**) and diorganoneopentylsilenes (R = Me, Ph) as far as polarity is concerned. **1** is more electron deficient than **2** and reacts with substrates that do not react with **2**, such as naphthalene[3] and acetylenes.[22] However, **2** does react in a [2 + 2 + 2] reaction with quadricyclane, which is not possible with diorganoneopentylsilenes.[8,13] Known [2 + 2 + 2] reactions of quadricyclane proceed only with dienophiles of low electron density,[23,24] e.g. dicyanoethene. **2** needs butadienes of lesser donor ability to form [2 + 2] cycloadducts than does **1** and forms no [2 + 2] cycloadducts with norbornadiene, a fact that shows the comparably lower LUMO energy of **2**. When the electron density in the diene is high enough, **2** prefers to react in a "concerted and allowed" fashion.[25]

We therefore conclude that **2** is a rather electron deficient silene having a polarity more comparable to that of **1**. The electron deficiency is caused mainly by the two chloro atoms at silicon, while the LUMO energy in comparison to **1** is lowered by the influence of the trimethylsilyl group at carbon. Work that will provide further proof of such influences is currently in progress.[25]

Experimental Section

All reactions were carried out with exclusion of moisture and oxygen. Solvents were dried by usual methods. Dienes and trapping reagents were used as purchased; chlorosilanes were distilled from K_2CO_3 prior to use.

Gas chromatography was carried out with a Chrompack CP 9000 chromatograph with a 10-m Chrompack CP Sil 5 CB resin; an all-glass splitter (200 °C, split ratio 1/30) was used as injector system. GC–MS analysis was carried out with a Chrompack CP 9000 system coupled with a Finnigan MAT ion trap 800 spectrometer. Chemical ionization (CI) used methanol as reactant gas. NMR spectra were recorded on JEOL JNM GX270 (^{1}H,^{29}Si) and Bruker WP100SY (^{13}C and ^{13}C-DEPT) instruments. $CDCl_3$ was used as internal standard. Assignment of the ^{13}C NMR spectral data of some cycloadducts was accomplished by comparison with compounds obtained from **1** which had been studied by 2D NMR spectroscopy (**10** see ref 2; **12** see ref 3; **13**, **14**, and **18**–**21** see refs 1 and 15). Mass spectra were obtained with Finnigan MAT 311A instrument.

X-ray Structure Determination. The X-ray measurement was made on an Enraf-Nonius CAD-4 diffractometer (graphite monochromator). Crystal data and details of measurement are summarized in Table I. The structure was solved by using direct methods followed by difference Fourier syntheses and subsequent least-squares refinement. The analysis was based on scattering factors for neutral atoms taken from ref 27. Anomalous dispersion was considered.[28] For all calculations the SDP program package was used.[29] All atoms but the hydrogens were refined anisotropically. The positions of the hydrogen atoms were calculated.

Synthesis of 1-(Trichlorosilyl)-1-(trimethylsilyl)ethene (4a). A 50-g (0.28-mol) sample of 1-bromo-1-(trimethylsilyl)ethene was used to form the Grignard reagent in 500 mL of THF.[26] This was added to 84.0 g (0.5 mol, 56.5 mL) of pure $SiCl_4$ and the resulting mixture refluxed for 3 h. After cooling, excess $SiCl_4$ and most of the THF were removed by distillation. The remaining slurry was extracted with three 200-mL portions of pentane. This solution was then distilled, the product boiling at 110 °C/130 mbar. The yield was 37.0 g (57%) of a colorless liquid. ^{1}H NMR: δ 0.48 (s, 9 H), 6.17, 6.71 (AB, ^{2}J = 4.8 Hz, 1 H each). ^{13}C NMR: δ −0.49 (SiMe$_3$, $^{1}J(^{13}C,^{29}Si)$ = 53.6, $^{3}J(^{13}C,^{29}Si)$ = 8.4 Hz), 147.50 ($C{=}CH_2$), 147.91 ($C{=}\mathit{C}H_2$). ^{29}Si NMR: δ −0.94 (SiCl$_3$), −2.07 (SiMe$_3$). MS: *m/e* 232 (M$^+$, 0%), 217 (45), 199 (12), 183 (10), 103 (41), 73 (100). Anal. Found/Calcd for $C_5H_{11}Cl_3Si_2$ (233.67): C, 25.98/25.70; H, 4.81/4.75.

Synthesis of 1-(Chlorodiisopropylsilyl)-1-(trimethylsilyl)ethene (17). The same procedure as above was applied. A 20.0-mmol amount of the above mentioned Grignard reagent and *i*-Pr$_2$SiCl$_2$ instead of $SiCl_4$ were used, and a catalytic amount of cuprous cyanide (0.5 g of CuCN) was added. The yield was 1.74 g (35%) of a colorless liquid boiling at 40 °C/10^{-2} mbar. It was contaminated by an unknown byproduct (<5%). ^{1}H NMR: δ 0.33 (s, 9 H), 1.00–1.25 (m, 14 H), 6.21, 6.79 (AB, ^{2}J = 15.4 Hz, 2 H). ^{13}C NMR: δ 0.0 (SiMe$_3$), 12.3, 13.3 (CH), 18.5, 18.8, 18.9, 19.8 (CH$_3$), 128.4 (C), 143.6 (CH$_2$). MS: *m/e* 248 (M$^+$, 0), 233 (100), 205 (61), 177 (48), 163 (83).

Trapping Reaction of 2 and 3. A solution of 2.32 g (10.0 mmol) of **4a** in 50 mL of pentane was cooled to −78 °C (CO$_2$/ethanol). A 5.9-mL aliquot of 1.7 M Li-*t*-Bu/pentane (10.0 mmol) was added dropwise. The clear reaction mixture was stirred at −78 °C for 2 h. Then 6.41 g (10.0 mmol, 5.6 mL) of trimethylsilyl triflate was added slowly. The mixture was allowed to warm up and the solution subjected to GC and GC–MS analysis.

The same procedure was followed for the trapping reaction of **2**, just that methoxytrimethylsilane was added at −25 °C. The clear solution immediately precipitated a colorless solid. After warming, the solid was removed by filtration and pentane was distilled. **6a** was obtained 100%, and distillation was not necessary. ^{1}H NMR: δ 0.35 (s, 18 H), 1.11 (s, 9 H), 2.08 (s, br, 2 H), 3.64 (s, 3 H). ^{13}C NMR: δ 3.25 (SiMe$_3$), 15.78 (Me$_3$Si–*C*–SiMe$_3$), 31.38 ($C(\mathit{C}H_3)_3$), 33.18 ($\mathit{C}(CH_3)_3$), 43.49 (CH$_2$), 50.08 (O–CH$_3$). MS (CI): *m/e* 358 (M$^+$, 0%), 343 (100), 323 (24), 213 (26), 193 (54), 105 (33). Anal. Found/Calcd for $C_{13}H_{32}Cl_2Si_3O$ (359.56): C, 43.21/43.43; H, 8.50/8.97.

General Procedure for Cycloadditions of 2. A 4.64-g (20.0-mmol) amount of **4a** and 3–10-fold excess of diene/ene were dissolved in 150 mL of pentane (exception: anthracene in toluene) and cooled to −78 °C (exception: anthracene in toluene, +60 °C). Then 11.8 mL of 1.7 M Li-*t*-Bu/pentane (20.0 mmol) were added dropwise. The reaction mixture was allowed to warm up (cool down). The solution was freed from precipitated LiCl by filtration. The solvent and excess diene were removed at ambient temperature and 10^{-2} mbar (anthracene was sublimed at +80 °C). The residue was distilled at 10^{-2} mbar (**5** was recrystallized from pentane). Only products containing no contamination by unknown substances as determined by GC and NMR spectroscopy were submitted to elemental analysis.

7: colorless solid; mp 165 °C; 1.94 g (45%); <4% anthracene. ^{1}H NMR: δ 0.28 (s, 9 H), 1.07 (s, 9 H), 1.55, 1.75 (AB, ^{2}J = 15.62 Hz, each 1 H), 3.85 (s, 1 H), 4.78 (s, 1 H), 6.85–7.08 (m, 8 H). ^{13}C NMR: δ 1.1 (SiMe$_3$), 26.2 (Si–C–Si), 33.0 ($C(\mathit{C}H_3)_3$), 34.5 ($\mathit{C}(CH_3)_3$), 48.1 (CH$_2$), 45.2, 52.6 (CH), 138.2, 139.3, 140.5, 141.8 (C), 125.8, 126.8, 126.9, 127.1, 127.4, 127.8 (CH). ^{29}Si NMR: δ 19.9 (SiCl$_2$), 3.35 (SiMe$_3$). MS: *m/e* 432 (M$^+$, 2.3), 375 (23.2), 324 (13.9), 268 (31.6), 197 (47.9), 178 (100), 73 (52.2).

10: slightly yellow viscous solid; bp 75 °C/10^{-2} mbar; 2.89 g (37%). ^{1}H NMR: δ 0.19, 0.25 (s), 0.39 (s, br), 0.71, 0.73, 0.95, 0.97 (s, br), 1.12, 1.14 (s, ratio of integrals 6/1), 1.20 (s, br), 1.62 (d, *J* = 1.5 Hz), 1.64 (d, *J* = 1.5 Hz), 1.81, 1.92 (AB, *J* = 15.0 Hz), 2.42 (q, *J* = 3.5 Hz), 0.9–1.2 (m). ^{13}C NMR: δ 6.0 (SiMe$_3$), 7.8, 9.7, 12.2, 14.3, 17.2 (CH$_3$), 31.7 (Si—C—Si), 33.1 ($C(\mathit{C}H_3)_3$), 33.3 ($\mathit{C}(CH_3)_3$), 44.4 (C), 61.7 (C—SiCl$_2$), 47.5 (CH$_2$), 52.3 (CH), 134.6, 138.0 (C=C). ^{29}Si NMR: δ 29.2 (SiCl$_2$), 2.03 (SiMe$_3$). MS (CI): *m/e* 391 (M$^+$ + 1, 50), 355 (100), 375 (18), 283 (13), 254 (14), 136 (37), 105 (40).

12: colorless viscous liquid; bp 80 °C/10^{-2} mbar; 3.61 g (54%). ^{1}H NMR: δ 0.17, 0.25 (s, integrals 1/1, 9 H), 1.00, 1.05 (s, integrals 1/1, 1 H), 1.3–2.4, 2.8, 3.1, 3.3 (m, 6 H), 5.4–6.4 (m, 2 H). ^{13}C NMR: δ 0.3, 2.0 (SiMe$_3$), 18.1, 20.3, 22.2, 23.0 (CH$_2$—CH$_2$), 33.1, 34.4 (Si—C—Si), 31.3, 31.5 ($C(\mathit{C}H_3)_3$), 40.1, 42.8 ($\mathit{C}(CH_3)_3$), 32.6, 35.5, 35.8, 37.3 (CH), 44.2, 45.1 ($\mathit{C}H_2$—$C(CH_3)_3$), 126.6, 128.3, 128.5, 129.6 (CH=CH). ^{29}Si NMR: δ 19.42, 21.31 ($SiCl_2$), 2.63, 3.33 ($SiMe_3$). MS (CI): *m/e* 334 (M^+, 0), 299 (100), 321 (17), 229 (12), 199 (13). Anal. Found/Calcd for $C_{15}H_{28}Cl_2Si_2$ (335.47): C, 53.89/53.71; H, 8.71/8.41; Si, 18.06/16.74; Cl, 19.25/21.14.

13: colorless viscous liquid; bp 80 °C/10^{-2} mbar; 4.44 g (66%); mixture with **14**. ^{1}H NMR: δ 0.3 (s, 9 H), 0.93 (s, 9 H), 1.2 (s, br, 1 H), 1.9–2.2 (m, 2 H), 2.5 (s, br, 3 H), 3.1 (s, br, 2 H), 6.8–7.2 (m, 4 H). ^{13}C NMR: δ 0.65 ($SiMe_3$), 13.27 (Si—C—Si), 21.17 (CH_3), 28.28 (Cl_2Si—CH_2), 29.74 ($C(\mathit{C}H_3)_3$), 31.72 ($\mathit{C}(CH_3)_3$), 36.94 ($\mathit{C}H_2$—$C(CH_3)_3$), 114.31, 114.54 (C=$\mathit{C}H_2$), 141.20, 142.92 (C=CH_2). ^{29}Si NMR: δ 4.88 ($SiMe_3$), 30.16 ($SiCl_2$). MS (CI): *m/e* 336 (M^+, 11.1), 321 (48.9), 301 (100). Anal. Found/Calcd for $C_{15}H_{30}Cl_2Si_2$ (337.48); C, 52.30/52.38; H, 8.92/8.96; Si, 17.24/16.64.

14. ^{13}C NMR: δ 1.02 ($SiMe_3$), 32.36 ($C(\mathit{C}H_3)_3$), 32.90 ($\mathit{C}(CH_3)_3$), 27.4, 38.4 (CH_2), 42.60 ($\mathit{C}H_2$—$C(CH_3)_3$), 125.2, 128.9 (C=C). ^{29}Si NMR: δ 6.58 ($SiMe_3$), 30.43 ($SiCl_2$). MS (CI): *m/e* 336 (M^+, 0), 321 (7), 301 (100), 229 (60), 121 (42), 105 (65).

18: colorless viscous liquid; bp 95 °C/10^{-2} mbar; 1.06 g (43%, based on 7.0 mmol of **17**); mixture with **19**. ^{1}H NMR: δ (**18** and **19**) 0.07, 0.12 (s, integrals 5/1), 1.02, 1.06 (s), 1.00–1.25 (m), 1.60–1.95 (m), 2.50 (m), 2.70 (m). ^{13}C NMR: δ 2.04 ($SiMe_3$), 11.91, 13.89 (CH), 15.89 (CH_2), 17.72 (Si—C—Si), 19.41, 19.70, 20.24, 20.29 (CH_3), 32.78 ($C(\mathit{C}H_3)_3$), 33.41 ($\mathit{C}(CH_3)_3$), 39.33 (CH_2), 45.10 ($\mathit{C}H_2$—$C(CH_3)_3$), 127.16, 127.23 (C=C). ^{29}Si NMR: δ 0.95, –0.74. MS: *m/e* 352 (M^+, 0), 337 (21), 309 (43), 295 (28), 73 (100), 57 (47). Anal. Found/Calcd for $C_{21}H_{44}Si_2$ (352.76): C, 71.21/71.50; H, 12.33/12.57.

19. ^{1}H NMR: δ additional signals 4.9–5.2 (m). ^{13}C NMR: δ 2.76 ($SiMe_3$), 4.54 (Si—C—Si), 13.24, 13.75 (CH), 17.64 (Si—CH_2), 19.34, 21.61, 22.16, 24.02 (CH_3), 30.37 ($C(\mathit{C}H_3)_3$), 31.90 ($\mathit{C}(CH_3)_3$), 38.90 ($\mathit{C}H_2$—$C(CH_3)_3$), 111.96, 113.31 (=CH_2), 144.61, 146.50 (=C). MS: *m/e* 352 (M^+, 0), 337 (5), 309 (5), 271 (18), 169 (47), 73 (100), 57 (21).

20: colorless viscous liquid; bp 70 °C/10^{-2} mbar; 2.03 g (33%). ^{1}H NMR: δ 0.12, 0.20 (s, integrals 1/1, 1 H), 0.98, 1.00 (s, integrals 1/1, 9 H), 1.05–2.2 (m, 4 H), 2.4–3.02 (m, 1 H), 4.60–4.90 (m, 2 H), 5.56–5.91 (m, 1 H). ^{13}C NMR: δ –0.38, 2.39 ($SiMe_3$), 22.29, 26.68 (CH_2), 29.36, 29.42 ($C(\mathit{C}H_3)_3$), 30.89, 31.01, 31.11, 31.21 (C), 41.29, 47.44 (CH), 42.01, 46.15 ($\mathit{C}H_2$—$C(CH_3)_3$), 139.05, 139.86 (CH=), 114.76, 114.83 (CH_2=). ^{29}Si NMR: δ –1.79, 0.06 ($SiMe_3$), 11.54, 15.24 ($SiCl_2$). MS (CI): *m/e* 308 (M^+, 5), 193 (100), 293 (17), 273 (62), 215 (48), 204 (51).

21: colorless liquid; bp 65 °C/10^{-2} mbar; 1.88 g (95% based on **20**). ^{13}C NMR: δ –1.19 ($SiMe_3$, $^1J(^{13}C,^{29}Si) = 52.1$ Hz), 0.76 ($SiMe_3$, $^1J = 52.4$ Hz), 20.84 (CH_2Si, $^1J = 58.7$ Hz), 23.12 (CH_2Si, $^1J = 55.5$ Hz), 30.10, 30.33 ($C(\mathit{C}H_3)_3$), 31.15, 32.68 ($\mathit{C}(CH_3)_3$), 37.23 (Si—C—Si, $^1J = 41.6$, $^1J = 59.8$ Hz), 39.97 (Si—C—Si, $^1J = 41.5$, $^1J = 56.5$ Hz), 38.62 (CH, $^2J = 17.5$ Hz), 42.33 (CH, $^2J = 17.5$ Hz), 44.45, 46.74 ($\mathit{C}H_2$—$C(CH_3)_3$), 49.92, 49.97 (O—CH_3), 112.89, 133.03 (=CH_2), 142.31, 143.46 (=CH). MS (CI): *m/e* 301 ($M^+ + 1$, 9.9), 286 (98.3), 270 (52.5), 242 (39.7), 189 (100), 159 (10.6).

22: colorless viscous liquid; bp 90 °C/10^{-2} mbar; 2.63 g (38%); mixture with **23**. ^{13}C NMR: δ 3.2 ($SiMe_3$), 12.4, 13.5, 13.9 ($\overline{\mathrm{CH{-}CH{-}C}}\mathrm{H}$), 29.1 (Si–C–Si), 32.1 ($C(\mathit{C}H_3)_3$), 33.1 ($\mathit{C}(CH_3)_3$), 34.2 (CH_2), 33.8, 37.8, 50.6 (CH), 46.7 ($\mathit{C}H_2$–$C(CH_3)_3$). ^{29}Si NMR: δ 2.21 ($SiMe_3$), 37.6 ($SiCl_2$). MS (CI): *m/e* 346 (M^+, 0), 344 (4), 333 (32), 311 (100), 181 (19), 121 (19).

23. ^{1}H NMR: δ 6.83 (s), 7.13–7.29 (m), integrals 1/2. ^{13}C NMR: δ 128.3, 136.8, 139.5 (=C), 177.3 (=CH). ^{29}Si NMR: δ 5.05 ($SiMe_3$), 19.98 ($SiCl_2$). MS (CI): *m/e* 346 (M^+, 0), 255 (12), 203 (7), 125 (20), 110 (29), 73 (100), 65 (63).

24: colorless viscous liquid; bp 90 °C/10^{-2} mbar; 2.01 g (29%). ^{1}H NMR: δ 0.25 (s, 9 H), 1.00 (s, 9 H), 1.19–2.30 (m, 6 H), 2.56–3.10 (m, 2 H), 5.88–6.13 (m, 2 H). ^{13}C NMR: δ 0.82 ($SiMe_3$), 30.72 (Si—C—Si), 31.81 ($C(\mathit{C}H_3)_3$), 33.51 ($\mathit{C}(CH_3)_3$), 40.80 (CH_2), 46.29 ($\mathit{C}H_2$—$C(CH_3)_3$), 42.25, 42.89, 44.49, 46.02 (CH), 136.77, 139.31 (HC=CH). ^{29}Si NMR: δ 0.77 ($SiMe_3$), 16.87 ($SiCl_2$). MS (CI): *m/e* 346 (M^+, 0), 331 (12), 311 (60), 289 (5), 239 (28), 182 (61), 105 (100).

25: colorless viscous liquid; bp 85 °C/10^{-2} mbar; 2.99 g (43%). ^{1}H NMR: δ 0.21 (s, 9 H), 1.05 (s, 9 H), 0.8–2.6 (diverse m, 11 H), 6.9 (s, 1 H). ^{13}C NMR: δ 2.11 ($SiMe_3$), 29.15 (CH_2), 30.68 ($C(\mathit{C}H_3)_3$), 37.94 ($\mathit{C}(CH_3)_3$), 33.14, 34.12, 38.02 (CH_2), 35.86, 36.98, 38.90 (CH), 131.55 (C=CH), 174.45 (C=$\mathit{C}H$). ^{29}Si NMR: δ 2.31 ($SiMe_3$), 16.09 ($SiCl_2$). MS (CI): *m/e* 348 (M^+, 0), 333 (72), 315 (100), 253 (3), 241 (13).

Gas Chromatographic Investigations of Rearrangements of the Cycloadducts. The GC system has been described above. A 25-μL aliquot of cycloadduct(s) was dissolved in 1.5 mL of solvent (pentane, acetone, THF, acetonitrile). For trapping reactions of intermediates, 200 μL of 2-methyl-1,3-butadiene or thiophenol was added. Then 1.0 μL of this solution was injected.

Synthesis of 16. Into a tube were placed 3.36 g of a mixture of **9**/**10** (10.0 mmol) in 3 mL of acetonitrile (two phases), and the mixture was degassed by three freeze/pump/thaw cycles. Then thiophenol was condensed onto this mixture (ca. 2 mL). The tube was sealed and left to itself for 2 months, after which just one liquid phase was present. Acetonitrile and thiophenol were condensed off, and the yellow viscous residue was used directly for NMR spectroscopy. The product decomposed when distillation was attempted (>120 °C/10^{-2} mbar). ^{1}H NMR: δ 0.53 (s, 9 H), 1.23 (s, 9 H), 1.30–2.10 (m, 11 H), 4.00 (m, 2 H), 7.22–8.05 (m, 5 H). ^{13}C NMR: δ 0.64 ($SiMe_3$), 14.34 (Si—CH—Si), 26.09 (Cl_2Si—CH_2), 29.71 ($C(\mathit{C}H_3)_3$), 31.63 ($\mathit{C}(CH_3)_3$), 36.72 ($\mathit{C}H_2$—$C(CH_3)_3$), 38.64 (CH_2—S), 20.51, 22.13 (CH_3), 126.33 (=C—S), 128.64, 130.40, 130.67 (CH), 136.72, 138.07 (C=C). MS (CI): *m/e* 447 ($M^+ + 1$, 11.1), 433 (15.4), 411 (100), 331 (17.5), 301 (14.1), 229 (68.8), 187 (20.8).

Acknowledgment. We thank the Hanns-Seidel-Stiftung eV. Munich (grant to J.B.) and the Stiftung Volkswagenwerk for support.

Supplementary Material Available: Complete listings of positional and thermal parameters, atomic coordinates, bond distances and bond angles, and root mean square amplitudes and a figure showing the cell plot (14 pages). Ordering information is given on any current masthead page.

OM910572F