δ -116.5 (tdd, $^1J_{PH}$ = 333 Hz, $^2J_{PH}$ = 6 Hz, J_{PW} = 219 Hz); ^{1}H NMR (C_6D_6) δ -0.08 and 0.28 (s, 18 H, $Si(CH_3)_3$), 1.1 (d, J_{HH} = 7.0 Hz, 1 H, CH), 4.08 (dd, J_{PH} = 333.0 Hz, J_{HH} = 6.0 Hz, 2 H, H_2P). Anal. Calcd for $C_{12}H_{21}O_5PSi_2W$: C, 27.91; H, 4.10. Found: C, 27.72; H, 4.00.

Synthesis of Zirconadiazaphosphetidine 31. Cp_2ZrHCl (257 mg, 1 mmol) was added to a solution of 1 mmol of (bis(trimethylsilyl)amino)bis((trimethylsilyl)imino)phosphorane **30** (453 mg) in 15 mL of THF at -20 °C. The yellow solution was stirred at this temperature for 30 min. After extraction of the solvent, the yellow residue was washed with benzene. The complex then precipitated as a white powder (82%): ^{31}P NMR (C_6D_6) δ 2.8 (d, $^1J_{PH}$ = 517 Hz); ^{1}H NMR (C_6D_6) δ 0.16 (s, 18 H, $N[Si(CH_3)_3]_2$), 0.43 and 0.61 (s, 9 H, $N-Si(CH_3)_3$), 6.31 (s, 5 H, Cp), 6.27 (s, 5 H, Cp), 7.54 (d, $^1J_{PH}$ = 517.0 Hz, 1 H, PH); ^{13}C NMR (C_6D_6) δ 6.1 (d, $^3J_{CP}$ = 8.2 Hz, $Si(CH_3)_3$), 6.2 (d, $^3J_{CP}$ = 4.6 Hz, $Si(CH_3)_3$), 8.0 (d, $^3J_{CP}$ = 4.1 Hz, $Si(CH_3)_3$), 114.3 (s, Cp), 116.3 (s, Cp); mass spectrum m/e 621. Anal. Calcd for $C_{22}H_{47}ClN_3PSi_4Zr$: C, 42.37; H, 7.60; N, 6.74. Found: C, 42.15; H, 7.25; N, 6.55.

Synthesis of Zirconadiazaphosphetidine Triflate 37. $Me_3SiOSO_2CF_3$ (222 mg, 1 mmol) was added dropwise with stirring to **31** (621 mg, 1 mmol) in 20 mL of CH_2Cl_2 at -20 °C. A clear yellow solution was formed within seconds. The reaction mixture was warmed to room temperature over 30 min. The solvent then was removed in vacuo to give a yellow light solid, **37** (75%): ^{31}P NMR (C_6D_6) δ -2.3 (d, $^1J_{PH}$ = 538 Hz); ^{1}H NMR (C_6D_6) δ 0.27-0.55 (m, 36 H, $Si(CH_3)_3$), 6.56 (s, 5 H, Cp), 6.59 (s, 5 H, Cp), 7.42 (d, $^1J_{PH}$ = 538.0 Hz, 1 H, PH); ^{13}C NMR (C_6D_6) δ 3.9 (d, $^3J_{CP}$ = 4.3 Hz, $Si(CH_3)_3$), 4.9 (s, $Si(CH_3)_3$), 115.3 (s, Cp), 116.8 (s, Cp), 120.0 (q, $^1J_{CF}$ = 320.0 Hz, CF_3SO_3). Anal. Calcd for $C_{23}H_{47}F_3N_3O_3PSSi_4Zr$: C, 37.47; H, 6.43; N, 5.70. Found: C, 37.06; H, 6.34; N, 5.61; IR (KBr) 1322 (ν_{SO_3}) cm^{-1}.

Synthesis of Cationic Zirconadiazaphosphetidine Triflate 38. Zirconadiazaphosphetidine triflate **37** was dissolved in acetonitrile. **38**: ^{31}P NMR (CD_3CN) δ 1.6 (d, $^1J_{PH}$ = 536 Hz); IR (CD_3CN) 1279 (ν_{SO_3} ionic) cm^{-1}.

Synthesis of Zirconadiazaphosphetidine 39. Cp_2ZrH_2 (1 mmol) was added at once to a solution of 1 mmol of (bis(trimethylsilyl)amino)bis((trimethylsilyl)imino)phosphorane (**30**) in 15 mL of toluene at -20 °C. The yellow solution was stirred for 30 min at this temperature. After extraction of the solvent, the yellow residue was washed with pentane. The complex **39** (80%) precipitated as a white powder: ^{31}P NMR (C_6D_6) δ -2.9 (dd, $^1J_{PH}$ = 509 Hz, $^2J_{PH}$ = 40 Hz); ^{1}H NMR (C_6D_6) δ 0.24, 0.30, 0.33, 0.40 (s, 36 H, $Si(CH_3)_3$), 4.68 (d, $^3J_{PH}$ = 40.0 Hz, 1 H, ZrH), 7.31 (d, $^1J_{PH}$ = 509.0 Hz, 1 H, PH), 5.74 (s, 5 H, Cp); 5.82 (s, 5 H, Cp); ^{13}C NMR (C_6D_6) δ 4.0-5.0 (m, $Si(CH_3)_3$), 104.3 (s, Cp), 105.6 (s, Cp). Anal. Calcd for $C_{22}H_{48}N_3PSi_4Zr$: C, 44.85; H, 8.21; N, 7.13. Found: C, 45.03; H, 7.97; N, 7.45.

Registry No. 1, 37342-97-5; **2a**, 50732-21-3; **2b**, 53787-01-2; **2c**, 72821-01-3; **3a**, 128337-85-9; **3b**, 131104-31-9; **3c**, 138694-46-9; **3d**, 138753-35-2; **6**, 63104-54-1; **7**, 138694-47-0; **9a**, 131104-37-5; **9b**, 131104-33-1; **10a**, 63104-56-3; **10b**, 138694-44-7; **10c**, 63104-57-4; **13**, 53973-90-3; **14**, 131104-34-2; **15**, 131104-36-4; **16**, 131130-18-2; **17**, 76173-65-4; **18**, 128337-84-8; **19**, 79454-85-6; **20**, 96043-64-0; **21**, 128429-18-5; **23**, 113389-13-2; **24**, 90500-31-5; **25**, 113192-44-2; **26**, 138694-50-5; **27**, 138694-45-8; **28**, 138694-48-1; **29**, 138694-49-2; **30**, 52111-28-1; **31**, 138694-51-6; **37**, 138694-52-7; **38**, 138694-54-9; **39A**, 138694-56-1; **39B**, 138694-55-0; Cp_2ZrH_2, 37342-98-6; Cp_2ZrMe_2, 12636-72-5; $Fe_2(CO)_9$, 15321-51-4; $Me_3SiOSO_2CF_3$, 27607-77-8.

Silaheterocycles. 14.[1] Regiospecific Cycloaddition Reactions of Dichloroneopentylsilene with Cyclohexa-1,3-diene. A Novel 7-Silabicyclo[4.2.0]oct-2-ene → 2-Silabicyclo[2.2.2]oct-5-ene Rearrangement

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Received August 15, 1991

In the presence of cyclohexa-1,3-diene (**2**), dichloroneopentylsilene (**1**), generated in situ from trichlorovinylsilane and *t*-BuLi, favors the regioselective formation of the anti/syn isomeric [2+2] cycloadducts (**3**, 74%) over the [4+2] addition, leading to the endo/exo isomer Diels-Alder compounds **4** (26%). On standing, the thermodynamically less stable silacyclobutane derivatives **3** completely isomerize to give the [4+2] products within several weeks. Possible reaction pathways, including a zwitterionic intermediate **A**, are discussed. In contrast, the dimethyl- and diphenyl-substituted [2+2] adducts (**7**, **8**), available from **3** by substitution reactions, show different isomerization behavior. They cannot be transformed into the Diels-Alder compounds, but the syn [2+2] isomers slowly form the thermodynamically more stable anti derivatives at room temperature. On thermolysis they yield open-chain products by a retro ene reaction. The high synthetic potential of strongly electrophilic **1** is demonstrated by the comparison of the cycloaddition behavior with diorgano-substituted neopentylsilenes $R_2Si{=}CHCH_2Bu$-*t*: Reaction of $Me_2Si{=}CHCH_2Bu$-*t* with **2** favors the [4+2] product formation, while $Ph_2Si{=}CHCH_2Bu$-*t* yields the Diels-Alder adducts exclusively.

Introduction

Our investigations on the cycloaddition behavior of dichloroneopentylsilene, $Cl_2Si{=}CHCH_2Bu$-*t* (**1**), formed by treating vinyltrichlorosilane with *t*-BuLi in nonpolar solvents,[2] revealed some surprising results, which have not been obtained in earlier work for diorgano-substituted derivatives by the group of Jones.[3] With cyclopentadienes,[4] aromatic dienes such as naphthalene[5] and

(1) Part 13: Auner, N.; Penzenstadler, E. *Z. Naturforsch.*, in press.
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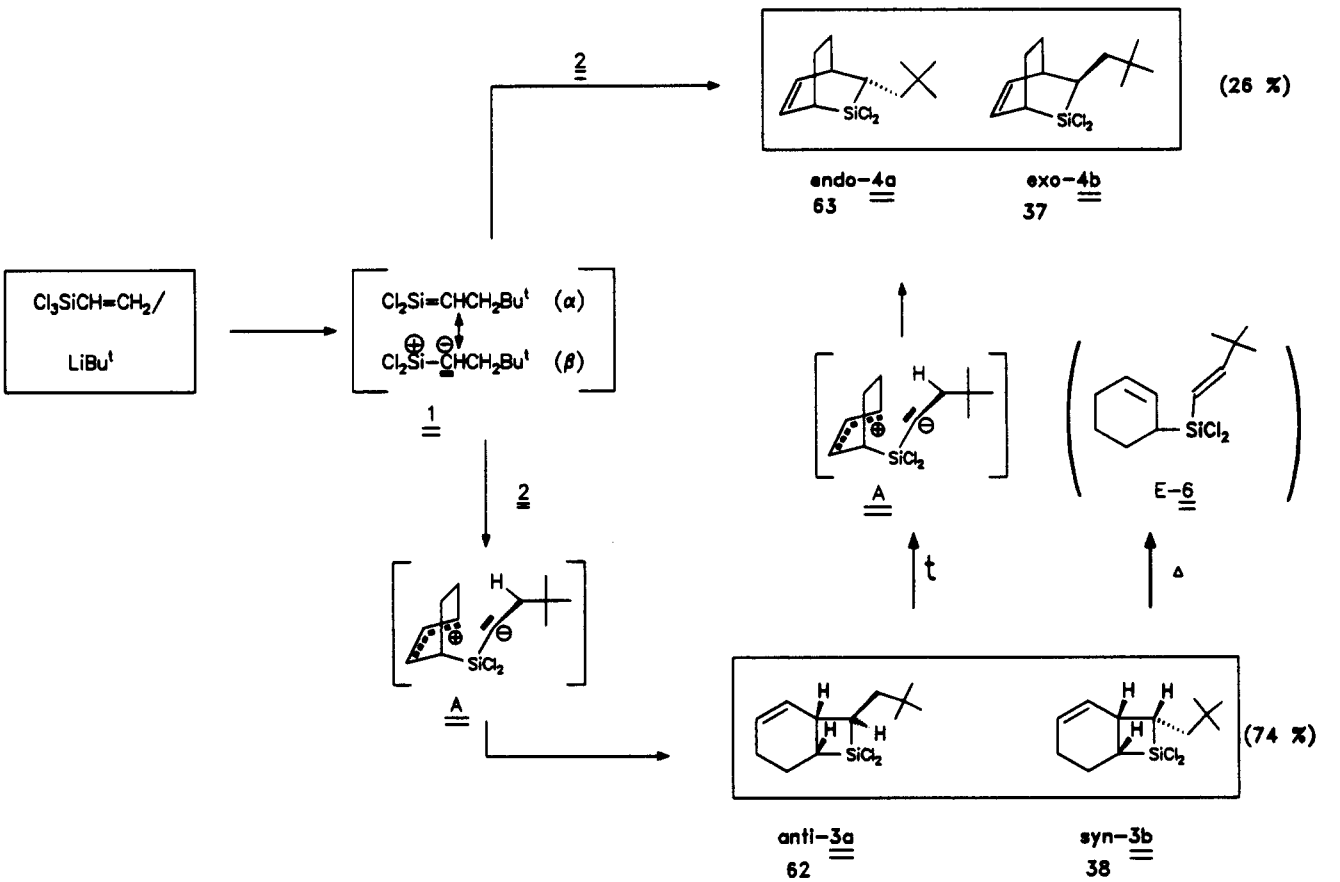
(4) Auner, N. *J. Organomet. Chem.* **1988**, *353*, 275.

0276-7333/92/2311-1137$03.00/0

Scheme I



anthracenes,[4] and heteroaromatics (i.e., furans),[6] the Diels–Alder products are formed; with norbornadiene, both [2+2] and [2+2+2] cycloadducts are obtained,[6] while with butadienes,[6] diorgano-substituted acetylenes,[7] norbornene, and quadricyclane,[6] the pure [2+2] and with the latter the [2+2+2] products are formed regioselectively. Furthermore, in some cases the [2+2] cycloadducts undergo rearrangements to the thermodynamically more stable [4+2] compounds and isomeric catenated retroene products.[5,6] Thus, **1** is best characterized by the combination of high dienophilicity with a strongly polarized Si=C double bond; this can be demonstrated by its reactivity toward cyclohexa-1,3-diene (**2**). Although this interesting diene forms Diels–Alder products with halogenated maleic anhydride[8] and butenes[9] and serves as a [4+2] trapping reagent for heterodienophiles such as P≡C,[10] P=C,[11] N=O,[12] C=O,[13] and C=S[14] bond systems, it reacts with *t*-Bu_2Si=$SiBu_2$-*t* to afford exclusively [2+2] products, which are favored because of steric reasons.[15] Evidently, the diene character of **2** is strongly dependent on the dienophiles reacted. This prompted us to study the cycloaddition behavior of silene **1**. In this paper we examine the reactivity of silene **1** toward **2**; both the selectivity of the reaction and the stability of the cycloadducts are compared to similar reactions involving diorgano-substituted derivatives (R_2Si=$CHCH_2Bu$-*t*).

Results and Discussion

I. Cycloaddition Reaction of 1 and 2 and the Stability of the Cycloadducts. When equimolar amounts of Cl_3SiCH=CH_2 and *t*-BuLi are mixed with a 3-fold excess of **2** at −78 °C in *n*-pentane, a reaction occurs at about −5 °C, as evidenced by the precipitation of LiCl. At first glance, the analytical and NMR spectroscopic investigations on a typical product mixture show divergent results: While the GC/MS analysis of the reaction solution and the isolated products indicates the formation of four cycloadducts (Scheme I) in nearly quantitative yield and an isomeric ratio of 4.4 (**3a**)/5.8 (**3b**)/56.8 (**4a**)/33 (**4b**), ^{13}C and ^{29}Si NMR spectroscopies suggest a very different product distribution with a relative isomer ratio of 46/28/16.4/9.6. Unfortunately, the products cannot be separated by distillation or gas chromatography. However, after the mixture was stored in daylight at room temperature for 8 weeks, only two isomeric compounds were detectable in a ratio of 63/37 by both GC and NMR methods; these products were identified (H,H and C,H COSY-NMR, see spectroscopic part) as endo/exo isomer [4+2] cycloadducts **4a** and **4b**, with the endo derivative **4a** as the major isomer. Obviously, this finding is different from the isomeric ratios of 3-neopentyl-2-silanorborn-5-enes reported in the literature (exo/endo = 55/45,[3] 60/40[4,16]) but is in good agreement with our results on the selective formation of the endo [4+2] adduct of **1** with naphthalene.[5]

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(6) Wolff, A. Dissertation, Technische Unversität München, **1991**. Publication in preparation.
(7) Auner, N.; Seidenschwarz, C.; Herdtweck, E. *Angew. Chem.* **1991**, *103*, 1172; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1151.
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(9) Huybrechts, G.; van Mele, B. *Int. J. Chem. Kinet.* **1978**, *10*, 1183.
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(14) Larson, C.; Hopp, D. N. *J. Org. Chem.* **1980**, *45*, 3713; Friedrich, K.; Gallmeier, H.-J. *Tetrahedron Lett.* **1981**, 2971.
(15) Weidenbruch, M.; Schäfer, A.; Thom, K.-L. *Z. Naturforsch.* **1983**, 38b, 1695.
(16) Auner, N. Habilitationsschrift, Münster, **1987**.

Comparison of the NMR data of pure **4a,b** with those of the original product mixture indicates that **4a,b** was originally present in 26% yield with the same 63/37 ratio and that the remaining two compounds are the anti/syn stereoisomeric [2+2] products **3a,b** formed in 74% yield. On the basis of GC and 2D NMR spectroscopic investigations, the anti/syn ratio was determined to be 62/38 on isolable diorgano-substituted pairs of the pure [2+2] derivatives, available by substituting the dichloroatoms of **3** by organo groups.

The reaction of **1** and **2** under comparable conditions, but in the dark,[17] leads to gradual changes in the product composition. The yield of **3** increases to more than 80% while that of **4** decreases to less than 20%. However, the endo/exo and anti/syn ratios, respectively, do not change for both isomeric pairs. The course of the cycloaddition between **1** and **2** and the isomerization of the [2+2] products is described in Scheme I. *t*-BuLi adds to the vinyl group of $Cl_3SiCH{=}CH_2$, giving the α-lithio compound $Cl_3SiCH(Li)CH_2Bu$-*t*; this species can be trapped by trimethylsilyl triflate quantitatively, forming $Cl_3SiCH(SiMe_3)CH_2Bu$-*t*.[6] LiCl 1,2-elimination generates **1**, which adds to Me_3SiOMe at −10 °C across the Si=C bond leading to $Cl_2Si(OMe)CH(Me_3Si)CH_2Bu$-*t* (**5**) (eq 1).

$$\underset{\mathbf{1}}{Cl_2Si{=}CHCH_2Bu^t} + Me_3SiOMe \longrightarrow \underset{\mathbf{5}}{Cl_2Si(OMe)CH(SiMe_3)CH_2Bu^t} \quad (1)$$

Silene **1** is a dienophile of significant reactivity, being strongly different from that of diorgano-substituted neopentylsilenes:[16] The two chlorine substituents as π donors at silicon not only increase its electrophilicity and the polarity of the Si=C bond in **1**—which is a Lewis acid in any case[18] —but also increase the energy level of the π^* orbital (LUMO) and the size of the orbital coefficients of the dienophile. We derive this comparison to $H_2Si{=}CH_2$ from ab initio calculations.[19] The energy difference between π and π^* orbitals is increased, thus rendering the [4+2] cycloaddition less favorable.[20] The participation of the strongly polarized Si=C bond in **1** (as examplified by the mesomeric formula $\alpha \leftrightarrow \beta$ in Scheme I) in the cycloaddition reaction results in competitive formation of [2+2] (from β) and [4+2] (from α) cycloadducts. We propose that the [2+2] addition occurs via a multiple-step mechanism including the dipolar intermediate A, which should be strongly favored by the chlorine substituent on silicon. The allylic carbocation is mostly stabilized by conjugation with the C–C double bond, while the α carbanion is stabilized by hyperconjugation and inductive effects of the dichlorosilyl group.[21]

The fact that the isomers *endo*-**4** and *anti*-**3**, in which the configuration of the neopentyl group in A is retained, are the main products may result from the reaction conditions (low reaction temperature, relatively short reaction time), which do not allow time for rotations around the Si–C bond in A. However, this result can also be explained on steric grounds; the C_1 bridge in the bicyclic [4+2] adducts 3-neopentyl-2-silanorborn-5-enes requires only a small steric space (exo > endo[3,4,16]), while the C_2 bridge in 2-silaoctenes forces the neopentyl group into the endo position[22] to reduce steric interactions with the bicyclic ring skeleton.

Scheme II. Stereochemistry of the Sigmatropic 1,3-Migration with Inversion of Configuration

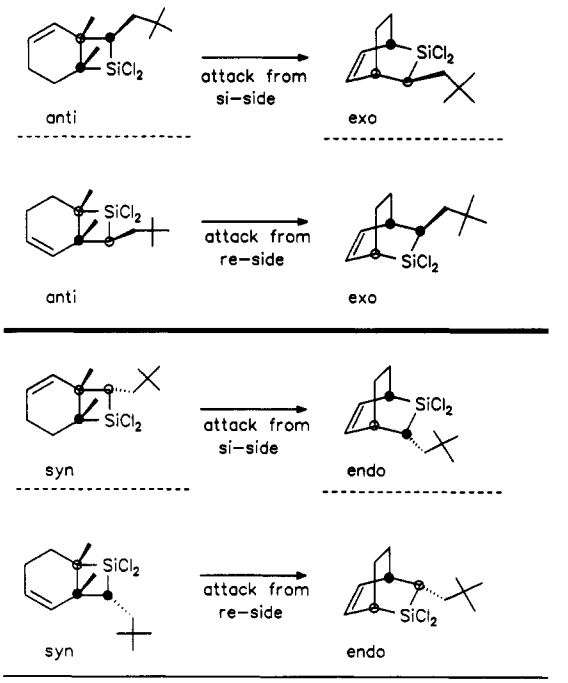

Table I

compound (%)				
3a	**3b**	**4a**	**4b**	conditions
46.0	28.0	16.4	9.6	after distillation
41.3	13.5	27.8	17.4	*n*-pentane, 35 °C
40.0	18.1	25.8	16.1	ether, 34.5 °C
9.7		58.8	31.5	THF, 66 °C
37.0	9.3	27.9	25.8	toluene, 110.6 °C
42.9	20.8	25.6	10.7	pure sample, 60 °C
		42.8	17.1	pure sample, 200 °C[a]

[a] (*E*)-**6**, 40.1%.

Force field calculations on the "steric stability" of **3** and **4** show[23] that the stability of *endo*-**4** is only slightly higher than that of the exo isomer. Compared to the [2+2] adducts, these Diels–Alder compounds are much more stable. The results also indicate a significantly higher stability of the anti isomer **3a** compared to the syn derivative **3b** in which the neopentyl group—hindered in its free rotation—interacts sterically with the annulated cyclohexene ring skeleton; consequently, this additional deformation results in further destabilization of the four membered ring.

The steric reasons, combined with the high thermodynamic stability of the Diels–Alder compounds and the Cl_2Si stabilization of A, may be responsible for the complete transformation of the liquid product mixture *anti/syn*-**3** into *endo/exo*-**4** without changing the endo/exo ratio (63/37). Moreover, an alternative explanation for the isomerization of **3** to **4** should be discussed involving a sigmatropic 1,3-rearrangement analogous to the conversion of C-homologous bicyclooctene ring skeleton derivatives.[24]

(17) The fast cycloaddition reaction is obviously not influenced by light, whereas the very slow rearrangement **3** → **4** reflects additional activation by daylight.
(18) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141.
(19) Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* **1984**, *106*, 6676.
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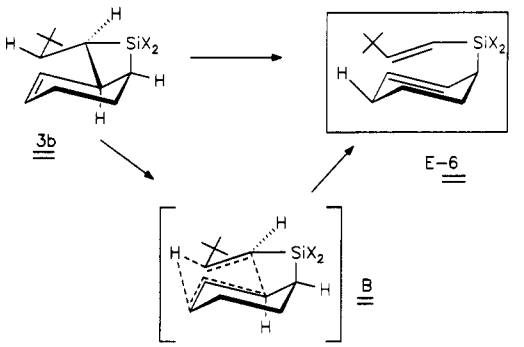
(23) Auner, N.; Selzle, H. Unpublished results.
(24) Fleming, I. *Grenzorbitale und Reaktionen organischer Verbindungen*; Verlag Chemie: Weinheim, 1988; p 257.

Scheme III



This is demonstrated for the enantiomeric pairs of **3a** and **3b** in Scheme II and shows that this rearrangement would favor the formation of the exo [4+2] products from the anti [2+2] adducts and vice versa. Consequently, a thermally allowed suprafacial sigmatropic 1,3-rearrangement (with inversion of configuration at the migrating carbon substituent) can be ruled out, as inverted product ratios should be obtained. Therefore, the product distribution from the reaction between **1** and **2** reflects the relative thermodynamic stabilities of the compounds and hints to a nonconcerted reaction pathway via a dipolar intermediate A.

The rearrangement of **3** → **4** is decisively influenced by the following conditions:

It is slowed by storing the pure sample in the dark[17] and accelerated at higher temperatures (e.g., 60 °C/12 h; see Table I).

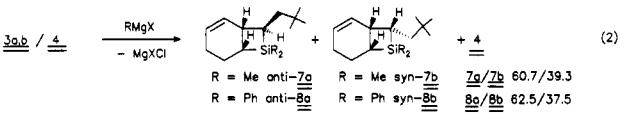
It does not occur when **3** is dissolved in a nonpolar solvent at 20 °C but is accelerated in more polar solvents. Table I gives the amounts of **3** and **4** (obtained from integration of the ^{29}Si NMR resonance signals) after the mixture was refluxed in different solvents for 5 days. The especially high yields of **4** obtained using THF as solvent confirms the rearrangement **3** → **4** occurring via dipolar intermediate A.

Under thermolysis conditions (200 °C/90 h) without a solvent, *anti/syn*-**3** are completely transformed into **4a,b** (60%, ratio 71.4/28.6)[25] and the isomeric catenated compound (*E*)-**6** (40%). The latter product is mostly generated from *syn*-**3**: Only **3b** can accommodate the conformative necessity to allow a thermally induced concerted retroene reaction leading to (*E*)-**6** via a cyclic six-electron transition state B (Scheme III).

The results from the thermolysis experiments suggest that there are two different routes for the isomerization of **3**. The low-temperature route favors the rearrangement of the 7-silabicyclo[4.2.0]oct-2-enes into the Diels–Alder products, while the more entropically favored retro ene reaction of **3b** becomes more attractive at higher temperatures.[26]

These findings are in good agreement with the gas chromatographic behavior of the mixture **3/4** described earlier. *anti/syn*-**3** are converted even in the injector of the GC ($T \sim 200$ °C) into the Diels–Alder derivatives, giving a product ratio [4+2]/[2+2] of 90/10. However, (*E*)-**6** is not detectable under these conditions. **4** and **6** are thermally very stable and remain unchanged even under drastic conditions (3 weeks, 200 °C). A common zwitterionic intermediate (A) may be responsible for the generation of **3**, as well as the isomerization of **3** to **4**.

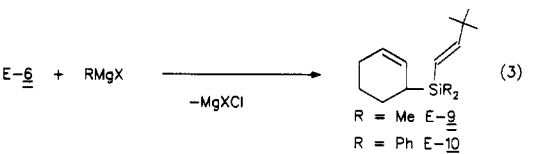
To compare the convertibility of **3** with that of diorgano-substituted derivatives, a mixture of **3/4** was treated with an excess of methyl or phenyl Grignard reagent. In all cases—even at reflux temperature of the solvent (Et_2O, THF)—only the [2+2] compounds were disubstituted; **4** remained unchanged (eq 2).



(2)

Considering (i) that monosilacyclobutanes are highly strained compounds with CSiC angles being smaller than 90°[27] and that this angle can increase to 100.3° for a 2-silabicyclo[2.2.2]octadiene derivative[5] (which may contribute to the fact that substitution reactions at Si in a four-membered ring are known to be faster than those in a six-membered one[28]) and, alternatively, (ii) that the easy cleavage of the Si–C bond in **3** forming A may facilitate the substitution reaction possibly going through an anionic Si pentacoordinated intermediate,[28] the course of the substitution reaction becomes understandable.

As expected, these derivatizations change the physical properties of the [2+2] products, making them easily separable from **4**. (**E**)-**6**, if present, is also substituted by the Grignard reagent (eq 3). The experimental result that substitution at Si in the open-chain compound goes faster than in the Diels–Alder derivative **4** is unexpected;[28,29] perhaps this is due to the fact that (*E*)-**6** is an allylvinylsilane.

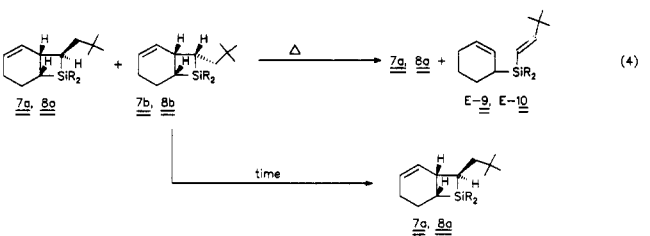


(3)

These results clearly show the different influence of the chloro substituents and the diorgano groups on the four-membered ring framework:

Under thermolysis conditions (200 °C/50 h) both anti derivatives **7a** and **8a** remain stable, while the syn isomers are completely transformed into (*E*)-**9** or (*E*)-**10** by retroene reactions as described for **3b**.

When the samples are stored without solvents for weeks, *syn*-**7b** and **8b** are fully converted into the anti compounds, the diphenyl-substituted **8b** reacting more slowly than the dimethyl derivative **7b**. This transformation is greatly accelerated at 60 °C, whereas dissolution of the samples in a nonpolar solvent slows the isomerization. This result again supports the existence of a dipolar intermediate (eq 4).



(4)

(25) These conditions evidently favor the formation of the endo derivative **4a**.

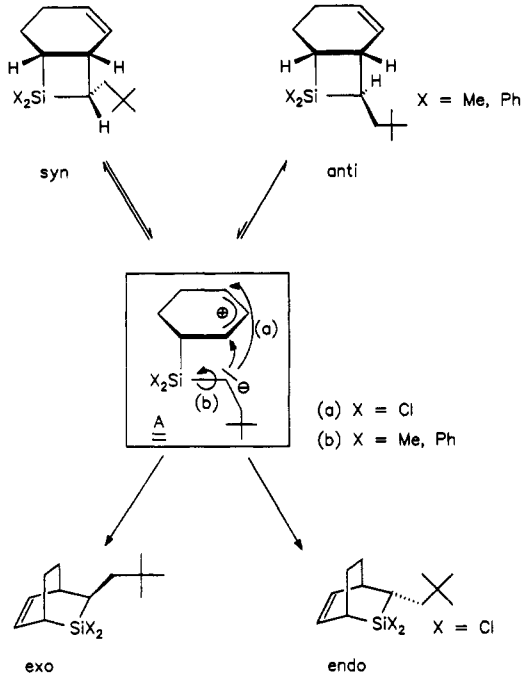
(26) It should be mentioned that we have found very similar results studying the isomerization behavior of the syn/anti isomeric [2+2] products derived from the reactions of **1** with butadienes,[6] cyclohepta-1,3-diene, and cyclohepta-1,3,5-triene: Auner, N.; Seidenschwarz, C.; Herdtweck, E. In preparation.

(27) Rempfer, B.; Pfafferott, G.; Oberhammer, H.; Auner, N.; Boggs, J. E. *Acta Chem. Scand.* **1988**, *A42*, 352.

(28) Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 20.

(29) Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. *Top. Stereochem.* **1984**, *15*, 43. We thank the reviewer for pointing out this fact.

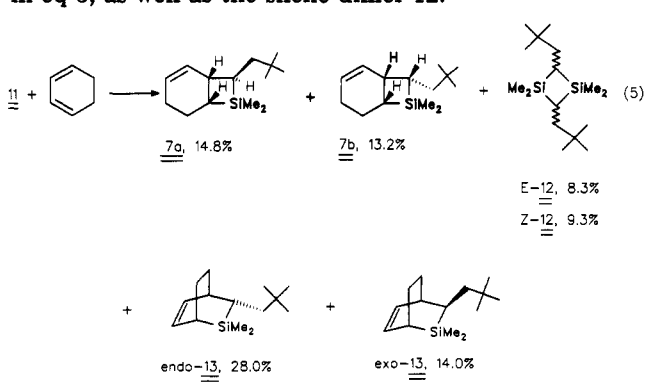
Scheme IV. Different Isomerization Behavior of Dichloro- and Diorgano-Substituted 7-Silabicyclo[4.2.0]oct-2-enes via Zwitterionic Intermediate A



No conversion of **7** and **8** into the Diels–Alder products can be observed even though the latter are thermodynamically and sterically more stable as can be shown by force field calculations.[23]

Lacking the stabilizing effect of the chloro atoms, the diorgano-substituted analogues of intermediate A are destabilized. Thus, the [2+2] → [4+2] rearrangement becomes impossible; only the faster syn [2+2] → anti [2+2] conversion occurs, evidently caused by steric reasons. This different isomerization behavior is illustrated in Scheme IV.

II. Cycloaddition Reaction of $Me_2Si{=}CHCH_2Bu$-*t* (11) and 2. The completely different cycloaddition behavior of diorgano-substituted neopentylsilenes compared to the dichloro analogue is clearly demonstrated by the exclusive formation of the endo/exo isomer [4+2] adducts from **2** and $Ph_2Si{=}CHCH_2Bu$-*t*.[22] The reaction of **11** (generated by treatment of $Me_2Si(CH{=}CH_2)Cl$ with *t*-BuLi[3,30]) and **2** gave the four isomeric cycloadducts shown in eq 5, as well as the silene dimer **12**.



In contrast to the [2+2] addition preferred by **1**, the [4+2] adducts *endo/exo*-**13** are obtained as main products (42%, isomeric ratio 66.8/33.2). (*E*/*Z*)-**12**, the cyclo dimer of **11**, was isolated as a crystalline solid and characterized by X-ray crystallography.[31] The ratio of E/Z 48/52 is in good agreement with ref. [30]. Two isomeric coupling compounds of $Me_2SiClCH(Li)CH_2Bu$-*t* with **2** (12.4%) are also observed in the product mixture, but they have not been fully characterized so far. While **12** and **13** are thermally stable, **7b** isomerizes to **7a** or (*E*)-**9** as described before.

Summarizing and comparing the cycloaddition reactions of neopentylsilenes with **2**, it is clear that silene **1** holds an exceptional position among this class of compounds and therefore is a useful building block in organosilicon chemistry:

Because of its electronic structure ($\alpha \leftrightarrow \beta$), [2+2] addition reactions are strongly preferred over [4+2] reactions.

Replacement of one chlorine atom by an organo group (e.g., $Vi(Cl)Si{=}CHCH_2Bu$-*t*[16]) increases the yields of the [4+2] products.

The same is true for diorgano-substituted neopentylsilenes; while the two "small" methyl groups of **11** may be responsible for the [2+2] product generation on a small scale, the presence of the more bulky phenyl groups in $Ph_2Si{=}CHCH_2Bu$-*t* results in the exclusive formation of the Diels–Alder products. This is also the case for diisopropylneopentylsilene.[32]

Reduction of the polarity of **1** by introducing a Me_3Si group at the α-C position [$Cl_2Si{=}C(SiMe_3)CH_2Bu$-*t*] leads exclusively to the expected formation of the [4+2] derivatives.[33]

NMR Spectroscopic Part[34]

I. NMR Signal Assignment of the Phenylated [2+2] Cycloadducts 8a,b.[35] According to chemical arguments there is evidence that the isomeric [2+2] cycloadducts **3**, **7**, and **8** are diastereomers. The following section will give proof of this thesis using 2D NMR techniques, i.e., H,H COSY,[36] ROESY,[38] NOESY,[40] and C,H COSY.[42] Figure

(30) Jones, P. R.; Lim, T. F. O. *J. Am. Chem. Soc.* **1977**, *99*, 2013. See also ref 3.

(31) Auner, N.; Seidenschwarz, C.; Herdtweck, E.; Behm, J. In preparation.

(32) Auner, N.; Weingartner, A. Unpublished results.

(33) Ziche, W.; Auner, N.; Behm, J. *Organometallics*, submitted for publication.

(34) All NMR experiments were performed on a Bruker AM 360 spectrometer (^1H, 360.134 MHz; ^{13}C, 90.556 MHz) in $CDCl_3$ as solvent at 23 °C. Chemical shifts (δ) are given (ppm) relative to TMS.

(35) All measurements were performed using two samples of **8a,8b**, which had been degassed during several freeze-thaw cycles. The ratio was 3/2 (sample used for H,H COSY, H,C COSY, and ROESY) and changed to 3/1 (sample used for NOESY) within some weeks by standing at room temperature.

(36) The double-quantum-filtered phase-sensitive COSY spectrum was recorded using the pulse sequence 90–t_1–90–δ–90 acquisition[37] with phase sensitivity achieved by the TPPI method. Eight scans (preceded by two dummy scans) were recorded into 2K data blocks for each of the 512 t_1 values with a relaxation delay of 2 s and spectral widths of 3067.5 Hz. The data matrix was zero-filled to 4K in f_2 and 1K in f_1 and apodized with shifted square sine bell functions in both dimensions. Coupling constants, as far as mentioned, are derived from a one-dimensional proton spectrum recorded with 64 scans, a pulse angle of 90°, and a relaxation delay of 5 s.

(37) (a) Marion, D.; Wuethrich, K. *Biochem. Biophys. Res. Commun.* **1983**, *113*, 967. (b) Rance, M.; Sorensen, O. W.; Bodenhausen, G.; Wagner, G.; Ernst, R. R.; Wuethrich, K. *Biochem. Biophys. Res. Commun.* **1983**, *117*, 479.

(38) Phase sensitivity was achieved by the TPPI method.[39] The longitudinal relaxation time T_1 was determined by an inversion recovery experiment. Sixteen scans (preceded by two dummy scans) were recorded into 2K data blocks for each of the 256 t_1 values with a mixing time of 250 ms, a relaxation delay of 2 s, and spectral widths of 3246.75 Hz. The data matrix was zero-filled to 4K in f_2 and 2K in f_1 and apodized with square sine bell functions in both dimensions. After phase correction, a base-line correction in both dimensions was applied.

(39) Bax, A.; Davis, D. G. *J. Magn. Reson.* **1985**, *63*, 207.

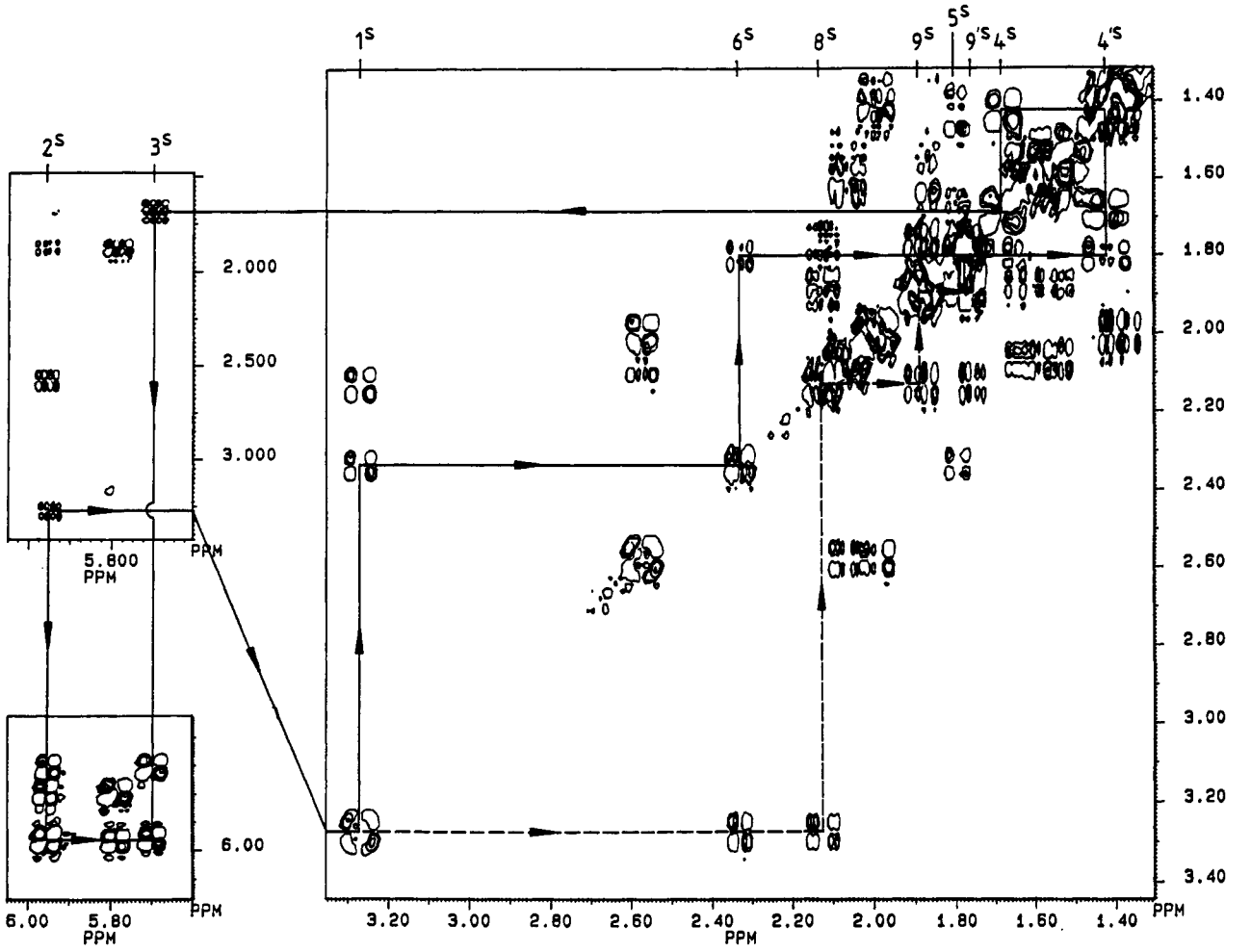
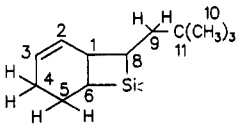


Figure 1.

Table II. Proton and Carbon NMR Signal Assignments of the Two Isomeric Diphenyl-Substituted [2+2] Cycloadducts 8 Due to H,H COSY



	anti-**8a** (62%)			*syn*-**8b** (38%)		
no.	$\delta(^1H)$ (ppm)	*J*(HH) (Hz)	$\delta(^{13}C)$ (ppm)	$\delta(^1H)$ (ppm)	*J*(HH) (Hz)	$\delta(^{13}C)$ (ppm)
1	2.57 ddm	10.3/8.6	39.09 CH	3.27 ddm	9.4/8.5	37.91 CH
2	5.96 dm	10.1	130.06 CH	5.95 dm	10.4	128.95 CH
3	5.79 dddd	10.1/5.2/2.6/2.6	126.76 CH	5.70 dddd	10.4/4.8/2.4/2.4	129.68 CH
4/4'	1.87 m		24.45 CH_2	1.43 m		23.73 CH_2
				1.69 m		
5/5'	1.55 m		21.44 CH_2	1.80 m		21.36 CH_2
	1.60 m					
6	2.07 ddd	8.6/8.6/5.6	23.79 CH	2.33 ddd	8.5/4.8/4.8	26.76 CH
8	2.00 ddd	11.5/10.3/4.2	30.68 CH	2.13 ddd	9.4/9.4/5.4	31.10 CH
9/9'	1.38 dd	13.3/11.5	44.30 CH_2	1.76 dd	13.7/5.4	40.89 CH_2
	1.45 dd	13.3/4.2		1.89 dd	13.7/9.4	
10	0.80 s		29.84 CH_3	0.83 s		29.76 CH_3
11			31.20 C			30.40 C

1 shows the double-quantum-filtered phase-sensitive COSY spectrum of **8a,b**[36] (the assignment pathway is outlined only for **8b**); the ^1H NMR signal assignments are listed in Table II.

(40) Phase sensitivity was achieved by the TPPI method.[41] The longitudinal relaxation time T_1 was determined by an inversion recovery experiment. Sixteen scans (preceded by two dummy scans) were recorded into 2K data blocks for each of the 128 t_1 values with a mixing time of 700 ms, a relaxation delay of 2.5 s, and spectral widths of 3424.66 Hz. The mixing time interval was randomly varied within ±21 ms. The data matrix was zero-filled to 4K in f_2 and in 1K in f_1 and apodized with square sine bell functions in both dimensions. After phase correction a base-line correction in both dimensions was applied.

(41) Bodenhausen, G.; Kogler, H.; Ernst, R. R. *J. Magn. Reson.* **1984**, *58*, 370.

(42) In this experiment[43] only geminal couplings are found in f_1. The 180 pulse was a composite pulse. A total of 96 scans were recorded into 4K data blocks for each of the 128 t_1 values with a relaxation delay of 2 s and spectral widths of 14 285.71 and 3419.97 Hz. The data matrix was zero-filled to 512W in f_1 and apodized with sine bell functions in both dimensions.

Table III. ROE or NOE Ratio between Selected Protons (8a/8b)

relation	product ratio	ROE or NOE ratio relative	absolute	expt
H1/H9	1.5	2.8	1.8	ROESY
H1/H10	1.5	2.0	1.3	ROESY
H1/H6	3.0	2.8	1.0	NOESY
H1/H8	3.0	2.1	0.7	NOESY
H1/H9	3.0	10.0	3.3	NOESY

The resonance signals of the phenyl substituents are found at 7.27–7.32 (meta, para) and 7.59–7.66 ppm (ortho). Starting the interpretation of the H,H COSY[36] with the resonances of the olefinic protons of both isomers, the allylic protons 1 (H1) are easy to localize. They show a cross peak to the olefinic region, and because of their position at the four-membered ring, they are the most deshielded aliphatic protons compared to the allylic protons 4 (H4) in the six-membered ring skeleton. Thus, the multiplet at 2.57 ppm is assigned to H1 of the anti isomer ($H1^a$), and the multiplet at 3.27 ppm is assigned to the analogous proton of the syn compound ($H1^s$). Notably, in the anti isomer H1 is more shielded than in the syn. $H1^a$ and $H1^s$ both show correlations to two further protons; this further corroborates the postulated regiochemistry. Both isomers are diastereomeric [2+2] cycloadducts with the same orientation of the silene unit. Otherwise, H1 should have only one more vicinal coupling partner each.

The cross peaks of H1 lead to H8 and H6 ($\delta(H8^a) = 2.00$; $\delta(H8^s) = 2.13$; $\delta(H6^a) = 2.07$; $\delta(H6^s) = 2.33$ ppm). H8 only shows correlations to the geminal protons of the neopentyl group, H9 and H9′, which have no further correlations. The protons H6 also have cross peaks leading to pairs of geminal protons (5,5′), but the correlations demonstrate that the spin system is continued to H4 and H4′ and then back to the olefinic H3. Probably because of the different steric demands, the geminal $H4^a$ are isochronic but not $H5^a$, whereas the situation in the syn isomer is vice versa. The coupling constants between the geminal H9 and their vicinal neighbors H8 are different (11.5 and 4.2 Hz for the anti and 9.4 and 5.4 Hz for the syn isomer), which is obviously a consequence of the hindered rotation of the neopentyl group around C8 and C9 in both isomeric compounds. As expected, the neopentyl moiety is directed away from the sterically demanding ring system. To assign the correct configuration to both isomers, a phase-sensitive ROESY[38] experiment was performed (Table III). In this experiment the decisive ROE cross peaks between protons $H1^a/H6^a$ and $H1^a/H8^a$ are perturbed by TOCSY signals, so the only information can be taken from the relations H1/H9 and H1/H10. Taking into account that the product ratio *8a/8b* is about 3/2, the absolute ROE ratio is 1.8/1 comparing the intensities of the cross peaks $H1^a/H9^a$ and $H1^s/H9^s$ and 1.3/1 for $H1^s/H10^a$ and $H1^s/H10^s$.

The information on the NOE relations H1/H6 and H1/H8 was completed by a phase-sensitive NOESY experiment (Table III).[40] Considering the product ratio of the sample to be ~3.0/1.0, the absolute NOE ratio for the relation H1/H6 is about 1, indicating that the distance between these protons is equal in both isomers as expected. The value for the relation H1/H8 (0.7) indicates that the distance between $H1^a$ and $H8^a$ is greater than that between $H1^s$ and $H8^s$. Finally, the ratio for H1/H9 of about 3.3 shows that $H1^a$ is closer to $H9^a$ than $H1^s$ to $H9^s$. This information had already been provided by the ROESY experiment mentioned above. In summary, these experiments prove that the major component of the stereoisomeric pair has anti and the minor one syn configuration at the four-membered ring.

To assign the carbon atoms, a C,H COSY experiment was performed.[42] The multiplicity of the ^{13}C NMR signals was determined by a combination of DEPT-90 and DEPT-135 experiments; the chemical shifts are listed in Table II.

All cross peaks confirm the assignment of the proton NMR signals.

II. NMR Signal Assignment of the Dichloro-Substituted [4+2] Cycloadducts 4.[44] A double-quantum-filtered phase-sensitive COSY spectrum was recorded;[45] assignments of the signals are listed in Table IV.

Starting with H5 and H6 in the olefinic region (δ = 6.20, 6.24, 6.27, 6.37 ppm), one correlation signal was found for each proton. According to the integrals of the one-dimensional spectrum, the resonance signals at δ = 6.20 and 6.27 ppm belong to the minor exo isomer. While the low-field olefinic resonances of both isomers show a correlation leading to signals at δ = 2.64 and 2.68 ppm, the latter belonging to the exo isomer, the cross peak of the high-field signals leads to one aliphatic proton signal each, situated at 2.22 (endo) and 2.31 ppm (exo isomer). These four NMR resonances have to be assigned to the bridgehead H1 and H4 of both isomers. Whereas the signals at 2.68 and 2.64 ppm show two further correlations to those at δ = 1.57 and 1.09 ppm (exo) and 1.35 and 1.16 ppm (endo), the NMR signals at 2.22 and 2.31 ppm have only one more correlation each, i.e., to protons at 2.01 (exo) and 1.96 ppm (endo isomer). Thus, the protons resonating at 2.64 and 2.68 ppm are $H4^{endo}$ and $H4^{exo}$ because they have one additional coupling partner compared to the protons $H1^{endo}$ and $H1^{exo}$ (resonating at δ = 2.22 and 2.31 ppm, respectively).

The additional correlation partners of H1 are found only in the C_2H_4 bridge ($H8^{endo}$ at 1.96 and $H8^{exo}$ at 2.01 ppm). Obviously the ring system is quite twisted because the value of the vicinal coupling constants H1–H8 and H1′–H8′ or H4–H7 and H4′–H7′ is different due to the different dihedral angles. For small coupling constants, consequently, there is no correlation signal of sufficient intensity, and only one vicinal coupling from H1 to H8 or from H4 to H7 is found in the routine two-dimensional spectrum. The diastereotopic methylene protons H9 of the neopentyl group are easy to identify; they give rise to pure double doublets, localized at δ = 1.86 and 1.70 ppm and two of them at 1.16 ppm. Both low-field resonances show very intensive cross peaks to the signals at 1.16 ppm due to the geminal coupling.

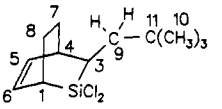
Because of multiple signal superposition in the area from 2.00 to 1.60 ppm, the remaining correlations are difficult to assign. At this stage it proved to be helpful first to assign the ^{13}C NMR signals using a C,H COSY.[46] The

(43) (a) Bax, A. *J. Magn. Reson.* **1983**, *53*, 517. (b) Rutar, V. *J. Magn. Reson.* **1984**, *58*, 306.

(44) All measurements were performed using a sample containing a mixture of two isomeric [4+2] cycloadducts in $CDCl_3$ as solvent in a ratio of about 63/37.

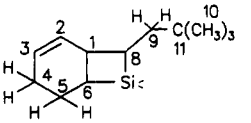
(45) A double-quantum-filtered phase-sensitive COSY spectrum was recorded using the pulse sequence 90–t_1–90–δ–90 acquisition[57] with phase sensitivity achieved by the TPPI method. The very intense signal of the *tert*-butyl groups was presaturated. A total of 32 scans (preceded by two dummy scans) were recorded into 2K data blocks for each of the 400 t_1 values with a relaxation delay of 1.5 s and spectral widths of 2808.99 Hz. The data matrix was zero-filled to 1K in f_1 and apodized with shifted square sine bell functions in both dimensions. These coupling constants, which could be measured, were derived from a one-dimensional proton spectrum recorded with 32 scans, presaturation of the *tert*-butyl group signal, and a relaxation delay of 2.5 s.

Table IV. Proton and Carbon NMR Signal Assignments of the Two Isomeric Dichloro-Substituted [4+2] Cycloadducts 4a,b



	endo-**4a** (63%)			*exo*-**4b** (37%)		
no.	$\delta(^1H)$ (ppm)	J(HH) (Hz)	$\delta(^{13}C)$ (ppm)	$\delta(^1H)$ (ppm)	J(HH) (Hz)	$\delta(^{13}C)$ (ppm)
1	2.22 dddd	7.6/5.0/1.0/1.0	27.11 CH	2.31 dddd	7.6/5.0/0.7/0.7	27.67 CH
3	1.16 m		27.11 CH	1.09 m		31.69 CH
4	2.64 m		40.27 CH	2.68 m		40.95 CH
5	6.37 ddm	8.0/7.6	136.40 CH	6.27 ddm	8.0/7.6	134.14 CH
6	6.24 ddm	8.6/8.0	130.11 CH	6.20 ddm	8.3/8.0	130.08 CH
7	1.35 m		20.79 CH_2	1.57 m		27.45 CH_2
7′	1.74 m			1.70 m		
8	1.68 m		21.15 CH_2	1.65 m		20.39 CH_2
8′	1.96 m			2.01 m		
9	1.16 dd	14.1/2.8	42.74 CH_2	1.16 dd	14.1/2.8	46.00 CH_2
9′	1.86 dd	14.4/8.7		1.70 dd	14.0/7.4	
10	0.8 s		29.38 CH_3	0.8 s		29.38 CH_3
11			31.01 C			31.11 C

Table V. Proton and Carbon NMR Signal Assignments (δ, ppm) of the Two Isomeric Dichloro-Substituted [2+2] Cycloadducts 3a,b in Comparison to the Data of the Diphenyl Analogues 8a,b



	anti-**8a**		*syn*-**8b**		*anti*-**3a**		*syn*-**3b**	
no.	$\delta(^1H)$	$\delta(^{13}C)$	$\delta(^1H)$	$\delta(^{13}C)$	$\delta(^1H)$	$\delta(^{13}C)$	$\delta(^1H)$	$\delta(^{13}C)$
1	2.57	39.09	3.27	37.91	2.49	38.42	3.14	33.74
2	5.96	130.06	5.95	128.95	5.91	130.27	5.82	127.60
3	5.79	126.76	5.70	129.68	5.74	126.00	5.82	127.60
4/4′	1.87	24.45	1.43	23.73	1.94	23.84	1.95	22.96
	1.87		1.69		2.05		1.99	
5/5′	1.55	21.44	1.80	21.36	1.78	20.01	1.68	19.77
	1.60		1.80		1.96		1.77	
6	2.07	23.79	2.33	26.76	2.21	35.52	2.31	34.87
8	2.00	30.68	2.13	31.10	2.01	44.58	2.26	39.54
9/9′	1.38	44.30	1.76	40.89	1.49	43.14	1.52	39.97
	1.45		1.89		1.71		1.58	
10	0.80	29.84	0.83	29.76	0.77	29.55	0.79	29.50
11		31.20		30.40		31.08		30.75

multiplicity of the ^{13}C NMR signals was determined by combining DEPT-90 and DEPT-135 experiments (Table IV).

The aliphatic region of the ^{13}C NMR spectrum contains three methylene group resonances for each isomer placed at 20.39, 20.79, 21.15, 27.45, 42.74, and 46.00 ppm, respectively. The latter two signals are assigned to the methylene group of the neopentyl moieties. The corresponding proton NMR signals are found at 1.16, 1.16, 1.70, and 1.86 ppm, as predicted from the H,H COSY spectrum. The remaining four carbon resonances belong to the carbon atoms $C7^{endo}$, $C7^{exo}$, $C8^{endo}$, and $C8^{exo}$. One proton of each methylene function H8 in both isomers has been established by the H,H COSY due to their cross peak to $H1^{endo}$ or $H1^{exo}$ ($H8^{endo}$, δ = 1.96; $H8^{exo}$, δ = 2.01 ppm). Using the information of the C,H COSY, their geminal pendants $H8^{endo}$ and $H8^{exo}$ are found at δ = 1.68 and 1.65 ppm. The carbon atoms attached to $H8^{endo}$ and $H8^{exo}$ give rise to signals at 21.15 and 20.39 ppm corresponding to $C8^{endo}$ and $C8^{exo}$. Consequently, the resonances of C7 at 20.79 and 27.45 ppm show corresponding proton absorption lines at 1.35/1.74 and 1.57/1.70 ppm. As mentioned above, in the H,H COSY, $H4^{endo}$ and $H4^{exo}$ are connected with correlation peaks at 1.35 and 1.57 ppm, which are assigned to $H7^{endo}$ and $H7^{exo}$. Thus, the protons $H7'^{endo}$ and $H7'^{exo}$ are localized according to the C,H COSY at 1.74 and 1.70 ppm. The remaining correlation partners of $H4^{endo}$ and $H4^{exo}$ at 1.16 and 1.09 ppm should be the protons $H3^{endo}$ and $H3^{exo}$. Indeed, $C3^{endo}$ and $C3^{exo}$ give rise to the NMR signals at 27.11 and 31.69 ppm with doublet multiplicity (CH group) according to the DEPT spectra.

III. NMR Signal Assignment of the Chlorinated [2+2] Cycloadducts 3a and 3b. To obtain a complete data set for the dichloro-substituted [2+2] cycloadducts **3** without separating **3** from **4**, a sample of 100 mg of **3**/**4** was dissolved in 400 μL of $CDCl_3$ and a C,H COSY was recorded.[47] The multiplicity of the ^{13}C NMR signals was determined by combining DEPT-90 and DEPT-135 experiments (Table V). The resonances of *endo*/*exo*-**4** were identified and neglected. The chemical shifts of **4** deviate only to a minimal extent from those mentioned earlier.

As expected, decisive changes of the chemical shifts on replacing the chlorine atoms attached to silicon by phenyl

(46) In this C,H COSY[43] with f_1 decoupling, only geminal couplings are still to find in f_1. The 180° pulse was a composite pulse. A total of 256 scans were recorded into 4K data blocks for each of the 128 t_1 values with a relaxation delay of 2 s and spectral widths of 15 151.52 and 2502.70 Hz. The data matrix was zero-filled to 1K in f_1 and apodized with sine bell functions in both dimensions.

(47) For this C,H COSY, 32 scans were recorded into 8K data blocks for each of the 512 t_1 values with a relaxation delay of 1.05 s and spectral widths of 12 195.12 and 3246.75 Hz. The data matrix was apodized with sine bell functions in both dimensions.

moieties can only be registered for the carbon atoms C8 and C6 of both isomers. Because the dichloro-substituted compounds have lower electron density at silicon, the carbon atoms attached to silicon in these cases are more deshielded.

Experimental Section

All reactions were performed under a nitrogen atmosphere. Solvents used were dry and oxygen free; $H_2C{=}CHSiCl_3$ and $(H_2C{=}CH)Me_2SiCl$ were obtained from Wacker Chemie GmbH, Burghausen. *t*-BuLi (1.7 M in *n*-pentane) was obtained from Aldrich-Chemie GmbH & Co. KG, Steinheim. Cyclohexa-1,3-diene and Me_3SiOMe were purchased from Fluka Chemie AG, Buchs.

Routine NMR spectra were recorded on a Bruker AM 360 (^1H, ^{13}C) and a Jeol JNM GX 270 (^{29}Si) FT NMR spectrometer. The samples were dissolved in $CDCl_3$, and TMS was used as standard. Special measurements and conditions are recorded in the spectroscopic part.

Gas chromatography was carried out with a Chrompack CP 9000 with a 10-m Chrompack CP Sil 5 CB; 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 coupled with a Finnigan MAT ion trap 800. Chemical ionization (CI) used methanol as reactant gas.

Elemental analyses were performed by Mikroanalytisches Laboratorium, Anorganisch-chemisches Institut der Technischen Universität München.

Cycloaddition Reaction between 1 and 2. An 18-mL (30-mmol) portion of *t*-BuLi was added with stirring to vinyltrichlorosilane (3.20 g, 30 mmol) and **2** (7.20 g, 90 mmol) in 500 mL of *n*-pentane at −78 °C. The mixture was then allowed to warm slowly to room temperature. After filtration and evaporation of the solvent, distillation of the residue under reduced pressure (10^{-2} mbar) yielded 7.82 g of a colorless liquid which was identified as a mixture of *anti/syn*-7,7-dichloro-8-neopentyl-7-silabicyclo-[4.2.0]oct-2-ene (**3**) and *endo/exo*-2,2-dichloro-3-neopentyl-2-silabicyclo[2.2.2]oct-5-ene (**4**): yield 99.3% (29.8 mmol); bp 60 °C/10^{-2} mbar.

^1H and ^{13}C NMR spectroscopic data are given in Tables IV and V.

3a: ^{29}Si NMR δ 19.7; mass spectrum (assignment (relative intensity, %)) *m/e* 262 (M^+, 6), 79 (C_6H_7, 100), 78 (C_6H_6, 72), 77 (C_6H_5, 40), 113 ($MeSiCl_2$, 12), 183 ($M^+ - C_6H_7$, 3), 205 (M^+ - Bu-*t*, 3).

3b: ^{29}Si NMR δ 14.2; MS *m/e* 262 (M^+, 5), 79 (C_6H_7, 100), 57 (Bu-*t*, 47), 227 (M^+ - Cl, 9), 205 (M^+ - Bu-*t*, 7), 78 (C_6H_6, 60), 77 (C_6H_5, 55).

4a: ^{29}Si NMR δ 25.6; MS *m/e* 262 (M^+, 12), 79 (C_6H_7, 100), 154 ($C_{12}H_{10}$, 82), 57 (Bu-*t*, 72), 78 (C_6H_6, 60), 205 (M^+ - Bu-*t*, 10), 247 (M^+ - Me, 8).

4b: ^{29}Si NMR δ 26.5; MS *m/e* 262 (M^+, 6%), 79 (C_6H_7, 100), 57 (Bu-*t*, 15), 113 ($MeSiCl_2$, 14), 183 ($M^+ - C_6H_7$, 4).

Anal. Calcd for $C_{12}H_{20}SiCl_2$ (**3**, **4**): C, 54.78; H, 7.60; Si, 10.67; Cl, 26.95. Found: C, 55.12; H, 7.84; Si, 10.47; Cl, 26.55.

Synthesis of 5. $Cl_3SiCH{=}CH_2$ (1.61 g, 10 mmol) was dissolved in 100 mL of *n*-pentane and the resultant mixture cooled to −78 °C. After addition of 6 mL of *t*-BuLi (10 mmol), the mixture was allowed to warm to −15 °C and Me_3SiOMe (3.3 mL, 30 mmol) was added dropwise with stirring. The reaction was completed by stirring for an additional 6 h at room temperature. The solution was freed from precipitated LiCl by filtration. The solvent and excess Me_3SiOMe were evaporated. **5** was isolated by distillation at 160 °C; 2.57 g, 9 mmol, 90%.

5: ^1H NMR (100 MHz) δ 0.13 (s, 9 H, $Si(CH_3)_3$), 0.88 (s, 9 H, *t*-Bu), 3.60 (s, 3 H, OCH_3), 1.93–1.23 (m, 3 H, $CHCH_2$); ^{13}C NMR δ 51.04 (OCH_3), 36.52 (CH_2), 31.65 ($C(CH_3)_3$), 29.50 ($C(CH_3)_3$), 13.90 (CH), −0.28 ($Si(CH_3)_3$); ^{29}Si NMR δ −8.5 ($Si(CH_3)_3$), 3.6 ($Si(Cl)_2OCH_3$); MS *m/e* 286 (M^+, <0.1), 73 ($SiMe_3$, 100), 57 (*t*-Bu, 38), 271 ($M^+ - CH_3$, 36), 229 (M^+ - *t*-Bu, 23), 251 (M^+ - Cl, 18), 121 ($ClSi(OMe)C_2H_3$, 10).

Preparation of *anti/syn*-7,7-Diphenyl-8-neopentyl-7-silabicylo[4.2.0]oct-2-ene (8). PhMgBr (50 mmol in 50 mL of THF) was added to **3** and **4** (4.0 g, 15 mmol) at room temperature. After the mixture was refluxed for 8 h, it was stirred at room temperature for an additional 12 h. Filtration of the precipitate, evaporation of the solvent, and distillation of the residue afforded **4** at 60 °C/10^{-2} mbar (0.95 g, 24.2%) and **8** at 170 °C/10^{-2} mbar as colorless, highly viscous liquids; 3.54 g, 66.7%. ^1H and ^{13}C NMR spectroscopic characterizations are given in Table II.

8a: ^{29}Si NMR δ 3.7; MS *m/e* 346 (M^+, 8), 209 ($Ph_2SiC_2H_3$, 100), 105 (PhSi, 42), 183 (Ph_2SiH, 41), 162 ($M^+ - Ph_2SiH_2$, 23), 79 (C_6H_7, 22), 259 ([(M^+ - Bu-*t*) - C_2H_6], 5).

8b: ^{29}Si NMR δ 0.2; MS *m/e* 346 (M^+, 6), 259 ([(M^+ - Bu-*t*) - C_2H_6], 100), 183 (Ph_2SiH, 30), 105 (PhSi, 28), 209 ($Ph_2SiC_2H_3$, 12), 162 ($M^+ - Ph_2SiH_2$, 8), 79 (C_6H_7, 8).

Anal. Calcd for $C_{24}H_{30}Si$ (**8**): C, 83.17; H, 8.73; Si, 8.10. Found: C, 80.83 (C value too low because of SiC formation); H, 9.47; Si 8.23.

Preparation of *anti/syn*-7,7-Dimethyl-8-neopentyl-7-silabicyclo[4.2.0]oct-2-ene (7). MeMgI (30 mmol in 50 mL of ether) was added dropwise to a solution of **3** and **4** (2.6 g, 10 mmol) in 50 mL of ether. Ether was evaporated, and pentane was added to force the precipitation of Mg salts. Filtration, evaporation of the solvent, and distillation of the yellow residue at 58–60 °C/10^{-2} mbar yielded a colorless liquid consisting of **4** and **7**. Although separation of the compounds by distillation or gas chromatographically failed, they could be spectroscopically characterized as a mixture.

7a: ^{13}C NMR δ 130.8 and 126.2 (CH olefin), 38.2, 32.2, and 24.0 (CH), 44.4, 24.8, and 21.3 (CH_2), 30.6 ($C(CH_3)_3$), 29.7 ($C(CH_3)_3$), −2.4 and −4.6 ($Si(CH_3)_2$); ^{29}Si NMR δ 9.6; MS *m/e* 222 (M^+, 10), 85 ($Me_2SiC_2H_3$, 100), 165 (M^+ - Bu-*t*, 18), 135 ([(M^+ - Bu-*t*) - 2Me], 10), 114 ($Me_2SiC_4H_8$, 5), 99 ($MeSiC_4H_8$, 3), 207 (M^+ - Me, 3).

7b: ^{13}C NMR δ 130.0 and 128.4 (CH olefin); 37.4, 27.6, and 27.1 (CH), 41.4, 24.6, and 21.7 (CH_2), 31.1 ($C(CH_3)_3$), 29.6 ($C(CH_3)_3$), 1.6 and − 1.9 ($Si(CH_3)_2$); ^{29}Si NMR δ 19.1; MS *m/e* 222 (M^+, 9), 85 ($Me_2SiC_2H_3$, 100), 73 ($SiMe_3$, 45), 165 (M^+ - Bu-*t*, 20), 135 ([(M^+ - 2Me) - Bu-*t*], 12), 207 (M^+ - Me, 3).

Thermolysis of 3 and 4. A mixture of **3** and **4** (4.0 g, 15 mmol) was heated in a sealed tube for 90 h at 200 °C. *anti/syn*-**3** completely isomerized into **4** and (*E*)-**6**. Distillation yielded a mixture of **4** and (*E*)-**6** (3.80 g, 14.5 mmol, 95%), which could not be separated; 58–60 °C/10^{-2} mbar.

(*E*)-**6:** ^1H NMR (270 MHz) δ 5.6 (H_A), 6.5 (H_B) (J_{AB} 18.6 Hz), 1.05 (s, Bu-*t*) (δ(CH_2) not separable from **4**); ^{13}C NMR δ 24.7, 22.5, and 21.7 (CH_2), 30.2 (CH), 129.0 and 123.0 (CH olefinic), 165.3 (=*C*HBu-*t*), 115.1 (=*C*HSiMe$_2$), 35.6 ($C(CH_3)_3$), 28.5 ($C(CH_3)_3$); ^{29}Si NMR δ 15.0; MS *m/e* 262 (M^+, 10), 79 (C_6H_7, 100), 80 (C_6H_8, 90), 181 ($M^+ - C_6H_7$, 20), 227 (M^+ - Cl, 3), 205 (M^+ - Bu-*t*, 3), 182 ($M^+ - C_6H_8$, 2).

Preparation of 2-(1′,1′,4′,4′-Tetramethyl-1′-silapent-2-(*E*)-enyl)cyclohexene ((*E*)-9). MeMgI (30 mmol in 50 mL of ether) was added dropwise to a solution of thermolysis products **4** and (*E*)-**6** (3.93 g, 15 mmol) in 50 mL of ether. The mixture was refluxed for 10 h. The isolation of (*E*)-**9** (together with **4**) was performed as described for **7**; yield 2.90 g.

(*E*)-**9:** ^1H NMR δ 5.6 (H_A), 6.5 (H_B) (J_{AB} 18.6 Hz), 0.1 and 0.2 (s, $Si(CH_3)_2$), 0.9 (s, Bu-*t*) (δ(CH_2) not separable from **4**); ^{13}C NMR δ 165.1 (=*C*HBu-*t*), 115.8 (=*C*HSiMe$_2$), 126.4 and 129.2, (CH olefinic), 24.4 (CH), 22.8, 24.2, and 25.2 (CH_2), 35.7 ($C(CH_3)_3$), 29.1 ($C(CH_3)_3$); ^{29}Si NMR δ −6.3; MS *m/e* 222 (M^+, 15), 85 ($Me_2SiC_2H_3$, 100), 59 (C_4H_{11}, 65), 83 (Me_2SiC_2H, 28), 135 (M^+ - $Me_2SiC_2H_5$, 20), 163 ($M^+ - C_4H_{11}$, 15), 207 (M^+ - Me, 7).

Thermolysis of 8. A mixture of *anti/syn*-**8** (1g, 0.3 mmol) was heated at 200 °C in a sealed tube for 5 days. *syn*-**8b** isomerizes completely to (*E*)-**10** while *anti*-**8a** remains unchanged.

(*E*)-**10:** ^1H NMR δ 1.0 (s, Bu-*t*), 5.5 (H_A), 6.4 (H_B) (J_{AB} 19 Hz), 7.9 (m, Ph) (δ(CH_2) not separable from **8a**); ^{13}C NMR δ 158.8 (=*C*HBu-*t*), 120.2 (=*C*HSiPh$_2$), 125.3 and 130.1 (CH olefinic), 27.4 (CH), 25.2, 24.0, and 22.7 (CH_2), 34.2 ($C(CH_3)_3$), 29.1 ($C(CH_3)_3$); ^{29}Si NMR δ −16.3; MS *m/e* 346 (M^+, 6), 209 ($Ph_2SiC_2H_3$, 100), 182 (Ph_2Si, 40), 105 (PhSi, 33), 77 (C_6H_5, 30), 79 (C_6H_7, 24).

Thermolysis of a Product Mixture of 4 and 7. A mixture of **4** and **7** (1 g) was heated at 200 °C in a sealed tube for 5 days. *syn*-**7b** isomerizes completely to (*E*)-**9** while **4** and **7a** remain unchanged.

Cycloaddition Reaction of Dimethylneopentylsilene (11) and 2. This reaction was performed as described previously for $H_2C{=}SiCl_2$, LiBu-*t*, and **2**: 18 mL of LiBu-*t* was added to vi-

nyldimethylchlorosilane (4.23 g, 30 mmol) and **2** (8 g, 100 mmol) in 500 mL of *n*-pentane at -78 °C. Isolation as before yields a colorless liquid (3.0 g; bp 55 °C/10^{-2} mbar) which could be identified as a mixture of (*E*/*Z*)-**12**, **13**, and **7**. The cycloadducts were separated from **12** by distillation.

(*E*)-**12**: ^{13}C NMR δ 39.8 (CH_2), 12.1 (CH), 31.5 ($C(CH_3)_3$), 29.3 ($C(CH_3)_3$), 0.7 ($Si(CH_3)_2$); ^{29}Si NMR δ 8.6.

(*Z*)-**12**: ^{13}C NMR δ 39.9 (CH_2), 12.7 (CH), 31.3 ($C(CH_3)_3$), 29.4 ($C(CH_3)_3$), 2.6 and -4.8 ($Si(CH_3)_2$); ^{29}Si NMR δ 10.3. For ^{1}H NMR and MS of **12** see ref 30.

13: ^{13}C NMR δ 134.0, 133.5, 133.1, and 131.6 (CH olefinic), 40.5, 40.1, 27.3, 23.6, 22.9, and 22.4 (CH), 43.6, 42.9, 24.4, 21.8, 21.5, and 20.9 (CH_2), 30.5 ($C(CH_3)_3$), 29.6 ($C(CH_3)_3$), -1.5 -2.7, -4.1, and -4.2 ($Si(CH_3)_2$); MS *m*/*e* 222 (M^+, 18), 85 ($Me_2SiC_2H_3$, 100), 59 (C_4H_{11}, 65), 135 ($M^+ - Me_2SiC_2H_5$, 20), 165 ($M^+ - C_4H_9$, 18), 137 ($M^+ - Me_2SiC_2H_3$, 10); MS *m*/*e* 222 (M^+, 20), 85 ($Me_2SiC_2H_3$, 100), 59 (C_4H_{11}, 95), 135 ($M^+ - Me_2SiC_2H_5$, 30), 137 ($M^+ - Me_2SiC_2H_3$, 18), 163 ($M^+ - C_4H_{11}$, 15).

Acknowledgment. This research has been supported by the Volkswagen-Stiftung, the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie.

Mechanism of the Photochemical C–C Coupling Reaction of Tricarbonyl(η^6-1,3,5-cycloheptatriene)chromium with Conjugated Dienes. IR Study in Liquid Noble Gases and Low-Temperature Matrices

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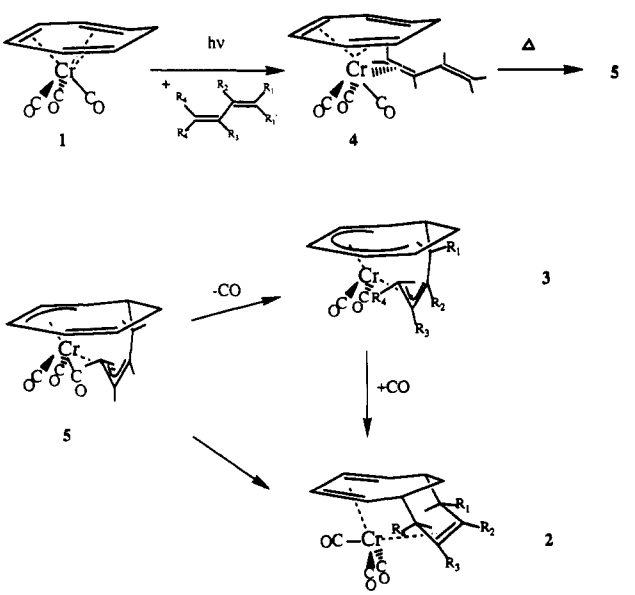
Received June 28, 1991

The mechanism of the photochemical C–C coupling reaction of $Cr(CO)_3(\eta^6\text{-}C_7H_8)$ (C_7H_8 = 1,3,5-cycloheptatriene) with conjugated dienes, producing a ($\eta^{4:2}$-bicyclo[4.4.1]undeca-2,4,8-triene)tricarbonyl- and/or a 1-butene-1,2-diylcyclohepta-2,4-dien-5-yldicarbonylchromium complex, has been investigated. The primary photoprocesses were studied in low-temperature matrices, and the secondary thermal reactions, in liquefied noble gases and organic solvents. The reactions were followed by infrared spectroscopy. Two primary photoprocesses have been observed: CO loss and $\eta^6 \rightarrow \eta^4$ hapticity change of the triene ligand. In solution only the CO loss reactions gave rise to the coupling reaction under study, which is independent of the wavelength of irradiation ($\lambda > 350$ nm). The new C–C bonds were formed stepwise. In the last step of the reaction the dissociated CO reacted back to form the final tricarbonyl product. Methyl substituents on the dienes destabilized the observed intermediates and hindered the formation of the C–C bonds and the back-reaction with CO.

Introduction

Kreiter and co-workers investigated the photochemical reactions of the cycloheptatrienechromium complex $Cr(CO)_3(\eta^6\text{-}C_7H_8)$ (**1**) and its heptafulvene derivative $Cr(CO)_3(\eta^6\text{-}C_{10}H_{12})$ (**1′**) with conjugated dienes at reduced temperatures.[1] They observed the formation of (bicycloundecatriene)tricarbonylchromium complexes **2** (out of **1**) and **2′** (out of **1′**) with two new C–C bonds[2] and/or, if sterically more hindered dienes were used, a dicarbonyl complex **3′** (out of **1′**) with one new bond[3] (compare with Scheme I). **3′** reacted with excess CO, forming **2′**, which process was favored by lowering the temperature.[4] The formation of **3′** indicated that the cycloaddition is not a concerted [6 + 4] cycloaddition but a stepwise process. A tentative mechanism for these reactions was proposed, which is depicted in Scheme I for the cycloheptatriene case. The first step of the reaction is a light-induced $\eta^6 \rightarrow \eta^4$ hapticity change of the triene ligand, leaving an open site for the diene, which binds to the metal in a η^2-coordination. This η^4–η^2-complex **4** (or **4′**) reacts further by a C–C coupling between the diene and the 1- or 6-carbon atom of the heptatriene ligand, resulting in the formation of an $\eta^{3,3}$-dienyl complex **5** (or **5′**); see Scheme I. **5** (or **5′**) can react in two ways: either by formation of **2** (or **2′**) or by loss of CO, producing **3** (or **3′**).[1,3]

Scheme I. Mechanism Proposed by Kreiter et al.[1] for the C–C Coupling Reaction between Tricarbonyl(η^6-1,3,5-cycloheptatriene)chromium Complexes and Conjugated Dienes



Complex **1** shows also a C–C coupling reaction with alkynes.[5] This reaction and the reaction with hydrogen,

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0276-7333/92/2311-1146$03.00/0