MNDO for 5. AM1 does appear to produce Sn-C bonds in stannocene that are somewhat too short, ranging from about 2.49 to 2.62 Å as compared to the experimental values which range from roughly 2.58 to 2.75 Å. The centroid-centroid angle for 4, 120°, is also smaller than that of the X-ray structure[18] (144° and 148°), although it is close to that derived from the GED study, 125°.[19] As the gas phase is the closest model to AM1, the discrepancy may be due to forces in the solid state not present in isolated systems, such as preferential packing arrangements.

The highest occupied orbitals of stannocene have been predicted by X_α calculations[23] to be the nearly degenerate $6a_2$ and $9b_2$[20] with the a_1 tin lone pair next highest in energy. Extended Huckel calculations reverse this ordering.[20] The X_α calculations, however, appear to be in accord with the UV PES spectrum of 4,[23] and in good agreement with the X_α calculations, AM1 predicts the nearly degenerate Cp ring MOs as the highest occupied MOs. AM1 does, unfortunately, overestimate the IP of stannocene, predicting a first ionization potential of 8.49 eV as compared to the experimentally observed value of 7.57 eV.[23] Overestimation of IPs in methods using the core approximation[25] is a common problem[26] due to the fact that repulsions between the valence and subvalence AOs are not specifically accounted for in these methods.

Conclusions

The AM1 formalism has been successfully extended to tin. In almost all cases, AM1 performs better than MNDO. The AM1 results for organometallic species are especially promising.

(25) The valence electrons are assumed to move in a fixed core of the nuclei and inner shell electrons.
(26) Dewar, M. J. S.; Rzepa, H. S. *J. Comput. Chem.* **1983**, *4*, 158.

Preparation and Structure of Silacycloheptatriene

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Received July 18, 1990

The first preparation of C-unsubstituted silacycloheptatrienes, silicon analogues of cycloheptatriene, is described along with spectroscopic properties. A 2,5-diphenyl derivative has been similarly prepared. The new and general preparative method for silacycloheptatriene is based on the reaction of the silacyclohexadienyl anion with chlorocarbene. The reaction pathway to silacycloheptatriene has been examined by the use of deuterium labeling.

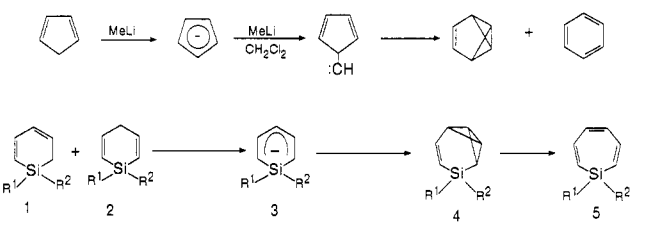
Introduction

Silacycloheptatrienes (silepins) have the possibility of delocalizing six π electrons in the ring through a vacant 3d orbital on a silicon atom, and in this respect, these may constitute neutral silicon analogues of the tropylium cation. Until our recent success in the preparation of 1,1-dimethylsilepin,[1] all silepins reported so far have been annelated derivatives such as mono-,[2] di-,[3] and tribenzosilepins[4] except for two examples,[5] which are monocyclic but C-substituted ones.

The UV spectrum of a dibenzosilepin[3a,c] does not reveal the existence of any significant cyclic delocalization of six π electrons through a silicon atom. Although in the ^1H NMR spectra of dibenzosilepin[3a] and 1,1-dimethyl-2,7-diphenylsilepin[5a] the SiMe signals appear as a singlet, these structures have been accounted for not by planar geometries but by rapidly inverting boat conformations. On the other hand, a tribenzosilepin has two distinct SiMe signals in accord with its rigid boat geometry.

These benzo- and C-substituted silepins are not always suitable for studies of subtle interaction between a triene unit and a silicon atom in a seven-membered ring. Therefore, the synthesis of C-unsubstituted silepins is an important goal. In this paper, the first successful synthesis of C-unsubstituted silepins and their structures are described in some detail.

Scheme I



Results and Discussion

Preparation of 1-Silacyclohepta-2,4,6-trienes (Silepins). One of the most important synthetic methods for the valence isomers of benzenoid hydrocarbons such as benzvalene and benzobenzvalene involves cyclization of the intermediate carbene species resulting from the reaction of a cyclohexadienyl or indenyl anion with CH_2Cl_2

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(1) Partly reported in a preliminary form: Nakadaira, Y. In *Organosilicon and Bioorganiosilicon Chemistry*; Sakurai, H., Ed.; Ellis Horwood: Chichester, U.K., 1984; Chapter 14, p 145.
(2) (a) Birkofer, L.; Haddad, H. *Chem. Ber.* **1966**, *102*, 432. (b) Birkofer, L.; Haddad, H.; Zamarlik, H. *J. Organomet. Chem.* **1970**, *25*, C57. (c) Birkofer, L.; Haddad, H. *Chem. Ber.* **1972**, *105*, 2101.
(3) (a) Barton, T. J.; Volz, W. E.; Johnson, J. *J. Org. Chem.* **1971**, *36*, 3365. (b) Corey, J. Y.; Dueber, M.; Bichlmeir, B. *J. Organomet. Chem.* **1971**, *26*, 167. (c) Cartledge, F. K.; Mollers, P. D. *Ibid.* **1971**, *26*, 175. (d) Corey, J. Y.; Farrell, R. L. *J. Organomet. Chem.* **1978**, *153*, 15.
(4) Corey, J. Y.; Corey, E. R. *Tetrahedron Lett.* **1972**, 4669.
(5) (a) Barton, T. J.; Kippenhan, R. C., Jr.; Nelson, A. J. *J. Am. Chem. Soc.* **1974**, *96*, 2272. (b) Ishikawa, M.; Fuchikami, T.; Kumada, M. *Tetrahedron Lett.* **1976**, 1299.

0276-7333/91/2310-0435$02.50/0

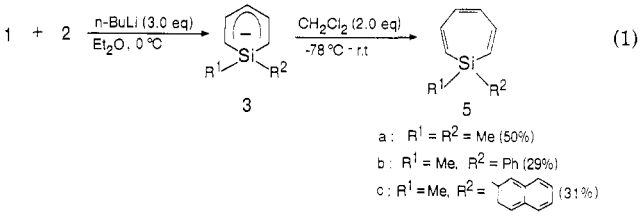
Table I. Coupling Constants (Hz) for 1a and 8

coupling const	1[a]	8
$J_{2,3}$	14.31	14.0
$J_{3,4}$	6.30	5.7 ($J_{5,6}$)
$J_{4,5}$	12.70	
$J_{2,4}$	0.61	0.3 ($J_{5,7}$)
$J_{2,5}$	0.70	0.8
$J_{2,6}$	−0.51	0.3 ($J_{3,7}$ = 0.4)
$J_{2,7}$	1.66	1.8
$J_{3,5}$	0.38	0.2
$J_{3,6}$	0.63	0.8

[a] Obtained by spectral simulation.

in the presence of alkyllithium to form the bicyclo[1.1.0]butane system.[6] These so-called Katz reaction products can be converted into the corresponding benzenoid hydrocarbons by thermal or metal-catalyzed skeletal rearrangement.

The method of the ring enlargement above may be applicable to the synthesis of a C-unsubstituted silepin in general. The silacyclohexadienyl anion **3**[7] is expected to



(1)

react with CH_2Cl_2 in the presence of BuLi to afford the bicyclobutane derivative **4**, which can isomerize to the silepin **5** without difficulty. The reaction of anions derived from a variety of silacyclohexadienes has been examined. The starting materials 1,1-dimethyl-1-silacyclohexa-2,4-diene (**1a**) and 1,1-dimethyl-1-silacyclohexa-2,5-diene (**2a**) were prepared as a mixture by flow copyrolysis of cyclopentadiene and 1,2-dimethoxy-1,1,2,2-tetramethyldisilane.[8] The ether solution of **1a** and **2a** (**1a**:**2a** = 3:2) was treated with BuLi (3.0 equiv) at 0 °C under an argon atmosphere, and then CH_2Cl_2 (2.0 equiv) in ether was added at −78 °C. After the usual treatment of the reaction mixture, extraction with ether, and evaporation of the solvent, the distillate obtained was purified by preparative GLC to give 1,1-dimethyl-1-silacyclohepta-2,4,6-triene (1,1-dimethylsilepin; **5a**) as a colorless oil in 50% yield free from byproducts such as bicyclobutane derivatives. **5a** is well characterized by various spectroscopic methods. The ^1H NMR spectrum of **5a** shows an [AA'BB'CC'] type signal due to the six ring protons at δ 5.79, 6.41, and 6.89 (Figure 1 and Table I), and the ^{13}C NMR spectrum shows three signals due to the ring carbons at δ 131.2 (d, C-2,7), 132.1 (d, C-4,5), and 140.4 (d, C-3,6). The last resonance was assigned by means of selective decoupling of the corresponding proton signals. In the mass spectrum measured at 60 °C, **5a** shows the molecular ion peak at m/z 136 (100%).

In a similar manner, 1-methyl-1-phenylsilepin (**5b**) was obtained from a mixture of 1-methyl-1-phenyl-1-silacyclohexa-2,4-diene (**1b**) and 1-methyl-1-phenyl-1-silacyclohexa-2,5-diene (**2b**) (**1b**:**2b** = 4:1) in 29% yield (TLC)

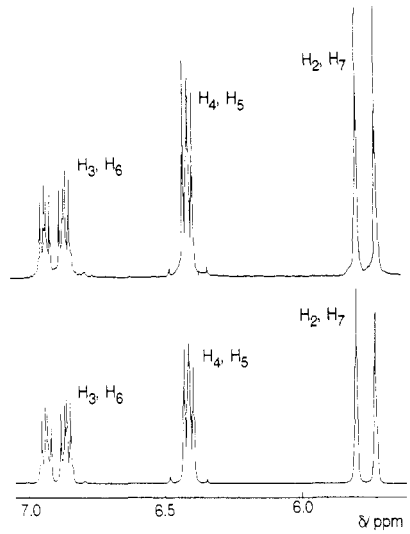
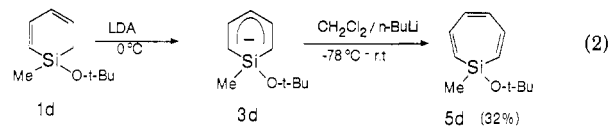
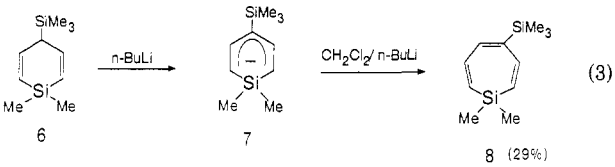


Figure 1. Experimental (top) and simulated (bottom) ^1H NMR spectra of **5a**. Only olefinic proton signals are shown.

and 1-methyl-1-(2-naphthyl)silepin (**5c**) was obtained from 1-methyl-1-(2-naphthyl)-1-silacyclohexa-2,4-diene (**1c**) in 31% yield. This method is also found to be applicable to the synthesis of a silacyclohexadiene having an alkoxy group on the silicon. Thus, at first, 1-methyl-1-*tert*-butoxy-1-silacyclohexa-2,4-diene (**1d**) was metalated with

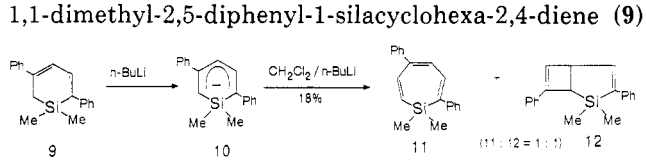


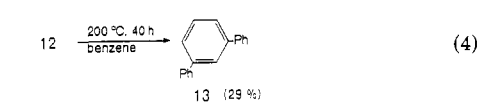
(2)



(3)

lithium diisopropylamide (LDA)[9] in ether at 0 °C, and then the resulting anion **3d** was treated with BuLi followed by CH_2Cl_2 at −78 °C to afford 1-methyl-1-*tert*-butoxysilepin (**5d**), which was isolated in 32% yield by TLC. Although no molecular ion peak in the mass spectrum was observed, the structure of **5d** was determined by characteristic ^1H NMR signals assignable to those of the six olefinic protons of the C-unsubstituted silepin. In fact, these signals are quite similar to those of **5a**. These procedures also serve as a general synthetic method for variously substituted silepins. Actually, 1,1-dimethyl-4-(trimethylsilyl)-1-silacyclohexa-2,5-diene (**6**) afforded the expected 1,1-dimethyl-4-(trimethylsilyl)silepin (**8**) in 29% yield. Together with its molecular ion peak at m/z 208 (3%) in the mass spectrum, **8** is well characterized by ^1H NMR coupling constants as summarized in Table I. On the other hand, 1,1-dimethyl-2,5-diphenyl-1-silacyclohexa-2,4-diene (**9**)





(4)

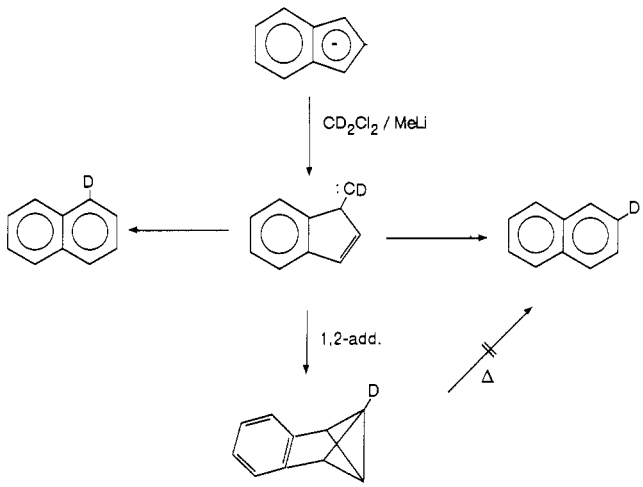
(6) (a) Katz, T. J.; Wang, E. J.; Acton, N. *J. Am. Chem. Soc.* **1971**, *93*, 3782. (b) Murata, I.; Nakatsuji, K. *Tetrahedron Lett.* **1973**, 47. (c) Burger, U.; Mazenod, F. *Ibid.* **1976**, 2881. (d) Pagni, R. M.; Burnett, M.; Hazell, A. C. *J. Org. Chem.* **1978**, *43*, 2750. (e) Gandillon, G.; Bianco, B.; Burger, U. *Tetrahedron Lett.* **1981**, *22*, 51.

(7) Barton, T. J.; Banasiak, D. S. *J. Organomet. Chem.* **1978**, *157*, 255.

(8) Hwang, R.-J.; Conlin, R. T.; Gasper, P. P. *J. Organomet. Chem.* **1975**, *94*, C34.

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

Scheme II



afforded a mixture of 1,1-dimethyl-2,5-diphenylsilepin (**11**) and an unexpected bicyclic isomer, 2,2-dimethyl-3,7-diphenyl-2-silabicyclo[3.2.0]hepta-3,6-diene (**12**), in 18% yield. The ratio of **11** to **12** was estimated to be around 1:1 from inspection of the ^{1}H NMR spectrum. Although **11** and **12** were susceptible to air oxidation and seemed to decompose at room temperature gradually, these were separated by means of HPLC. Both **11** and **12** show molecular ion peaks at m/z 288, the relative intensities of which are 19 and 42%, respectively. The structures of **11** and **12** are supported on the basis of ^{1}H NMR spectra; i.e., the coupling constants between the four ring protons of **11** are quite similar to those of **5a**. The presence of the two types of methine and vinyl protons in the ^{1}H NMR spectrum indicates **12** to be a bicyclic compound. The coupling constants between these protons ($J_{1,5}$ = 3.8 Hz, $J_{1,6}$ = 0.8 Hz, $J_{4,5}$ = 3.2 Hz, $J_{5,6}$ = 1.3 Hz) are well rationalized on the basis of the substitution pattern of the two phenyl groups in **12**. This is further supported by the experimental fact that pyrolysis of **12** at 200 °C for 40 h gives *m*-terphenyl (**13**) in 29% yield.

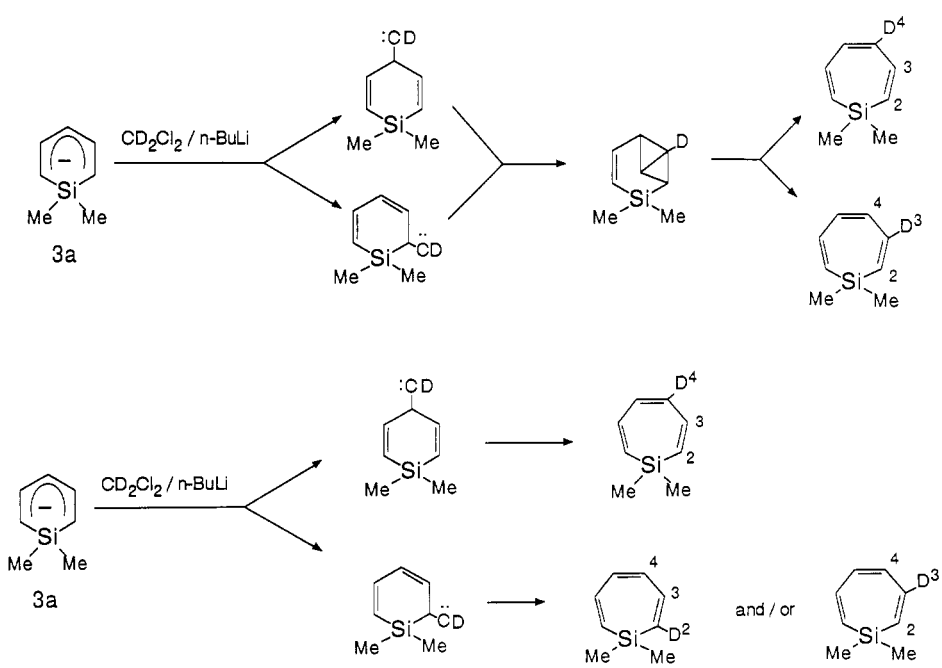
Mechanisms for the Formation of Silepins. Lithium salts of the cyclopentadienyl anion have been known to be converted into benzenoid hydrocarbons and their isomers such as benzvalene-type compounds by reactions with a chlorocarbene generated from CH_2Cl_2 and alkyllithium. The mechanistic studies reveal that benzvalene-type compounds should be formed through intramolecular 1,2-addition of the carbene centers of the key intermediates which arise from the reaction of aromatic anions with chlorocarbene as depicted in Scheme II.[6c] On the other hand, 1,2-vinyl migration to the carbene center of the intermediate leads to the benzenoid compounds.

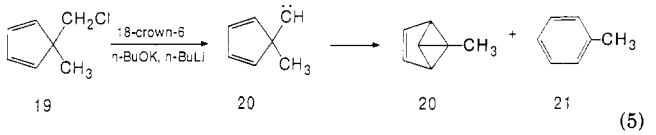
In order to determine the location of the carbon atom derived from CH_2Cl_2, the silepin synthesis has been carried out by the use of CD_2Cl_2. If **5a** is formed via a bicyclobutane derivative, it should be labeled equally at C-3 and C-4 (Scheme III, top). On the other hand, if it is formed via rearrangement of a skeletal atom to the carbene center, the deuterium should be located at C-2, C-3, and/or C-4 (Scheme III, bottom).

Then, **3a** was treated with CD_2Cl_2 in the presence of BuLi under conditions similar to those described above. 2-Deuterio-1,1-dimethylsilepin (**16**) was obtained exclusively, and no other isomers were detected. The position of the deuterium incorporated in **16** can readily be assigned on the basis of the ^{1}H NMR spectrum. As shown in Figure 1, the ^{1}H NMR spectrum of **5a** shows three sets of olefinic proton signals centered at δ 5.79, 6.41, and 6.89 with equal intensity, while in **16**, the intensities of the two signals at δ 6.41 and 6.69 remain unchanged but the signal at δ 5.79 reduces to half of its original intensity observed in **5a**.

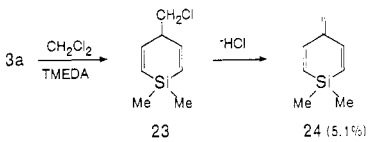
The reaction path to **16** can be explained as shown in Scheme IV. First, a deuterated chlorocarbene species generated from the reaction of CD_2Cl_2 with BuLi adds to the carbon at the 2-position of **3a** to give the anion **14**, and then a β-silylcarbene is formed by elimination of a chloride ion. The subsequent migration of the silyl group to the carbene center produces silepin **16**. Under these reaction conditions, the intermediacy of a carbene species such as **15** is well documented. For example, carbene **20**, generated from haloalkene **19**, produces **21** with intramolecular carbene addition, accompanied by **22**.[10] On the other

Scheme III

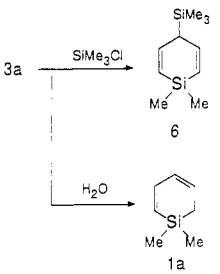




(5)



(6)

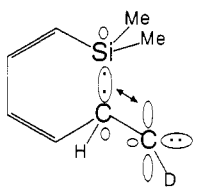


(7)

hand, the treatment of **3a** with CH_2Cl_2 in the presence of tetramethylethylenediamine afforded only 4-methylene-1,1-dimethyl-1-silacyclohexa-2,5-diene (**24**) possibly by way of **23**, no silepin **5a** being detected in the reaction mixture. This fact indicates that the direct coupling reaction between **3a** and CH_2Cl_2 is not involved in the reaction pathway to silepin **5a**.

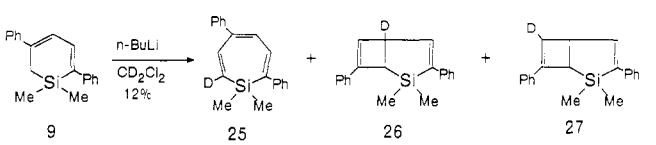
According to the ESR study of the 1,1-dimethyl-1-silacyclohexadienyl radical,[11] the spin density at C-4 is larger than those at C-2 and C-6. This agrees with the fact that **3a** reacts with chlorotrimethylsilane only at C-4 to give the 4-(trimethylsilyl)silacyclohexadiene **6**.[12] However, **3a** is protonated at C-2 with water to yield the 1,3-diene **1**. It turns out that an electrophilic chlorocarbene adds to the anion **3a** at C-2 in the same manner as a proton.

The preferential migration of the silyl group to the carbene center of **15** may be rationalized in terms of the σ–π conjugation between the filled Si–C σ orbital and the vacant p orbital of the electrophilic carbene shown in **15**.



15

Next, the reaction of **9** with CD_2Cl_2 was examined. The reaction afforded 7-deuterio-1,1-dimethyl-2,5-diphenylsilepin (**25**) and a mixture of **26** and **27**, deuterated at C-5 and C-6, respectively. The ratio of **26** to **27** was estimated



25 : (26 + 27) = 1 : 1 ; 26 : 27 = 9 : 1

(8)

to be around 9:1 on the basis of the ^1H NMR spectrum.

(10) Burger, U.; Gandillon, G. *Tetrahedron Lett.* **1979**, 4281.
(11) Kobayashi, T. Master Thesis, Tohoku University, 1975.
(12) Cernyshev, E. A.; Komalenkova, N. G.; Bashkirova, S. A.; Kishin, A. V.; Smironava, T. M.; Mironova, V. A. *Zh. Obshch. Khim.* **1974**, *44*, 226.

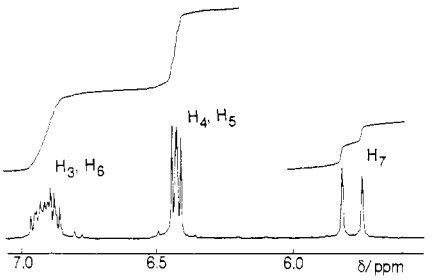
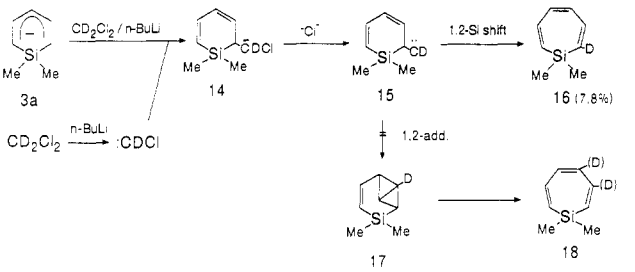


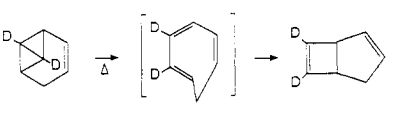
Figure 2. ^1H NMR spectrum of **16** in $CDCl_3$. Only olefinic proton signals are shown.

Scheme IV



The positions of the deuteriums incorporated in these three isomers are assigned unequivocally by means of ^1H NMR and ^2H NMR spectroscopy. In the latter spectra, **25**–**27** have signals at δ 6.17, 4.05, and 6.68 corresponding to D-7 of **25**, D-5 of **26**, and D-6 of **27**, respectively.

The mechanism for the formation of these isomers can be explained by the sequence of reactions shown in Scheme V. First, chlorocarbene adds to the sterically less hindered position C-6 of **10**, to give the common intermediate **28**. Again, the attacking positions of electrophiles in the products depend on the nature of the electrophiles employed. That is, protonation of **10** with water also occurs at C-6, and quenching with chlorotrimethylsilane occurs at C-4.[11] Silepin **25** is formed by 1,2-migration of the silyl group to the carbene center of **28** as in the case of **16**. In **28**, the HOMO level of the vinyl moiety should be raised because of its conjugation with the phenyl group and electrophilic addition of the carbene center of **28** should be promoted to produce the bicyclobutane derivative **29**. Probably **29** is a common intermediate for **26** and **27**. Homolytic cleavage of the central bond of the bicyclobutane ring leads to the formation of **26** by way of the diradicals **30** and **31**, which are stabilized by two phenyl groups. On the other hand, ring opening of **29**, by way of thermal symmetry-allowed [σ2s + σ2a] isomerization, gives the distorted *trans,cis,cis*-silepin **32**, which should undergo ring closure in a conrotatory fashion to give **27** rapidly. The latter has already been identified in the isomerization of **33** to **35**.[13]



(9)

Structure of 1,1-Dimethylsilepin (5a). The ^1H NMR studies on cycloheptatrienes permit discussion about their conformations. The ^1H NMR spectrum of C-unsubstituted **5a** shows an [AA'BB'CC'] signal due to the ring protons and consists of three complex multiplets, which are analyzed by means of computer simulation. The observed and

(13) Christl, M.; Heinemann, U.; Kristof, W. *J. Am. Chem. Soc.* **1975**, *97*, 2299.

Scheme V

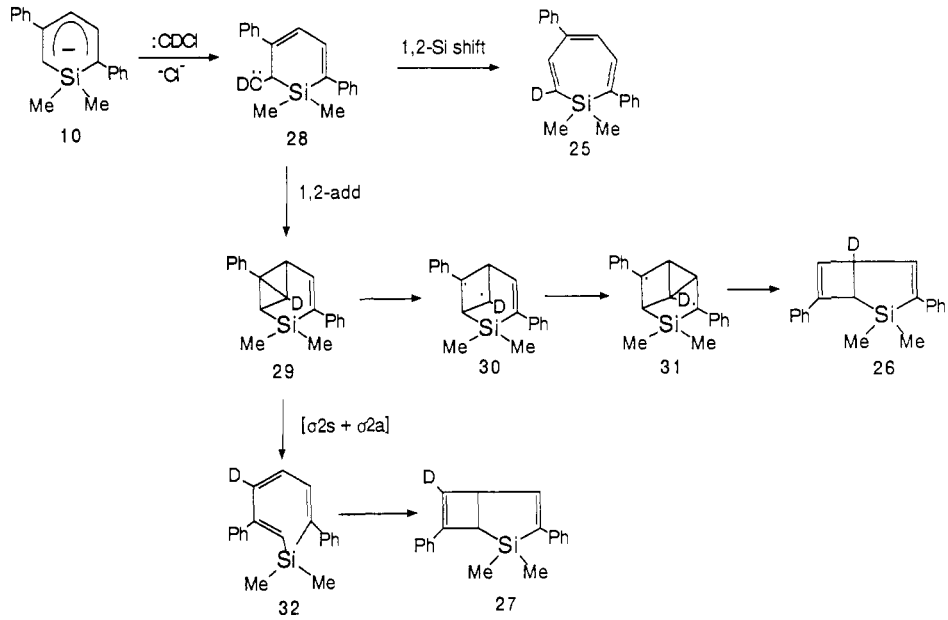
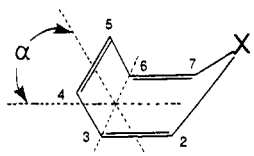


Table II. Correlation between the Dihedral Angle α (deg) and ^{1}H NMR Coupling Constants (Hz) in Cycloheptatriene Systems



compd	 45	 46	 47	 5a	 48	 49
$J_{3,4}$	5.36[15]	5.5[16]	5.51[14]	6.30[a]	6.96[18]	8.3[20]
$J_{3,6}$	0.66[15]		0.69[14]	0.63[a]	0.44[18]	0.1[20]
α	28.5[15]	28.0[16]	29.5 ± 4[17]	25[a]	22.8[19]	0[21]

[a] This paper.

simulated spectra are shown in Figure 1. The coupling constants obtained are summarized in Table I and are found to be strongly alternating and to be in close agreement with those of other nonplanar seven-membered cyclic trienes (vide infra).

According to Karplus,[14] the magnitude of the vicinal coupling constant $J_{3,4}$ should increase as the dihedral angle α between the base plane [C(2), C(3), C(6), C(7)] and the stern plane [C(3), C(4), C(5), C(6)] decreases. The $J_{3,4}$ values listed in Table II show that the dihedral angle α of **5a** is around 25°. Furthermore, according to Günther,[15] the angle α is related also to $J_{3,6}$ and the angles estimated from $J_{3,6}$ in cycloheptatrienes agree with those observed. Consequently, **5a** is inferred to have a boat conformation. The ^{1}H NMR spectra of **5a** over the substantial range of temperature, +30 to −122 °C, remain unchanged, and signals due to the two SiMe groups appear as a singlet. Therefore, the ^{1}H NMR evidence gives no indication of the presence of 7-silanorcaradiene in equilibrium with **5a** and this can be accounted for by rapidly inverting boat geometries. The methylene protons of the parent compound cycloheptatriene give rise to two chemically shifted signals below −143 °C, and this shows the molecule is also nonplanar.[23] 1,1-Dimethyl-2,3,4,5,6,7-tribenzosilepin shows no evidence of line broadening of the two signals due to the two SiMe groups even at 200 °C.[4]

Generally, the UV absorption maxima of a variety of silyl-substituted unsaturated compounds show bathochromic shifts to the extent of several nanometers relative to those of their carbon analogues.[24] The absorption maximum of **5a** is located at a wavelength 20 nm longer than that of the carbon analogue cycloheptatriene **47**, as shown in Table III.[25] The shapes and absorption coefficients of the maxima for **47**, **8**, and **5a** are very similar

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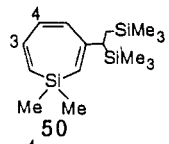
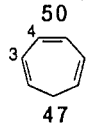
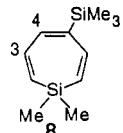
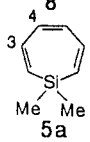
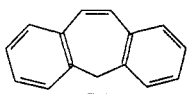
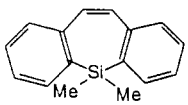
(25) Judging from the $J_{3,4}$ values, the marked difference in UV maxima between **41** and the silepins prepared here may be attributable to the difference in their molecular geometry.

Table III. UV Absorption Maxima (λ_{max}, nm) and ^{1}H NMR Coupling Constants $J_{3,4}$ (Hz) of Silepin and Related Compounds

compd	λ_{max}	ϵ	$J_{3,4}$
 50	223[a]		2.6
 47	261[b]	2800	5.51
 8	276[b]	3800	5.7
 5a	281[b]	2100	6.30
 51	284[c]	10960	
 52	291[c]	10530	

[a] In cyclohexane. [b] In *n*-hexane. [c] In ethanol.

to each other. This implies that these absorption bands are assigned to the π–π^* transitions. In addition to more efficient orbital overlap in the cyclic π system, the large red shift of the UV maxima observed in these silepins may be due to the possible participation of σ–π conjugation between the Si–Me σ bond and the cyclic triene π system.[26] In dibenzocycloheptatrienes **51** and **52**, the UV absorption is reasonably considered to arise from the chromophore having stilbene rather than cycloheptatriene character, and so the smaller red shift of 7 nm is obtained.

We have demonstrated the first preparation of C-unsubstituted silepins, the silicon analogue of cycloheptatriene, along with a description of their spectroscopic properties. The new and general preparative method for the silepin is based on the reaction of silacyclohexadienyl anion with chlorocarbene. The reaction pathway to the silepin has been examined by use of deuterium labeling.

Experimental Section

^{1}H NMR spectra were recorded with Varian EM-390 and XL-200 spectrometers. ^{2}H, ^{13}C, and ^{29}Si NMR spectra and variable-temperature ^{1}H NMR spectra of **5a** in trichlorofluoromethane–dichloromethane-d_2 (1:1) were recorded with a JEOL FX -90Q spectrometer. Infrared spectra were obtained with a Hitachi EPG-G2 spectrophotometer. Mass spectra were measured on JMS-D 300 and Hitachi RMU-670 spectrometers. Ultraviolet spectra were recorded on a Hitachi 323 spectrophotometer.

The ^{1}H NMR spectral simulation has been achieved on the XL-200 spectrometer using the LAME system which is the LAOCOON program with magnetic equivalence added.

Experiments were carried out under an argon or nitrogen atmosphere with use of solvents that were dried and distilled prior to use from the following drying agents: THF and diethyl ether (Na/benzophenone), benzene (Na/benzophenone), CH_2Cl_2 (CaH_2).

Materials. A mixture of 1-chloro-1-methyl-1-silacyclohexa-2,4-diene (**1e**) and 1-chloro-1-methyl-1-silacyclohexa-2,5-diene (**2e**) was prepared by copyrolysis of cyclopentadiene and 1,1,2,2-tetrachloro-1,2-dimethyldisilane according to the reported method[27] with **1e** as a major isomer. 1,1-Dimethyl-4-(trimethylsilyl)-1-silacyclohexa-2,5-diene (**6**) was prepared by the reported method.[12]

1-Methyl-1-(2-naphthyl)-1-silacyclohexa-2,4-diene (1c). A mixed solvent of THF–ether–benzene (1:2:3) was used in this experiment. In a 30-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a reflux condenser, and a dropping funnel were placed a mixture of **1e** and **2e** (1.0 g, purity ca. 85%, 5.9 mmol) and 6 mL of the mixed solvent. To the stirred solution was added dropwise 10 mL of 0.9 N 2-naphthylmagnesium bromide (9.0 mmol, 1.5 equiv) in the mixed solvent, and the mixture was stirred at room temperature overnight and refluxed for 3 h. The reaction mixture was hydrolyzed and extracted with ether. The organic layer was washed with water and aqueous NaCl and dried over anhydrous Na_2SO_4. After evaporation of the solvent in vacuo, the residue was subjected to flash chromatography (eluent hexane) to give **1c** (0.85 g, purity ca. 85%, 53% yield): colorless oil; ^{1}H NMR (CCl_4) δ 0.62 (s, 3 H, SiMe), 1.8–2.0 (m, 2 H, CH_2), 6.0–6.2 (m, 3 H, vinyl), 6.8–7.1 (m, vinyl), 7.3–8.0 (m, 7 H, arom); MS *m/z* (%) 236 (M^+, 100), 221 (84), 208 (53), 171 (59), 155 (56); high-resolution MS found 236.1006, calcd for $C_{16}H_{16}Si$ 236.1021.

1-Methyl-1-*tert*-butoxy-1-silacyclohexa-2,4-diene (1d). To an ether solution (50 mL) of a mixture of **1e** and **2e** (8.2 g, purity ca. 80%, 45 mmol) were added dropwise *t*-BuOH (5.7 g, 77 mmol, 1.7 equiv) and pyridine (6.3 g, 80 mmol, 1.8 equiv) in ether. The resulting precipitate was filtered off. After evaporation of the solvent, the residue was subjected to flash chromatography (eluent hexane) to afford **1d** (7.7 g, 42 mmol, 93%): colorless oil; ^{1}H NMR (CCl_4) δ 0.22 (s, 3 H, SiMe), 1.26 (s, 9 H, Bu), 1.51 (m, 1 H), 1.64 (m, 1 H), 5.8–6.1 (m, 3 H, vinyl), 6.6–6.9 (m, 1 H, vinyl); MS *m/z* (%) 182 (M^+, 27), 167 (13), 126 (52), 111 (100), 61 (53); high-resolution MS found 182.1116, calcd for $C_{10}H_{18}OSi$ 182.1126.

1,1-Dimethyl-1-silacyclohepta-2,3,6-triene (1,1-Dimethylsilepin) (5a). In a 100-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a reflux condenser, and a dropping funnel was placed a mixture of **1a** and **2a** (**1a**:**2a** = ca. 3:2, 2.01 g, 16.2 mmol) in absolute ether (20 mL). To the stirred solution was added 35 mL of 1.4 N BuLi in ether (49 mmol, 3.0 equiv) dropwise slowly at 0 °C. The solution turned deep yellow and was cooled to −78 °C. Then dry CH_2Cl_2 (2.75 g, 32.3 mmol, 2.0 equiv) in ether (4 mL) was added dropwise over 10 min. The stirred solution was warmed to room temperature gradually. After hydrolysis followed by extraction with ether, a large amount of ether was distilled off and the residue was submitted to bulb-to-bulb distillation. Most of the ether was further distilled at atmospheric pressure. The separation of the residue by means of preparative GLC with the injector and detector kept below 150 °C afforded pure **5a** (446 mg, 3.27 mmol, 20%): colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 6 H, SiMe), 5.79 (br d, 2 H, H-2,7), 6.41 (m, 2 H, H-4,5), 6.89 (m, 2 H, H-3,6); ^{13}C NMR ($DCCl_3$) δ −3.00 (q, SiMe), 131.2 (d, C-2,7), 132.1 (d, C-4,5), 140.4 (d, C-3,6); ^{29}Si NMR ($CDCl_3$) δ −17.2; IR (neat, cm^{-1}) 3000, 2970, 1600, 1525, 1370, 1250, 890, 845, 790, 745, 670, 630; UV (*n*-hexane) λ_{max} 216 nm (ϵ 5300, sh), 281 nm (ϵ 2100); MS (11 eV, 60 °C) *m/z* (%) 136 (M^+, 100), 121 (30), 58 (89). Anal. Calcd for $C_8H_{12}Si$: C, 70.51; H, 8.88. Found: C, 70.31; H, 9.03.

1-Methyl-1-phenylsilepin (5b). In a 30-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a reflux condenser, and a dropping funnel was placed a mixture of **1b** and **2b** (**1b**:**2b** = ca. 4:1, 496 mg, 2.66 mmol) in ether (5 mL). To the stirred solution was added 6.0 mL of 1.4 N BuLi in ether (8.4 mmol, 3.2 equiv) dropwise over 50 min at 0 °C. The solution turned deep yellow and was cooled to −78 °C. Then CH_2Cl_2 (457 mg, 5.38 mmol, 2.0 equiv) in ether (0.5 mL) was added dropwise over 5 min. The stirred solution was warmed to room temperature gradually. The reaction mixture was hydrolyzed and extracted with ether. The organic layer was washed with water three times

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and once with aqueous NaCl and dried over anhydrous Na_2SO_4. After evaporation of the solvent in vacuo, the residue was subjected to TLC on silica gel to give **5b** (154 mg, 0.776 mmol, 29%): colorless oil; ^1H NMR ($CDCl_3$) δ 0.35 (s, 3 H, SiMe), 5.59 (br d, 2 H, H-2,7), 6.42 (m, 2 H, H-4,5), 7.02 (m, 2 H, H-3,6), 7.3–7.6 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ −3.79 (q), 127.7 (d), 129.2 (d), 129.8 (d), 132.1 (d), 134.0 (d), 137.3 (d), 141.7 (d); ^{29}Si NMR ($CDCl_3$) δ −21.4; IR (neat, cm^{-1}) 1600, 1530, 1430, 1370, 1250, 1115, 800, 735, 705; MS m/z (%) 198 (M^+, 17), 183 (7), 120 (100), 105 (75); high-resolution MS found 198.0866, calcd for $C_{13}H_{14}Si$ 198.0864.

1-Methyl-1-(2-naphthyl)silepin (5c). In a 30-mL two-necked round-bottom flask equipped with a magnetic stirring bar, a reflux condenser, and a dropping funnel was placed **1c** (0.40 g, purity ca. 85%, 1.4 mmol) in ether (5 mL). To the stirred solution was added 3.2 mL of 1.6 N BuLi in ether (1 mL) dropwise. The stirred solution was warmed to room temperature gradually. The reaction mixture was hydrolyzed and extracted with ether. The organic layer was washed with water and aqueous NaCl and dried over anhydrous Na_2SO_4. After evaporation of the solvent in vacuo, the residue was subjected to TLC on silica gel to give **5c** (0.11 g, 0.44 mmol, 31%): colorless oil; ^1H NMR ($CDCl_3$) δ 0.48 (s, 3 H, SiMe), 6.03 (br d, 2 H, H-2,7), 6.45 (m, 2 H, H-4,5), 7.06 (m, 2 H, H-3,6), 7.4–8.0 (m, 7 H, arom); MS m/z (%) 248 (M^+, 23), 233 (6), 170 (80), 155 (100); high-resolution MS found 248.1020, calcd for $C_{17}H_{16}Si$ 248.1021.

1-Methyl-1-*tert*-butoxysilepin (5d). In a 50-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a serum cap, and a reflux condenser was placed diisopropylamine (193 mg, 1.91 mmol, 1.4 equiv) in ether (12 mL) under an argon atmosphere. To the stirred solution, cooled to −78 °C was added 1.6 mL of 1.2 N BuLi in ether (1.9 mmol, 1.4 equiv) with a syringe. Then the LDA solution formed was warmed to 0 °C and a solution of **1d** (246 mg, 1.35 mmol) in ether was added. The solution turned pale brown and was cooled to −78 °C again, upon which the solution turned green. To the solution was added 5.0 mL of 1.2 N BuLi in ether (6.0 mmol, 4.4 equiv) followed by CH_2Cl_2 (0.27 mL, 4.2 mmol, 3.1 equiv). The reaction mixture was warmed to 0 °C gradually and hydrolyzed. After the usual workup, the mixture was subjected to TLC on silica gel to give **5d** (83.4 mg, 0.429 mmol, 32%): colorless oil; ^1H NMR ($CDCl_3$) δ 0.23 (s, 3 H, SiMe), 1.20 (s, 9 H, Bu), 6.09 (br d, 2 H, H-2,7), 6.41 (m, 2 H, H-4,5), 6.92 (m, 2 H, H-3,6).

1,1-Dimethyl-4-(trimethylsilyl)silepin (8). In a 30-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a reflux condenser, and a dropping funnel was placed **6** (356 mg, 1.81 mmol) in ether (5 mL). To the stirred solution was added 3.4 mL of 1.4 N BuLi in ether (5.4 mmol, 3.0 equiv) dropwise slowly at 0 °C. The solution became pale yellow and was cooled to −78 °C. Then CH_2Cl_2 (321 mg, 3.78 mmol, 2.1 equiv) was added dropwise. The solution was warmed to room temperature gradually, hydrolyzed, and extracted with ether. The organic layer was washed with water and aqueous NaCl and dried over Na_2SO_4. Then, the ether was distilled off and the residue was subjected to TLC on silica gel followed by HPLC (eluent CH_3CN) to afford **8** (110 mg, 0.528 mmol, 29%; the ^{13}C NMR signals were assigned by means of selective decoupling of the corresponding proton signals): colorless oil; ^1H NMR ($CDCl_3$) δ 0.05 (s, 6 H, $SiMe_2$), 0.15 (s, 9 H, $SiMe_3$), 5.74 (d, 1 H, H-2), 5.82 (d, 1 H, H-7), 6.68 (d, 1 H, H-5), 6.88 (dd, 1 H, H-6), 6.98 (d, 1 H, H-3); ^{13}C NMR ($CDCl_3$) δ −3.72 (q, $SiMe_2$), −1.57 (q, $SiMe_3$), 130.4 (d, C-2), 132.9 (d, C-7), 138.0 (C-5), 140.9 (d, C-6), 142.8 (d, C-3), 146.4 (s, C-4); ^{29}Si NMR ($CDCl_3$) δ −1.40 ($SiMe_3$); IR (neat, cm^{-1}) 2950, 1570, 1515, 1250, 1045, 960, 835, 815, 795; UV (*n*-hexane) λ_{max} 276 nm (ϵ 3800); MS m/z (%) 208 (M^+, 3), 193 (7), 150 (4), 135 (100), 105 (6), 73 (25). Anal. Calcd for $C_{11}H_{20}Si_2$: C, 63.38, H, 9.67. Found: C, 63.21; H, 9.59.

1,1-Dimethyl-2,5-diphenylsilepin (11) and 2,2-Dimethyl-3,7-diphenyl-2-silabicyclo[3.2.0]hepta-3,6-diene (12). In a 50-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, reflux condenser, and dropping funnel was placed **9** (282 mg, 1.02 mmol) in ether (10 mL). To the stirred solution was added 3.4 mL of 1.2 N BuLi in ether (4.1 mmol, 4.0 equiv) dropwise at 0 °C. The solution became red and was cooled to −78 °C. Then CH_2Cl_2 (0.20 mL, 3.1 mmol, 3.1 equiv) in ether (1 mL) was added to the anion solution, which was warmed to room temperature gradually. The reaction mixture was hydrolyzed and extracted with ether. After evaporation of the solvent in vacuo, the residue was subjected to TLC on silica gel to give a mixture of **11** and **12** (54.1 mg, 0.118 mmol, 18%). The ratio of **11** to **12** was estimated to be around 1:1 by means of ^1H NMR spectroscopy. These isomers were successfully separated into **11** (5.6 mg, 0.019 mmol, 1.9%) and **12** (6.3 mg, 0.0218 mmol, 2.1%) by means of HPLC. Both compounds gradually decomposed in air even at −20 °C. **11**: colorless oil; ^1H NMR ($CDCl_3$) δ 0.18 (s, 6 H, SiMe), 5.92 (d, 1 H, $J_{6,7}$ = 14.4 Hz, H-7), 6.84 (dd, 1 H, $J_{3,4}$ = 7.0 Hz, $J_{3,6}$ or $J_{4,6}$ = 1.0 Hz, H-3 or H-4), 6.91 (d, 1 H, $J_{3,4}$ = 7.0 Hz, H-3 or H-4), 7.11 (dd, 1 H, $J_{3,6}$ or $J_{4,6}$ = 1.0 Hz, $J_{6,7}$ = 14.4 Hz, H-6), 7.2–7.6 (m, 10 H, Ph); MS m/z (%) 228 (M^+, 19), 273 (48), 230 (100), 58 (32); high-resolution MS found 288.1322, calcd for $C_{20}H_{20}Si$ 288.133. **12**: colorless crystals; ^1H NMR ($CDCl_3$) δ 0.09 (s, 3 H, SiMe), 0.42 (s, 3 H, SiMe), 2.91 (dd, 1 H, $J_{1,5}$ = 3.8 Hz, $J_{1,6}$ = 0.8 Hz, H-1), 3.93 (ddd, 1 H, $J_{1,5}$ = 3.8 Hz, $J_{4,5}$ = 3.2 Hz, $J_{5,6}$ = 1.3 Hz, H-5), 6.55 (dd, 1 H, $J_{1,6}$ = 0.8 Hz, $J_{5,6}$ = 1.3 Hz, H-6), 7.03 (d, 1 H, $J_{4,5}$ = 3.2 Hz, H-4), 7.2–7.5 (m, 10 H, Ph); MS m/z (%) 288 (M^+, 42), 273 (100), 230 (41), 58 (40); high-resolution MS found 288.1335, calcd for $C_{20}H_{20}Si$ 288.1333.

Pyrolysis of 12. A benzene solution of **12** (9.9 mg, 0.34 mmol) was heated at 200 °C for 40 h in an evacuated sealed tube. The pyrolysate was subjected to TLC on silica gel followed by HPLC to give *m*-terphenyl (**13**; 2.4 mg, 0.010 mmol, 29%) as colorless crystals. The signal pattern of the ^1H NMR spectrum of **13** was in agreement with that of an authentic sample. The mass spectrum of **13** showed the molecular ion peak at m/z 230 (100%).

Reaction of (1,1-Dimethyl-1-silacyclohexadienyl)lithium (3a) with CD_2Cl_2 in the Presence of BuLi. In a 50-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a reflux condenser, and a dropping funnel was placed a mixture of **1a** and **2a** (**1a**:**2a** = ca. 3:2, 1.30 g, 10.5 mmol) in ether (10 mL). To the stirred solution was added 20 mL of 1.6 N BuLi in ether (32 mmol, 3.0 equiv) slowly dropwise at 0 °C over 45 min. The solution turned deep yellow and was cooled to −78 °C. Then CD_2Cl_2 (1.88 g, 21.6 mmol, 2.1 equiv) in ether (1 mL) was added dropwise. After addition was complete, the stirred solution was warmed to room temperature gradually. The reaction mixture was hydrolyzed and extracted with ether. The organic layer was washed with water and aqueous NaCl and dried over anhydrous Na_2SO_4. Then, most of the ether was distilled. After bulb-to-bulb distillation, preparative GLC with the injector and detector kept below 150 °C afforded 2-deuterio-1,1-dimethylsilepin (**16**; 113 mg, 0.823 mmol, 7.8%): colorless oil; ^1H NMR ($CDCl_3$) δ 0.09 (s, 6 H, SiMe), 5.79 (d, 1 H, H-7), 6.89 (m, 2 H, H-4,5), 6.89 (m, 2 H, H-3,6); MS (11 eV, 30 °C) m/z (%) 137 (M^+, 100), 122 (89), 79 (35), 58 (83).

Quenching of (1,1-Dimethyl-1-silacyclohexadienyl)lithium (3a) with Dichloromethane and Water. In a 30-mL two-necked round-bottomed flask equipped with a magnetic bar, a reflux condenser, and a dropping funnel was placed a mixture of **1a** and **2a** (**1a**:**2a** = ca. 3:2, 470 mg, 3.78 mmol) in ether (5 mL). To the stirred solution was added 2.5 mL of 1.6 N BuLi in ether (4.0 mmol, 1.1 equiv) dropwise at 0 °C. The solution turned deep yellow, and the solution of **3a** prepared above was added over 40 min at 0 °C. After addition was complete, the solution was warmed to room temperature and stirred for 30 min. However, the yellow color remained. The mixture was hydrolyzed and extracted with ether. The organic layer was washed with water and aqueous NaCl and dried over anhydrous Na_2SO_4. Then, most of the ether was distilled off. After bulb-to-bulb distillation, the distillate afforded only **1a** (166 mg, 1.34 mmol, 35%): colorless oil; ^1H NMR ($CDCl_3$) δ 0.07 (s, 6 H, SiMe), 1.47 (dd, 2 H, CH_2), 5.8–6.0 (m, 3 H, vinyl), 6.67 (dd, 1 H, $J_{2,3}$ = 13.3 Hz, $J_{3,4}$ = 5.5 Hz, H-3).

Reaction of 3a with Dichloromethane in the Presence of *N,N,N',N'*-Tetramethylethylenediamine (TMEDA). In a 30-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a reflux condenser, and a dropping funnel were placed a mixture of **1a** and **2a** (**1a**:**2a** = ca. 3:2, 118 mg, 0.950 mmol) and an excess amount of TMEDA in ether. To the stirred solution was added 0.7 mL of 1.4 N BuLi (0.98 mmol, 1.0 equiv) dropwise at 0 °C. Then to the solution cooled to −78 °C was added dropwise an excess amount of CH_2Cl_2 in ether (5 mL). The solution was stirred overnight at room temperature and refluxed

for 4 h. After bulb-to-bulb distillation, most of the ether was distilled off under atmospheric pressure. The residue afforded 1,1-dimethyl-4-methylene-1-silacyclohexa-2,5-diene (**24**; 6.5 mg, 0.048 mmol, 5.1%) by means of preparative GLC: oil; ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 6 H, SiMe), 5.27 (s, 2 H, $=CH_2$), 6.05 (d, 2 H, $J_{2,3} = J_{5,6} = 14.5$ Hz, H-2,6), 7.03 (d, 2 H, $J_{2,3} = J_{5,6} = 14.5$ Hz, H-3,5); IR (neat, cm^{-1}) 2980, 2950, 1615, 1550, 1245, 895, 840, 805, 765, 710; MS m/z (%) 136 (M^+, 17), 121 (100), 95 (14), 69 (12); high-resolution MS found 136.0702, calcd for $C_8H_{12}Si$ 136.0708.

Reaction of (1,1-Dimethyl-2,5-diphenyl-1-silacyclohexadienyl)lithium (10) with CD_2Cl_2 in the Presence of BuLi. In a 50-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a reflux condenser, and a dropping funnel was placed **9** (313 mg, 1.13 mmol) in ether (20 mL) under an argon atmosphere. To the stirred solution was added 3.8 mL of 1.2 N BuLi in ether (4.6 mmol, 4.0 equiv) dropwise at 0 °C over 10 min. Then the solution was cooled to −78 °C. Dry CD_2Cl_2 (302 mg, 3.47 mmol, 3.1 equiv) in ether (1 mL) was added to the anion solution, which was warmed to room temperature gradually. The reaction mixture was hydrolyzed and extracted with ether. After evaporation of the solvent in vacuo, the ^{1}H NMR spectrum of the residue showed signals due to the deuterated **11** and **12** as the main products. Then the residue was subjected to TLC on silica gel to give a mixture of 7-deuterio-1,1-dimethyl-2,5-diphenylsilepin (**25**), 5-deuterio-2,2-dimethyl-3,7-diphenyl-2-silabicyclo[3.2.0]hepta-3,6-diene (**26**), and 6-deuterio-2,2-dimethyl-3,7-diphenyl-2-silabicyclo[3.2.0]hepta-3,6-diene (**27**) (839.2 mg, 0.135 mmol, 12%). The ratio of **25** to the mixture of **26** and **27** was estimated to be ca. 1:1 by means of ^{1}H NMR spectroscopy. These isomers were separated into **25** (9.1 mg, 0.031 mmol, 2.7%) and a mixture of **26** and **27**, which was estimated to be ca. 9:1 by means of ^{1}H NMR spectroscopy. **25**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 6 H, SiMe), 6.84 (dd, 1 H, $J_{3,4} = 7.0$ Hz, $J = 1.0$ Hz, H-3 or H-4), 6.91 (d, 1 H, $J_{3,4} = 7.0$ Hz, H-3 or H-4), 7.11 (d, $J = 1.0$ Hz, H-6), 7.2–7.6 (m, 10 H, Ph); ^{2}H NMR ($CHCl_3$, internal standard $CDCl_3$ δ 7.26) δ 6.10 (D-7); MS m/z (%) 289 (M^+, 20), 274 (55), 231 (100), 58 (21); high-resolution MS found 289.1379, calcd for $C_{20}H_{19}DSi$ 289.1398. **26** and **27**: colorless oil; MS m/z (%) 289 (M^+, 42), 274 (100), 231 (37), 58 (39); high-resolution MS found 289.1395, calcd for $C_{20}H_{19}DSi$ 289.1398. **26**: ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 3 H, SiMe), 0.42 (s, 3 H, SiMe), 2.91 (br s, 1 H, H-1), 6.55 (br s, 1 H, H-6), 7.03 (s, 1 H, H-4), 7.2–7.5 (m, 10 H, Ph); ^{2}H NMR ($CHCl_3$, internal standard $CDCl_3$ δ 7.26) δ 4.05 (D-5). **27**: ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 3 H, SiMe), 0.42 (s, 3 H, SiMe), 2.91 (d, 1 H, $J_{1,5} = 3.8$ Hz, H-1), 3.93 (dd, $J_{1,5} = 3.8$ Hz, $J_{4,5} = 3.2$ Hz, H-4), 7.03 (d, 1 H, $J_{4,5} = 3.2$ Hz, H-4), 7.2–7.5 (m, 10 H, Ph); ^{2}H NMR ($CHCl_3$, internal standard δ 7.26) δ 6.68 (D-4).

Structural Evidence for Ligand Backbonding in Distortions from Octahedral Geometry of Complexes of d^6 ML_4 Fragments with π-Ligands

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Received June 27, 1990

Variations in the structure of the ML_4 portion of d^6 ML_4(π-ligand) complexes are explored through a survey of structures in the literature and qualitative molecular orbital theory, supported by calculations at the extended Hückel level. The π-ligands considered are allyl anion, nonconjugated diene, conjugated diene, and alkyne. There are systematic distortions from octahedral geometry in the ML_4 fragment, characterized by a bending back of the axial ligands from the π-ligand and an opening up of the angle for the equatorial ligands. Little bendback of the axial ligands occurs for allyl anion and nonconjugated diene complexes, where π-backbonding is a modest component of the metal–π-ligand bonding. A much larger bending back occurs when the π-ligand is a conjugated diene or an alkyne. These ligands have low-lying π^* orbitals and are excellent π-acids, which stabilizes the distortion through a stronger metal-to-ligand backbond. Equatorial distortion is influenced by steric effects. The equatorial ligands are opened up to an angle greater than 100° in most of the allyl anion, 1,3-diene, and alkyne complexes, but not with the nonconjugated complexes. This is because substituents on the nonconjugated diene ligand only are pointed toward the equatorial sites, preventing the opening up of the equatorial angle. A relationship between a significant ground-state distortion and a low barrier for formal rotation of the π-ligand is discussed in terms of the ability of the π orbitals on the metal to switch roles when the ligand is a good π-acceptor, as detected in changes in fragment orbital populations. The structures of certain other complexes, with chelation among the ML_4 set or with more symmetric π-ligands (cyclobutadiene, trimethylenemethane, dienyl cation), are shown to be consistent with the trends observed.

Introduction

Backbonding, where d-electron density is transferred from a transition metal to an unoccupied ligand orbital, is an important part of many metal–ligand interactions. This is especially true with unsaturated organic ligands, and backbonding is a key element of the Dewar–Chatt–Duncanson model of the metal–olefin bond.[1] There have been several structural studies of the influence of backbonding on *ligand* bond lengths, angles, and bond strengths.[2] This was critical, for example, to the evidence advanced by Chatt and Duncanson to support partial occupation of the C–C π^*-bond in platinum olefin complexes.[1b]

The historical emphasis on the effect of backbonding on a ligand's structure neglects the effect the same interaction must, ispo facto, have on the metal fragment. Just as an olefin, for example, undergoes pyramidalization

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0276-7333/91/2310-0442$02.50/0