The First Detection of an Exclusive 1,2-Silatropic Shift in the Enantiopure Silylcyclopentadiene [$C_5H_5(SiMe_2(1R)$-*endo*-(+)-$OC_{10}H_{17})$]

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The enantiopure silylcyclopentadiene **1** was obtained as a mixture of regioisomers where the dominant isomer 5-(**1**) had the silyl substituent located on the allylic or 5-position of the cyclopentadiene ring. The full characterization of **1** by ^{1}H, ^{13}C{^{1}H}, ^{13}C{^{1}H} DEPT, ^{29}Si{^{1}H} DEPT, ^{1}H−^{1}H NOESY, ^{1}H−^{1}H COSY, ^{1}H−^{13}C HMQC, ^{1}H−^{29}Si HMBC, and ^{1}H-difference NOE spectroscopy was accompanied by trapping of 5-(**1**) as well-characterized Diels−Alder adducts with DMAD and TCNE. Above 250 K, compound 5-(**1**) undergoes a degenerate [1,5]-sigmatropic silyl rearrangement which exchanges the five sites of the cyclopentadiene ring. The rate of silyl migration around the CpH ring increased with temperature, leading to coalescence of the allylic and vinylic CpH ^{1}H NMR resonances above 410 K in biphenyl-d_{10}. When the fluxional process was monitored by VT ^{1}H and VT ^{13}C{^{1}H} experiments in toluene-d_8, line shape analysis of the allylic region for 5-(**1**) afforded the activation energy $E_a = 17.4$ kcal mol^{-1} for the sigmatropic rearrangement. The mechanism for the rearrangement was independent of solvent polarity and was found to occur exclusively by a 1,2-Si shift at 250 K in toluene-d_8 by ^{1}H−^{1}H EXSY in combination with a resonance-selective ^{1}H-NOE difference experiment at 200 K.

Introduction

Metallocenes are recognized as catalysts for various polymeric[1] and organic processes[2] where the capabilities of such catalysts are often dependent on the nature of the cyclopentadienyl substituent.[3] Main-group-substituted cyclopentadienes are thus versatile precursors in the synthesis of novel functionalized metallocenes where the steric and electronic properties of the metallocene catalyst can ultimately be tailored by the choice of element (E) and substituents (R) (Figure 1a).[4] As a result, extensive study into the synthesis and characterization of new cyclopentadienes is an area of significant interest.

The properties of functionalized cyclopentadienes, which are synthons to metallocenes, are also associated with the type of substituent incorporated into the five-membered unsaturated ring.[5] For example, in terms of regioisomerism, the predominant placement of a metalloid in an allylic or vinylic position of the ER_xCpH ($Cp = C_5H_4$) ring is a function of both the main-group element (E) and the substituents (R) on E.[5] Furthermore, this class of compounds is subject to two fluxional processes—1,2-metallotropic and 1,2-prototropic shifts—whose energetics and mechanisms are intricately linked to the identity of the substituent ER_x. Previously characterized (alkylsilyl)cyclopentadienes such as $SiMe_3$-CpH were found by NMR spectroscopy to exist predomi-

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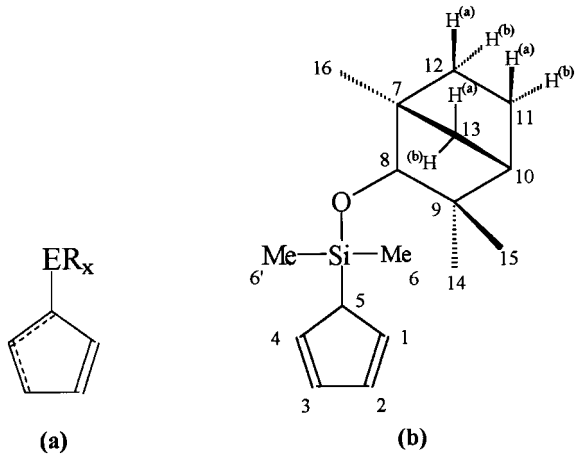


Figure 1. (a) Representation of E(R)$_x$CpH, a typical monosubstituted cyclopentadiene which exists as three possible regioisomers. E = main-group element, R = element substituent, and Cp = C_5H_4. (b) Representation of [CpH(SiMe$_2$(1*R*)-*endo*-(+)-OC$_{10}$H$_{17}$)] (5-(**1**)). Compound **1** is displayed with the silyl group in the allylic or 5-position of the CpH ring. The atomic labeling corresponds to the labeling for the NMR data of **1** provided in Tables 1 and 2.

nantly (90%) as the allylic or 5-isomer at ambient temperatures.[6] However, upon successive replacement of the methyl silyl substituents with more electronegative chloride ligands, the vinylic isomers were found to increase steadily to the 65% observed for CpHSiCl$_3$.[7] Significantly, the degree of vinylic isomers present also increases above ambient temperature due to an increase in the rate of the prototropic shift. At ambient temperatures and below, both the silatropic and prototropic shifts occur; however, the silatropic shift tends to predominate for silylcyclopentadienes and the energetics of this fluxional process have been investigated by line shape analysis of the variable-temperature (VT) NMR spectra.[8] Temperatures in excess of 393 K are usually necessary to increase the rate of the prototropic shift so that it can be suitably monitored by VT NMR spectroscopy.[9]

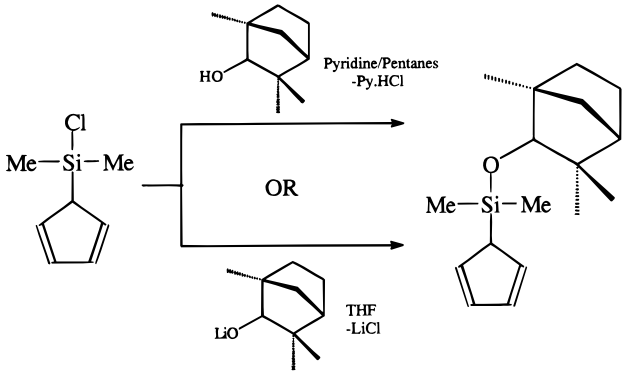
The determination of this classical silatropic shift mechanism has remained elusive because there has been no clear method to distinguish between rapid 1,2- or 1,3-silatropic rearrangements.[9,10] From a VT-^{13}C NMR study of chiral silylcyclopentadienes such as $C_5H_5Si^*H(^iPr)(Me)$, a distinction between proximal and distal ring carbons was proposed on the basis of the larger diastereotopic shift observed for the nuclei closest to the chiral center. Under this assumption, simulation of the migration of the silyl group over five sites of exchange indicated that the silatropic shift occurred by a 1,2- rather than a 1,3-pathway.[11a] Anisochronicity of the two methyls of the isopropyl substituent remained throughout the temperature range studied and supported a rearrangement that proceeded with retention of configuration.

In the current study the chiral site was incorporated into a substituent at silicon in the cyclopentadiene derivative [C_5H_5(SiMe$_2$(1*R*)-*endo*-(+)-OC$_{10}$H$_{17}$)] (**1**). This places diastereotopic Me groups directly on the migrating silicon center. With the advent of more sophisticated NMR spectroscopy, studies of **1** established that the [1,5]-sigmatropic rearrangement occurs by a 1,2-shift of the silyl substituent at 250 K with retention of configuration at the migrating silicon center. The activation energies for this process in solvents of differing polarities were found in the range $17.9 > E_a > 17.1$ kcal mol^{-1}.

Results and Discussion

We have recently examined the substituent effects in metallocenes that act as catalysts in the dehydropolymerization of silanes to polysilanes and sought to develop a series of new enantiopure silyl-substituted metallocenes for this purpose.[11b] To accomplish this goal, it was necessary to synthesize the new chiral silylcyclopentadiene **1** as shown in Figure 1b; this compound was fully characterized by elemental analysis and ^{1}H, ^{13}C{^{1}H}, ^{29}Si{^{1}H}, and various forms of 2D and VT NMR spectroscopy. To establish the dominant regioisomer of **1**, the compound was trapped as the Diels−Alder (D−A) products with the activated dienophiles DMAD (dimethyl acetylenedicarboxylate) and TCNE (tetracyanoethylene). We were interested in examining how a silyl substituent bearing a large electronegative enantiopure alkoxy group affected the characteristics of the cyclopentadiene molecule from the standpoint of isomer ratios and, in particular, the intramolecular dynamics outlined previously.

Synthesis of [C_5H_5(SiMe$_2$(1*R*)-*endo*-(+)-OC$_{10}$H$_{17}$)] (1). Compound **1** was successfully synthesized by addition of fenchol to freshly distilled chlorocyclopentadienyldimethylsilane (eq 1) in a mixture of pentanes and pyridine, since the use of THF as a solvent resulted in the formation of several byproducts. The best yields of



(1)

1 were obtained when the reaction was halted after 10 min, because prolonged reaction times resulted in the

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growth of minor impurities, as indicated by the GC traces of the reaction mixture. Filtration of the py·HCl salts and removal of the solvents provided a pale green oil from which pure **1** could be isolated as a liquid in good yield by simple Kugelrohr distillation or by column chromotography. It was found by ^{1}H NMR spectroscopy that freshly chromatographed **1** existed predominantly (>90%) as the allylic isomer. Upon standing at room temperature in the presence or absence of air and/or light, the colorless liquid was found to gradually change color to a fluorescent yellow. If distilled, **1** was obtained as a fluorescent yellow liquid. When **1** was monitored by ^{1}H NMR spectroscopy in chloroform-*d* or benzene-d_6, an increase in the concentration of the vinylic isomers was found to accompany this color change. After equilibration at ambient temperature, **1** was found to have a 4.2:1 ratio of allylic to vinylic isomers, which is similar to that observed for other silylcyclopentadienes.[6a,7,12] However, it could be stored for a period of months at −50 °C without significant decomposition or isomerization. In an alternative synthesis, **1** could also be generated from $ClSiMe_2C_5H_5$ and $C_{10}H_{17}OLi$ in THF solvent, but with lower isolated yields (eq 1). Compound **1** is soluble in all common organic solvents.

Synthesis and Characterization of $C_{11}H_{11}O_4$-($SiMe_2$(1*R*)-*endo*-(+)-$OC_{10}H_{17}$) (2) and $C_{11}H_5N_4$-($SiMe_2$(1*R*)-*endo*-(+)-$OC_{10}H_{17}$) (3). To determine the dominant regioisomer of **1** at ambient temperature, it was trapped as two fully characterized D−A adducts of DMAD and TCNE.[13] In both cases, ^{1}H NMR established that the products **2** and **3** contained the silyl substituent in the bridging position of the norbornyl framework.[14] Additionally, ^{1}H−^{1}H NOE studies confirmed that the silyl group was in a 7-*exo* orientation with respect to the ester functionality for **2** or cyano functionality for **3**.[15]

Since the NMR studies comprehensively showed that 7-*exo*-silyl products were generated as the major regioisomers of both **2** and **3**, it was concluded that the dominant isomer of **1** was the allylic or 5-isomer,[16] an assignment which is in agreement with the NMR studies carried out on **1** and from the data available on related silylcyclopentadienes.[5a]

Table 1. NMR Data in the Fenchoxy Region for Compound 1 ($CDCl_3$, 303 K)[a]

atom	^{1}H (ppm)	^{13}C{^{1}H} (ppm)
7		49.79/49.65
8	3.31/3.30	86.26/85.65
9		39.76/39.55
10	1.67	48.53
11a	1.39	26.40/26.44
11b	1.67	
12a	1.79	25.69
12b	0.93	
13a	1.44	41.11
13b	1.10	
14	1.05/0.93	30.71/30.57/30.46
15	0.94/0.87	21.46/21.36/21.31
16	0.83/0.76	20.25/20.07

[a] See Figure 1b for atomic labeling.

Spectroscopic Studies of 1. Compound **1** was characterized by ^{1}H, ^{13}C{^{1}H}, ^{29}Si{^{1}H}, and various two-dimensional experiments in order to fully assign all the resonances observed. In agreement with other silylcyclopentadienes, the allylic isomer of **1** (designated 5-(**1**)) was found to undergo degenerate [1,5]-sigmatropic silyl rearrangements at lower temperatures (>250 K) and nondegenerate [1,5]-sigmatropic proton rearrangements at temperatures above 400 K.[6a,10a,13] The line broadening of the cyclopentadienyl ^{1}H and ^{13}C{^{1}H} resonances between 250 and 450 K allowed estimation of the activation energies for these fluxional processes.

The ^{1}H NMR spectrum of **1** in chloroform-*d*, benzene-d_6, or toluene-d_8 has four regions of note. In chloroform-*d*, between δ −0.08 and 0.70 ppm three sets of signals were observed for the $Si(CH_3)_2$ groups of the allylic and vinylic cyclopentadiene isomers. Each exists as a set of diastereotopic resonances, since the chiral alcohol substituent renders the $SiCH_3$ signals anisochronous.[17] The resonances for the fenchol substituent lie slightly further downfield between δ 0.83 and 1.79 ppm. Three distinct fenchol methyl singlets were observed in a region of mostly complex multiplets which correspond to the remaining protons of the norbornyl framework. The allylic cyclopentadiene protons for each of the three isomers could be found between δ 3.03 and 3.54 ppm in addition to the resonances associated with the alcoholic carbon C(8). Finally, the signals for the Cp vinylic protons are located furthest downfield as two broad signals (centered at δ 6.61 and 6.68 ppm) at 303 K.

The assignments for each of the resonances of the fenchoxy protons were based on several techniques. The literature assignments for the carbon signals of fenchol and the fenchoxy residue of **1** were found to be practically identical due to the small change in their magnetic environment.[18] Under the assumption that these resonances were indeed unchanged, a HMQC study allowed the correlation of these resonances to their attached protons. Lists of relevant chemical shifts for **1** are provided in Tables 1 and 2 with a full illustration of the atomic labeling for 5-(**1**) in Figure 1b. The NOE contacts throughout the fenchoxy component in combi-

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(13) Compound **1** was subject to slow D−A reactions with activated dienophiles to give three regioisomeric D−A products.[6a,10a] A mixture of **1** and a slight excess of the dienophile DMAD or TCNE in CH_2Cl_2 at ambient temperature was monitored by GC. Over the course of 3 days, the corresponding 7-*exo*-silylnorbornadiene (**2**) and 7-*exo*-silylnorbornene (**3**) products were respectively generated. In each case, the major isomer isolated was conclusively established by NMR studies to be the 7-*exo*-silyl product, which arises from reaction of the dienophiles with the *allylic* isomer of compound **1**: i.e., 5-(**1**).[6a,10a] For similar examples, see: (a) Abel, E. W.; Dunster, M. O. *J. Organomet. Chem*. **1971**, *33*, 161. (b) Kraihanzel, C. S.; Lossee, M. L. *J. Am. Chem. Soc*. **1968**, *86*, 4701.

(14) This conclusion was reached by virtue of the 2:2:1 intensity ratio of the resonances for H_a (vinyl), H_b (bridgehead), and H_c (bridging), respectively.

(15) For both compounds, the correlation of NOE effects between the H_a and $Si(CH_3)_2$ protons indicated that these groups were close enough to establish through-space contacts. Furthermore, NOE contacts from H_c to only H_b and not to H_a were observed. If the H_c and H_a protons were located *endo* to one another, they would have been sufficiently close to one another to also display NOE contacts. The model implicated by the NOESY studies is only possible in the case of the 7-*exo*-silyl regioisomer.

(16) As a further note, the GC ratios of the three regioisomers of **2** remained constant throughout the Diels−Alder reaction of **1** and DMAD. This suggested that the prototropic shifts of the isomers for **1** occurred at an ambient temperature rate which was greater than the corresponding rate of the Diels−Alder reaction. In effect, the equilibrium composition of **1** as it was converted to **2** remained effectively constant throughout the reaction period as measured by GC.

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Table 2. NMR Data in the $SiMe_2CpH$ Region for Compound 1 ($CDCl_3$, 303 K)

assignment	^1H (ppm)	$^{13}C\{^1H\}$ (ppm)	$^{29}Si\{^1H\}$ DEPT (ppm)[b]
allylic[c] Me_2Si (11)	−0.08/−0.07	−2.57/−2.42	9.90
vinylic[a] Me_2Si	0.70	−0.40/−0.14	0.52
	0.69	−0.76/−0.58	0.14
allylic bridgehead CH (5)	3.54 (br)	53.84 (br)	
vinylic[a] bridgehead CH_2	3.03	43.82	
	3.10	45.63	
allylic olefin CH (1,4; 2,3)	6.61	131.03	
	6.68	132.87	
vinylic[a] olefin CH	6.70/6.77/ 6.92	132.98/138.36/ 143.10 135.69/144.41/ 146.65	

[a] Two vinylic isomers are present and are listed as major and minor isomers, respectively. [b] Evidence for assignments is based on HMBC correlations of the ^{29}Si resonances to the distinguishable $SiMe_2$ signals. [c] Two chemical shifts are listed to represent the diastereotopic nature of the $SiMe_2$ region.

nation with a COSY spectrum verified that the assignments of the proton chemical shifts as given in Table 1 were corrct. Unfortunately, the assignments of the resonances for protons H(11a) and H(11b) as well as H(12a) and H(12b) were not fully established using these methods.

A $^{13}C\{^1H\}$ DEPT experiment in combination with the previously mentioned HMQC data demonstrated absolutely that the major silylcyclopentadiene isomer of **1** at ambient temperatures was the allylic isomer.[19] Integration of the three signals for both the allylic and the $Si(CH_3)_2$ ^1H NMR resonances at 303 K provided an allylic to vinylic isomer ratio of 4.2:1. The isomer composition was found to be 90% for the allylic or 5-isomer of $(SiMe_3)CpH$,[6a] whereas it is only 81% with 5-(**1**), 79% for $(SiMe_2Cl)CpH$,[7] and 35% for 5-$(SiCl_3)$-CpH.[7] This would tend to agree with previous reports that the tautomer ratios depend on the number of electronegative groups attached to the silyl substituent, where more electronegative substituents result in a decrease in the concentration of the 5-isomer present at ambient temperatures.[4,7]

The $^{29}Si\{^1H\}$ DEPT spectrum in chloroform-*d* displayed three resonances with the signal for 5-(**1**) at δ 9.90 ppm and the resonances for the vinyl isomers appearing further upfield at δ 0.52 and 0.14 ppm. The assignment of these resonances was confirmed by a $^1H-^{29}Si\{^1H\}$ HMBC experiment which displayed a strong correlation between the $Si(CH_3)_2$ and C(8) protons of 5-(**1**) to the resonance at δ 9.90 ppm.

Silatropic and Prototropic Shifts in 1. At ambient temperature in toluene-d_8, the ^1H NMR resonances for the allylic and two vinylic protons of 5-(**1**) were broad, due to the degenerate silatropic shift about the cyclopentadiene ring. When the temperature was lowered to 200 K, these resonances became sharper and well-resolved as the fluxional process was slowed. When the temperature was raised above 250 K, the signal line width increased and began to approach coalescence at the temperature limit (384 K) of the solvent (Figure 2). To observe the coalescence at higher temperatures, biphenyl-d_{10} was employed as a solvent and convergence of the allylic and vinylic signals for 5-(**1**) was noted at ~410 K with a corresponding value for the free energy of activation, $\Delta G^{\ddagger} = 17.4(\pm 0.3)$ kcal/mol. The activation parameters obtained by line shape analysis for the silatropic shift were estimated under a slow exchange regime by measuring the line broadening of the allylic proton and carbon signals between 250 and 320 K and assuming that the considerably slower rate of the prototropic shift does not significantly contribute to the line broadening observed at these temperatures.[20] This assumption was substantiated by the fact that the ratio of the three $Si(CH_3)_2$ signals was invariant in the temperature range used. Furthermore, a $^1H-^1H$ EXSY experiment did not show exchange correlations between the $Si(CH_3)_2$ peaks (see later). The results are summarized in Table 3.

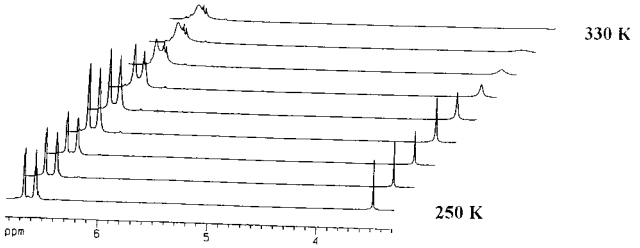

Figure 2. ^1H VT NMR spectra of 5-(**1**) in toluene-d_8 (250−330 K). The allylic proton of 5-(**1**) broadens upon heating above 250 K. This broadened line shape occurs as the rate of the degenerate silatropic shift increases with temperature.

The dynamic behavior of 5-(**1**) was also examined in chloroform-*d*, acetone-d_6, and acetonitrile-d_3 to determine if there was any dependence of the rate of silyl migration on solvent polarity. As shown in Table 3, the activation parameters obtained for the silatropic shift for these solvents over the same temperature regime as used for toluene-d_8 were invariant within experimental error in all cases. A plot of log k^{300} as a function of internal pressure (*d*) (Figure 3) illustrated that the silyl migration rate was independent of solvent polarity and would tend to eliminate the possibility of highly polarized transition states such as that associated with silyl dissociation leading to intermolecular silyl transfer during the rearrangement.[21]

The typical activation energies for the silatropic shift in other silyl-substituted cyclopentadiene compounds have values of $E_a \approx 13.1-18.6$ kcal mol^{-1}. The activation parameters for 5-(**1**) ($E_a = 17.1-17.9$ kcal mol^{-1}) compare well with the range derived for related moieties, indicating no significant departure in the energetic

(19) The 5-isomer of **1** is the only case where the allylic carbon is tertiary; for the remaining vinylic isomers the allylic carbon must be secondary. Thus, the $^{13}C\{^1H\}$ DEPT spectrum differentiated between vinylic and allylic isomers of **1** by the nature of the 180° phase-shifted resonances for the allylic carbon atoms of 1- or 2-isomers in comparison to the signal for the carbon atom of the 5-isomer of **1**. The HMQC experiment provided a correlation from the allylic carbon for 5-(**1**) to the major allylic resonance in the ^1H NMR spectrum, verifying that 5-(**1**) was the dominant isomer. For a related example, see: Huhmann, J. L.; Corey, J. Y.; Rath, N. P. *Organometallics* **1996**, *15*, 4063. For a general description of the DEPT experiment, see: Friebolin, H. P. *Basic One- and Two-Dimensional NMR Spectroscopy*; VCH Publishers: New York, 1991; p 192.

(20) It was first established by Ustynyuk et al. that prototropic shifts do occur in silylcyclopentadienes: Ustynyuk, Y. A.; Kisin, A. V.; Oksinoid, D. E. *Zh. Obshch. Khim.* **1968**, *38*, 391. However, this process competes with the silatropic shift at temperatures higher than those used to monitor the silicon migration in 5-(**1**).

(21) (a) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism: A Study of Homogeneous Chemical Reactions*, 3rd ed.; Wiley-Interscience: New York, 1981; p 246. (b) For an example, see: Stefani, A. P. *J. Am. Chem. Soc.* **1968**, *90*, 1694.

Table 3. Activation Parameters for the 1,2-Silatropic Shift in 5-(1)

	int press,δ^a	E_a (kcal/mol)	$\Delta G_c^{\ddagger}$ (kcal/ mol)^b	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (J/(K mol))^c
toluene-d_8	8.91	17.1(±0.4)	17.4	16.5(±0.4)	4.3(±0.1)
chloroform-d_1	9.24	17.4(±0.3)	>14.1	16.6(±0.3)	5.4(±0.1)
acetone-d_6	9.66	17.9(±0.3)	>13.9	17.2(±0.3)	7.1(±0.1)
acetonitrile-d_3	11.80	17.2(±0.3)	>14.9	16.5(±0.3)	4.7(±0.1)

[a] Internal pressure parameter (δ) used as a gauge of solvent polarity. Hildebrand, J. H.; Scott, R. L. *Solubility of Non-Electrolytes*, 3rd ed.; Dover: New York, 1950. [b] When coalesence occurred above the solvent temperature limit, the lower limit of $\Delta G_c^{\ddagger}$ was estimated.[8] For the toluene-d_8 entry, the value of $\Delta G_c^{\ddagger}$ was measured in biphenyl-d_{10} because signal coalescence occurred at a temperature which was beyond the boiling point of toluene-d_8. [c] Entropy of activation values calculated at 300 K.

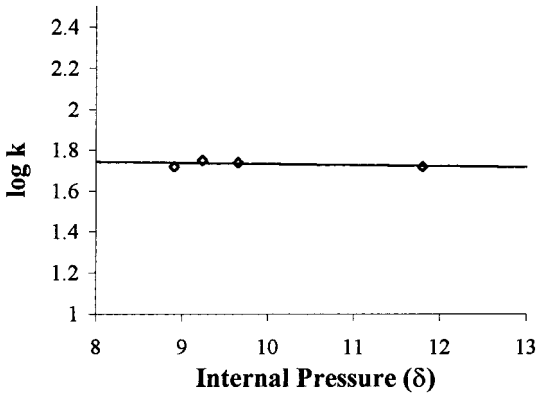

Figure 3. Plot of log k^{300} vs internal pressure (δ) for 5-(**1**). The rate of the silatropic shift at 300 K was measured in toluene-d_8, choloroform-d, acetone-d_6, and acetonitrile-d_3 and the log of each rate plotted as a function of solvent polarity represented by the internal pressure (δ). The increase in solvent polarity had no significant impact on the rate of the silatropic shift, indicating a nonpolarized transition state.

nature of the silatropic shift. However, the values obtained for 5-(**1**) appear nominally increased upon inclusion of the dimethylfenchoxysilyl substituent when compared to 5-($SiMe_3$)CpH (E_a = 15.2 kcal mol^{-1}), 5-($SiMe_2Cl$)CpH (E_a = 15.9 kcal mol^{-1}), and 5-($SiCl_3$)-CpH (E_a = 16.3 kcal mol^{-1}).[7] The increased value of E_a may be linked to the combined presence of the electronegative oxygen silyl substituent and the steric element of the fenchol residue during the migration event. As can be seen for 5-($SiCl_3$)CpH and 5-($SiMe_2$-Cl)CpH, electron-withdrawing chloride substituents (Cl has a 3.0 electronegativity value on the Pauling scale[22]) enhance the activation energy of the silatropic shift in comparison to permethyl substituents (C is 2.5 on the Pauling scale). Thus, an oxygen substituent (O is 3.5 on the Pauling scale) could also be expected to increase E_a, as was observed for 5-(**1**), where the activation energy for the silyl group migration was raised by ~2.0 kcal mol^{-1}. It is also likely that the increase of E_a can be attributed in part to the presence of the large alkyl portion of the fenchol substituent, although surprisingly, no direct comparisons to related sterically hindered silylcyclopentadienes are available to our knowledge.

The mechanism of the silatropic shift in related 5-silylcyclopentadienes such as 5-($SiMe_3$)CpH, which are symmetrical (by virtue of a mirror plane within the molecule) has been subject to some speculation, although it is generally believed that a 1,2-silatropic shift accounts for the observed fluxionality rather than a 1,3-shift.[5a] This was rationalized by the unsymmetrical collapse of the two vinyl carbon and proton signals which represent the positions that are proximal (1,4) and distal (2,3) to the 5-silyl substituent. For instance, the signals corresponding to positions 1 and 4 of 5-($SiMe_3$)CpH were found to broaden and collapse twice as quickly as the resonances for positions 2 and 3, which statistically supported a 1,2-shift and has been discussed in full elsewhere.[23] The crucial designation of the resonances to positions 1 and 4 was based on an empirical argument of chemical shift shielding as a function of proximity to the silyl group and coupling constant information, but if the assignments were reversed, i.e., to positions 2 and 3, then the mechanism would also be reversed to a 1,3-shift. However, there are also some contrasting cases where a 1,3-mechanism was suggested as the mode of the silyl transfer.[10a,c]

We chose to employ ^{1}H difference NOE and ^{1}H−^{1}H EXSY techniques as another means to verify the important assignment of the vinylic resonances to the 1,4- and 2,3-positions of 5-(**1**) and to establish the mechanism of the silyl migration. By examination of several ^{1}H−^{1}H EXSY experiments at low temperatures, further evidence for the 1,2-silatropic shift mechanism was obtained.

The resonances corresponding to the various vinylic protons were unequivocally assigned using a line selective difference NOE method. A sample of **1** was cooled to 200 K in toluene-d_8, and a nonspinning ^{1}H NMR control spectrum was recorded. The ^{1}H NMR spectrum of 5-(**1**) clearly displayed two resonances corresponding to the distal and the proximal vinyl protons at δ 6.70 and 6.58 ppm and a further multiplet for the single allylic proton at δ 3.55 ppm in the cyclopentadiene region of 5-(**1**). Upon irradiation of the 5-(**1**) allylic proton signal at δ 3.55 ppm and subtraction of the control spectrum, only the vinylic resonances at δ 6.58 ppm displayed signal enhancement, as shown by the diagram in Figure 4. Due to the close proximity of the proximal 1,4-protons to the allylic proton of 5-(**1**), substantial Overhauser enhancement between those nuclei is possible; however, due to the greater distance between H(5) and the distal 2,3-protons there is no observable dipolar coupling.[24] By utilizing this technique, it was therefore possible to unequivocally assign the resonances at δ 6.58 ppm to the proximal 1,4-protons and thus infer that the resonances at δ 6.70 ppm correspond to the distal 2,3-protons.

(22) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

(23) Mann, B. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 3, Chapter 20.

(24) (a) Kessler, H.; Gehrke, M.; Griesinger, C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 490. (b) Benn, R.; Gunther, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 350. (c) Williams, D. H.; Fleming, I In *Spectroscopic Methods in Organic Chemistry*, 4th ed.; McGraw-Hill: London, U.K., 1989; p 114. (d) Akitt, J. W. In *NMR and Chemistry, an Introduction to Modern NMR Spectroscopy*, 3rd ed.; Chapman and Hall: New York, 1992.

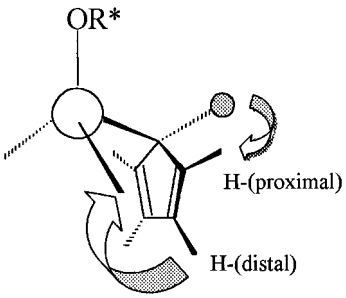

Figure 4. Illustration of the critical NOE effects in 5-(**1**). The line selective excitation of the allylic proton resulted in selective enhancement of the proximal protons of 5-(**1**), which allowed absolute assignment of the proximal and distal Cp resonances. A $^1H-^1H$ NOE demonstrated strong NOE contacts between the distal and $SiMe_2$ protons, whereas only a weak exchange was noted between the proximal and $SiMe_2$ protons. This indicated how the $SiMe_2$ was located over the Cp ring. The methyl groups were oriented closest to the distal protons, and consequently the silicon atom was found closest to the proximal carbons. This model was consistent with the geometry necessary for 1,2-silatropic shifts of the silyl group.

At 250 K, a $^1H-^1H$ EXSY (D_8 = 1.2 s) experiment revealed strong NOE contacts between the $Si(CH_3)_2$ and the distal vinyl 2,3-protons, whereas weaker through-space contacts were obtained between the $Si(CH_3)_2$ fragment and the proximal 1,4-protons. This observation illustrated how the silyl substituent was poised over the cyclopentadiene ring with the methyl silyl substituents lying closer to the distal protons and the silicon atom oriented above the proximal substituents of the CpH ring (Figure 4).

Although NOE contacts between the vinyl and $Si(CH_3)_2$ protons were observed, no through-space interactions associated with the allylic proton of 5-(**1**) were detected. However, exchange cross-peaks were observed only between proton 5 and the proximal protons 1 and 4. Additionally, exchange correlations between protons 1, 4 and 2, 3 were noted, which confirmed that the silatropic shift occurred *exclusively* by a 1,2-migratory pathway at 250 K. If the alternative 1,3-silatropic shift took place, exchange correlations between proton 5 and protons 2 and 3 would have been observed. At higher temperatures (260 and 303 K with D_8 = 0.8 s), the EXSY spectra showed exchange cross-peaks from proton 5 to protons 1, 4 *and* 2, 3. Given the exclusive 1,2-Si migration at 250 K, it is most likely that this is due to consecutive 1,2-silatropic shifts rather than a 1,3-shift.

The diastereotopic nature of the $Si(CH_3)_2$ groups was diagnostic in revealing another aspect of the mechanism of the silyl group migration. As shown in Figure 5, there are two possible modes by which the 1,2-silyl migration could occur, depending upon which set of the degenerate frontier molecular orbitals is used. During the first suprafacial mechanism (Figure 5a) inversion of stereochemistry at the Si center occurs, whereas with the second mechanism (Figure 5b) there is retention of stereochemistry.[25] For the migration in Figure 5a, the $Si(CH_3)_2$ methyl groups (Me_a and Me_b) are exchanged during the sigmatropic rearrangement with inversion at the Si center. However, no exchange of the anisotropic $SiCH_3$ groups was observed by $^{13}C\{^1H\}$ VT NMR (Figure 6) and $^1H-^1H$ EXSY experiments through the temperature range established for the 1,2-silatropic shift. The $^{13}C\{^1H\}$ VT NMR in toluene-d_8 as shown in Figure 6 clearly indicates no broadening or coalesence of the $Si(CH_3)_2$ peaks from 250 to 330 K, which would tend to eliminate the inversion mechanism (A) and support the occurrence of the least-motion pathway (B). This evidence agrees with the data collected by Stobart et al. for 5-[SiMe(i-Pr)(Ph)]CpH, who originally proposed mechanism B.[11a]

(25) Woodward, R. B.; Hoffmann, R. *Angew. Chem.* **1969**, *81*, 797.

Conclusion

The chiral silylcyclopentadiene **1** was thoroughly characterized by chemical derivatization and various spectroscopic techniques, which indicated that the allylic isomer 5-(**1**) was the dominant isomer at ambient temperatures. At temperatures ranging from 250 to 330 K, 5-(**1**) was subject to an exclusive 1,2-silatropic shift, whose mechanism was monitored by 1D and 2D NMR techniques. This work represents the first case where the 1,2-mechanism for this classical fluxional process has been unambiguously established.

Experimental Section

General Comments. All reactions were run under an atmosphere of dry nitrogen using Schlenk techniques or a glovebox, unless otherwise stated. Reaction vessels were flame-dried under a stream of nitrogen, and anhydrous solvents were transferred by oven-dried syringes or cannula. Tetrahydrofuran was distilled from calcium hydride and then from sodium benzophenone ketyl; diethyl ether was distilled from sodium benzophenone ketyl. Toluene and hexanes were distilled from calcium hydride; dichloromethane was washed with sulfuric acid, neutralized with K_2CO_3, washed with water, and distilled from calcium hydride. The compounds DMAD (dimethyl acetylenedicarboxylate) and TCNE (tetracyanoethylene) were purchased from Aldrich; DMAD was passed through silica before use. The compound (1*R*)-*endo*-(+)-$OC_{10}H_{18}$ was purchased from Aldrich and used as supplied. The enantiopurity of (1*R*)-*endo*-(+)-$OC_{10}H_{17}$ was established to be >99% ee by isothermal GC analysis at 90 and 110 °C using a CYCLODEX-B chiral column. The compound $C_5H_5SiMe_2Cl$ was prepared according to a modified literature procedure and distilled immediately before use.[26] The chlorosilane Me_2SiCl_2 (Gelest) was distilled from K_2CO_3 before use, and C_5H_6 was freshly cracked from dicylopentadiene (Acros) before use. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Data Collection. Proton, carbon-13, and silicon-29 (^1H, ^{13}C, ^{29}Si) nuclear magnetic resonance spectra were recorded using either a Varian Unity + 300 equipped with a tuneable broadband probe or a Bruker ARX-500 equipped with a broadband or inverse probe. Two-dimensional studies were performed using a Bruker ARX-500. Unless otherwise stated, spectra were recorded in $CDCl_3$ and referenced internally to residual solvent peaks ($CHCl_3$) or to TMS. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hertz. ^1H NMR spectra used for accurate determination of signal ratios were run with a delay of 0.5−1.0 s to minimize the effects of differential relaxation periods.

Low-resolution mass spectra were obtained at 70 eV on a Hewlett-Packard Model 5988A GC-MS instrument and are reported as *m/z* (relative intensity) [fragment]. Accurate masses for the parent ion (M^+) or suitable fragment ions are reported. Gas chromatographic separations were conducted on a Shimadzu GC-14A instrument using a DB5 capillary column.

(26) Siemling, U.; Jutzi, P.; Neumann, B.; Stammler, H.-G.; Hursthouse, M. B. *Organometallics* **1992**, *11*, 1328.

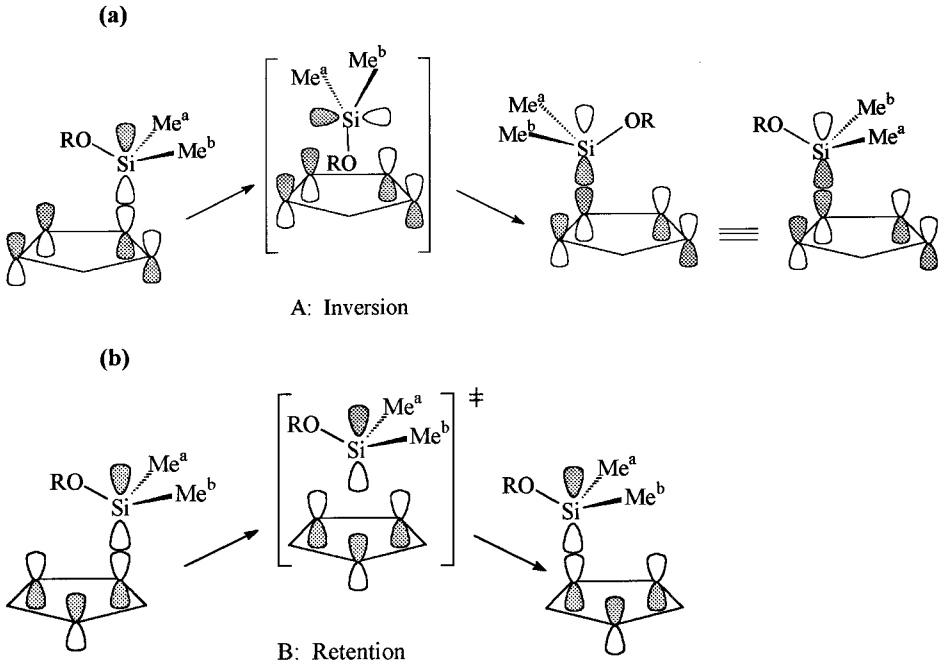

Figure 5. Possible retention and inversion mechanisms of silatropic shifts for 5-(**1**). With the retention mechanism B, the diastereotopic methyl groups of the migrating Si center are not exchanged. With the inversion mechanism A, the diastereotopic methyl groups undergo exchange during the silyl group migration.

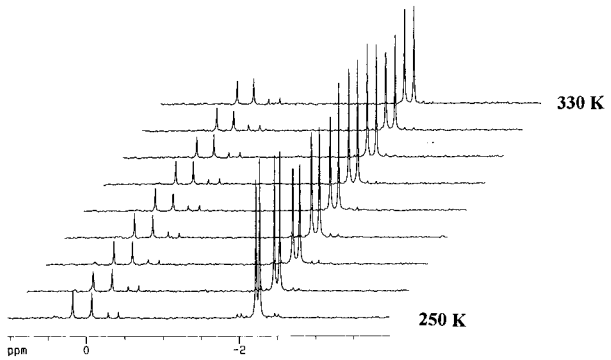

Figure 6. $^{13}C\{^1H\}$ VT NMR spectra in the $Si(CH_3)_2$ region for 5-(**1**) in toluene-d_8 (250−330 K). The diastereotopic methyl groups of 5-(**1**) failed to broaden or begin to coalesce during the sigmatropic shift which was clearly observed in the allylic and vinylic regions by VT ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. This suggests that the retention mechanism B in Figure 5a is responsible for the observed [1,5]-sigmatropic silyl rearrangement.

Synthesis of [$C_5H_5(SiMe_2(1R)$-*endo*-(+)-$OC_{10}H_{17})$] (1). A sample of (1*R*)-*endo*-(+)-$OC_{10}H_{18}$ (fenchol; 6.2 g, 40 mmol) and $C_5H_5SiMe_2Cl$ (8.1 g, 50 mmol) were dissolved in pentanes (20 mL), and the solution was cooled to 0 °C. Upon dropwise addition of pyridine (8.0 mL) over 10 min, the precipitation of a colorless solid was observed. The further addition of pentanes (50 mL) was followed by stirring at room temperature for 30 min. Filtration through Celite and removal of the volatiles in vacuo provided a pale green oil, which was transferred to a Kugelrohr apparatus. Distillation (80−90 °C, 0.1 mmHg) afforded **1** as a colorless liquid (9.2 g, 84% yield, >99% purity by GC). Compound **1** can also be isolated (>99% purity by GC) by silica gel chromatography (34% yield, $R_f = 0.6$, pentanes eluant). LR-MS (EI): *m*/*z* 276 (8.0) [M^+], 211 (30.9) [$M^+ - C_5H_5$]. Anal. Calcd for $C_{17}H_{28}OSi$: C, 73.85; H, 10.81. Found: C, 73.15; H, 10.04. NMR data are provided in Tables 1 and 2.

Synthesis of [$C_{11}H_{11}O_4(SiMe_2(1R)$-*endo*-(+)-$OC_{10}H_{17})$] (2). A sample of freshly distilled **1** (0.50 g, 1.8 mmol) and DMAD (0.27 g, 1.9 mmol) were dissolved in CH_2Cl_2 (40 mL), and the solution was stirred at room temperature. After 24 h GC analysis of the reaction mixture indicated 65% consumption of **1** and formation of three new compounds in a ratio of 3:1:20. A further aliquot of DMAD (0.10 g, 0.7 mmol) was added and the reaction mixture stirred. After a total reaction time of 36 h, GC analysis of the reaction mixture indicated 94% consumption of **1** and a ratio of the three product compounds of 3:1:18. After 60 h the reaction was complete and the solvent removed under reduced pressure, providing three regioisomers of the crude target compound **2** in a ratio of 3:1:22. The remaining DMAD was removed by distillation, and **2** was isolated by silica gel chromatography ($R_f = 0.6$, elutant 1:1 Et_2O/pentanes) as a colorless oil (0.54 g, 70% yield). Note that ^1H and ^{13}C resonances for the minor isomers were too weak to be suitably distinguished; therefore, resonances for the minor isomers are listed in the $^{29}Si\{^1H\}$ DEPT spectrum only. ^1H NMR (500 MHz, $CDCl_3$, 303 K): δ 6.88 (m, 2H), 4.02 (m, 2H), 3.12 (d, $^3J = 1.6$ Hz, 1H, C*H*OSi), 2.39 (s, 1H), 1.68 (m, 1H), 1.62 (m, 2H), 1.38 (m, 1H), 1.34 (m, 1H), 1.06 (m, 1H), δ0.95 (s, 3 H, CH_3), 0.91 (s, 3 H, CH_3), 0.77 (s, 3 H, CH_3), 0.01 (s, 3 H, SiCH_3), 0.00 (s, 3 H, SiCH_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 303 K): δ 165.81 (*C*O_2), 156.02 (*C*CO_2), 142.96 (*C*H_a/*C*$H_{a'}$), 85.70 (*C*HOSi), 81.3 (*C*HSi), 56.80 (*C*H_b/*C*$H_{b'}$), 52.16 (CO_2CH_3), 49.64, 48.49, 41.06, 39.53, 30.61, 26.37, 25.64, 21.43, 20.11, 0.72 (SiCH_3), δ 0.13 (SiCH_3). $^{29}Si\{^1H\}$ DEPT NMR (99 MHz, $CDCl_3$, 303 K): δ 9.98 (minor), 7.93 (major), 1.67 (minor). LR-MS (EI): *m*/*z* 403 (3.6) [$M^+ - CH_3$], 266 (35.0) [$M^+ - C_{10}H_{16}O$]. Anal. Calcd for $C_{23}H_{34}O_5Si$: C, 65.99; H, 8.19. Found: C, 66.15; H, 8.25.

Synthesis of [$C_{11}H_5N_4(SiMe_2(1R)$-*endo*-(+)-$OC_{10}H_{17})$] (3). A sample of freshly distilled **1** (0.50 g, 1.8 mmol) and TCNE (0.23 g, 1.8 mmol) were dissolved in CH_2Cl_2 (40 mL), and the solution was stirred at room temperature. After 72 h, GC analysis of the reaction mixture indicated complete consumption of **1** and the presence of three new compounds in a ratio of 1:1:12. The solvent was removed under reduced pressure, providing the crude target compound **3** as an off-white solid. Compound **3** was dissolved in EtOH (20 mL) and the solution filtered through a Celite pad. Storage at −50 °C over 7 days precipitated colorless crystals of **3** (0.63 g, 86% yield) as essentially one regioisomer. Only trace amounts of the other two regioisomers were detected by GC and ^1H NMR. For NMR

spectroscopy, only resonances for the major isomer are listed. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ 6.63 (m, 2H), 4.03 (m, 2H), 3.18 (d, $^3J = 1.6$ Hz, 1H, C*H*OSi), 1.88 (s, 1H), 1.62−1.68 (m, 3H), 1.62 (m, 2H), 1.40 (m, 2H), 1.12 (m, 1H), 1.06 (m, 1H), 0.98 (s, 3 H, CH_3), 0.91 (s, 3 H, CH_3), 0.75 (s, 3 H, CH_3), 015 (s, 3 H, SiCH_3), 0.14 (s, 3 H, SiCH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 303 K): δ 137.30, 137.16, 112.23, 111.13, 86.67, 59.36, 50.35, 49.40, 48.11, 40.72, 39.38, 30.43, 26.08, 25.43, 21.37, 19.94, 0.59 (Si*C*H$_3$), 0.12 (Si*C*H$_3$). ^{29}Si{^{1}H} DEPT NMR (99 MHz, $CDCl_3$, 303 K): δ 9.91. Anal. Calcd for $C_{23}H_{28}N_4OSi$: C, 68.28; H, 6.98. Found: C, 68.05; H, 6.90.

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Supporting Information Available: Figures giving selected regions of ^{1}H−^{1}H NOE data for **3** accompanied by selected regions of the ^{1}H−^{13}C HMQC and ^{13}C DEPT spectra for **1**, selected regions of the line selective ^{1}H NMR spectrum, control ^{1}H NMR spectrum and the difference spectrum at 200 K for 5-(**1**), selected regions of the ^{1}H EXSY data collected at 250 K for 5-(**1**), and Arrhenius and Eyring plots used in the calculation of the activation parameters for the silatropic shift of 5-(**1**) in chloroform-*d*, toluene-d_8, acetonitrile-d_3, and acetone-d_6 solvents. This material is available free of charge via the Internet at http://pubs.acs.org.

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