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[1,5]-Silatropic shifts in disilyl substituted indenes: an NMR spectroscopic and computational study

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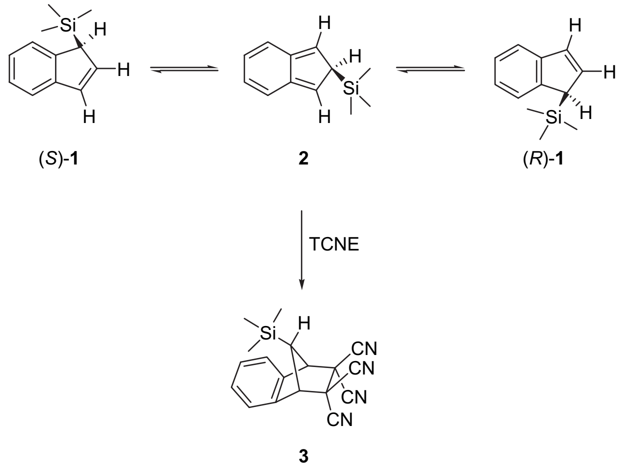
Abstract—The equilibrium profiles for [1,5]-silatropic shifts in a series of 1,3-/1,1-disilyl substituted indenes were studied by NMR and computational methods based on density functional theory. Both methods indicate higher activation parameters for the [1,5]-shifts than observed in monosilyl substituted indene analogues.

1. Introduction

In main group chemistry, migrations of R_3E substituents (E=Si, Ge, Sn) in organic molecules have been studied for several years.[1] Such substituents, especially when E=Si, often form essential parts of group 4 metallocene catalysts utilized for stereoselective polymerization of α-olefins.[2] Accordingly, there is considerable recent interest in the study of the dynamic and migratory processes in these compounds.

The migration of σ-bonded silyl fragments over indenyl surfaces was first reported over three decades ago.[3] The mechanism of this silicon migration can be explained by two successive [1,5]-sigmatropic shifts; molecule (*S*)-**1** interconverts to its enantiomer (*R*)-**1** via the *iso*-indene intermediate **2** (Scheme 1).[4] The aromaticity is lost in **2** and this highly reactive non-aromatic intermediate rapidly isomerizes to the more stable structure. While this intermediate is unstable it can be trapped with tetracyanoethylene as the Diels–Alder adduct **3**.[5]

The experimentally determined barrier energy for [1,5]-shifts in **1** is ∼25 kcal mol^{-1}.[3a,c] In earlier work it has been demonstrated that the activation energy for the [1,5]-silatropic shifts in indenyl moieties can be decreased by 3–7 kcal mol^{-1} by fusing aromatic rings to the system.[6] Likewise, the activation energies for the [1,5]-silatropic shifts in several monosilyl substituted indene derivatives have been determined previously,[7] while just in few cases the corresponding shifts in disubstituted indenes have been studied. Davison and Rakita reported the activation energy for such [1,5]-silatropic shifts in 1,2-bis(trimethylsilyl)-indene (26 kcal mol^{-1})[3c] and 1-trimethyl-2-methylindene (26.5 kcal mol^{-1}),[3d,e] whereas the activation energy for silicon migration in 1,3-dimethyl-1-(trimethylsilyl)indene was reported by Stradiotto et al. (23 kcal mol^{-1}).[8] In the previous work, attempts have been made to determine the activation energies for the corresponding shifts in both 1,3-bis(trimethylsilyl)indene [(*R*/*S*)-**9**, vide infra][3c] and bis(trimethylsilyl)benz[*e*]indene[6a] by variable temperature or single selective inversion NMR technique. However, in neither of the cases could the coalescence temperature or the exchange of protons be observed.



Scheme 1. [1,5]-Sigmatropic shifts in silyl substituted indenes.

In the context of our recent studies on the synthesis and functionalization of alkenyl substituted indenes[9] we have prepared the racemic bis(silyl)indenes (*R*/*S*)-**4** and (*R*/*S*)-**7**

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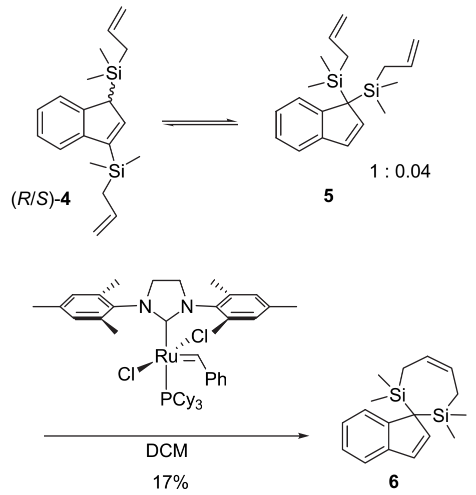
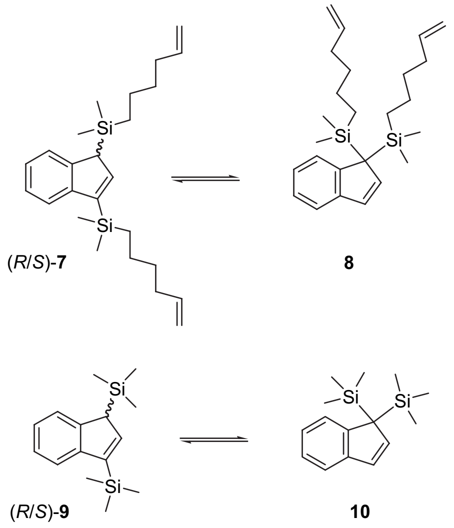
as displayed in Schemes 2 and 3, respectively.[9b] In both the cases, the initially formed, geminally substituted compounds **5** and **8** are expected to rearrange to their predominant 1,3-disubstituted analogues via [1,5]-silatropic shifts. When, however, the isolated 1:0.04 mixture from the synthesis of (*R*/*S*)-**4** and **5** was subjected to the Grubbs' second generation ruthenium metathesis catalyst (NHC)(PCy$_3$)Cl$_2$Ru=CHR,[10] instead of the expected 1,3-ring bridged product, the only ring-closure product spirocyclic 1,1-substituted indene **6** was isolated and obtained in fair yield (17%) (Scheme 2).[9b] Thus, during the course of the ring-closure, the amount of the 1,1-substituted compound must have been enriched. An alternative driving-force is that the seven-membered ring is more easily formed than the corresponding nine-membered ring, as only a slight bias in product stability would be required, even if the equilibrium is in favor of the 1,3-substituted form of (*R*/*S*)-**4**. It could also be considered that the 1,3-substituted isomer ring closes directly followed by the silatropic shifts, although this can be considered highly unlikely due to the imminent strain in the hypothetical nine-membered ring formed at first.[9b]



Scheme 2. [1,5]-Silatropic shifts in (*R*/*S*)-**4**/**5** and the corresponding ring-closing metathesis reaction with Grubbs' second generation catalyst.



Scheme 3. [1,5]-Silatropic shifts in (*R*/*S*)-**7**/**8** and (*R*/*S*)-**9**/**10**.

Considering the scarce amount of reports on silyl migration in disilylindenes[3c,6a] prompted us to study the energy and equilibrium profiles of the (*R*/*S*)-**4**/**5** mixture. By evaluation of the activation energy for the silyl migration in this system, we wished to determine whether the second silyl group facilitates the conversion between the two isomers by decreasing the activation energy for migration. This, in turn, could be the facilitating factor for the formation of the 1,1-spiro product in the metathesis reaction.[11] Studies of the equilibrium between (*R*/*S*)-**4** and **5** should also give more insights into the concentration of the geminal form, which is a precursor to the spiro compound **6**.

We present here a detailed study on the [1,5]-silatropic shifts in (*R*/*S*)-**4**/**5**, as well as its close analogues 1,3-/1,1-bis(hexenyldimethyl)silylindenes (*R*/*S*)-**7**/**8** and 1,3-/1,1-bis(trimethylsilyl)indenes (*R*/*S*)-**9**/**10**. The equilibria between the geminally and 1,3-substituted forms were studied with advanced NMR spectroscopic techniques and the connection between the equilibrium constant and free-energy was used to determine the direction of the reaction and the energetic difference between the equilibrating isomers. In addition, changes in enthalpy and entropy in the equilibria were determined. The activation parameters and thermodynamical equilibria were also obtained computationally by using density functional theory.

2. Results and discussion

2.1. NMR spectroscopic studies

The equilibrium constant at a given temperature was determined by dissolving the compound in question in 1,1,2,2-tetrachloroethane-d_2, letting the sample reach the thermal equilibrium and integrating the peaks corresponding to olefinic CH-resonances in the five-membered rings of both isomers. The equilibrium constants for dialkenylsilylindenes (*R*/*S*)-**4**/**5** and (*R*/*S*)-**7**/**8**, and for 1,3-/1,1-bis(trimethylsilyl)-indene (*R*/*S*)-**9**/**10** were measured at several temperatures between 64.5 (337.7 K) and 108.4 °C (381.6 K). By utilizing the basic equations of thermodynamics, the enthalpy change for the equilibrium was calculated from the slope of the straight line obtained by plotting $\ln K$ versus $1/T$ (Table 1). In addition, the changes in free-energy and entropy for the (*R*/*S*)-**4**/**5**, (*R*/*S*)-**7**/**8**, and (*R*/*S*)-**9**/**10** equilibria were calculated at 64.5 °C (337.7 K) (Table 1).

As expected, the enthalpy changes for (*R*/*S*)-**4**/**5**, (*R*/*S*)-**7**/**8**, and (*R*/*S*)-**9**/**10** were of the same order of magnitude. The ΔH obtained for the 1,3-/1,1-bis(trimethylsilyl)indene (*R*/*S*)-**9**/**10** equilibrium (0.44 kcal mol^{-1}) differs from the value reported earlier (2.1 kcal mol^{-1}).[3c] However, in contrast to

Table 1. Equilibrium parameters for (*R*/*S*)-**4**/**5**, (*R*/*S*)-**7**/**8**, and (*R*/*S*)-**9**/**10**

Equilibrating isomers	ΔH (cal mol^{-1})[a]	ΔG (kcal mol^{-1})[b]	ΔS (cal mol^{-1} K^{-1})[b]
(*R*/*S*)-**4**/**5**	−465	1.1	−4.5
(*R*/*S*)-**7**/**8**	−402	1.3	−5.0
(*R*/*S*)-**9**/**10**	−436	0.4	−2.4

[a] Error limit for $\Delta H \pm 1$ cal mol^{-1} based on linear regression analyses.
[b] Determined at 64.5 °C (337.7 K).

the earlier report, we observed that the rate of the [1,5]-silatropic shifts in these disilylindenes is *very low*, taking hours to reach the thermal equilibrium at low temperatures. The earlier work by Davison and Rakita reports that the equilibrium for (*R*/*S*)-**9/10** was reached in approximately 5 min.[3c] The difference in ΔH reported for this compound by us and Davison and Rakita most likely stems from the fact that in the earlier work the thermal equilibrium had not been reached at the time the equilibrium constants were measured.

All the values of free-energy were positive indicating that the reaction is favored toward the 1,3-disubstituted product (Schemes 2 and 3). This verifies the assumption that the initially formed, geminally substituted disilylindene rearranges to the 1,3-substituted analogue.[9b] By comparing the ΔG values for (*R*/*S*)-**4/5** and (*R*/*S*)-**7/8** with the value obtained for (*R*/*S*)-**9/10** it can be observed that ΔG for (*R*/*S*)-**9/10** is approximately three times smaller than the values for (*R*/*S*)-**4/5** and (*R*/*S*)-**7/8** (Table 1). Thus, the energy difference between the geminally substituted compound and its 1,3-substituted analogue is much larger for (*R*/*S*)-**4/5** and (*R*/*S*)-**7/8** than in (*R*/*S*)-**9/10**. Consequently, the equilibrium concentration of the geminally substituted form is much larger in the case of 1,3-/1,1-bis(trimethylsilyl)indene (*R*/*S*)-**9/10** than in the cases of the dialkenylsilylindenes (*R*/*S*)-**4/5** and (*R*/*S*)-**7/8**.

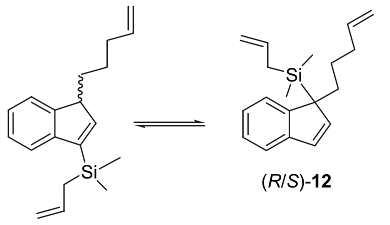
According to Davison and Rakita the (*R*/*S*)-**9/10** ratio at ambient temperature is approximately 1:1 whereas at higher temperatures the 1,3-isomer predominates.[3c] Our NMR studies show that in the case of (*R*/*S*)-**9/10**, the equilibrium concentration of the geminally substituted isomer indeed decreases on increasing the temperature but the ratio of **10** at ambient temperature is less than 50%, being approximately 38%.

The same trend was observed for the dialkenylsilylindenes (*R*/*S*)-**4/5** and (*R*/*S*)-**7/8**; the equilibrium is driven toward the direction of the 1,3-substituted isomer at higher temperatures. When (*R*/*S*)-**4/5** is treated with the Grubbs' second generation Ru catalyst at ambient temperature, the formation of the spiro compound **6** (Scheme 2) can be explained as follows. While the initial mixture of (*R*/*S*)-**4/5** only contains 4% of compound **5**, a slow rearrangement toward the equilibrium containing approximately 19% of **5** takes place. Compound **5** then directly cyclizes to form **6** in the presence of the Grubbs' catalysts.

The dynamic processes can also be investigated by 2D EXSY NMR where the chemical exchange is detected before the occurrence of line broadening.[12] While the activation energies for the [1,5]-silatropic shifts in (*R*/*S*)-**4/5**, (*R*/*S*)-**7/8**, and (*R*/*S*)-**9/10** are far too high for reaching the coalescence points within the operational temperature limits of the NMR probe employed ($T \leq 134$ °C, 407 K), the occurrence of the [1,5]-silatropic shifts could nevertheless be demonstrated by exchange spectroscopy (EXSY). Thus, we investigated the dynamic behavior of (*R*/*S*)-**4/5**, (*R*/*S*)-**7/8**, and (*R*/*S*)-**9/10** by 2D EXSY NMR at several temperatures. In the cases of (*R*/*S*)-**4/5** and (*R*/*S*)-**7/8**, the corresponding cross-signals could not be observed at temperatures below 134 °C (407 K) indicating that the exchange rate is slower than what is observable on the NMR time scale. The rate of exchange can be increased by raising the observation temperature, and for both compounds (*R*/*S*)-**4/5** and (*R*/*S*)-**7/8** cross-signals between the exchanging C(1) and C(3) protons were detected by 2D EXSY NMR at 134 °C (407 K) with 0.5 s mixing time. For (*R*/*S*)-**9/10**, however, the exchange rate is faster and can be detected at lower temperatures providing cross-peaks between the exchanging C(1) and C(3) protons at 110 °C (383 K). For comparison with the results reported earlier, we measured the 2D EXSY spectrum for trimethylsilylindene (*R*/*S*)-**1** at 110 °C (383 K) and obtained clear cross-peaks between the exchanging C(1) and C(3) protons. Obviously, [1,5]-silatropic shifts take place in disilyl substituted indenes such as (*R*/*S*)-**4/5**, (*R*/*S*)-**7/8**, and (*R*/*S*)-**9/10**, but the rates of the rearrangements are slow, especially in the case of (*R*/*S*)-**4/5** and (*R*/*S*)-**7/8**. The results obtained indicate that the activation energy for the silicon migration in disilylindenes is higher than ~25 kcal mol^{-1}, which is the experimentally determined barrier for [1,5]-silatropic shifts in (*R*/*S*)-**1**.[3a,b] Corresponding results were obtained computationally, as described below.

As a further proof for the silatropic shifts, we attempted to trap the presumed *iso*-indene intermediates as Diels–Alder adducts in analogy to Scheme 1 by using the methods described earlier.[5b,7a,b] After five days of reaction time, only marginal amounts of the Diels–Alder products were formed as verified by mass spectrometry.[13] This may be due to the slow rates of the [1,5]-shifts in these compounds at ambient temperature, or simply the low stabilities of the corresponding *iso*-indene intermediates.

In the previous synthetic study, we also prepared the 1,3-disubstituted indene (*R*/*S*)-**11** having one alkyl and one silyl substituent (Scheme 4).[9b] Consequently, it was of interest to investigate the activation energy for the potential silyl migration in this compound as well. This could provide further information on whether the hypothetical equilibrium and silyl migration between (*R*/*S*)-**11** and (*R*/*S*)-**12** are either facilitated or slowed down by replacing one silyl group in the indenyl five-membered ring with an alkyl chain. Accordingly, 2D EXSY experiments were carried out at temperatures ranging from 100 to 134 °C (373–407 K) yielding no observable cross-peaks, most likely due to the slow reaction rates for [1,5]-shifts in these compounds. Thus, the activation barrier for [1,5]-silatropic shifts in (*R*/*S*)-**11** is much higher than in (*R*/*S*)-**4/5**, (*R*/*S*)-**7/8**, and (*R*/*S*)-**9/10**, which all bear in common two silyl subsituents. A possible contributing factor for the higher activation energy in (*R*/*S*)-**11** is the increased steric crowding in the 1,1-substituted analogue



(*R*/*S*)-**11**

(*R*/*S*)-**12**

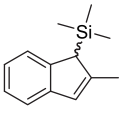
Scheme 4. Potential [1,5]-Silatropic shifts between (*R*/*S*)-**11** and (*R*/*S*)-**12**.

(*R*/*S*)-**12** resulting from the shorter bond length of the C–C (approx. 1.53 Å) bond as compared to the corresponding C–Si (approx. 1.87 Å) bond in compounds **5**, **8**, and **10**. This in turn could somewhat increase the energy difference and barrier for migration between the positional isomers (*R*/*S*)-**11** and (*R*/*S*)-**12**.

2.2. Computational studies

Theoretical calculations of some silyl shifts were carried out for comparison with the experiments. The transition state energies, enthalpies, entropies, and the reaction Gibb's energies ($\Delta G^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$, and ΔG, respectively) were calculated at 1 bar and 51.9 °C (325 K) for (*R*/*S*)-**1**, (*R*/*S*)-**4/5**, (*R*/*S*)-**9/10**, and 1-trimethylsilyl-2-methylindene (*R*/*S*)-**13** (Fig. 1). The results are given in Table 2. The earlier published activation energies for the [1,5]-silatropic shifts in (*R*/*S*)-**1** and (*R*/*S*)-**13**, determined using the variable temperature NMR technique, are well in line with our computational results.[3a,c–e] However, the theoretical calculations predicted rather different thermodynamic equilibria for (*R*/*S*)-**4/5** and (*R*/*S*)-**9/10** (ΔG=8.9 and 4.1 kcal mol^{-1}, respectively) compared to the results obtained experimentally.[14]

The transition state energy $\Delta G^{\ddagger}$ increases with the number or bulkiness of the substituents. The transition state energies for the [1,5]-silicon shifts are comparable to the experiment's, varying from 25.8 for (*R*/*S*)-**1** to 30.1 kcal mol^{-1} for (*R*/*S*)-**4/5**. The *iso*-indene intermediate structures resulting from [1,5]-silicon shifts in (*R*/*S*)-**9/10** and (*R*/*S*)-**4/5** are very unstable with ΔG being at 51.9 °C (325 K) and 1 bar, 21.1 and 28.2 kcal mol^{-1} compared to **9** and **4**, respectively. The corresponding ΔG for the equilibria between (*R*/*S*)-**1** and (*R*/*S*)-**13** is also high, being 17.3 and 26.0 kcal mol^{-1}, respectively. This is understandable, since the aromatic nature of the indene structure is lost in the *iso*-indene intermediates. As there exists two energetically different [1,5]-silatropic shifts in (*R*/*S*)-**9/10** and (*R*/*S*)-**4/5**, there are also two different transition states. The second transition state between the *iso*-indene intermediate and the geminal isomer is always the rate determining step being approximately 4 kcal mol^{-1} higher than the first transition state in (*R*/*S*)-**9/10** and (*R*/*S*)-**4/5**.



(*R*/*S*)-**13**

Figure 1. 1-Trimethylsilyl-2-methylindene (*R*/*S*)-**13**.

Table 2. Activation parameters for the [1,5]-silatropic shifts in (*R*/*S*)-**1**, (*R*/*S*)-**4/5**, (*R*/*S*)-**9/10**, and (*R*/*S*)-**13** calculated at the B3LYP/cc-pVDZ level

Equilibrating isomers	$\Delta G^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})
(*R*/*S*)-**1**	25.8	−4.2	24.4
(*R*/*S*)-**13**	28.0	−6.2	26.0
(*R*/*S*)-**9/10**	29.6	−6.3	27.6
(*R*/*S*)-**4/5**	30.1	−5.7	28.2

3. Summary and conclusions

We have presented here the equilibrium profiles for [1,5]-silatropic shifts in a series of disilyl substituted indenes by determining the equilibrium constants for these migrations at several temperatures. The equilibrium parameters for bis(trimethylsilyl)indene (*R*/*S*)-**9/10** are well in line with the results published earlier.[3c] For the di(alkenylsilyl)indenes, however, the activation energies were higher than what we expected at the outset of this study, based on purely sterical arguments. In the cases of (*R*/*S*)-**4/5** and (*R*/*S*)-**7/8**, both of which contained silyl substituents larger than TMS, the geminally substituted 1,1-isomer became considerably more unfavorable than in the case of the 1,1-TMS-substituted analogue **10**. The equilibrium amounts of the 1,1-substituted compounds **5** and **8** at ambient temperature were under 20% compared to 38% of **10** under the same migratory conditions. The larger substituents at silicon thus bear a considerable effect on both the equilibrium and the energetic differences between the exchanging isomers. Additionally, we studied the [1,5]-silatropic shifts in (*R*/*S*)-**4/5**, (*R*/*S*)-**7/8**, and (*R*/*S*)-**9/10** by utilizing 2D EXSY NMR techniques. It can be concluded that the activation energies for (*R*/*S*)-**4/5**, (*R*/*S*)-**7/8**, and (*R*/*S*)-**9/10** were higher than the activation energy for 1-(trimethylsilyl)indene (*R*/*S*)-**1**. A similar trend was also observed computationally. The additional silyl substituent in position C(3) of the indene increases the barrier for silicon migration. The activation barrier for migration is further increased by replacing one of the silyl substituents with an alkyl group as in (*R*/*S*)-**11**. In this case, the rate of the [1,5]-silatropic shifts was lower than could be detected with the NMR techniques available. The computational studies verify the conclusions made from the 2D EXSY experiments. The additional silyl substituent at C(3) position possibly unstablilizes the *iso*-indene intermediate leading to an increase in the activation energy for the [1,5]-silatropic shift in disilylindenes. The substituents on the silicon do not significantly affect the activation energy, the difference in activation energy of (*R*/*S*)-**4/5** and (*R*/*S*)-**9/10** being only 0.5 kcal mol^{-1}, as determined by the calculations.

4. Experimental

4.1. General considerations

The compounds investigated, (*R*/*S*)-**4/5**,[9b] (*R*/*S*)-**7/8**,[9b] (*R*/*S*)-**9/10**,[3c] (*R*/*S*)-**11/12**,[9b] and 1*H*-inden-1-yltrimethylsilane (*R*/*S*)-**1**,[15] were prepared as previously described. NMR spectra were recorded using a Bruker Avance 600 (^{1}H NMR 600 MHz) spectrometer equipped with Magnex 14.1 T standard bore superconducting magnet and Bruker Avance 400 (^{1}H NMR 400 MHz) spectrometer equipped with Oxford 9.4 T standard bore superconducting magnet. The probe used in all the experiments was Bruker 5 mm straight broad band BBO-probe with *z*-gradient. In all the cases, NMR spectra were referenced against residual ^{1}H-impurities in the solvent. The NMR spectra were recorded in δ values with 1,1,2,2-tetrachloroethane-d_2 as the solvent. Sample temperatures were maintained throughout the measurements by using the Bruker BVT-3000 temperature controlling unit with BCU-05 precooling unit. The temperature calibration of the instrument was performed externally by using 80%

ethylene glycol in DMSO. The mass spectrometric analyses of the Diels–Alder products were performed on an Agilent 1100 Series LC/MSD SL Trap Instrument. The compounds were analyzed by direct inlet infusion to the source by a syringe pump at a rate of 5 $\mu L\ min^{-1}$ and at a concentration of about 10 $mg\ mL^{-1}$. The operation parameters were as follows: drying gas temperature, 325 °C (598 K); drying gas flow rate, 5 $L\ min^{-1}$; nebulizer gas pressure, 15 psi. The instrument was operated in positive mode.

4.2. 2D EXSY measurements

2D EXSY spectra were recorded in the phase-sensitive mode using the pulse sequence for NOESY (90°–t_1–90°–t_m–90°–ACQ).[12] In a typical experiment, 256 increments were recorded in the f_2 dimension in 2K data points. Each increment was acquired in 8–16 scans over a 6.8 kHz spectral width. The acquired data were Fourier transformed with qsine window function in both f_1 and f_2. The relaxation delay was set to 2 s. Experiments were carried out at temperatures ranging from 100 to134 °C (373–407 K) using 1,1,2,2-tetrachloroethane-d_2 as the solvent. Mixing times ranging from 0.3 to 3 s were used. The best results were obtained with a 0.5 s mixing time.

4.3. Computational details

All of the stationary points on the potential energy surfaces were optimized at the DFT level of the theory. The Becke three-parameter hybrid method[16] with the Lee–Yang–Parr correlation functional approximation (B3LYP)[17] and the Dunning correlation consistent polarized valence double-ξ (cc-pVDZ) basis set were used.[18,19] All the calculations were carried out spin restricted. Vibrational analyses were carried out at the same level of theory to prove that the optimized structures are true minima (as no negative frequencies were found) or transition states (when only one negative frequency was found relevant to the silicon shift). Vibrational analysis (scaled by 0.9806,[20] 1 bar, 325 K) provided also thermodynamic contributions to the electronic energies to obtain $\Delta G^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$, and ΔG. In the case of (*R*/*S*)-**4**/**5**, potential minima conformations with respect to the allyl substituents were optimized by a grid search using Sybyl 7.1 software[21] and Tripos force field as implemented in the software. Found minima structures were used as starting geometries for the DFT optimization. All calculations were done with the Gaussian98/03 software.[22]

Acknowledgements

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Supplementary data

Plots of ln *K* versus 1/*T* for (*R*/*S*)-**4/5**, (*R*/*S*)-**7/8**, and (*R*/*S*)-**9/10** and 2D EXSY spectra for (*R*/*S*)-**4/5**, (*R*/*S*)-**7/8**, (*R*/*S*)-**9/10**, and 1*H*-inden-1-yltrimethylsilane (*R*/*S*)-**1** as well as a table reporting the ΔG for (*R*/*S*)-**9/10** obtained with various computational methods are available from the authors as supplementary material free of charge. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.07.040.

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14. It is notable that the calculated Gibb's free energies defining the equilibrium for the [1,5]-silatropic shifts in (*R*/*S*)-**9/10** as well as in (*R*/*S*)-**4/5** are far too high compared to the experimentally obtained values reported in Table 1. The ΔG and difference in the electronic energy ΔE were therefore calculated for (*R*/*S*)-**9/10** with several methods and are tabulated in Supplementary data with related discussion.
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