Mechanism and Kinetics of Sigmatropic Rearrangements in Cyclononatetraenyl(trimethyl)tin

Ilya D. Gridnev,*[a] Peter R. Schreiner,*[b] Oleg L. Tok,[a] and Yuri N. Bubnov[a]

Abstract: The dynamic behavior of cyclononatetraenyl(trimethyl)tin (**3**) was analyzed in detail by a combination of dynamic NMR techniques and high-level, ab initio, density functional calculations {Becke3–Lee–Yang–Parr (B3LYP) in conjunction with 6-31G* (C and H) and 3-21G* (Sn) basis sets for optimizations as well as 6-311G* (C and H) and 3-21G* (Sn) basis sets for single-point energy evaluations on the optimized geometries}. Complete ^{1}H and ^{13}C NMR spectra of **3** were assigned at 173 K; a comparison of computed and measured NMR data was used to elucidate the peak assignments of the *endo* ground-state structure of **3**. 2D ^{13}C,^{13}C-EXSY experiments in the temperature range 173–195 K provide strong evidence for [1,9]-SnMe$_3$ migrations in **3**. The experimental activation energy for this process (25.1 ± 2.5 kJ mol^{-1}), obtained from a series of 2D EXSY spectra, is in excellent agreement with the computed value (26.4 kJ mol^{-1}). The analysis of the selectivities of sigmatropic migrations in a series of cycloheptatrienyl and cyclononatetraenyl derivatives of boron and tin suggests that orbital control is the dominant factor governing the selectivities and mechanisms of these rearrangements. If several nearly degenerate migrations are possible, the least-motion principle favors the rearrangement which involves minimal motion of the migrating group. Hence, the barrier of a particular migration is determined by the properties of the carbon cycle rather than by the nature of migrating group.

Keywords: density functional calculations · least-motion principle · NMR spectroscopy · sigmatropic migrations · tin

Introduction

The concept of orbital control in organic chemistry, first envisaged by Woodward and Hoffmann in 1965,[1] is now widely used when dealing with problems concerning chemical reactivity and stereochemistry. However, molecular orbitals are not the only element governing chemical transformations, other factors, such as steric demand or the least-motion principle (LMP), may become decisive. Since the theoretical treatment of sigmatropic [1,*j*] migrations in conjugated carbocycles is rather straightforward, these rearrangements provide clear-cut examples for probing qualitative molecular orbital arguments which allow the prediction of a mechanism for a particular system.[2] However, experimental data for the validation of such theoretical analyses are still rather scarce.

With regard to these questions, many cyclopentadienyl[3] and indenyl[4] derivatives that involve various elements at the migrating center were extensively studied in the late 1960s to early 1970s. Despite sophisticated approaches, these systems are still particularly challenging when it comes to the analysis of the *topology* of a particular intramolecular sigmatropic migration by, for instance, NMR spectroscopy. Even in the most recent studies on the fluxional behavior of some indenyl derivatives, the rearrangement mechanism could not be established unequivocally from the available experimental data.[5] A further complication is that [1,5]-sigmatropic shifts in cyclopentadienyl and indenyl systems are indistinguishable from [1,2] migrations to the nearest position, so that the exact analysis of orbital control is difficult.

The NMR study of the dynamic behavior of cycloheptatrienyl derivatives is much easier; however, these compounds are sometimes difficult to prepare. In 1971 Larabee found facile [1,5]-Sn sigmatropic shifts in triphenylcycloheptatrienyltin (**1a**).[6] This observation was later confirmed twice;[7] the same mechanism was recently found for trimethylcycloheptatrienyltin (**1b**) (Scheme 1).[8] These results clearly demonstrate the importance of orbital control in sigmatropic migrations, since the tin moiety migrates selectively to the most remote position in the ring. Nevertheless, until now **1b** is the only cycloheptatrienyl derivative which displays a [1,5]-

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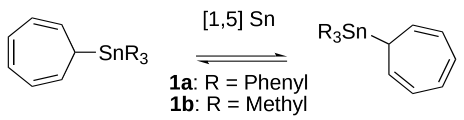
Abstract in Russian:

*Динамическое поведение циклононатетраенил-(триметил)олова **3** подробно исследовано комбинацией методов динамического ЯМР и теоретических расчетов ab initio {метод B3LYP с использованием базисов 6-31G* (C и H) и 3-21G(*) (Sn) для оценки энергий стационарных состояний}. Полное отнесение сигналов в ^{1}H и ^{13}C спектрах ЯМР было осуществлено при 173 K. Сравнение экспериментальных и рассчитаных величин хим. сдвигов ^{13}C указывает на то, что эндо-конформация **3** является преимущественной. Эксперименты 2D ^{13}C—^{13}C EXSY, проведенные в температурном интервале 173-195 K указывают на механизм последовательных [1,9] миграций $SnMe_3$ группы. Экспериментально найденная энергия активации этого процесса (25.1 ± 2.5 кДж моль$^{-1}$), полученная из серии 2D EXSY спектров, находится в хорошем соответствии с рассчитаной величиной (26.4 кДж моль$^{-1}$). Анализ наблюдаемых сигматропных миграций в ряде циклогептатриенильных и циклононатетраенильных производных бора и олова указывает на то, что основным фактором, регулирующим селективность и механизмы этих перегруппировок является орбитальный контроль. Если несколько типов миграций соответствуют орбитальным требованиям, то с наибольшей скоростью протекает перегруппировка, требующая минимального перемещения мигрирующей группы. Величина активационного барьера перегруппировки в большей степени зависит от природы углеродного цикла, чем от природы мигрирующей группы.*

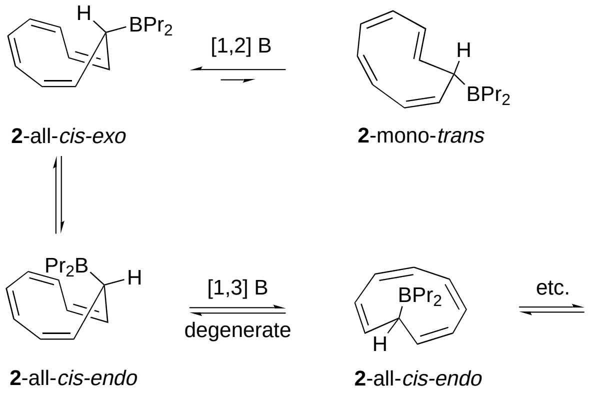
Abstract in German: *Das dynamische Verhalten von Cyclononatetraenyl-Trimethyl-Zinn (**3**) wurde durch eine Kombination von dynamischer NMR-Spektroskopie und Dichtefunktionaltheorie-Rechnungen {Becke3–Lee–Yang–Parr (B3LYP)-Funktional in Verbindung mit 6-31G* (C,H) und 3-21G(*) (Sn) Basissätzen für die Optimierungen und mit den 6-311G* (C und H) bzw. 3-21G(*) (Sn) Basissätzen für Energie-Einzelrechnungen} untersucht. Die ^{1}H- und ^{13}C-NMR Signale von **3** konnten bei 173 K vollständig zugeordnet werden; ein Vergleich zwischen berechneten und gemessenen NMR-Daten zeigt, dass **3** einen endo-Grundzustand besitzt. 2D ^{13}C,^{13}C-EXSY-Experimente im Temperaturbereich von 173–195 K weisen deutlich auf [1,9]-$SnMe_3$ Verschiebungen in **3** hin. Die damit verbundene experimentelle Aktivierungsenergie (25.1 ± 2.5 kJ mol^{-1}), die aus einer Serie von 2D EXSY-Spektren ermittelt wurde, stimmt ausgezeichnet mit dem berechneten Wert von 26.4 kJ mol^{-1} überein. Die Analyse der Selektivitäten sigmatroper Umlagerungen in einer Serie von Cycloheptatrienyl- und Cyclononatetraenyl-Derivaten von Bor und Zinn zeigt, dass Orbital-Auswahlregeln die Selektivitäten und Mechanismen dieser Verschiebungen klar bestimmen. Sofern mehrere, nahezu entartete Umlagerungen möglich sind, favorisiert das „least-motion principle“ diejenige, welche der geringsten Umorganisation der Atompositionen bedarf. Folglich wird die Umlagerungsbarriere einer bestimmten Verschiebung weniger durch die wandernde Gruppe selbst, als vielmehr durch die Eigenschaften des Kohlenstoffrings bestimmt.*



Scheme 1. [1,5]-Sn sigmatropic shifts in trialkylcycloheptatrienyltin compounds.

sigmatropic migration. Substituted B,[8] Re,[9] Ru,[10] and S[11] fragments all rearrange in a [1,7] fashion, which again is formally equal to the [1,2] shifts to the nearest position and can thus be rationalized by both orbital control and the „least motion principle“ (LMP).

Recently, we studied the dynamic behavior of the cyclononatetraenylboron derivative **2**, experimentally and computationally;[12] all data agree that the [1,3]-B shift is the fastest rearrangement in this compound (Scheme 2).[12] This may be regarded as a second example for clear orbital control.



Scheme 2. Dynamic behavior of the cyclononatetraenylboron derivative **2**.

However, our accompanying ab initio computations also suggested an almost equally facile [1,9]-B shift,[12b] which is not predicted by the Woodward–Hoffmann rules but follows the LMP. Apart from that, a facile rearrangement to **2**-mono-*trans*, a key intermediate in further rearrangements of **2**,[13] was characterized.[12b]

With regard to these apparent problems with sigmatropic migrations, we became interested in a detailed theoretical and experimental analysis of the dynamic behavior of cyclononatetraenyl(trimethyl)tin (**3**). This compound was first prepared in 1976 by Boche and Heidenhain,[14] who had also reported its fluxional character judged by the appearance of the ^{1}H NMR spectrum at ambient temperatures. In the following three years two efforts were directed towards the resolution of the ^{1}H[15] and ^{13}C[16] NMR spectra of **3** at low temperatures; however, both were unsuccessful on account of spectrometer limitations. We now report the detailed characterization of the low-temperature NMR spectra of **3**, experimental studies of its fluxional behavior in conjunction with density functional theory computations and a discussion of the relative importance of orbital control, as well as other factors governing the rearrangement pattern in **3**.

Results and Discussion

Assignment of the signals in the low-temperature NMR spectra of 3: Compound **3** was prepared from lithium cyclononatetraenide and trimethyltin chloride as described previously.[14–16] Since **3** is thermally unstable, its synthesis and all further operations were carried out at temperatures below 253 K. We obtained the narrow-line NMR spectra of **3** at 173 K (400 MHz); 2D correlation experiments at this temperature allowed the assignment of the signals (Figure 1 and Figure 2). Protons H4 and H5 appear as an unresolved multiplet in the ^{1}H NMR spectrum; an individual assignment of their positions was not possible at this stage (vide infra).

Figure 3 shows the 2D ^{13}C-EXSY spectrum of **3** at 173 K at a mixing time of 50 ms; the spectrum contains four cross-peaks. Carbon atom C1 exchanges only with C2, which also exchanges with C3. This clearly indicates the [1,2]-migration of the trimethyltin group, which corresponds to a [1,9]-Sn sigmatropic shift in **3** (Scheme 3). Therefore, C3 produces a second exchange cross peak with C4; the last signal belongs to C5. With this data and the C–H correlation (Figure 2) we obtained the relative positions of H4 and H5 protons in the ^{1}H NMR spectrum (Figure 1).

At higher temperatures or longer mixing times, additional cross peaks are observed in the EXSY spectra of **3**. However, we were not able to differentiate between [1,3]-, [1,5]-, and [1,7]-, or several consecutive [1,9]-Sn shifts. While [1,3]- and [1,7]-Sn shifts in **3** could not be excluded on the basis of the 2D EXSY data, the [1,9]-Sn sigmatropic shift is most likely to be the fastest rearrangement.

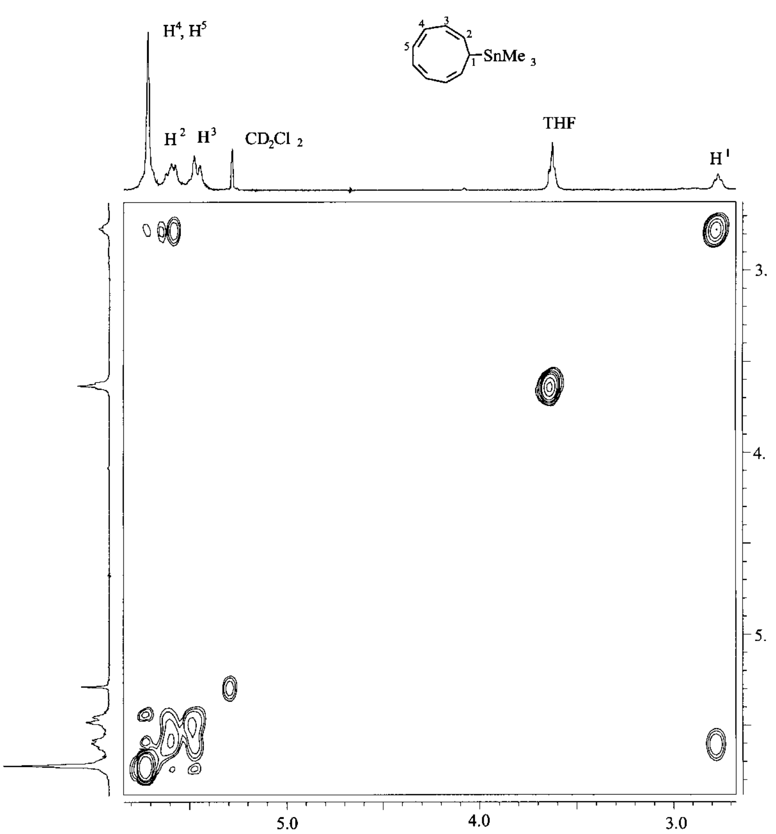


Figure 1. ^{1}H,^{1}H-COSY spectrum of cyclononatetraenyl(trimethyl)tin (400 MHz, 173 K, $CCl_4/CDCl_3/CD_2Cl_2$).

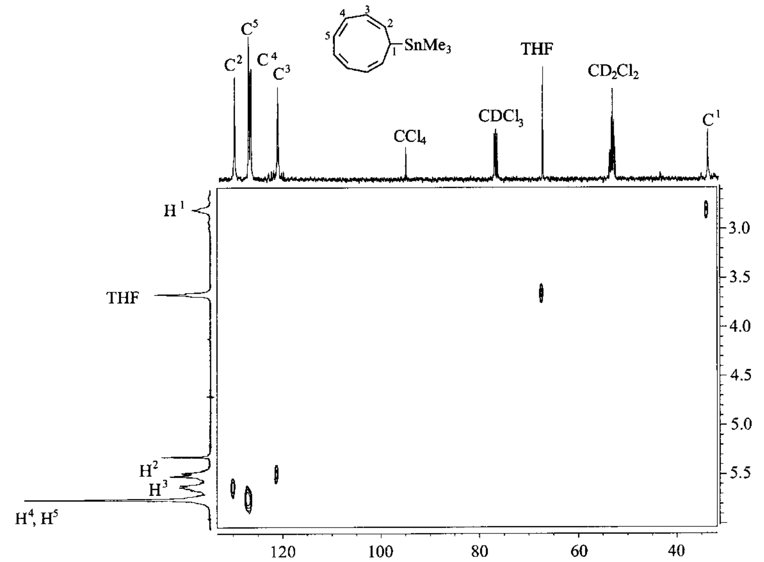


Figure 2. ^{1}H,^{13}C-XHCORR spectrum of **3** (400 MHz, 173 K, $CD_2Cl_2/CDCl_3/CCl_4$).

To elucidate the various possible sigmatropic shifts, we employed density functional theory (DFT) computations (see Computational Methods). In perfect agreement with experiment, the computations (Figure 4) clearly show that the [1,9]-Sn shift is most favorable (experimental barrier (E_A) = 25.1 ± 2.5 kJ mol^{-1} (see below), computed $\Delta H^{\neq} = 26.4$ kJ mol^{-1}, **TS19**, Figure 4). All other possible shifts are much higher in energy and cannot be of significance regarding the sigmatropic shifts in **3**.

Study of the conformational equilibria in 3: Spectral changes in the temperature interval 173–225 K are in accord with the [1,9]-Sn shifts in **3** (Figure 5). However, the reversible broadening of C3 and C5 at lower temperatures indicates the presence of another intramolecular dynamic process, which

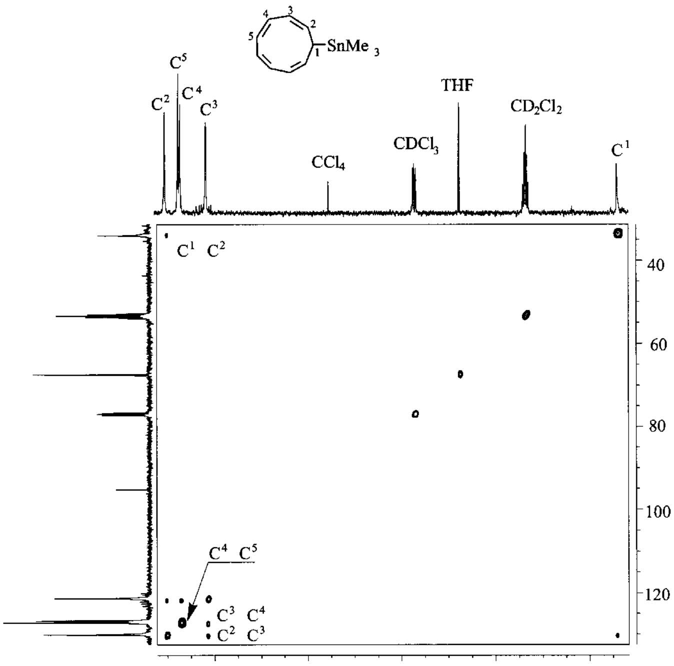
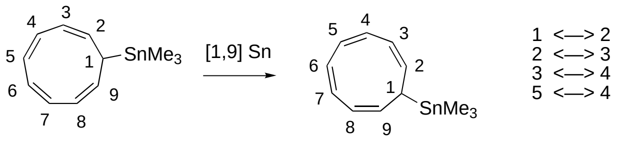


Figure 3. Phase-sensitive ^{13}C,^{13}C-EXSY spectrum of **3** (100 MHz, 173 K, CD_2Cl_2/$CDCl_3$/CCl_4).



Scheme 3. [1,9]-Sn sigmatropic shift in **3** and carbon atom exchanges which give rise to the cross peaks in the 2D ^{13}C-EXSY NMR spectrum.

most probably involves conformational changes. An obvious explanation would be the equilibration between **3**-*exo* and **3**-*endo* (Scheme 4). Since we were unable to record the NMR spectra at even lower temperatures, we performed ab initio computations on the conformers of **3** (see Computational Methods for details).

A decrease in temperature within the 153–173 K temperature interval affects the linewidths for C3 and C5 most dramatically (Figure 5). On the contrary, the computed chemical shifts display the greatest difference for C2. The computed relative energies for **3**-*endo* and **3**-*exo* are rather similar and very sensitive to basis set effects; we conclude that both structures are similar in energy. The transition structure for their interconversion could not be located because it was computationally not feasible to compute second derivatives at points along the reaction coordinate.

It is more likely that the observed spectrum should be attributed to averaging between the enantiomers of **3**-*endo*, which belongs to the C_1 point group; note that **3**-*exo* is C_s symmetric. Enantiomers have identical NMR spectra; however, the fast exchange between them, which results in the time-averaged loss of asymmetry, would equalize the chemical shifts for pairs C2/C9, C3/C8, C4/C7, and C5/C6. This process was examined theoretically by computing and averaging the chemical shifts for the carbons which become equivalent as a result of fast exchange (Table 1). Taking into account that the computed chemical shifts are uniformly somewhat too high because of the neglect of solvent and temperature effects, the agreement between the averaged experimental and computed NMR data for **3**-*endo* is quite good. As the deviation between these two data sets and the NMR peaks for **3**-*exo* is large, the latter is unlikely to be involved in this exchange process. We conclude, therefore, that only **3**-*endo* is observed in the

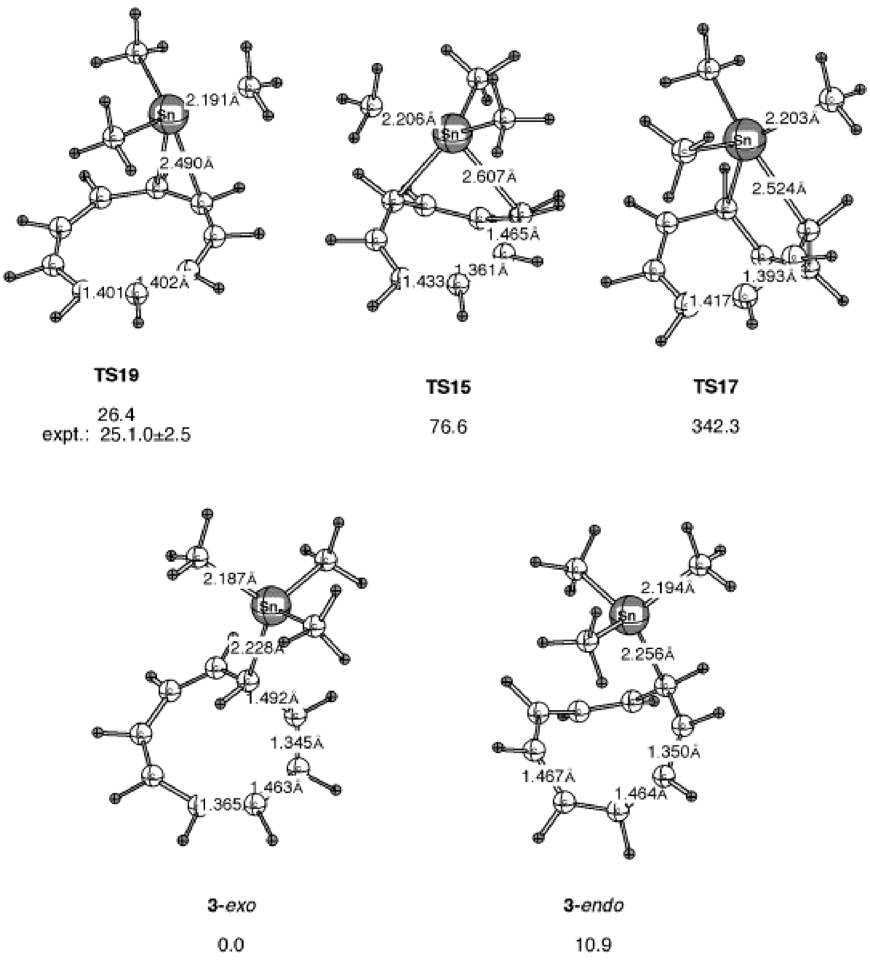


Figure 4. B3LYP/6-31G* (3-21G* on Sn) optimized structures of the trimethylcyclononatrienyltin compounds discussed in the present work. Final relative energies in kJ mol^{-1} were computed at the B3LYP/6-311G* level (3-21G* on Sn).

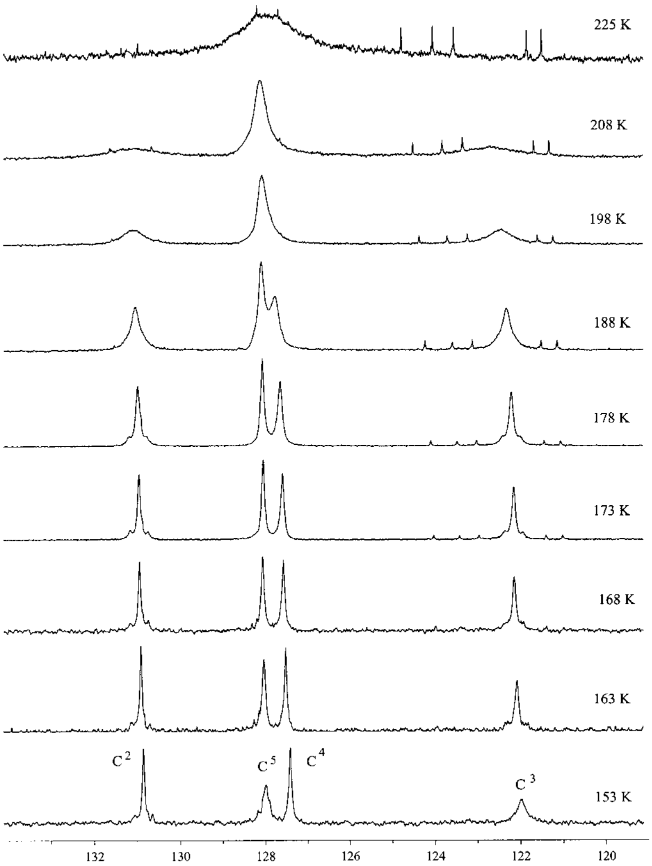
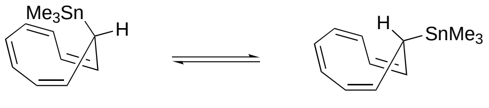


Figure 5. Section plots of ^{13}C NMR spectra of **3** (100 MHz, $CDCl_3/CD_2Cl_2/CCl_4$) at different temperatures.



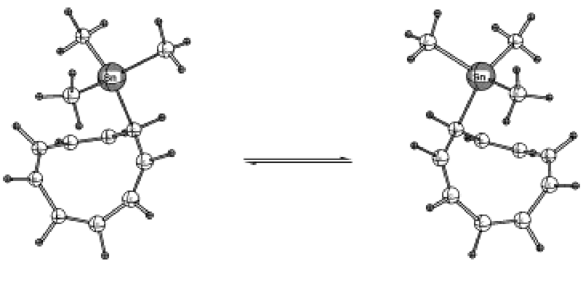
3-*endo* **3**-*exo*

Scheme 4. Conformational equilibrium between **3**-*exo* and **3**-*endo*.

Table 1. Experimental and computed ^{13}C chemical shifts in $C_9H_9SnMe_3$ (**3**).

Carbon atom	Experimental δ	Computed δ **3**-*exo*	**3**-*endo*	**3**-*endo*, averaged
1	34.0	53.9	42.5	42.5
2	130.1	157.0	133.4, 121.0	127.2
3	121.4	131.3	123.6, 133.4	128.5
4	126.8	135.3	134.8, 131.2	133.0
5	127.2	130.9	129.6, 140.6	135.1
Me	7.9	10.0, 13.2	4.1, 7.4, 11.9	7.8

^{13}C NMR spectra and that the lineshape dependence below 173 K may be interpreted by the conformational changes in the C2–C9 section of the cyclononatetraene moiety (Scheme 5).



3-*endo* **3**-*endo*

Scheme 5. Conformational changes in the C2–C9 section of the cyclononatetraene moiety in **3**.

Kinetics of the [1,9]-Sn shift in 3: The conformational equilibrium discussed above and the satellites from C–Sn coupling observed in the ^{13}C NMR spectrum of **3** complicate lineshape analyses for the determination of the activation parameters for the rearrangement. This encouraged us to use the 2D EXSY NMR techniques for the kinetic studies of this rearrangement. For small mixing times, the rate constant of the exchange reaction can be derived as the slope of the linear dependence of the relative volume of a cross peak and the mixing time.[17, 18]

We have carried out a series of 2D ^{13}C-EXSY experiments in the temperature interval 162–183 K and have measured the dependence of the relative volume of each cross peak on the mixing time at each temperature. Linear dependence was found for the cross peak between C3 and C4, normalized by the C3 diagonal peak at each temperature. The signals C4 and C5 are too close to allow accurate integration of the cross peak between them. For other cross peaks strong deviations from linear dependence were observed, which may be the result of inaccurate integration caused by direct Sn–C coupling. Arrhenius treatment of the rate constants for the [1,9]-Sn shifts in **3** gave the activation energy for the [1,9]-Sn sigmatropic shift (Figure 6, Table 2). Note the very good agreement between the experimental and calculated values.

Selection rules for sigmatropic migrations in conjugated monocycles: As already noted in the Introduction, [1,5] migrations are almost exclusively observed in cyclopentadienyl derivatives;[4] numerous examples of [1,7]-sigmatropic shifts in cycloheptatrienes[6–8] led to the conclusion that sigmatropic migrations may be ruled by LMP rather than by orbital control;[3b, 15] the lack of additional experimental evidence did not allow a more definitive conclusion. In the following section we will argue that both factors have to be considered: orbital symmetry and spatial separation of the involved atoms or groups.

Figure 7 depicts the Hückel-type p-molecular orbitals of fully conjugated cycloheptatrienyl and cyclononatetraenyl moieties for a qualitative analysis of the orbital selection rules. As we pointed out earlier,[8] the migrating groups (alkylboron or alkyltin fragments) are partially positively charged; hence, one has to consider the LUMOs (degenerate set of two in both cases) in order to determine which migrations are favorable, based on orbital phases and coefficients. This is an extension of the original formulation of the Woodward–Hoffmann rules which are based on the consideration of bonding in the transition state from a union of two hypothetical radical fragments (where the degenerate SOMOs would have to be considered in the present case). We found no

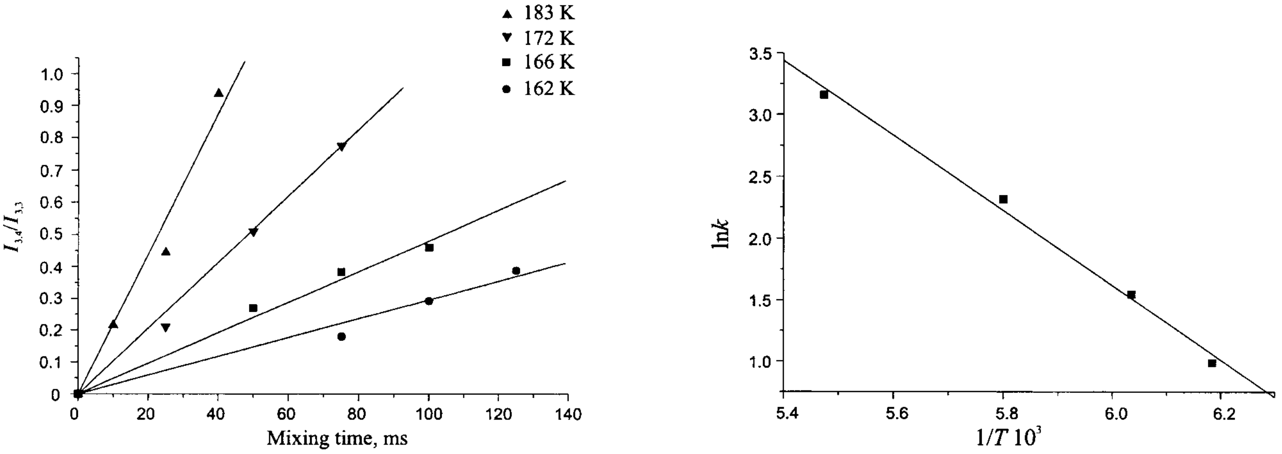
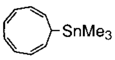
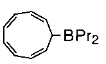
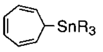
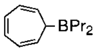
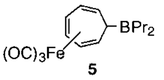


Figure 6. Kinetic analysis of the [1,9]-Sn shift in **3**: Left: kinetic curves obtained from 2D ^{13}C,^{13}C-EXSY experiments. Right: Arrhenius plot.

Table 2. Experimental data on sigmatropic migrations of boron and tin groups in cyclic conjugated molecules.

Compound	Type of rearrangement	G(T) [kJ mol^{-1}]	E_a [kJ mol^{-1}]	Reference
 **3**	[1,9]-Sn[a]	38.0 ± 0.4 (173)	25.2 ± 2.5[e]	This work
 **2**	[1,3]-B[a]	36.8 ± 0.4 (195)	26.1 ± 2.2[f]	[12b]
 **1a,b**	[1,5]-Sn[a]	75.2 ± 0.2	65.4 ± 0.3	[12b]
 **4**	[1,7]-B[a]	77.0[b]		[8]
 **5**	[1,7]-B[c]	65.3 ± 0.3[d]	71.2 ± 2.1	[19]
	[1,3]-B[d]			

[a] The fastest rearrangement. [b] Computed value (B3LYP/6-311 + G*//B3LYP/6-31G* + ZPVE, ref. [8]. [c] Accompanied by [1,2]-Fe haptotropic migration. [d] At 298 K the [1,3]-B shift in **5** is about 10 times slower than the [1,7]-B shift. [e] Computed value (B3LYP/6-311G*(3-21G* on Sn)//B3LYP/6-31G* (3-21G* on Sn) = 26.4 kJ mol^{-1}. [f] Computed value (B3LYP/6-311 + G*//B3LYP/6-31G*) = 25.1 kJ mol^{-1}.

indication for diradical-type transition structures; the restricted B3LYP solutions are stable with respect to the expansion to an unrestricted (UB3LYP) approach. While inversion of configuration is observed for boryl-group migrations (i.e. a p-orbital *perpendicular* to the plane of the π system connects the migrating termini), the configuration is retained in the case of SnR_3 (i.e. an sp^n or a p-orbital *parallel* to the plane of the π system connects the migrating termini). This is also confirmed by our computations (Figure 4), where the $SnMe_3$ moiety remains pyramidal throughout the migration. Thus, alkylboryl groups (or other isolobal fragments) shift with one orbital phase inversion; alkyltin moieties migrate between orbitals with the same sign. In the cycloheptatrienyl case, both LUMOs show clearly that [1,3]- and [1,7]-boryl migrations are allowed; only [1,5] shifts are likely to occur in trialkyl tin group migrations as a consequence of orbital constraints: the coefficients for allowed [1,7] shifts differ significantly in size or are simply too small, which leads to high barriers.

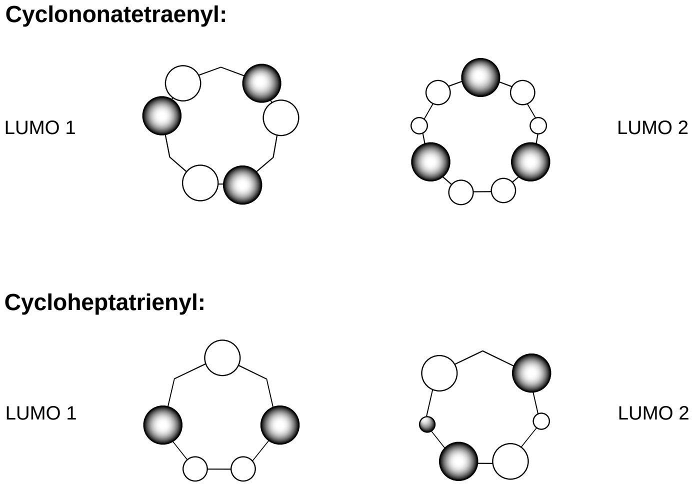


Figure 7. Simple qualitative presentation of the degenerate Hückel LUMOs for the analysis of allowed suprafacial shifts in conjugated cycloheptatrienyl and cyclononatetraenyl systems.

On the other hand, in the cyclononatetraenyl system (Figure 7), the situation is somewhat more complicated because of the larger number of p-orbitals. Based on orbital phases only, [1,3]-, [1,5]-, and [1,9]-boryl shifts are allowed with inversion of configuration, while [1,5] shifts are disfavored because of mismatches in orbital size or small orbital coefficients. However, only the [1,3]-boryl shift connects orbitals with the same coefficient so that this mode is preferred, despite the fact that the LMP would suggest that the [1,9]-boryl shift is the lowest in energy. The situation is rather different for migrating trialkyltin groups, where in-phase orbitals must be connected to the p-orbital at SnR_3. Hence, [1,9]-, [1,7]-, and [1,5]-alkyltin shifts are orbital-allowed. All, except for the [1,9] shifts, are accompanied by out-of-phase orbital interactions, as demonstrated clearly in

LUMO 2. Hence, the [1,9]-SnR_3 migrations are highly favored and only involve a barrier of 25.2 ± 2.5 kJ mol^{-1}, which is in nearly perfect agreement with the computed value of 26.4 kJ mol^{-1}. The computed barriers for the [1,5]- and [1,7]-Sn group migrations are prohibitively high in energy (76.6 kJ mol^{-1} and 342.3 kJ mol^{-1}, respectively, Figure 4).

The data (Table 2) show impressively that these qualitative considerations also hold true for the compounds **1**–**5**: [1,3] and [1,7] shifts are observed for boron compounds (**2**, **4**, **5**), whereas the corresponding tin derivatives (**1** and **3**) only show [1,5] (cycloheptyl case) and [1,9] (cyclononyl case) migrations. If the symmetry of the bonding orbitals for boron and tin is taken into account, the sigmatropic shifts with inversion (Möbius-type transition state) for boron and with retention (Hückel-type transition state) for tin agree nicely with the qualitative predictions from molecular orbital theory.

Furthermore, the selectivity *among allowed processes* may be rationalized by means of the LMP. The [1,7]-B shifts (migration to the nearest position of cycloheptatriene) proceed faster than [1,3]-B shifts in the same compounds; the orbitally allowed [1,7]-B migration in cyclononatetraenyl boron is strongly energetically disfavored compared to [1,3]-B and [1,9]-B shifts, for which the small distance between the reaction termini allows the formation of flat homoaromatic transition structures.

Nevertheless, the barriers for sigmatropic shifts in cyclic polyolefins are not controlled directly by the distance between the migration termini. Thus, the [1,7]-B shift (migration to the adjacent position) in cycloheptatrienyl borane **4** is about 30 kJ mol^{-1} higher in energy than the [1,3]-B shift in cyclononatetraenyl borane **2**.[8, 12b] Moreover, despite the different nature of the migrating groups, the rearrangement barriers for the cycloheptatrienyl boron and tin compounds **1**, **4**, and **5**, as well as for the cyclononatetraenes **2** and **3** are rather similar. Hence, the energetics of sigmatropic migrations is mainly determined by the properties of the carbon cycle rather than by the nature of the migrating group.

Conclusions

Our combined experimental and computational data on the sigmatropic migrations in cycloheptatrienyl and cyclononatetraenyl derivatives of tin and boron show that orbital control is the dominant factor governing the selectivity and mechanisms of these rearrangements. If several nearly degenerate migrations are possible, the least-motion principle favors the rearrangement which involves minimal motion of the migrating group. Consequently, the barrier of a particular migration is determined by the properties of the carbon cycle rather than by the nature of migrating group.

Experimental Section

Computational methods: Geometries of all stationary points were optimized by means of analytical energy gradients of self-consistent field theory[20] and density functional theory (DFT).[21] The latter utilized Becke's three-parameter exchange-correlation functional[22] and included the nonlocal gradient corrections described by Lee–Yang–Parr (LYP),[23] as implemented in the Gaussian 94 program package.[24] All geometry optimizations were performed with the 6-31G* (C and H) and 3-21G(*) (Sn) basis sets.[25] Single-point energies were evaluated with the more flexible 6-311G* (C and H) and standard 3-21G(*) (Sn) basis sets;[26] final energies thus refer to B3LYP/6-311 + G*(C, H); 3-21G*(Sn)//B3LYP/6-31G* (C,H); 3-21G* (Sn). Standard notation is used, that is „//“ means energy computed at // geometry.[27]

NMR chemical shifts were computed with the gauge-including atomic orbital (GIAO) approach[28] in conjunction with the B3LYP functional;[22, 23] the B3LYP/6-31G*(C,H); 3-21G*(Sn) geometries were used to compute the chemical shifts. The absolute shift (s) of tetramethylsilane (TMS) was used to compute the relative chemical shifts $\delta = \sigma_{\text{reference}} - \sigma_{\text{compound}}$.

Physical measurements: All operations were performed in a dry argon atmosphere. NMR spectra were obtained on a Bruker AMX-400 spectrometer (400 MHz for protons, 100 MHz for carbon). The synthesis, signal assignments, and EXSY spectra of cyclononatetraenyl(dipropyl)borane was described previously[12a].

Trimethylcyclononatetraenyltin (**3**): A solution of 9-chlorobicyclo[6.1.0]-nona-2,4,6-triene (1.04 g) in THF (5 mL) was added to lithium (1.0 g) at −50 °C. The reaction mixture was allowed to warm to ambient temperature and then stirred for 1 h. The resulting dark red solution of lithium cyclononatetraenide was decanted from the excess of lithium and the solvent was removed in vacuum. The solid residue was suspended in pentane (30 mL) and the suspension was cooled to −70 °C. A solution of Me_3SnCl (1.36 g) in pentane (10 mL) was added dropwise, while the temperature of the reaction mixture was kept below −40 °C. The color of the reaction mixture slowly turned light yellow and a white solid precipitated. To prepare a sample for NMR investigation, 1–2 mL of the resulting solution (without precipitate) was taken, the solvent was removed in vacuo at −30 °C, and the residue was dissolved in a mixture of $CD_2Cl_2/CDCl_3/CCl_4$ (60:27:13 by volume). Samples thus obtained contained **3** and some amounts of pentane and THF. ^{1}H NMR (400 MHz, 173 K, $CD_2Cl_2/CDCl_3/CCl_4$): $\delta = 0.03$ (s, 9H, 3 CH_3, $^2J(\text{H,Sn}) = 25.9$ Hz), 2,76 (t, 1H, H1, $^3J(\text{H,H}) = 7.1$ Hz, $^2J(\text{H,Sn}) = 49.3$ Hz), 5.48 (dd, 2H, H3, $^3J(\text{H,H}) = 2 \times 11.9$ Hz), 5.59 (dd, 2H, H2, $^3J(\text{H,H}) = 7.1$, 11.9 Hz), 5.71 (m, 2H, H4, H5); ^{13}C NMR (100 MHz, 173 K, $CD_2Cl_2/CDCl_3/CCl_4$): $\delta = 7.9$ (CH_3, $^1J(\text{C,Sn}) = 320.9$, 306.9 Hz), 34.0 (C1, $^1J(\text{C,Sn}) = 267.0$, 253.2 Hz), 121.4 (C3, $^3J(\text{C,Sn}) = 41.6$ Hz), 126.8 (C4), 127.2 (C5), 130.1 (C2, $^2J(\text{C,Sn}) = 43.0$ Hz).

Dynamic NMR studies: All 2D NMR spectra were obtained on a Bruker AMX-400 spectrometer from the samples sealed under argon. 2D ^{13}C-EXSY spectra were acquired with a NOESYTP pulse program slightly modified to allow the decoupling of protons during the acquisition. Areas of cross peaks and diagonal peaks were obtained by volume integration of appropriate voxels surrounding the peaks.

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