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Synthesis and Dynamic Properties of Cycloheptatrienyl(dipropyl)borane. Equilibrium with 7-Dipropylborylnorcaradiene

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Abstract: The synthesis of cycloheptatrienyl(dipropyl)borane (**2a**) was accomplished via the exchange reaction of trimethyl(cycloheptatrienyl)tin (**6**) and dipropylchloroborane. Compound **2a** was found by NMR spectroscopy to equilibrate with its valence tautomer 7-*exo*-(dipropylboryl)norcaradiene (**2b**). The equilibrium between **2a** and **2b** was studied in detail experimentally by variable temperature NMR and theoretically by *ab initio* calculations of size-reduced molecular systems (***2a*** and ***2b***, with methyl instead of *n*-propyl groups) at the B3LYP/6-311+G*//B3LYP/6-31G* + ZPVE level. Experimentally determined thermodynamic parameters of the equilibrium ($\Delta H = 2.4 \pm 0.1$ kcal mol^{-1}; $\Delta S = -5.5 \pm 0.3$ cal mol^{-1} K^{-1}) and the activation barriers at 228 K ($\Delta G^{\ddagger}_{228}(\mathbf{2a} \rightarrow \mathbf{2b}) = 8.2 \pm 0.1$ kcal mol^{-1}, $\Delta G^{\ddagger}_{228}(\mathbf{2b} \rightarrow \mathbf{2a}) = 9.4 \pm 0.1$ kcal mol^{-1}) are in reasonable agreement with the computed results ($\Delta H = 2.0$ kcal mol^{-1}, $\Delta S = -3.7$ cal mol^{-1} K^{-1}; $\Delta G^{\ddagger}_{228}(\boldsymbol{2a} \rightarrow \boldsymbol{2b}) = 3.2$ kcal mol^{-1} and $\Delta G^{\ddagger}_{228}(\boldsymbol{2b} \rightarrow \boldsymbol{2a}) = 6.7$ kcal mol^{-1}). The computations also indicate that 7-*endo*-(dimethylboryl)norcaradiene (***2c***) is 7.6 kcal mol^{-1} less stable than the *exo*-isomer ***2b*** due to more favorable overlap of the unoccupied boron 2p AO with the Walsh orbital of the three-membered ring moiety in ***2b***. Line shape analyses together with 2D ^{1}H EXSY data for the equilibrating system of **2a** and **2b** allowed the detection of a [1,7] sigmatropic shift in **2a** at temperatures above 293 K. This is confirmed by the computations identifying the [1,7] B shift to have the lowest activation enthalpy (***2a***, $\Delta H^{\ddagger} = 18.4$ kcal mol^{-1}). In the unsymmetrical deuteriopyridine complex **9**, the empty boron 2p AO interacts strongly with the nitrogen lone pair. This reduces the stabilization of the *exo*-norcaradiene skeleton, yielding only the "pure" cycloheptatrienyl form **9** in the NMR spectra. Both NMR data and the computations show that the rotation about the B−C bond in **9** is hindered.

Introduction

Cycloheptatrienes display a large variety of dynamic processes which in most cases can be understood in terms of qualitative molecular orbital theory. The sigmatropic[1j] migrations of 7-η^{1} derivatives of cycloheptatriene afford typical examples.[1] The nature of a particular rearrangement depends on the migrating atom: while [1,5] sigmatropic shifts are observed for the proton[1d−g] and groups containing tin as the migrating center,[1a−c] substituted Ru,[1h] Re,[1i] and S[1j,k] atoms only rearrange in a [1,7] fashion. Polyhapto−metal complexes of cycloheptatriene are also known to undergo haptotropic shifts.[2]

Recently we have found that three independent processes take place in the iron tricarbonyl complex of cycloheptatrienyl(dipropyl)borane (**1**): a [1,3] B sigmatropic shift, a [1,7] B sigmatropic shift accompanied by [1,2] migration of the iron tricarbonyl group, and a [1,3] Fe haptotropic shift.[3] The inherent symmetry of **1** allowed us to exclude simultaneous [1,5] B migrations. We concluded that [1,3] and [1,7] boron migrations are allowed, whereas [1,5] B shifts are prohibited.[3] However, the question of whether the observed selectivity is only due to the presence of the transition metal in **1** remained unanswered. The synthesis of an uncoordinated cycloheptatrienylboron derivative was therefore of particular interest.

Another motivation for synthesizing and studying boron cycloheptatrienyls is to elucidate further on the long-standing discussion over the tautomerism between cycloheptatrienes (CHT) and norcaradienes (NCD).[4] Despite Willstätter's formulation of the problem as early as 1901,[5] it has been tackled experimentally only after NMR techniques developed into a powerful tool for physical organic chemistry in the 1960s.[4a,b] Examples were found where either norcaradienes[6] or cycloheptatrienes predominate,[7] but also where rapid equilibria between

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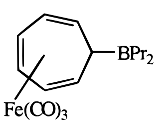
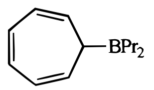
these two forms exist.[8] This stimulated extensive studies of steric and electronic substituent effects on CHT−NCD equilibria.[9] The first explanation of the observed stability of 7,7-dicyanonorcaradiene proposed by Ingold,[10] *viz*. "quasi-conjugation of the cyclopropane ring with the cyano-group", was supported theoretically by Hoffmann[11a] and Günther,[11b] who showed that NCD is stabilized by electron donation from the cyclopropane Walsh orbital into an unoccupied π MO. It was shown recently that CHT−NCD equilibria can be controlled differentially through substitution.[12] For instance, NCD can be stabilized by introducing weak π donors in 3,5-positions.[13] Nevertheless, it is still impossible to differentiate between the steric and electronic effects operative in CHT−NCD equilibria. The study of related new systems allowing these effects to be analyzed more cleanly is desirable, especially in view of the fundamental importance of this problem for the synthesis[14] and understanding of similar equilibria in larger molecules, such as 1,6-methano[10]annulenes,[15] as well as fullerenes and fulleroids.[16]

The present work describes the synthesis of cycloheptatrienyl(dipropyl)borane (**2**) as well as its analysis by NMR and electronic structure methods.



1

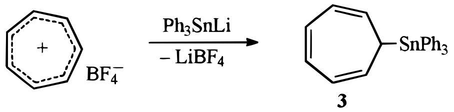


2

Results and Discussion

Synthesis of Cycloheptatrienyl(dipropyl)borane. Synthesis of Trimethylcycloheptatrienyltin (6) and the Kinetics of the [1,5] Sn Shift. Borylation of appropriate lithium or potassium precursors for the synthesis of allylic boranes was accomplished previously.[3,17] Unfortunately, this approach failed for the preparation of the target compound **2** since the corresponding antiaromatic cycloheptatrienyl anion is highly unstable.[18,19] Therefore, only covalent cycloheptatrienyl metals could be considered as suitable synthetic precursors for the desired borane. Among those, the tin compounds are most readily accessible via reaction of tin−lithium derivatives with tropylium salts. Thus, triphenylcyclo-heptatrienyltin (**3**) was prepared by reacting Ph_3SnLi with tropylium tetrafluoroborate (Scheme 1).[1a−c]

Scheme 1



Although the yields are low and many byproducts form, stannane **3** is stable and can be purified by column chromatography. However, the triphenyl derivative **3** is an unsuitable starting compound for the synthesis of the boron analogue via transmetalation, since phenyl radicals in organotin compounds are more labile than alkyl groups,[20] and the expected product of a reaction between **3** and a dialkylboron halide is a dialkylphenylboron species. Therefore, a trialkyltin derivative of cycloheptatriene was needed; unsuccessful syntheses of trimethyl- or triethylcycloheptatrienyltin are described in the literature.[1c] In these experiments bicycloheptatrienyl (**4**) and ditin compound **5** were the only products of the reaction of R_3SnLi (R = Me,Et) with tropylium tetrafluoroborate (Scheme 2). Thus, we decided to try the less ionic tropylium bromide for the synthesis of trimethylcycloheptatrienyltin (**6**).

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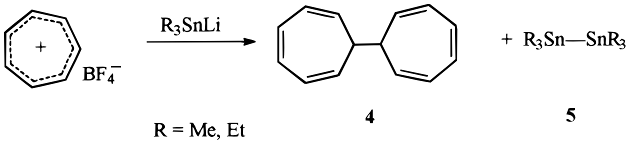
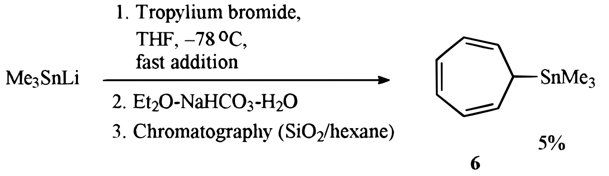
Scheme 2



Scheme 3



The reaction between tropylium bromide and lithium trimethyltin proved to be very sensitive to the reaction conditions. As found in earlier reports, only **4** and **5** (R = Me) were detected in the reaction mixtures when a solution of Me_3SnLi was added to a suspension of tropylium bromide at either 0 or −78 °C. Reversing the order of addition also was unsuccessful. Only when tropylium bromide was added very quickly at once to a solution of Me_3SnLi at −78 °C, followed by immediate treatment with $Et_2O-H_2O-NaHCO_3$, could **6** be detected by NMR (Scheme 3). In some experiments the yield for **6** was 35−40%; however, **6** is rather unstable, and the best preparative yield after purification did not exceed 5%. The only satisfactory way of purification was by column chromatography on silica gel in hexane; attempts to distill **6** in vacuo led to complete decomposition.

Triphenylcycloheptatrienyltin (**3**) was the first fluxional cycloheptatrienyl derivative.[1a] The nature of tin sigmatropic migrations in this compound was the key question in the discussions of the factors governing the reaction pathways in cyclic polyunsaturated organometallic compounds.[1f] Two independent investigations on the dynamic behavior of **3** showed that a [1,5] Sn shift occurs in **3**, clearly indicating orbital control of sigmatropic tin migrations.[1b,c] There is some discrepancy in the activation parameters reported for the [1,5] Sn shift in **3**, but the values given in the most recent work seem more reliable[1c] ($\Delta H^{\ddagger} = 13.8 \pm 0.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = -5.6 \pm 1.2$ cal mol^{-1} K^{-1}, $\Delta G^{\ddagger}_{300} = 15.4 \pm 0.1$ kcal mol^{-1}).

We have studied the fluxional behavior of trimethylcycloheptatrienyltin (**6**). The 2D EXSY NMR experiments (e.g., Figure 1) carried out in the 298−338 K temperature interval provided strong evidence for a [1,5] Sn shift in **6**. Kinetic data for the [1,5] Sn migration in **6** were deduced from 2D EXSY ^{13}C NMR spectra. It is known that at small mixing times the rate constant can be obtained from the slope of the linear dependence of the volume of a cross-peak on the temperature.[21,22] The result of such a treatment for four different temperatures is shown in Figure 2. The activation parameters found from these data by the Eyring approach are shown in Scheme 4. A decrease of the rate of the [1,5] Sn shift in **6** compared to that in **3** is due to the known tendency of the phenyl groups increasing the migratory aptitude of a tin atom.[20]

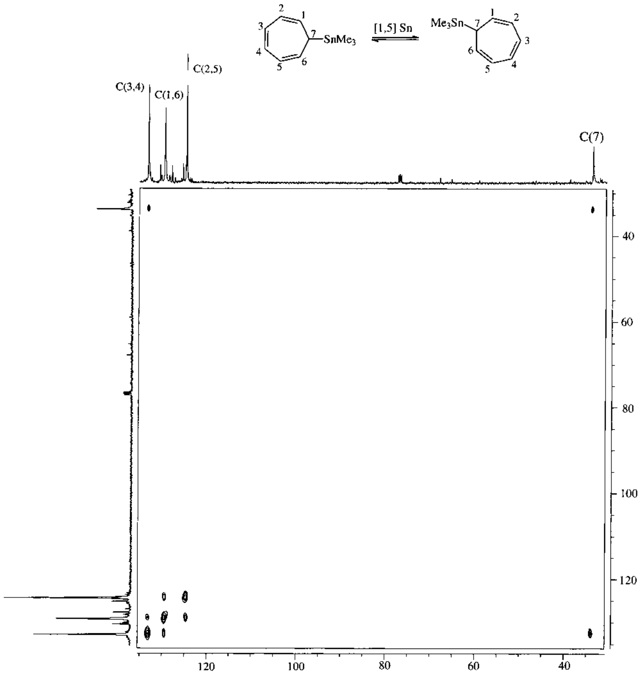


Figure 1. ^{13}C NMR EXSY spectrum of trimethylcycloheptatrienyltin (**6**) (100 MHz, $CDCl_3$, 328 K): mixing time 0.08 s, initial delay 1 s, number of scans 256, a matrix 512 × 256 was acquired by the TPPI technique and zero-filled to the size 1024 × 1024.

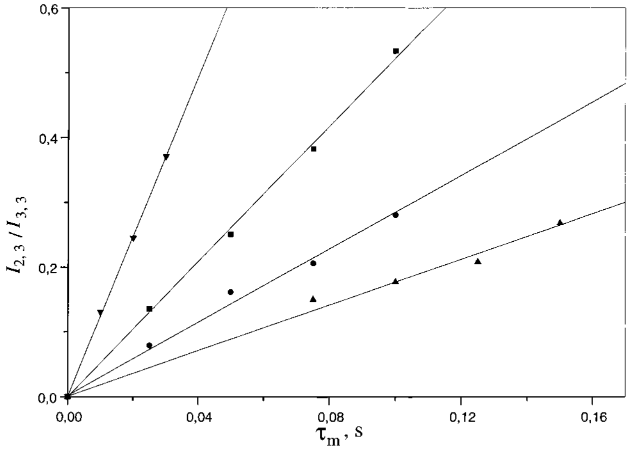
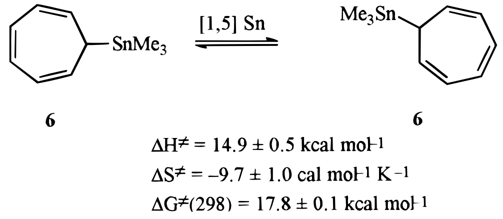


Figure 2. Kinetic curves for the [1,5] tin shift in **6**.

Scheme 4



Replacement of Tin with Boron in Trimethylcycloheptatrienyltin (6). Preliminary experiments showed that transmetalation of **6** readily proceeds at room temperature in deuteriochloroform (monitored by NMR). However, when approximately half of **6** is consumed, side reactions (i.e., the exchange of the radicals between **6** and trimethyltin chloride (**7**), giving chlorodimethylcycloheptatrienyltin (**8**), and tetramethyltin (Scheme 5)) become more significant. Compound **8** was characterized by one- and two-dimensional ^{1}H, ^{13}C, and ^{119}Sn NMR spectra. Interestingly, 2D EXSY experiments showed that the [1,5] Sn shift in **8** is significantly faster than that in **6**. This observation is in agreement with the reported

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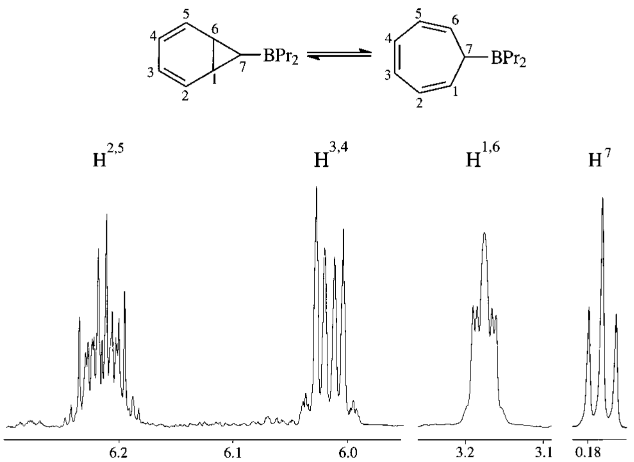
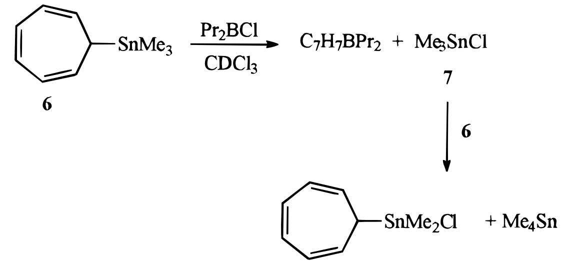
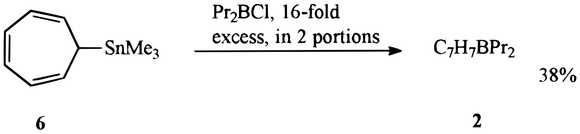


Figure 3. ^{1}H NMR spectrum of **2** (400 MHz, $CD_2Cl_2-CDCl_3-CCl_4$, 298 K).

Scheme 5



Scheme 6



acceleration of tin sigmatropic shifts when an alkyl group at the tin atom is replaced by chlorine.[23]

Further experiments showed that the amount of **8** produced in the reaction of **6** with Pr_2BCl is reduced when an excess of dipropylboron chloride is used. The synthesis of the pure organoboron compound was accomplished by treating **6** with an 8-fold excess of dipropylboron chloride without solvent for 30 min followed by evaporation of volatile compounds in vacuo, treatment with an additional 8 equiv of Pr_2BCl, and vacuum distillation (Scheme 6).

Dynamic Equilibrium between Cycloheptatrienyl(dipropyl)borane (2) and 7-(Dipropylboryl)norcaradiene (2b). Analysis of the NMR Spectra of 2. Figure 3 displays the ^{1}H NMR spectrum of the transmetalation product **2** recorded at room temperature. In contrast to a typical 7-monosubstituted cycloheptatriene NMR spectrum, it contains a high-field triplet at 0.16 ppm, a multiplet at 3.18 ppm, and two multiplets in the olefinic region—at 6.02 and 6.22 ppm. The proton at 0.16 ppm is attached to a carbon atom ($\delta = 23$ ppm) adjacent to boron; this follows from the CHCORR spectrum and the characteristic broadening of the signal in the ^{13}C NMR spectrum caused by C−B coupling. Figure 4 displays the temperature dependence of the ^{13}C NMR spectra of **2**. Particularly dramatic changes are observed for the signal at $\delta = 59.7$ ppm at 313 K. When the temperature is decreased to 273 K, the chemical shift of this signal decreases and it becomes much broader. The signal almost disappears at 228 K but reappears as a very broad signal at 203 K; a relatively sharp resonance at $\delta = 33.6$ ppm is observed at 153 K.

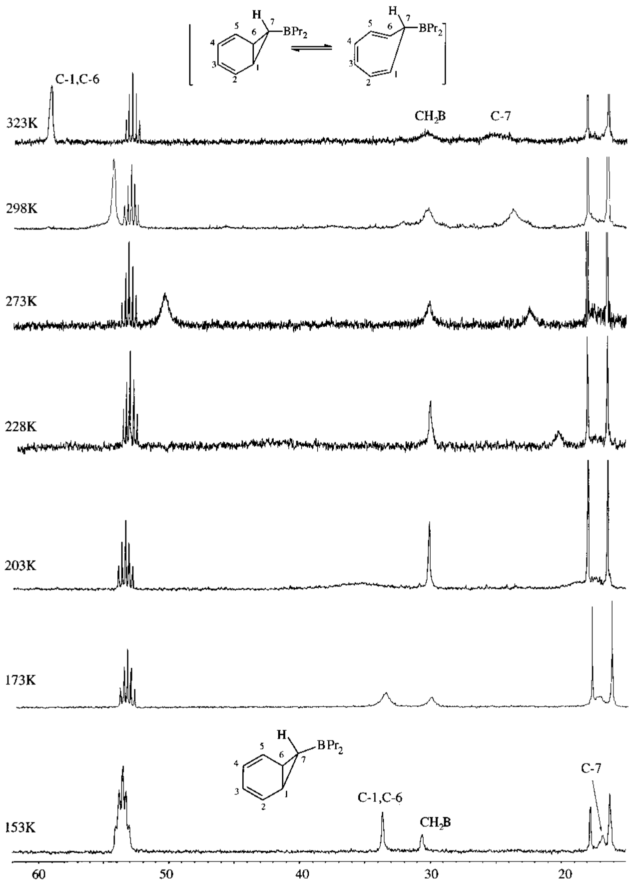
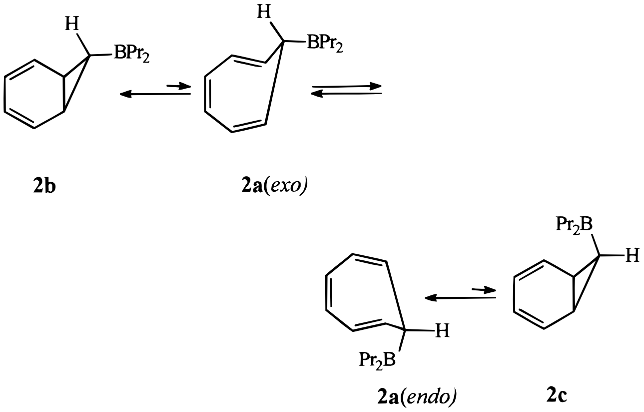


Figure 4. Temperature dependence of the high-field region of the ^{13}C NMR spectrum (100 MHz, $CD_2Cl_2-CDCl_3-CCl_4$) of compound **2**.

Scheme 7



The temperature-dependent spectra correspond to an equilibrium between cycloheptatrienylborane **2a** (*endo* and *exo* forms) [the eqilibrium between the *exo* and *endo* forms of **2a** is fast on the NMR time scale in the studied temperature range; only at 153 K can some indications of this process be detected, viz., the broadening of the signals of the propyl groups in the ^{13}C NMR spectrum, the other signals remaining relatively narrow] and its valence tautomer 7-(dipropylboryl)norcaradiene (**2b**) (Scheme 7).[9] However, the ^{1}H and ^{13}C NMR spectra measured at the lowest temperature (153 K, Figure 4) display only one set of signals easily assigned to the norcaradienyl **2b**. Attempts to detect the exchange cross-peaks between **2a** and

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(23) Naruta, Y.; Nishigaichi, Y.; Maruyama, K. *Tetrahedron* **1990**, *45*, 1067.

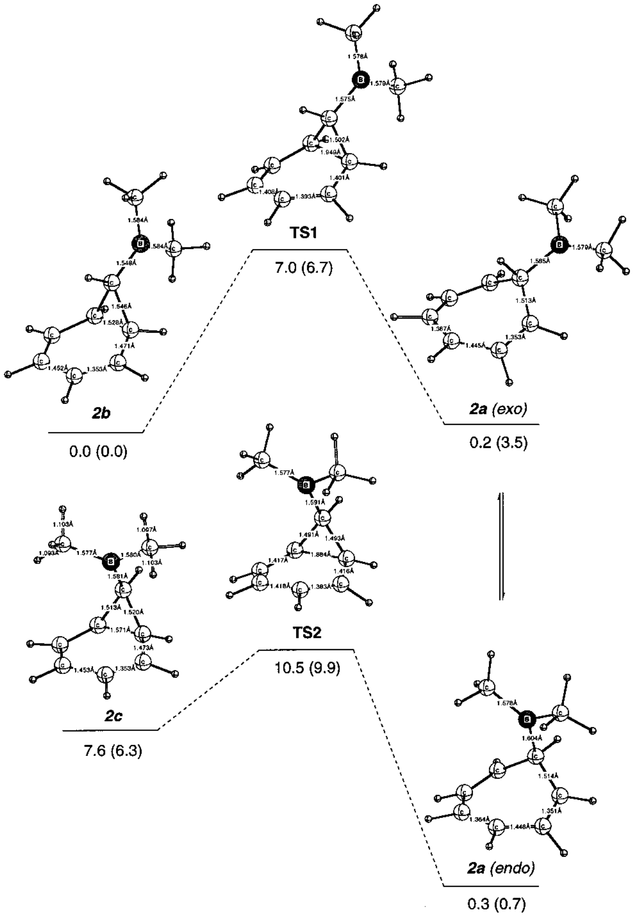

Figure 5. B3LYP/6-311+G*//B3LYP/6-31G* + ZPVE structures and energies (ΔG values at 228 K at B3LYP/6-31G* in parentheses, cf. Table 1) for the cycloheptatrienyl(dimethyl)borane → 7-(dimethylboryl)norcaradiene rearrangement.

2b in ^{1}H and ^{13}C 2D EXSY experiments at 153 K were unsuccessful, although we had observed the exchange cross-peaks between two tautomers with a ratio of 24:1 previously.[17f] Therefore, the equilibrium must be shifted even more toward **2b** at lower temperatures.

Only the *exo* isomer of the norcaradienyl form **2b** was observed in the NMR spectra. This assignment has been made on the basis of $\delta(H^7)$ which is -0.47 ppm at 153 K, owing to its orientation over the shielding cone of the conjugated π system; larger $\delta(H^7)$ values (2.0−2.5 ppm) are characteristic for *exo* H^7 protons in the corresponding *endo* isomers[8b,9b] {which could form from **2a** (*endo*)}. Since **2c** was not detected in the NMR spectra, it must be thermodynamically less stable than **2b**.

To elaborate further on these considerations, we carried out density functional computations on the isomers of **2** and their transition states for interconversion; computational details can be found below. To reduce the size of the problem, we replaced the propyl groups by methyl groups in our computational studies; to remain consistent with the structure numbering, we labeled the computed "reduced" systems in bold italics {e.g., ***2b*** refers to $C_7H_7B(CH_3)_2$}. All structures are depicted in Figures 5 and 6; energies are listed in Table 1.

From the computed geometries of ***2b*** vs ***2c*** one can easily deduce why the latter must be higher in energy. While the empty p AO on boron is perfectly aligned with the Walsh orbital of the cyclopropane moiety in ***2b***, this interaction is essentially "switched off" in ***2c*** due to a perpendicular orientation resulting from minimization of steric repulsion between the alkyl groups and the cyclohexadiene moiety. This is analogous to the bisected and perpendicular geometries of the cyclopropylcarbinyl cation.[24] The relative energy difference (7.6 kcal mol^{-1}) between the two isomers ***2b*** and ***2c*** (note that both are minima), however, is only about half of that found experimentally (NMR at 253 K) for the (1,1-dimethylcyclopropyl)carbinyl cation (13.7 kcal mol^{-1}),[25] owing to the greater electron demand of the positively charged carbon system.

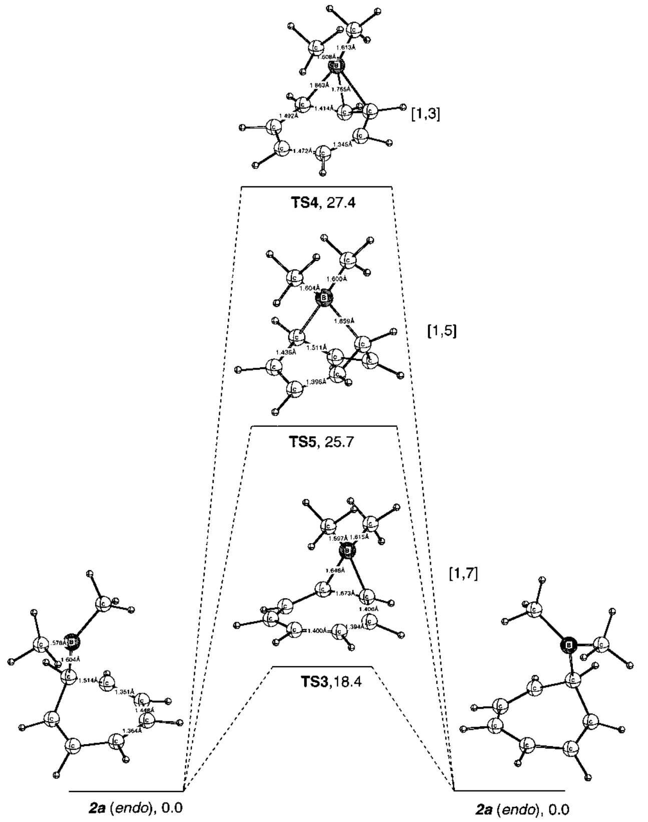

Figure 6. B3LYP/6-311+G*//B3LYP/6-31G* + ZPVE structures and energies for the [1,*n*] boron shifts (n = 1, 3, 7) in 7-(dimethylboryl)-norcaradiene.

The temperature dependence of the stabilities of ***2a*** and ***2b*** (see NMR data above) is well reproduced by our computations. While ***2b*** is 0.5 kcal mol^{-1} more stable than ***2a*** (*endo*) at 298 K, this difference increases to 0.7 kcal mol^{-1} at 228 K, mostly due to entropic effects favoring ***2b*** (Table 1). The nearly exclusive formation of **2b** is also supported by the computed NMR data (Table 2). The observed and computed proton chemical shifts agree remarkably well; the largest deviation of only 0.3 ppm is found for the proton experiencing the ring current of the π system (measured, -0.5 ppm; computed, -0.8 ppm). The computed ^{13}C shifts are systematically somewhat too high, but agree qualitatively quite well.

The thermodynamic parameters for the equilibrium between **2a** and **2b** were derived from six ^{13}C NMR spectra at 263−313 K, i.e., in the temperature interval where the chemical shifts of the averaged C(1,6) signals could be measured accurately. The chemical shift of C(1,6) in **2a** was estimated as being approximately that of the structurally similar cyclononatetraenyl-(dipropyl)borane (135.8 ppm).[17e] Since the difference between chemical shifts of C(1,6) in **2a** and **2b** (approximately 100 ppm) is about 2 orders of magnitude larger than the possible error in

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[24] Hehre, W. *J. Acc. Chem. Res.* **1975**, *8*, 369.

[25] Kabakoff, D. S.; Namanworth, E. *J. Am. Chem. Soc.* **1970**, *92*, 3234.

Table 1. Energies and Thermodynamic Quantitites of $C_7H_7B(CH_3)_2$ Isomers Related to **2** at B3LYP

species	abs energy (6-31G*), −au	ZPVE,[a] kcal mol^{-1}	entropy, eu[a]	abs energy incl thermal corrections to ΔG^a(−au)	rel energy[a,b] (6-31G*), kcal mol^{-1}	abs energy[c] (6-311+G*), −au	rel energy[c] (6-311+G*), kcal mol^{-1}
2*a* (*exo*)	375.59855	122.4	96.8	375.43857	2.0	375.68335	0.2
		109.3	90.0	375.44697	3.5		
2*a* (*endo*)	375.59877	122.5	103.8	375.44093	0.5	375.68317	0.3
		109.4	96.8	375.45138	0.7		
2*b*	375.60204	123.3	100.5	375.44177	0.0	375.68359	0.0
		110.1	93.6	375.45254	0.0		
2*c*	375.58993	122.7	103.8	375.43202	6.1	375.67154	7.6
		109.5	96.8	375.44247	6.3		
TS1	375.58870	122.1	102.9	375.43150	6.4	375.67208	7.2
		109.1	96.0	375.44191	6.7		
TS2	375.57380	121.9	100.9	375.42616	9.8	375.66690	10.5
		108.8	94.1	375.43675	9.9		
TS3	375.57196	122.3	95.3	375.41134	19.1	375.65382	18.7
		109.2	88.4	375.4226	18.8		
TS4	375.55786	123.4	95.2	375.39564	28.9	375.63940	27.7
		110.2	88.1	375.40708	28.5		
TS5	375.56004	122.3	92.3	375.39849	27.2	375.64210	26.0
		109.2	89.6	375.41003	16.7		

[a] First entry at 298.15 K; second entry at 228 K, unless noted otherwise. [b] Including energy corrections. [c] Uncorrected.

Table 2. Selected Measured (298 K) and Computed (GIAO-B3LYP/6-311+G**//B3LYP/6-31G*) NMR Chemical Shifts (vs TMS and $F_3B{\cdot}OEt_2$) of **2b** and Complex **9**[a]

	C-1	C-2	C-3	C-7	B	H_{C1}	H_{C2}	H_{C3}	H_{C7}
2b[b,c]									
exptl	33.6	128.3	121.1	16.8	76.3	2.5	6.2	5.9	−0.5
theor	39.3	137.5	129.1	22.9	85.9	2.4	6.5	6.1	−0.8
9[d]									
exptl	124.5	124.9	129.0	129.4	8.2[e]	5.1	6.1	6.5	1.1
theor	133.6	138.5	140.9	143.6	0.8	5.1	6.6	6.9	0.5

[a] The computed species were slightly reduced in size (*n*-propyl groups replaced by methyl groups) due to computational limitations. Thus, the boron shifts are slightly shifted downfield in the computed chemical shifts. [b] For numbering see Scheme 9. [c] Averaged with slight traces of **2a** (*endo*); see the text. [d] For numbering see Figure 12. [e] At 303 K.

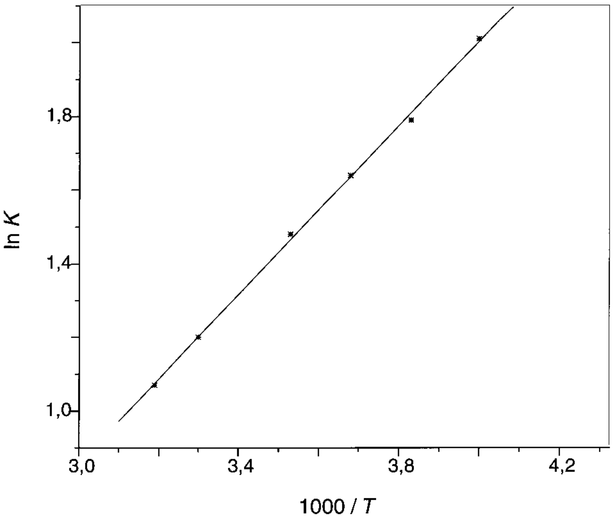

Figure 7. Dependence of ln *K* versus 1/*T* for the equilibrium between **2a** and **2b**.

the estimation of the corresponding chemical shift in **2a** (about ±1 ppm), this treatment should not result in a significant error. The thermodynamic equilibrium parameters, determined through a linear correlation of ln *K* vs 1/*T* (Figure 7), are as follows: $\Delta H = 2.4 \pm 0.1$ kcal mol^{-1}; $\Delta S = -5.5 \pm 0.3$ cal mol^{-1} K^{-1}. These thermodynamic equilibrium parameters are in excellent agreement with our computations (at 298 K) which give $\Delta H =$ 2.0 kcal mol^{-1} and $\Delta S = -3.7$ cal mol^{-1} K^{-1}. Note, however, that it is quite difficult to reliably recover such small relative energy differences computationally. A much more elaborate electron correlation treatment (e.g., the coupled cluster method) and a larger basis set would be needed for absolute quantitative agreement, but this is currently not feasible computationally. The equilibrium constant at 153 K calculated from these data equals 182; therefore, the failure to observe exchange cross-peaks at this temperature is quite understandable.

The rate constants for the rearrangement of **2a** to **2b** and the reverse reaction at the coalescence temperature were derived by the method of Anet and Basus[26] for systems with unequally populated sites. It has been shown that when the differences in both the populations and the chemical shifts are large, the use of eqs 1a and 1b for determining the rate constants at the

$$k_A = k(\text{major} \rightarrow \text{minor}) = 2\pi p_B \delta\nu \qquad (1a)$$

$$k_B = k(\text{minor} \rightarrow \text{major}) = 2\pi p_A \delta\nu \qquad (1b)$$

maximum broadening temperature does not lead to significant errors. p_A and p_B are the populations of the major and the minor components, respectively, and $\delta\nu$ is the difference in the chemical shifts in hertz.

In our case $p_A = 0.93$, $p_B = 0.07$ (calculated from the thermodynamic parameters of the equilibrium found above), $\delta\nu = 10\,220$ Hz (for the signals C(1,6) in **2a** and **2b**), and the temperature of maximum broadening is 228 K (Figure 8). This gives $k_A(228) = 4.5 \times 10^3$, $k_B(228) = 6.0 \times 10^4$ s^{-1}, $\Delta G^{\ddagger}_{228}$(**2a**→**2b**) = 8.2 ± 0.1 kcal mol^{-1}, and $\Delta G^{\ddagger}_{228}$(**2b**→**2a**) = 9.4 ± 0.1 kcal mol^{-1}.[27]

The corresponding transition states for electrocyclic ring opening of ***2a*** and ***2b*** also were computed to calibrate theoretical with experimental results (Figure 5). We computed $\Delta G^{\ddagger}_{228}${***2a(exo)*** → **TS1**} = 3.2 kcal mol^{-1} and $\Delta G^{\ddagger}_{228}$(***2b*** → **TS1**) = 6.7 kcal mol^{-1} at B3LYP/6-31G*, in reasonable agreement with experiment. Note that the corresponding barrier for electrocyclic ring closure of ***2a*** (*endo*) is significantly higher ($\Delta G^{\ddagger}_{228} = 9.2$

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(26) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1984.

(27) Friebolin, H. *Ein- und zweidimensionale NMR-Spectroskopie*, 2nd ed.; VCH: Weinheim, 1992.

(28) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev. (Washington, D.C.)* **1988**, *88*, 899.

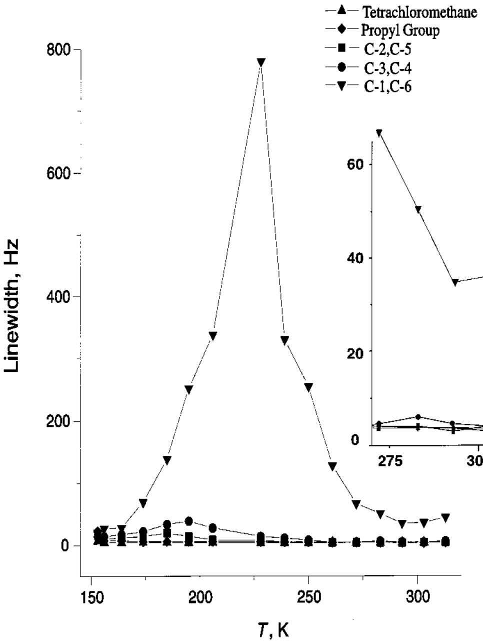


Figure 8. Dependence of the line width of the various resonances in the ^{13}C NMR spectrum of 2 on temperature.

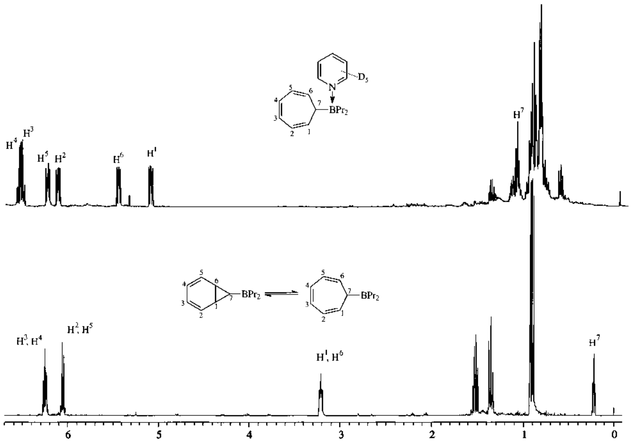


Figure 9. ^{1}H NMR spectra of **2** (400 MHz, 298 K): (a) in CD_2Cl_2−$CDCl_3$−CCl_4; (b) in pyridine-d_5.

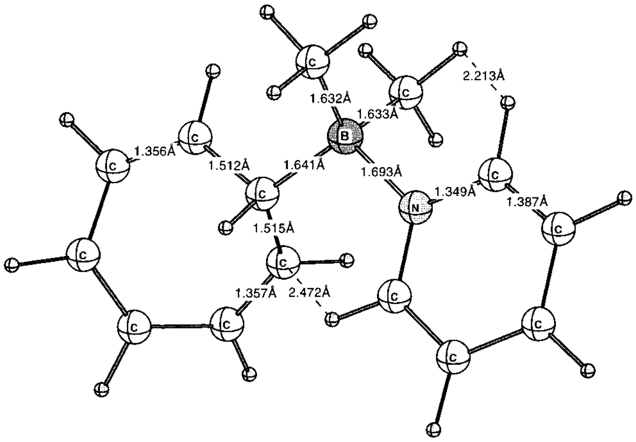


Figure 10. Structure of complex *9* at B3LYP/6-31G*.

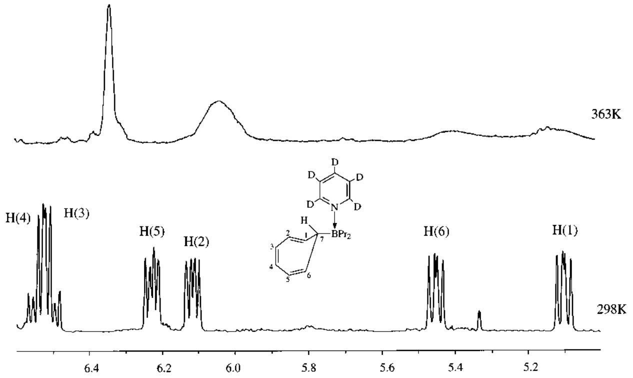
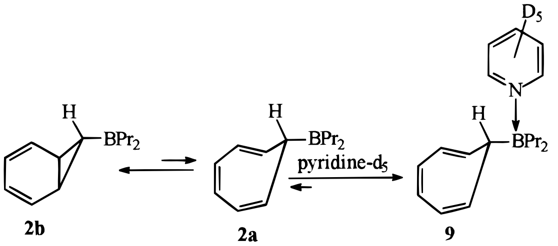


Figure 11. Temperature dependence of the olefinic part of the ^{1}H NMR spectrum of **9** (400 MHz, pyridine-d_5).

Scheme 8



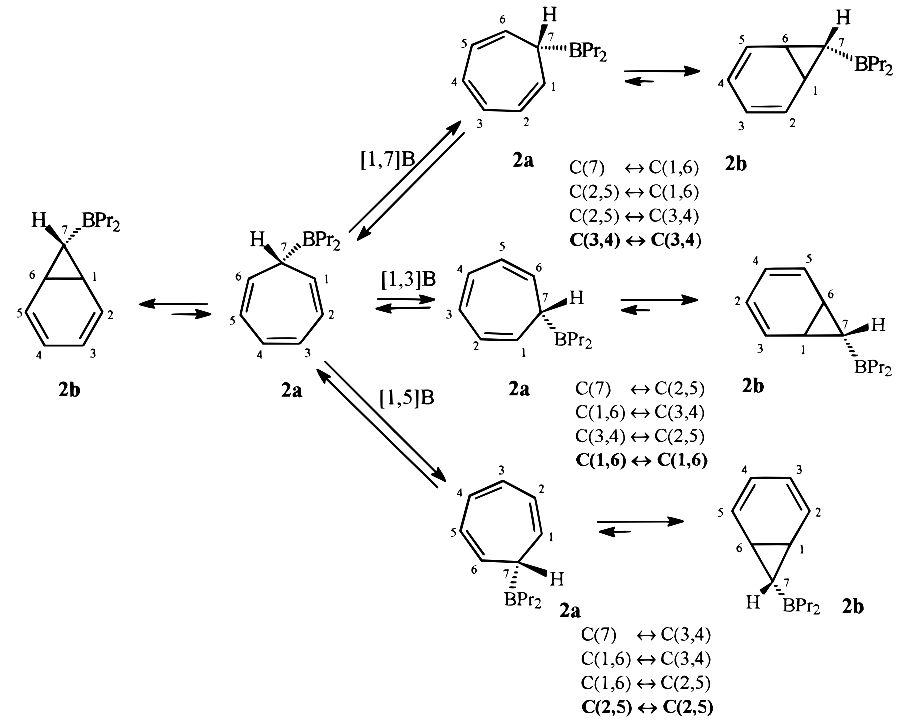
kcal mol^{-1}) whereas the barrier for ring opening of ***2c*** is small ($\Delta G^{\ddagger}_{228}$ = 3.6 kcal mol^{-1}).

Dynamic Behavior of the Deuteriopyridine Complex 9. Since the increased thermodynamic stability of **2b** vs **2a** is due to overlap of the empty boron 2p AO with the Walsh orbital of the cyclopropane moiety (note that there is no evidence for norcaradienyl forms in cycloheptatrienyl derivatives of silicon, germanium, tin, rhodium, and ruthenium due to the absense of empty orbitals of proper size and symmetry), we speculated that filling the empty boron 2p AO with an electron pair donor would lead to exclusive formation of the cycloheptatrienyl form. Figure 9 illustrates impressively that this is indeed the case: the ^{1}H NMR spectrum of **2** changes dramatically when the neutral solvent is changed to deuteriopyridine. The cycloheptatrienyl moiety in the deuteriopyridine complex **9** (Scheme 8) is evidenced by 2D correlation experiments. However, initially somewhat unexpected is the lack of symmetry in the spectrum of **9**: all nuclei are magnetically inequivalent. This observation is confirmed by the nonsymmetrical (C_1 point group) minimum energy structure for the optimized complex **9** (Figure 10). Although the B−C bonds lengthen upon complexation with pyridine by 0.054−0.056 Å, complex **9** is rather "tight" with some particularly short atom−atom distances. The pyridine *ortho*-hydrogen pointing toward the cycloheptatrienyl moiety has an optimized distance of only 2.472 Å to one of the carbons. The other *ortho*-hydrogen also has a close contact with one of the methyl group hydrogens (2.213 Å).

Upon raising the temperature, reversible dynamic effects were observed in the ^{1}H and ^{13}C NMR spectra of **9** (e.g., Figure 11). The 2D EXSY experiments suggest that the exchange between the positions 1 and 6, 2 and 5, and 3 and 4 in the cycloheptatrienyl moiety of **9** is observed. The activation barrier for this process was derived from the 2D ^{1}H EXSY spectrum of **9** at 313 K. Each pair of exchanging signals in **9** can be regarded as the exchange between two equally populated sites, and the rate constant can be calculated from the intensities of diagonal and off-diagonal peaks by eq 2,[21,22] where I_{AA} and I_{BB} are the intensities of the diagonal peaks and I_{AB} and I_{BA} are the intensities of the cross-peaks.

$$k = \frac{1}{t_m} \ln \frac{r+1}{r-1} \qquad r = \frac{I_{AA} + I_{BB}}{I_{AB} + I_{BA}} \tag{2}$$

Scheme 9



Application of eq 2 to the ^{1}H 2D EXSY spectrum of **9** afforded the rate constant for the oserved dynamic process in **9**: $k_{313} = 1.75\ \mathrm{s}^{-1}$ ($\Delta G^{\ddagger}{}_{313} = 18.0 \pm 0.1$ kcal mol^{-1}). The chemical shifts for **9** were computed (Table 2) and show good qualitative agreement with the measured, highly temperature dependent NMR spectrum. Again, the proton shifts agree exceptionally well, while the computed ^{13}C shifts are uniformly somewhat too high.

The measured values of the ^{11}B chemical shift at 303 and 313 K for complex **9** differ considerably from the calculated value at 0 K. Moreover, $\delta(^{11}\mathrm{B})$ increases noticeably from 8.2 at 303 K to 10.4 at 313 K. These findings indicate that complex **9** is probably somewhat less stable than other pyridine complexes of triorganoboranes. A considerable amount of uncomplexed **2a** equilibrates with **9** already at 303 K. Therefore, the dynamic effects observed in the ^{1}H and ^{13}C NMR spectra of **9** are most likely due to a dissociation−association mechanism, and the determined activation barrier corresponds probably to the dissociation step.

Analysis of the Mechanism of Boron Sigmatropic Migrations in 2. As noted above, cycloheptatrienylborane **2a** cannot be observed in its pure form because of equilibration with its tautomer **2b**. However, since at temperatures above 300 K this equilibrium is fast on the NMR time scale and the content of **2a** is about 30%, some conclusions about the mechanism and approximate rates of sigmatropic boron migrations in **2a** may be drawn from an analysis of the equilibrium mixture. If a sigmatropic boron migration occurs in **2**, it should lead to mixing of the chemical shifts in **2a**, which would inevitably affect the line shape of the averaged spectrum. We conclude that the barrier for such migrations must be comparatively high (see computations below), since no changes in the line shapes besides the ones belonging to the equilibrium between **2a** and **2b** were observed at temperatures below 293 K. Nevertheless, such changes were detected at higher temperatures (Figure 8). The line width of C(1,6) displays a minimum at 293 K and increases by 10 Hz in the 293−313 K temperature regime. The sharpening of the averaged C(1,6) signal when the temperature is raised from 228 to 293 K is due to a rate increase for the equilibrium between **2a** and **2b**. However, significant broadening of this signal at higher temperatures can only be due to the existence of another dynamic process, viz., sigmatropic migration of the dipropylboryl group in **2a**. In the same temperature interval (293−313 K) the width of the C(2,5) signal changes from 4.0 to 7.5 Hz, whereas the widths of those for C(3,4) and the other resonances in the spectrum remain constant—4.0 Hz (the signal of C(7) broadens significantly, but the same effect is expected due to the quadrupolar coupling with boron). Scheme 9 displays the analysis of the exchange patterns for the three possible mechanisms of boron migration in **2a**.

In each case one of the signals must display a relatively weak line width broadening since one of the exchanges transforms it into itself. For each type of boron migration this signal is different, C(3,4) for [1,7] B shift, C (1,6) for [1,3] boron migration, and C(2,5) for [1,5] boron migration. Hence, we conclude that a [1,7] B shift must occur.

The same conclusion follows from the phase-sensitive 2D ^{1}H EXSY spectrum recorded at 323 K (Figure 12). Since the positions of the protons relative to the position of the dipropylboryl group remain unchanged when **2a** interchanges with **2b** (Scheme 9), the exchange cross-peaks between the averaged signals directly indicate the mode of the sigmatropic boron migration in **2a**. The H(7) resonance gives a cross-peak with the H(1,6) resonance, corresponding to a formal [1,2] migration, i.e., a [1,7] B shift in **2a**. The positions of other cross-peaks in the 2D EXSY spectrum at 323 K are also in agreement with a sigmatropic [1,7] B shift in cycloheptatrienyl(dipropyl)borane (**2a**) (Scheme 9).

The computed relative energies also identify the [1,7] B shift as the most favorable shift mechanism ($\Delta H^{\ddagger} = 18.4$ kcal mol^{-1}, Table 1, Figure 6), followed by the [1,5] ($\Delta H^{\ddagger} = 25.7$ kcal mol^{-1}) and the [1,3] B shift ($\Delta H^{\ddagger} = 27.4$ kcal mol^{-1}). The [1,7] B transition structure **TS3** can be rationalized as a favorable Möbius aromatic system with eight electrons in eight active orbitals connected in a circle with one phase inversion. This circle consists of the seven p orbitals on carbon and the boron

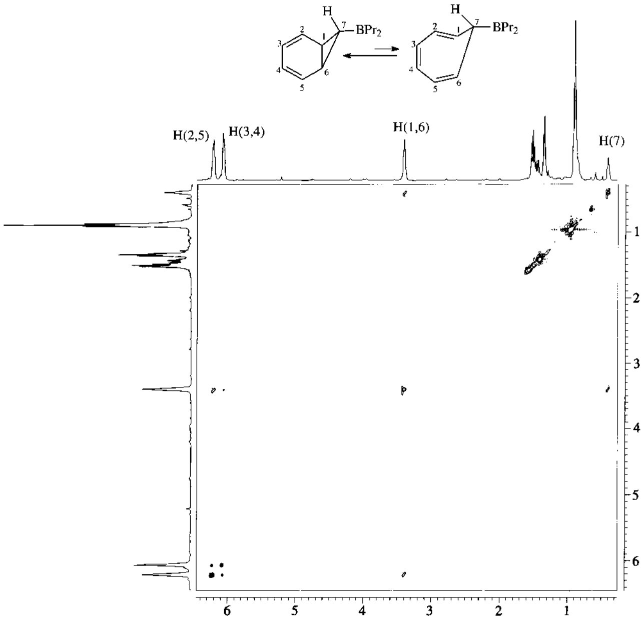


Figure 12. ^{1}H NMR EXSY spectrum of compound **2** (400 MHz, $CD_2Cl_2-CDCl_3-CCl_4$, 323 K): mixing time 0.5 s, initial delay 1 s, number of scans 256, a matrix 512 × 256 was aquired by the TPPI technique and zero-filled to the size 1024 × 1024.

p AO; the latter has a nodal plane (phase inversion). This leads to electron delocalization which causes a reduction of the positive charge (NBO) on boron (+0.6 in **TS3**) vs ***2a*** (+1.0) and bond length equalization from C1 to C7, but not between these two (note the long C1−C7 bond, 1.673 Å, Figure 6). In contrast, **TS4** and **TS5** are strongly alternating and considerably higher in energy (Figure 6, Table 1).

Conclusions

The synthesis as well as the study of the dynamic behavior of a boron cycloheptatrienyl (**2**) allows the analysis of several important problems. Compound **2** is the first organometallic derivative of cycloheptatriene in which the norcaradiene form predominates. Many compounds with the organometallic group in the 7-position are known to exist exclusively as cycloheptatrienes. *Ab initio* computations show that the donor−acceptor interaction between the boron 2p AO and the Walsh orbital of the cyclopropane is most effective in the *exo*-norcaradiene form **2b**. Our results clearly demonstrate that the boron 2p AO is necessary for stabilizing the norcaradiene form. The deuteriopyridine complex **9** only exists in its cycloheptatrienyl form. Note that in the iron tricarbonyl complex **1** the corresponding norcaradiene is not detected[3] owing to the effect of the iron tricarbonyl forcing the dipropylboryl group into the *endo* position.

The mechanism of boron migrations in **2a** has also been clarified. Both experimental and computational data indicate that the [1,7] B shift is the fastest borotropic rearrangement in **2a**. Since the same type of sigmatropic boron shift has previously been found in the iron tricarbonyl complex **1**, one can conclude that a suprafacial [1,7] B shift is a facile process, regardless of the presence of the iron tricarbonyl group. Orbital control but more importantly charge distribution and geometric factors are dominating. However, the data concerning two other possible boron shifts in cycloheptatrienylboranes are not entirely conclusive. While a relatively slow [1,3] B migration was detected in **1** ([1,5] B shift was not observed), computational data for **2a** energetically favor [1,5] B over [1,3] B shifts, but only by 1.7 kcal mol^{-1}. Several factors can account for such a difference, for instance the presence of a transition metal atom in **1** or inevitable *endo* orientation of the dipropylboryl substituent in **1**. Studies on the effects governing the selectivity of the sigmatropic migrations of organometallic groups in cyclononatetraene compounds are well underway in our laboratories.

Experimental Section

All experiments were performed under dry argon atmosphere. ^{1}H, ^{13}C, ^{11}B, and ^{119}Sn NMR spectra were recorded using a Bruker AMX-400 spectrometer. ^{1}H and ^{13}C 2D EXSY NMR spectra were acquired using a NOESYTP pulse program, slightly modified in the case of ^{13}C EXSY to allow the ^{1}H decoupling during acquisition. Areas of cross-peaks and diagonal peaks were obtained by volume integration of appropriate voxels surrounding the peaks.

Trimethyl(cyclohepta-1,3,5-trien-7-yl)tin (6). To a 0.25 M solution of Me_3SnLi in THF (110 mL, 27.5 mmol) at −60 °C was added tropylium bromide (1.28 g, 7.5 mmol) in one portion, and the solution was then poured into water (200 mL). The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel with hexane as the eluent, affording 0.36 g (5.1%) of **6** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 0.10$ (s, 9H, CH_3, $^{2}J(\mathrm{H},^{119}\mathrm{Sn}) = 51.2$ Hz); 2.79 (t, 1H, H-4, $^{3}J(\mathrm{H,H}) = 9.0$ Hz, $^{2}J(\mathrm{H},^{119}\mathrm{Sn}) = 63.3$ Hz); 5.40 (dd, 2H, H-1, $^{3}J(\mathrm{H,H}) = 9.3$ Hz, $^{3}J(\mathrm{H,H}) = 9.0$ Hz, $^{3}J(\mathrm{H},^{119}\mathrm{Sn}) = 38.0$ Hz); 5.76 (ddd, 2H, H-2, $^{3}J(\mathrm{H,H}) = 9.3$ Hz, $^{3}J(\mathrm{H,H}) = 3.5$ Hz, $^{4}J(\mathrm{H,H}) = 2.8$ Hz, $^{4}J(\mathrm{H},^{119}\mathrm{Sn}) = 28.9$ Hz); 6.20 (dd, 2H, H-3, $^{3}J(\mathrm{H,H}) = 3.5$ Hz, $^{4}J = 2.8$ Hz, $^{5}J(\mathrm{H},^{119}\mathrm{Sn}) = 23.4$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): $\delta = -6.32$ (CH_3, $^{1}J(^{13}\mathrm{C},^{119}\mathrm{Sn}) = 305.5$ Hz); 33.29 (C-4, $^{1}J(^{13}\mathrm{C},^{119}\mathrm{Sn}) = 328.1$ Hz); 124.59 (C-2, $^{4}J(^{13}\mathrm{C},^{119}\mathrm{Sn}) = 31.2$ Hz); 129.62 (C-1, $^{2}J(^{13}\mathrm{C},^{119}\mathrm{Sn}) = 38.5$ Hz); 133.26 (C-3). ^{119}Sn NMR (149 MHz, $CDCl_3$, 298 K): $\delta = 12.41$.

NMR Experiments on the Exchange Reaction between 6 and Dipropylchloroborane. Pr_2BCl (0.1 g, 0.8 mmol) was added to a solution of 0.15 g (0.6 mmol) of trimethylcycloheptatrienyltin (**6**) in 0.5 mL of $CDCl_3$. NMR spectra taken immediately at room temperature showed 50% conversion of **6** into **2** (see below). Further storage of the sample at room temperature or heating to 343 K for several hours led to complete conversion of **6**; however, the amount of **2** in the reaction mixture did not increase. Instead, equal amounts of chlorodimethylcycloheptatrienyltin (**8**) and tetramethylstannane were detected by ^{119}Sn NMR. The structure of compound **8** was confirmed by 2D chemical shift correlation experiments. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 0.62$ (s, 6H, CH_3, $^{2}J(\mathrm{H},^{119}\mathrm{Sn}) = 57.2$ Hz); 3.49 (t, 1H, H-4, $^{3}J(\mathrm{H,H}) = 8.7$ Hz, $^{2}J(\mathrm{H},^{119}\mathrm{Sn}) = 77.4$ Hz); 5.84 (t, 2H, H-1, $^{3}J(\mathrm{H,H}) = 9.1$ Hz, $^{3}J(\mathrm{H},^{119}\mathrm{Sn}) = 70.4$ Hz); 6.13 (m, 2H, H-2); 6.56 (m, 2H, H-3). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): $\delta = 3.9$ (CH_3, $^{1}J(^{13}\mathrm{C},^{119}\mathrm{Sn}) = 256.5$ Hz); 41.47 (C-4); 125.70 (C-2); 128.69 (C-1, $^{2}J(^{13}\mathrm{C},^{119}\mathrm{Sn}) = 34.3$ Hz); 134.52 (C-3).

Dipropyl(cyclohepta-1,3,5-trien-7-yl)borane (2a) in Equilibrium with 7-(Dipropylboryl)norcaradiene (2b). Pr_2BCl (6.2 g, 48 mmol) was added in one portion to trimethylcycloheptatrienyltin (**6**) (1.5 g, 6 mmol). The reaction mixture was stirred at room temperature for 1 h, and then the volatile products were removed in vacuo. An additional portion of Pr_2BCl (6.2 g, 48 mmol) was added to the reaction mixture, and the above treatment was repeated. The residue was distilled in vacuo, and a fraction collected at 45−55 °C (0.5 mmHg) afforded 0.3 g (27%) of **2** as a colorless extremely air-sensitive liquid. ^{1}H NMR (400 MHz, $CCl_4-CDCl_3-CD_2Cl_2$ (13:27:60), 298 K): $\delta = 0.28$ (t, 1H, H-4, $^{3}J(\mathrm{H,H}) = 5.5$ Hz); 0.96 (t, 6H, $CH_2CH_2C\boldsymbol{H}_3$, $^{3}J(\mathrm{H,H}) = 7.3$ Hz); 1.41 (t, 4H, $C\boldsymbol{H}_2CH_2CH_3$, $^{3}J(\mathrm{H,H}) = 7.8$ Hz); 1.58 (m, 4H, $CH_2C\boldsymbol{H}_2CH_3$); 3.28 (m, 2H, H-1), 6.11 (dd, 2H, H-3, $^{3}J(\mathrm{H,H}) = 6.5$ Hz, $^{3}J(\mathrm{H,H}) = 3.0$ Hz); 6.31 (m, 2H, H-2). ^{13}C NMR (100 MHz, $CCl_4-CDCl_3-CD_2Cl_2$ (13:27:60), 298 K): $\delta = 16.45$ (Pr); 18.02 (Pr); 23.01 (br, C-4); 30.12 (br, Pr); 52.55 (br, C-1); 123.65 (C-3); 128.05 (C-2). ^{11}B NMR (128 MHz, $CCl_4-CDCl_3-CD_2Cl_2$ (13:27:60), 298 K): $\delta = 76.3$. When **2** was dissolved in deuteriopyridine, quantitative formation of complex **9** was observed. ^{1}H NMR (400 MHz, $CCl_4-CDCl_3-CD_2Cl_2$ (13:27:60), 298 K): $\delta = 1.10$ (t, 1H, H-4, $^{3}J(\mathrm{H,H}) =$

6.3 Hz); 0.6−1.4 (m, 14H, Pr); 5.08 (dd, 1H, H-1, ^3J(H,H) = 8.9 Hz, ^3J(H,H) = 6.4 Hz); 5.43 (dd, 1H, H-6, ^3J(H,H) = 9.1 Hz, ^3J(H,H) = 6.1 Hz); 6.09 (dd, 1H, H-2, ^3J(H,H) = 9.2 Hz, ^3J(H,H) = 4.8 Hz); 6.20 (dd, 1H, H-5, ^3J(H,H) = 9.3 Hz, ^3J(H,H) = 5.2 Hz); 6.49 (m, 2H, H-3,4). ^{13}C NMR (100 MHz, CCl_4−$CDCl_3$−CD_2Cl_2 (13:27:60), 298 K): δ = 16.91 (Pr); 17.77 (Pr); 28.76 (br, Pr); 34.51 (br, C-7); 124.45 (C-5); 124.51 (C-1); 124.90 (C-2); 125.96 (C-6); 129.04 (C-3); 129.36 (C-4). ^{11}B NMR (128 MHz, pyridine-d_5, 313 K): δ = 10.4.

Computational Methods. Geometries of all stationary points were optimized using analytical energy gradients of self-consistent field[29] and density functional theory (DFT).[30] The latter utilized Becke's three-parameter exchange-correlation functional[31] including the nonlocal gradient corrections described by Lee−Yang−Parr (LYP),[32] as implemented in the Gaussian 94 program package.[33] All geometry optimizations were performed using the 6-31G* basis set.[34] Previous studies showed convincingly that DFT methods in conjunction with double-ζ basis sets are quite suitable for studying transition states of pericyclic reactions[35] and electron-deficient rearrangements.[36]

Thermodynamic corrections (228 and 298 K) and zero-point vibrational energy corrections (ZPVE) were derived from analytical vibrational frequencies at B3LYP/6-31G*. Single-point energies were evaluated using a standard 6-311+G* basis set;[37] final energies thus refer to B3LYP/6-311+G*//B3LYP/6-31G* + ZPVE, unless noted otherwise. Standard notation is used, i.e., "//" means energy computed at//geometry.

NMR chemical shifts were computed with the gauge-invariant atomic orbital (GIAO) approach[38] in conjunction with the B3LYP functional.[31,32] Since a flexible valence basis plus polarization functions is needed for accurate chemical shifts, we utilized the 6-311+G** basis for chemical shift calculations on the B3LYP/6-31G* geometries. The absolute shifts (σ) of tetramethylsilane (TMS) and the etherate of boron trifluoride ($Et_2O{\cdot}BF_3$) were used to compute the relative chemical shifts $\delta = \sigma_{\text{reference}} - \sigma_{\text{compound}}$.

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