

Sigmatropic migrations in cyclononatetraenyl(dipropyl)borane: a combined experimental and computational study

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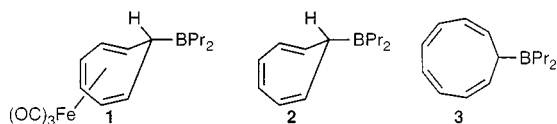
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Large-ring sigmatropic migrations do not necessarily follow the 'least motion principle' and can only be rationalized by a combination of experimental and computational techniques.

Despite the formulation of the Woodward–Hoffmann rules nearly 30 years ago,¹ the selectivities in sigmatropic migrations in conjugated carbocycles are not easily predictable. The difficulties in rationalizing a particular shift mechanism arise from the neglect of, for instance, orbital coefficients and the 'least motion principle' (LMP), when the Woodward–Hoffmann rules are applied. The possible importance of the LMP is emphasized by the large number of studies on cyclopentadienyl² and indenyl³ derivatives, where mostly [1,5]- and very few [1,3]-sigmatropic migrations are observed. Since [1,5]- and [1,2]-shifts in cyclopentadienyl systems are formally equal, the LMP cannot be probed.⁴ To the best of our knowledge, the [1,5]-Sn shifts in triphenyl-⁵ and trimethyl-(cycloheptatrienyl)tin^{6a} are the only examples violating the LMP.

Our recent studies on cycloheptatrienyl(dialkyl)boron derivatives⁶ showed that both orbital *and* distance factors govern the selectivities of sigmatropic migrations. For instance, in the tricarbonyliron complex of cycloheptatrienyl(dipropyl)borane **1** both [1,3]- and [1,7]-B shifts are observed, whereas [1,5]-B shifts were not detected.^{6a} This is in accord with orbital control because dialkylboryl groups migrate with inversion of configuration utilizing the unoccupied boron 2*p* atomic orbital (AO).^{6b} On the other hand, the [1,7]-B shift is considerably faster than the [1,3]-B shift in **1**;^{6a} the [1,7]-B migration is substantially energetically favored in uncomplexed **2**.^{6b} Hence, as for the cyclopentadienyl system, the LMP seems to be effective, but could not be differentiated from other effects. We therefore present here a combined experimental and computational study on cyclononatetraenyl(dipropyl)borane **3**, which clearly displays a fast [1,3]-B shift.⁷



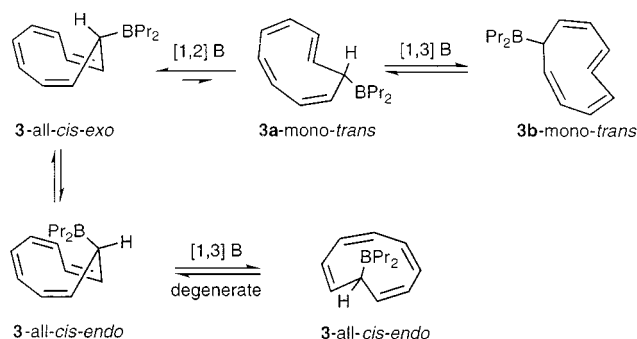
The experimental [1,3]-B shift barrier in **3** is rather low; the ¹H NMR data indicate dynamic processes even at $-100\text{ }^{\circ}\text{C}$.⁷ Our density functional theory (DFT) computations[†] show that the *endo*-conformer of **3** (the propyl groups were replaced by methyl groups to speed up the computations) is favored by only 0.3 kcal mol^{-1} over the *exo*-conformer due to overlap between the empty boron 2*p* AO and the π -system of the ring. While the degenerate [1,3] dipropylboryl migration in **3-all-cis-endo** could be confirmed computationally, we were unable to localize

a [1,3]-B TS for **3-all-cis-exo**, despite extensive searches. Instead, we found that **3-all-cis-exo** undergoes a [1,2]-B shift to **3a-mono-trans-exo** (Scheme 1 and Fig. 1). However, **3-mono-trans** is thermodynamically unfavorable by 6.5 kcal mol^{-1} and the [1,2]-B shift is accompanied by a rather high activation barrier ($17.3\text{ kcal mol}^{-1}$; all energies relative to **3-all-cis-exo**). Hence, the observed temperature dependence of the NMR spectra and the results of EXSY experiments may be explained by degenerate [1,3]-B shifts in **3-all-cis-endo** only.

Although it was impossible to observe the completely averaged ¹³C NMR spectrum due to the thermal instability of **3**, the spectrum is well resolved at low temperatures (Fig. 2). The pronounced lineshape–temperature dependence in the temperature interval 173–233 K allowed the [1,3]-B shift activation parameters in **3-all-cis-endo** to be determined. Lineshape calculations⁸ gave: $E_a = 6.2 \pm 0.5\text{ kcal mol}^{-1}$, $\Delta_{195\text{ K}}G^{\ddagger} = 8.8 \pm 0.1\text{ kcal mol}^{-1}$; the computed E_a for **3** is 6.6 kcal mol^{-1} .

As we pointed out earlier,^{6b} the dialkylboron moiety is partially positively charged; hence, one has to consider the two degenerate LUMOs (schematically depicted in Fig. 3) to determine which migrations are favorable based on orbital phases *and* coefficients. 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). Based on orbital phases only [1,3], [1,5] and [1,9] shifts are symmetry allowed with inversion of configuration in the cyclononatetraenyl system. LUMO 1 indistinguishably only allows for [1,3] and [1,9] shifts, while LUMO 2 permits all three. However, [1,5] migrations are highly unfavorable due to small orbital coefficients. Hence, a clear prediction cannot be made from these considerations.

For direct comparisons, we computed the transition states for [1,*j*]-B sigmatropic migrations in cyclononatetraenyl(dimethyl)borane **3**. As noted above, the E_a for the [1,3]-B shift in **3** agrees very well with the experimental value for **3**. The activation barriers for [1,9]- and [1,3]-B migrations are very



Scheme 1

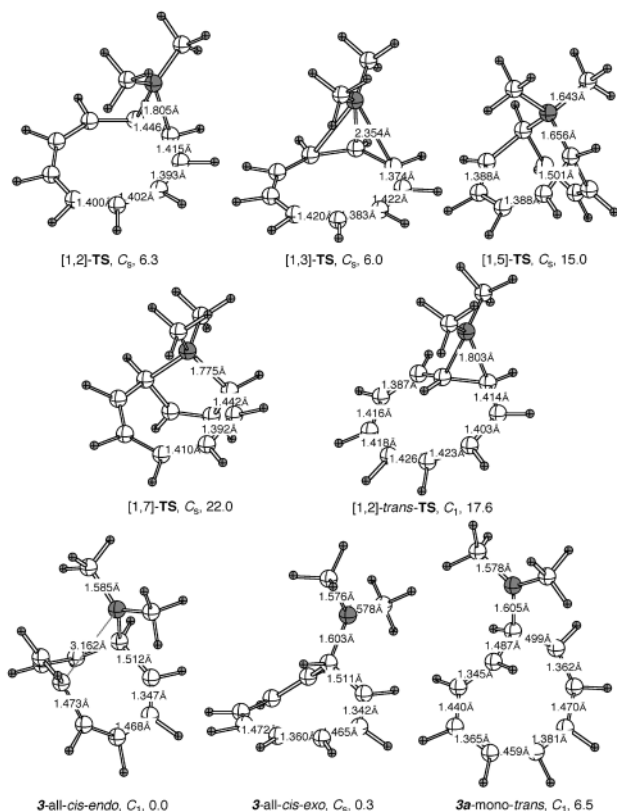


Fig. 1 B3LYP/6-311G**//B3LYP/6-31G* computed ground and transition state structures for dimethylboroyl group migrations relative to **3**-all-*cis*-endo. Relative energies (ΔH) in kcal mol⁻¹.

similar (within 0.3 kcal mol⁻¹). It should be stressed that in symmetrically conjugated molecules like **3** only the fastest sigmatropic rearrangement can be reliably characterized by NMR analysis. At 188 K and a mixing time of 10 ms, all possible cross-peaks of comparable intensity are observed in the EXSY spectra of **3**. That means that the E_a for the [1,9]-B migration may be only about 1.1 times higher than that for [1,3]-B shifts, in agreement with the computed data. The [1,5] and [1,7] migrations are clearly disfavored by 15.0 and 22.0 kcal mol⁻¹, respectively. They also do not allow the cyclononatetraenyl moiety to become planar and therefore pseudo-Hückel-aromatic in the transition structure.

In summary, we have shown that [1,3]-dialkylboroyl shifts in cyclononatetraenyl systems are facile and are slightly favored

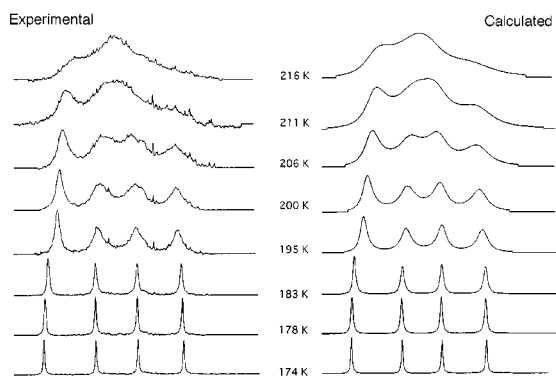


Fig. 2 Temperature-dependent experimental and computed ¹³C NMR spectra of **3**.

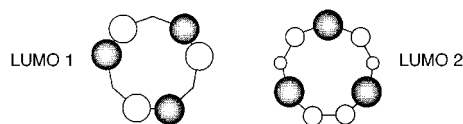


Fig. 3 Simple qualitative presentation of the degenerate Hückel LUMO orbitals for the analysis of allowed suprafacial shifts in conjugated cyclononane systems.

over [1,2]-shifts. Neither Woodward–Hoffmann rules nor the ‘least motion principle’ alone can be used for the prediction or rationalization of the migration pathways. Adequate analyses require a combination of dynamic NMR techniques and high-level *ab initio* calculations.

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Notes and references

† *Computations*: Geometries of all stationary points were optimized using analytical energy gradients (ref. 9, 10). We utilized Becke’s three-parameter exchange-correlation functional (ref. 11) including the nonlocal gradient corrections described by Lee–Yang–Parr (LYP) (ref. 12), as implemented in the GAUSSIAN 94 program package (ref. 13). All geometry optimizations were performed with the 6-31G* basis set (ref. 14); stationary structures were characterized by inspecting the updated Hessian matrices. Single point energies were evaluated using a standard 6-311G* basis set (ref. 15); final energies thus refer to B3LYP/6-311+G**//B3LYP/6-31G*. Standard notation is used, *i.e.* // means energy computed at // geometry (ref. 15). Computational results are available as supplementary data: see <http://www.rsc.org/suppdata/cc/1998/2507>.

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- The lineshapes were calculated utilizing a self-written computer program designed for direct iterative search of the activation parameters from the whole set of experimental spectra as proposed by R. Laatikainen, *J. Magn. Res.*, 1985, **64**, 375. Iterations were made for two independent NMR operating frequencies (50 and 100 MHz for ¹³C, Fig. 2); temperature calibration was carried out using a standard calibration sample (4% MeOH in [2H₄]MeOH), providing an approximate accuracy of ±1 K. Temperature coefficients of the chemical shifts were determined by spatial iteration cycles where they were regarded as variable parameters. Linear coefficients were found to be approximately 1 Hz K⁻¹ for C-1–4 and 2 Hz K⁻¹ for C-5; second order coefficients were less than 0.001 Hz K⁻².
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