Two different [1,3]-B shifts in phenalenyl(dipropyl)borane

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Both possible [1,3]-B sigmatropic shifts are observed in the title compound; benzylic rearrangement to position 9 is much faster than allylic migration to position 3.

Twenty years ago Butcher and Pagni argued that the phenalenyl ring system is an excellent choice for the exploration of fluxionality in its organometallic derivatives.[1] However, the trimethylsilyl and trimethylstannyl compounds prepared in their work were non-fluxional on the NMR time scale at temperatures up to 185 °C.[1] Due to orbital restrictions, both silicon[2] and tin[3–5] prefer to rearrange *via* [1,5]- or [1,9]-migration pathways (thermal [1,3]-Si shifts have very high activation barriers[6,7] and known [1,3]-Sn rearrangements are intermolecular).[3,4,8] However, there is only one possibility of intramolecular [1,5]-M migration in a molecule of monosubstituted phenalene, *i.e.* non-degenerate rearrangement to the central position. This is difficult to observe due to the obvious relative instability of the corresponding isomer.

On the other hand, introducing a [1,3]-migrating substituent into position 1 of phenalene provides the first example of a molecule where two different [1,3]-sigmatropic migrations may occur. Being interested in the regularities of the sigmatropic migrations of BR_2 groups,[9] which often migrate by the [1,3]-B shift mechanism,[10–14] we have synthesized a phenalenyl derivative of boron and studied its fluxional behaviour.

1-Phenalenyl(dipropyl)borane **1** was prepared by the reaction of phenalenyllithium **2**[1] with chloro(dipropyl)borane in pentane. Borane **1** is a light-yellow extremely air- and moisture-sensitive oil. It has only limited thermal stability that retards its purification. We failed to distil borane **1** and used samples of approximately 95% purity (main admixture is phenalene), obtained after evacuation of volatile products in vacuum, for the NMR studies.

Assignment of signals in the ^1H and ^{13}C NMR spectra of **1** was carried out by standard homo- and heteronuclear 2D chemical shift correlation techniques. The signal of H^9 in the ^1H NMR spectrum was distinguished from H^4 by its long-range coupling with H^1 [$^4J(H^1–H^9)$ = 1.1 Hz, confirmed by double resonance].

The NMR spectra of **1** show reversible temperature dependence and are not affected by changes in concentration. Therefore, intramolecular rearrangements take place in **1**. The mechanism of these was elucidated by 2D $^1H–^1H$ EXSY (exchange spectroscopy) NMR experiments. Fig. 1 shows the chemical exchange NMR spectrum of **1** taken at 298 K. Four exchange cross-peaks observed in this spectrum unequivocally prove the mechanism of [1,3]-B sigmatropic migrations from position 1 to position 9 of the phenalene ring. The 2D EXSY experiments carried out at higher temperatures also show cross-peaks of lower intensity, corresponding to the second possible degenerate [1,3]-B migration from position 1 to position 3 (Fig. 2, Scheme 1). Thus, both [1,3]-B shifts are observed in **1**, but their rates differ significantly.

The kinetics of the $[1,3]^9$-sigmatropic migrations of the dipropylboryl group in **1** were measured from a series of 2D ^1H EXSY spectra recorded in the temperature interval 290–318 K. At this temperature, the second dynamic process does not manifest itself in the EXSY spectra at short mixing times (τ_m) and therefore, may be neglected. Rate constants were obtained from eqn. (1),[15] 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. Rate constants and activation parameters so obtained, derived by Arrhenius and Eyring treatments of the kinetic data, are listed in Table 1.

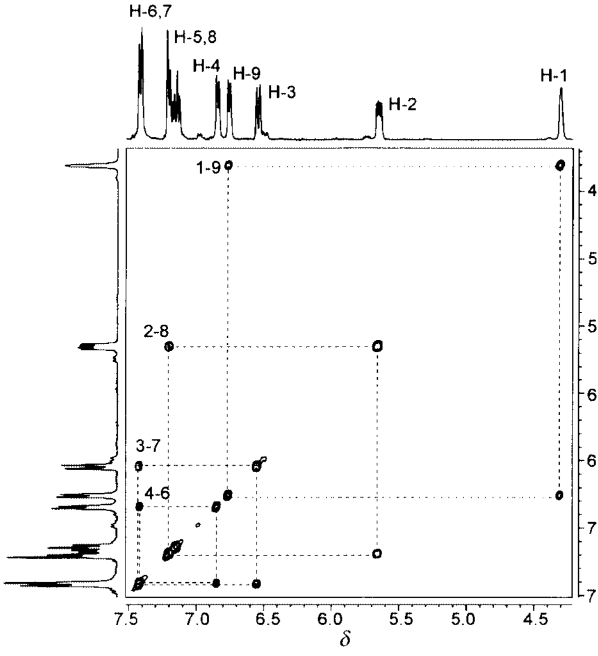


Fig. 1 2D $^1H–^1H$ EXSY spectrum (400 MHz, benzene-d_6) of dipropyl(phenalenyl)borane **1** at 298 K with a mixing time of 0.5 s.

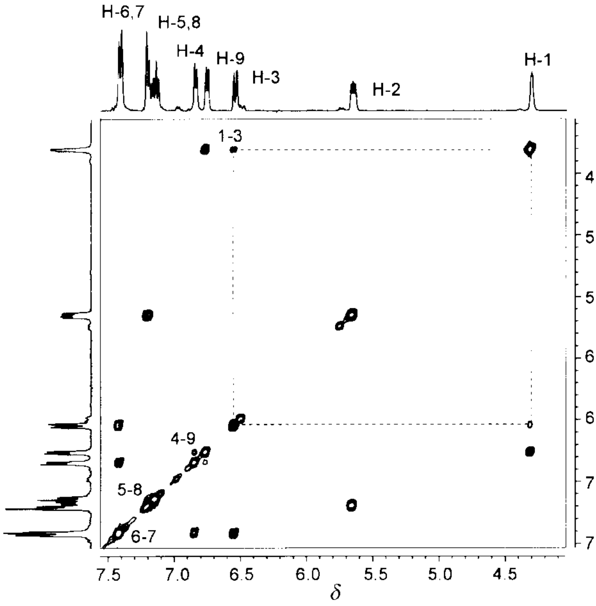
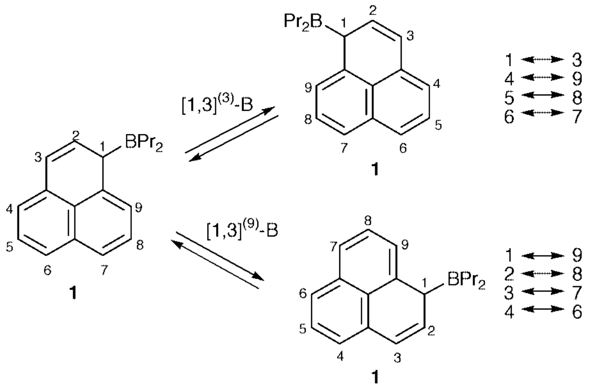


Fig. 2 2D $^1H–^1H$ EXSY spectrum (400 MHz, benzene-d_6) of dipropyl(phenalenyl)borane **1** at 313 K with a mixing time of 0.5 s.

$$k = \frac{1}{\tau_{\mathrm{m}}}\ln\frac{r+1}{r-1},\quad r = \frac{I_{\mathrm{AA}}+I_{\mathrm{BB}}}{I_{\mathrm{AB}}+I_{\mathrm{BA}}} \qquad (1)$$

The kinetic analysis of simultaneous dynamic processes is possible *via* matrix analysis.[15] However, in the present case this approach is complicated by a considerable difference in the rates of the two borotropic migrations and the overlap of some diagonal and cross-peaks. Approximate evaluation of the available data shows that the $[1,3]^3$-borotropic migration in **1** at 323 K is about 10 times slower the $[1,3]^9$-B shift.

Either of two [1,3]-B shifts in isolation is spatially fixed to one allylic or benzylic fragment of **1**. However, the *combination of both* results in the possibility for the dipropylboryl group to wander around the whole molecule. This is experimentally illustrated by difference SST (spin saturation transfer) ^{1}H NMR spectra (Fig. 3). Irradiation of the H^1 signal leads to a decrease in the intensities of all signals due to α-protons in **1** (Fig. 3a). Similarly, irradiation of H^2 shows that it is in exchange with both remaining β-protons, H^5 and H^8 (Fig. 3b).



Scheme 1 Two possible borotropic migrations in **1**.

Table 1 Kinetic data and activation parameters for the [1,3]-B shift in borane **1**

T/K	k/s^{-1}	τ_{m}/s	
290	0.95	0.500	E_{A} = 19.1 ± 0.4 kcal mol^{-1}
295	1.41	0.300	ln A = 33.0 ± 0.7
298	1.97	0.200	$\Delta H^{\ddagger}_{298}$ = 16.6 ± 0.2 kcal mol^{-1}
303	3.33	0.050	$\Delta S^{\ddagger}_{298}$ = 5.0 ± 0.1 cal mol^{-1} K^{-1}
308	6.06	0.050	$\Delta G^{\ddagger}_{298}$ = 15.1 ± 0.2 kcal mol^{-1}
313	9.86	0.025	
318	14.80	0.010	

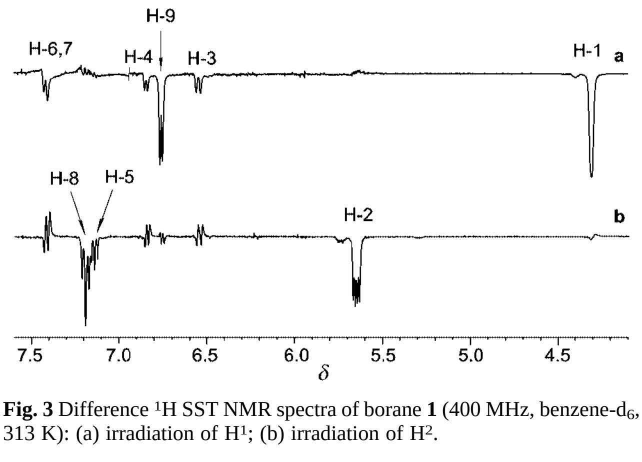
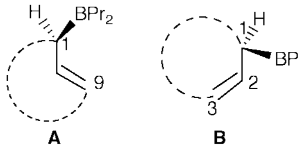


Fig. 3 Difference ^{1}H SST NMR spectra of borane **1** (400 MHz, benzene-d_6, 313 K): (a) irradiation of H^1; (b) irradiation of H^2.



Scheme 2 Schematic representation of the geometries of allylic fragments for $[1,3]^9$-B (**A**) and $[1,3]^3$-B (**B**) shifts in **1**.

Since the configurations of the starting compounds and the product are equal for both observed rearrangements,[16] the difference in the activation barriers is exactly the difference in the energies of the corresponding transition states (TS). Therefore, one can conclude that the spatial arrangement of the allylic fragment **A** is much nearer in configuration to the TS than that of **B** (Scheme 2). This conclusion is in agreement with computational results for the [1,3]-B shift.[17]

Thus, we have observed for the first time two different [1,3]-B sigmatropic shifts in one molecule, *viz.* phenalenyl(dipropyl)borane. Further studies on the fluxional behaviour of organometallic derivatives of phenalene are underway in our laboratory.

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