First Observation of a [1,7] Boron Shift—Three Independent Fluxional Processes in the Tricarbonyliron Complex of Cycloheptatrienyl(dipropyl)borane

Ilya D. Gridnev, Oleg L. Tok, Mikhail E. Gurskii, and Yuri N. Bubnov*

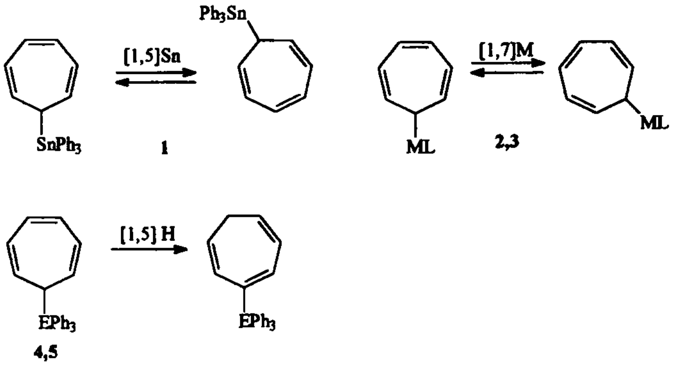
Abstract: The fluxional behavior of [1–4-η^4-*exo*-7-dipropylborylcyclohepta-1,3,5-triene]tricarbonyliron (**14**) has been studied by dynamic NMR. The 2D ^{1}H and ^{13}C EXSY NMR experiments carried out at various temperatures revealed that three independent fluxional processes occur in **14**. The fastest rearrangement is a [1,7] B sigmatropic shift accompanied by [1,2] Fe migration ($E_A = 71.2 \pm 2.3$ kJ mol^{-1}, $\ln A = 32 \pm 1$). Two other rearrangements also take place: [1,3] B sigmatropic and [1,3] Fe haptotropic migrations. The analysis of the observed selectivity towards [1,*j*] B sigmatropic shifts ([1,3] and [1,7] B shifts are observed, but [1,5] B shifts are not) in terms of theoretical predictions gives reason to assume that the [1,*j*] boron migrations occur with inversion of configuration at the migrating atom.

Keywords
boron compounds · fluxionality · iron complexes · NMR spectroscopy · rearrangements

Introduction

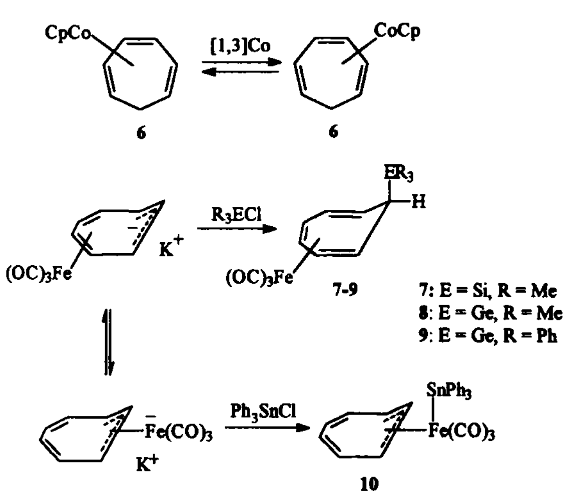
Systems undergoing sigmatropic [1,*j*] shifts present excellent models for investigating the scope and limitations of the rules for conservation of orbital symmetry.[1] In this respect the sigmatropic migration of organometallic groups is of particular interest, because it often occurs under mild conditions.[1b]

The dynamic behavior of the organometallic derivatives of cycloheptatriene has been extensively studied.[2–8] In η^1-cycloheptatrienylmetals various [1,*j*] sigmatropic migrations of the organometallic group can occur. Thus, in (η^1-7-cycloheptatrienyl)triphenyltin (**1**) a sigmatropic [1,5] Sn shift took place (Scheme 1).[2] In η^1-cycloheptatriene derivatives of Re (**2**)[3] and Ru (**3**)[4] [1,7] Re and [1,7] Ru sigmatropic shifts were observed. On the other hand, no silicon or germanium migration was detected in (η^1-7-cycloheptatrienyl)triphenylsilane (**4**)[5] and (η^1-7-cycloheptatrienyl)triphenylgermane (**5**).[6] At temperatures higher than 400 K a [1,5] hydrogen shift occurred in the compounds **4** and **5**.[5, 6]



Scheme 1. Sigmatropic migrations of organometallic groups. ML = Re(CO)$_5$ (**2**), RuCp(CO)$_2$ (**3**); E = Si (**4**), Ge (**5**).

Another kind of fluxionality takes place in polyhapto metal complexes of cycloheptatriene. For example, a reversible haptotropic [1,3] shift of the (η^5-Cp)Co group was observed in complex **6** (Scheme 2).[7] Similarly, a haptotropic [1,3] shift of the tricarbonyliron fragment was found in the [1–4-η^4-*exo*-7-(R$_3$E)-cyclohepta-1,3,5-triene]tricarbonyliron complexes **7–9**



Scheme 2. Haptotropic migrations of organometallic groups.

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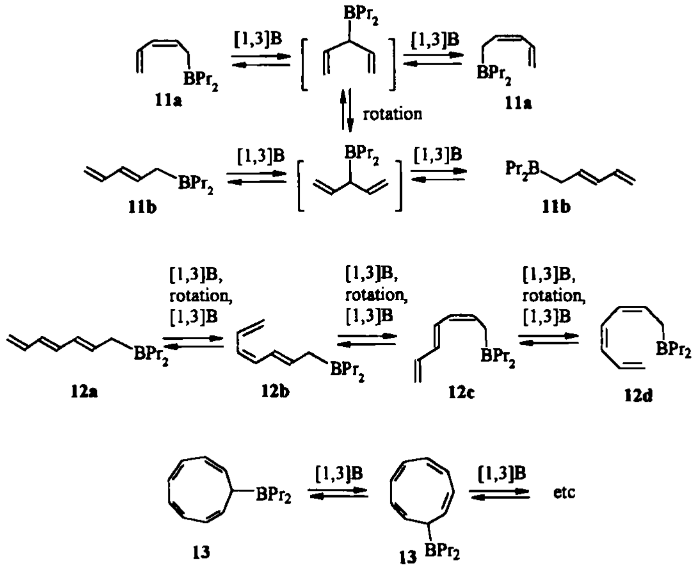
(R_3E = Me_3Si, Me_3Ge, Ph_3Ge).[8] The complexes **7**–**9** contain both η^1- and η^4-bonded organometallic groups in one molecule and might be expected to exhibit a more complex fluxional behavior; however, sigmatropic rearrangements do not proceed in these compounds, at least not below 400 K (at still higher temperatures irreversible [1,5] hydrogen shifts occur).[8] The apparent reason for this is a rather high activation barrier for sigmatropic migrations of Si and Ge.[9] The activation barriers to [1,5] Sn migrations are comparatively low;[2] however, attempts to synthesize a tin analogue of **7**–**9** failed, presumably because the allyliron complex **10** was formed instead.[10]

Boryl groups are also known to be capable of sigmatropic rearrangements with low activation barriers. Facile [1,3] boron sigmatropic shifts have been observed in all known triorganoboranes of allylic type.[11] Of the various possible [1,*j*] sigmatropic boron shifts, the [1,3] shift is the fastest in polyunsaturated 2,4-pentadienyl-,[11c] 2,4,6-heptatrienyl-,[11d,e] and 9-cyclononatetraenyl(dialkyl)boranes[11g] (**11**–**13**) (Scheme 3). However, cycloheptatrienyl derivatives of boron are unknown. Therefore, the synthesis of a boron analogue of the compounds **7**–**9** was of particular interest, since one might expect to find both types of the above-discussed metallotropic migrations in such a molecule, namely, a sigmatropic [1,3] B and a haptotropic [1,3] Fe shift. Here we report the first synthesis of [1–4-η^4-*exo*-7-(Pr_2B)-cyclohepta-1,3,5-triene]tricarbonyliron (**14**) and the investigation of its fluxional behavior by dynamic NMR.

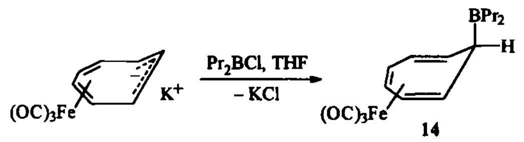


Scheme 3. [1,3] Shifts in polyunsaturated boranes.

Results

Synthesis and NMR spectra of 14: The complex **14** was synthesized by the reaction between $[C_7H_7Fe(CO)_3]K^+$ and Pr_2BCl at −40 °C in THF (Scheme 4). Attempts to purify **14** by distillation failed, probably owing to a self-carbonylation of **14**.[12] Reasonably pure samples of **14** (about 95% purity) were prepared by extracting the crude material with hexane or pentane followed by additional filtration and evaporation of the solvents.

Complex **14** is an extremely air-sensitive greenish brown oil. The ^{11}B NMR chemical shift (δ = 79.4) is somewhat lower than the values characteristic of other allylic triorganoboranes (δ = 81–83);[11] nevertheless, it clearly indicates the presence of three B–C bonds in the molecule of **14**. Confirmation and unequivocal proof for structure **14** come from the ^1H and ^{13}C NMR spectra of the complex taken at 268 K (see Table 1), which are in complete accord with the presence of a static 1–4-η-bonded and 7-substituted cycloheptatriene ring, where all protons and carbon atoms have different chemical environments.



Scheme 4. Synthesis of cycloheptatrienylborane 14.

Table 1. Chemical shifts δ and coupling constants J [Hz] for compound **1** (without BPr_2 groups) [a].

Atom No.	$\delta(^1H)$	Coupling constants, Hz	$\delta(^{13}C)$ [b]
1	3.17	[c]	63.5
2	4.65	4.5 ($J_{1,2}$); 7.5 ($J_{2,3}$); 1.1 ($J_{2,4}$)	87.0
3	4.57	7.5 ($J_{2,3}$); 4.5 ($J_{3,4}$); 1.3 ($J_{1,3}$)	92.2
4	3.14	[c]	60.1
5	5.90	8.3 ($J_{4,5}$); 9.8 ($J_{5,6}$); 0.9 ($J_{5,7}$)	127.9
6	5.27	9.8 ($J_{5,6}$); 4.3 ($J_{6,7}$)	129.0
7	2.79	4.5 ($J_{1,7}$), 4.3 ($J_{6,7}$)	44.6

[a] ^{11}B NMR (128 MHz, [D_8]toluene, $BF_3\cdot Et_2O$): δ = 79.4. [b] $\delta(^{13}C)$ (C≡O) = 213.8. [c] Coupling constants were extracted from other signals.

The signals in the ^1H and ^{13}C NMR spectra of compound **14** were assigned at 268 K by means of two-dimensional correlation NMR spectroscopy (standard procedures COSY-45 and HETCOR). The chemical shift of H^7 in **14** (δ = 2.79) is close to those found for structurally related chromium complexes [(η^6-7-RC_7H_7)$Cr(CO)_3$] with *exo* configuration (δ = 2.7–3.2). In the *endo* isomers the H^7 nucleus is more shielded ($\delta \approx 1.8$).[13] The value of the long-range coupling constant $^4J_{5,7}$ = 0.9 Hz (confirmed by the corresponding crosspeak in the COSY-45 spectrum) also supports the *exo* configuration of complex **14**. The narrow range of the allyl coupling of quasiequatorial protons in 7-*exo*-substituted cycloheptatriene complexes (0.92–0.94 Hz) has been reported.[14,15] For the quasiaxial protons in 7-*endo*-substituted complexes, somewhat greater absolute values of the allyl couplings have been observed (1.3–1.4 Hz).[15,16] Therefore, it is concluded that complex **14** possesses *exo* configuration, which means that the $Fe(CO)_3$ and the BPr_2 group occupy opposite faces of the cycloheptatriene ring. This result is in accord with the stereochemistry of complexes **7**–**9**, which were also prepared by transmetalation of $[C_7H_7Fe(CO)_3]K^+$.[8]

^1H and ^{13}C NMR spectra of compound **14** are temperature dependent. Thus, at 298 K the ^1H NMR signals of the ring protons are broadened (compared to the signals of the B-propyl groups). Corresponding broadening is observed for the ^{13}C (ring) NMR signals. At 308 K the signals become still broader, whereas at 268 K sharp lines are observed in the ^1H and ^{13}C NMR spectra. The appearance of these spectra did not change when a tenfold diluted sample was measured. These changes in the line shape indicate that compound **14** is fluxional and undergoes some intramolecular degenerate rearrangement.

Analysis of exchange processes in 14: A fascinating property of complex **14** is the fact that different [1,*j*] migrations of the BPr_2

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group (j = 3, 5, 7) lead to completely different sets of exchanging atoms (Scheme 5). This feature provides a unique opportunity for the analysis of various degenerate rearrangements of **14** by means of dynamic NMR. Indeed, in other cyclic polyunsaturated fluxional molecules like **1**–**3** or **13** two consecutive [1,j] shifts cannot be distinguished from a one [1,i] shift: for example, in **1** two [1,5] Sn shifts lead to a formal [1,7] Sn shift. Therefore, only the fastest process can be examined by 2D EXSY NMR spectroscopy or SST experiments, whereas other (slower) [1,j] shifts cannot be proved experimentally. In complex **14** the situation differs dramatically. Compound **14** contains two groups capable of migration, namely, the dipropylboryl and the tricarbonyliron groups, and in Scheme 5 all possible degenerate rearrangements are shown. Since all carbon atoms of the cycloheptatrienyl cycle are nonequivalent, the dipropylboryl group has six different ways for changing its position (two α-migrations, two β-migrations, and two γ-migrations). For each of these six possibilities two different locations of the tricarbonyliron group are possible; this doubles the total number of conceivable rearrangements (see Scheme 5). In the 13th possible rearrangement the location of the tricarbonyliron fragment changes, while the position of the dipropylboryl is retained. All thirteen of these intramolecular rearrangements are degenerate in terms of NMR spectroscopy (seven rearrangements marked by asterisks in Scheme 5 lead to the interconversion of the enantiomers of **14**).

In the phase-sensitive ^{1}H and ^{13}C EXSY NMR spectra of compound **14** taken at 268 K, three crosspeaks are observed (e.g., Fig. 1), corresponding to a single exchange reaction at this temperature, namely, the process **A** → **D** in Scheme 5. At 298–323 K thirteen crosspeaks of various intensity are observed (e.g., Fig. 2). The best spectra are detected at 298 K, since the exchange processes affect the lineshape at higher temperatures.

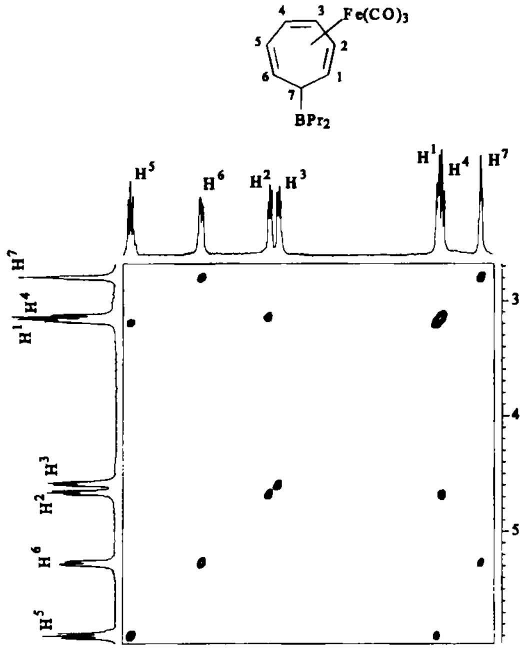
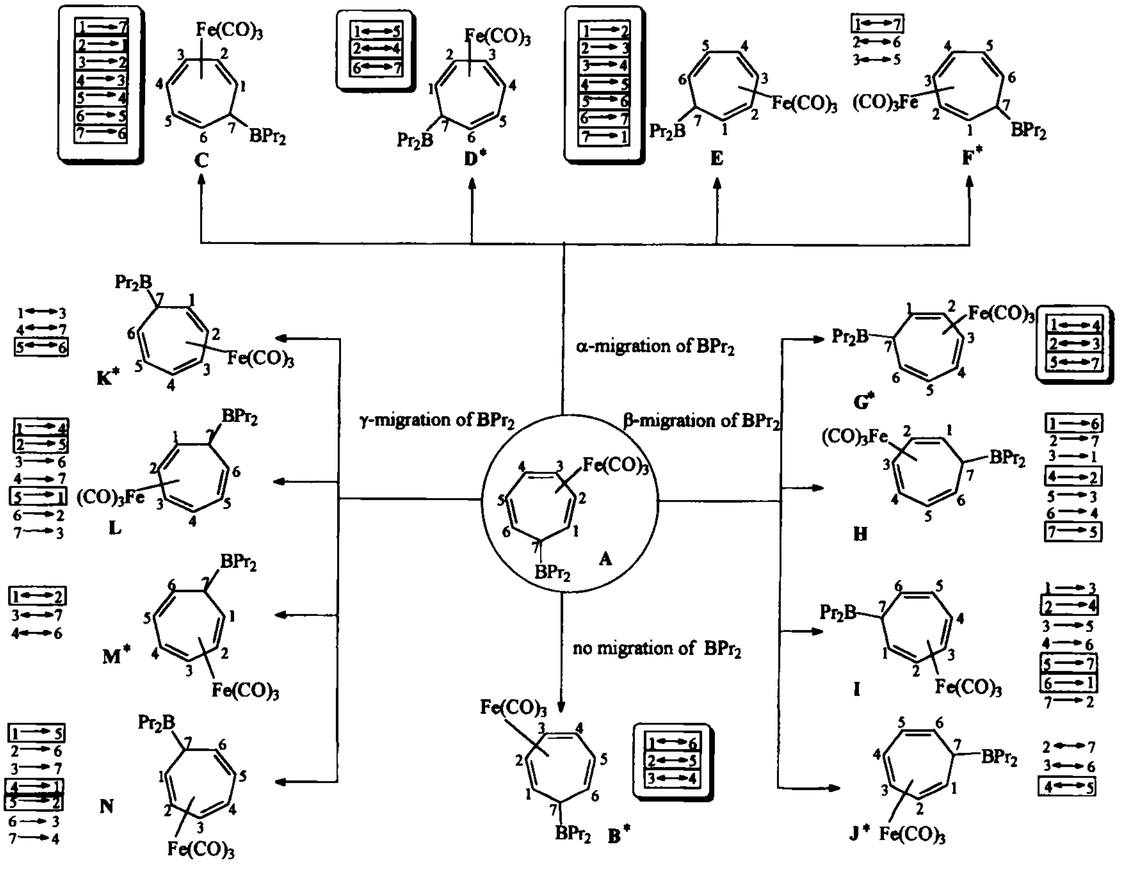


Fig. 1. ^{1}H EXSY NMR spectrum of **14** (400 MHz, [D$_8$]toluene, 268 K); mixing time 1 s, initial delay 2 s, number of scans 16; a matrix 512 × 256 was acquired by the TTPI technique and zero-filled to the size 1024 × 1024 to give, after the Fourier transformation, a digital resolution of 2.77 Hz per point in both dimentions.

The matrix in Figure 3 displays the experimental intensities of the diagonal and crosspeaks obtained from the ^{13}C EXSY NMR spectrum of **14** at 298 K (mixing time 1 s). The three most



Scheme 5. All possible degenerate rearrangements of **14**.

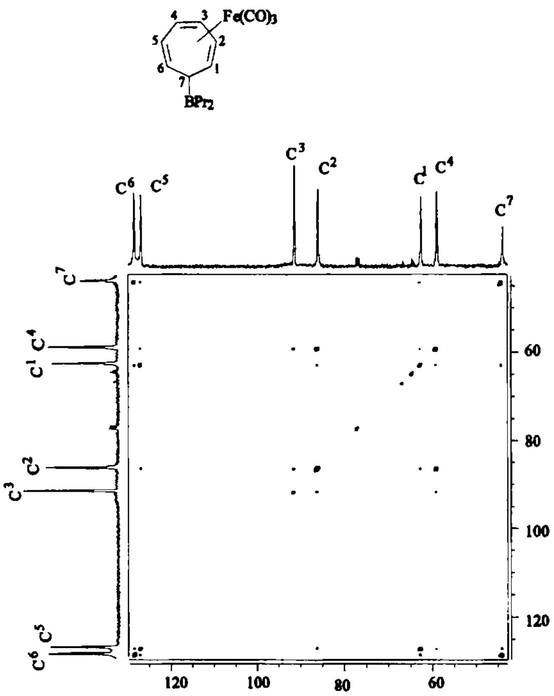
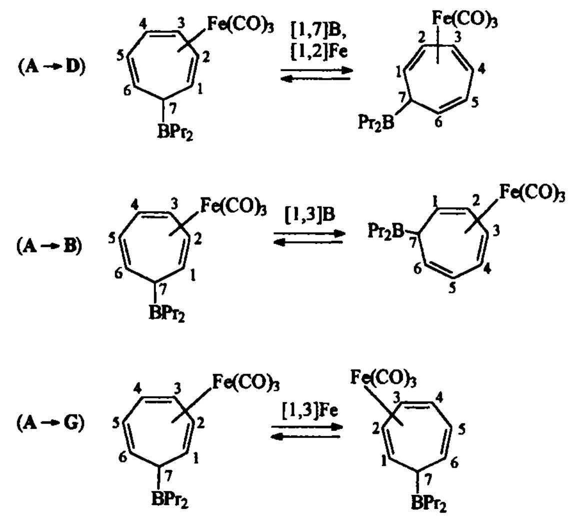


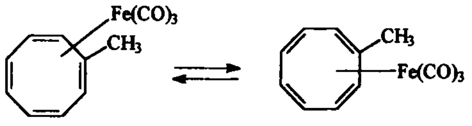
Fig. 2. ^{13}C EXSY NMR spectrum of **14** (100 MHz, $CDCl_3$, 298 K); mixing time 1 s, initial delay 1 s, number of scans 256; a matrix 512 × 256 was acquired by the TPPI technique and zero-filled to the size 1024 × 1024 to give, after the Fourier transformation, digital resolution of 5.13 Hz per point in both dimentions.

	1	2	3	4	5	6	7
1	243	18		11	128	18	21
2	16	211	21	159	32		
3		19	365	48			
4	8	163	54	226	8		
5	137	24		8	208	20	14
6	23				20	225	169
7	21				11	155	205

Fig. 3. Experimental intensities of the diagonal and crosspeaks obtained from the ^{13}C EXSY NMR spectrum of **14**.



Scheme 6. Mechanisms of processes A → D, A → B, and A → G.



15 **15**

Scheme 7. Example of a migration accompanied by the simultaneous shift of double bonds.

intense crosspeaks (between C^1 and C^5; C^2 and C^4; C^6 and C^7) correspond to the already observed exchange **A** → **D**. Ten other crosspeaks indicate the occurrence of slower processes.

A set of the expected crosspeaks is given beside each process in Scheme 5. If a rearrangement takes place, the whole set of expected crosspeaks should be observed. Therefore, the absence of even a single crosspeak from a particular set in the experimental spectrum is sufficient reason to exclude the whole process. In Scheme 5 the experimentally observed crosspeaks are framed; for five processes, namely, for **A** → **B**, **A** → **C**, **A** → **D**, **A** → **E**, and **A** → **G**, all of the expected crosspeaks are present in the 2D EXSY NMR spectra, while for each of the remaining eight possible rearrangements at least two of the expected crosspeaks are absent in the experimental ^{1}H and ^{13}C EXSY NMR spectra.

The nature of the processes **A** → **B** and **A** → **G** is clear (see Scheme 6): they are explained by [1,3] B sigmatropic shift and [1,3] Fe haptotropic shift, respectively, both of which are well documented (see Introduction). However, the fastest observed exchange reaction (**A** → **D**) is a new type of rearrangement, namely, a [1,7] B sigmatropic shift accompanied by simultaneous [1,2] migration of the tricarbonyliron group (Scheme 6). Previously, a similar [1,2] migration of the $Fe(CO)_3$ group was observed by Günther et al. in complex **15** (Scheme 7),[17] accompanied by the simultaneous shift of the double bonds in the cyclooctatetraene ring. Since a pure [1,7] boron shift requires a similar change in the positions of the double bonds, one can assume that the [1,2] migration of the tricarbonyliron group in compound **14** is the consequence of the [1,7] B shift. In the same way as in **15**, it may be the result of the fluctuation of double bonds, characteristic for all cyclooctatetraenes.[18]

The kinetics of the [1,7] boron shift (accompanied by the [1,2] Fe migration) in compound **14** was measured from the series of 2D ^{13}C EXSY NMR spectra by integration of the diagonal and crosspeaks corresponding to the exchange between C^1 and C^5. The rate constants (Table 2) were obtained by Equation (1),[19, 20] where I_{AA}, I_{BB} are the intensities of the diagonal

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

peaks and I_{AB}, I_{BA} are the intensities of the crosspeaks. The Arrhenius plot presented in the Figure 4 shows a linear correlation, and gives the activation parameters (Table 2) for the [1,7] boron shift in **14**.

The appearance of the crosspeaks formally corresponding to the processes **A** → **C** and **A** → **E** is apparently explained by con-

Table 2. Kinetic data and activation parameters for the [1,7] boron shift in **14** ($CDCl_3$).

T, K	t_m, s	k, s^{-1}	Activation parametres
258	1	0.25	$E_A = 71.2 \pm 2.1\ kJ\,mol^{-1}$
263	0.75	0.49	$\ln A = 32 \pm 1$
268	0.5	0.97	$\Delta H^{\neq} = 68.9 \pm 2.3\ kJ\,mol^{-1}$
273	0.5	1.38	$\Delta S^{\neq} = 12 \pm 3\ J\,mol^{-1}\,K^{-1}$
278	0.2	3.13	
283	0.2	4.90	
288	0.1	8.32	

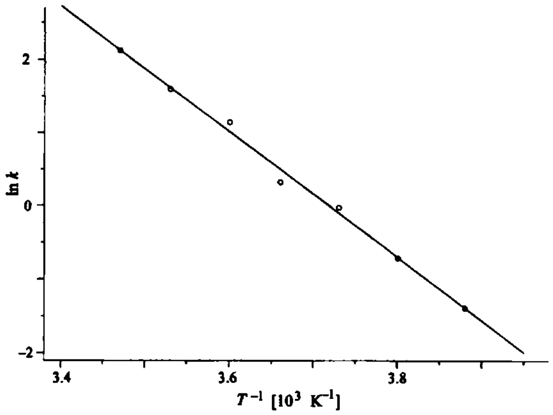
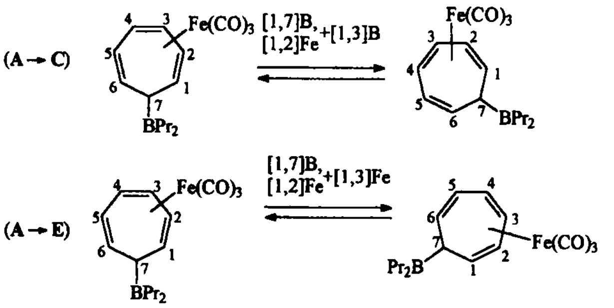


Fig. 4. Arrhenius plot for the [1,7] boron shift in **2**.

secutive reactions **A** → **D** + **A** → **G** and **A** → **D** + **A** → **B**, respectively (see Scheme 8), since they are the result of fast and slow reactions, which are observed independently. This assumption can be supported with the data of the matrix in Figure 3. Generally speaking, the rate constants matrix for a multisite exchange can be deduced from the matrix intensities by known equations;[19,20] however, in the present case, such a complete analysis of the matrix would be incorrect, since all of the low-intensity peaks can be observed only at 298 K (mixing time 1 s), that is, under the conditions for which the main process is too fast for accurate measurement (the rate constant for [1,7] B shift **A** → **D** at 298 K calculated from the data of Table 2 is 21.6 s^{-1}). Nevertheless, it can be deduced from the available data that the rate of [1,3] Fe shift (**A** → **G**) is about 8–10 times lower than the rate of [1,7] B shift (compare, for example, the intensities I_{24} and I_{16} in the matrix). The [1,3] B shift (**A** → **B**) proceeds still slower than the [1,3] Fe shift (compare the intensities I_{14} and I_{16} in the matrix). If the above conclusion about the nature of the processes **A** → **C** and **A** → **E** is correct, then the overall rates of two consecutive reactions should be approximately equal to the rates of the slow steps; this is in reasonable accordance with the observed intensities of the corresponding crosspeaks (I_{12}, I_{45}, I_{56}).



Scheme 8. Mechanisms of processes **A** → **C** and **A** → **E**.

Since there is no indication that the processes **A** → **B**, **A** → **D**, and **A** → **G** give a crossing multitude of the expected crosspeaks, we can conclude from the study of the fluxional behavior of **14** by 2D EXSY NMR spectroscopy that three independent rearrangements are operating, namely, a [1,7] B shift accompanied by a [1,2] Fe shift, a [1,3] B shift, and a [1,3] Fe shift.

Discussion

In all triorganoboranes of allylic type studied so far, a [1,3] sigmatropic shift of boron has been observed.[11] Complex **14** is no exception, since a [1,3] B shift also occurs in this compound. However, the fastest boron migration is a [1,7] B shift, which has not been observed previously, apparently because of the difficulty of finding appropriate compounds. One can therefore assume that both types of boron migrations observed in **14** are allowed processes, whereas a [1,5] B shift is prohibited.

The [1,7] B and [1,3] B shifts in **14** are inevitably suprafacial, in contrast to the [1,7] hydrogen shifts, which are antarafacial.[1,11d,e,21] In the case of [1,7] Re and [1,7] Ru shifts in complexes **2** and **3** the suprafacial nature of the [1,7] migrations was accounted for by a relaxation in the orbital symmetry restrictions when the migrating group possesses valence-shell d orbitals.[3,4] However, a boron atom cannot use d orbitals, and another explanation is therefore necessary. Theory predicts the possibility of suprafacial [1,*j*] shifts (*j* = 3 or 7) for elements other than hydrogen if the reaction proceeds with inversion at the migrating atom.[22,1a] Therefore, we can conclude that this mechanism operates in the case of the [1,3] and [1,7] boron sigmatropic shifts.

It is interesting to note that, in the case of cyclononatetraenyl(dipropyl)borane (**13**), a [1,3] boron shift is the fastest process, while in **14** the [1,7] B shift proceeds faster than the [1,3] B shift. This corresponds to the modified "least motion" theory,[6] recently reformulated as *"the necessity of a close relationship between migration origin and migration terminus to maintain simultaneous bonding of these centers to the migrating group, as is required for the transition state of a truly pericyclic reaction"*.[22] In compound **13** the [1,3] migration requires a shorter pathway than the [1,7] migration, and the former is faster than the latter. In contrast, in compound **14**, the pathway of [1,7] migration is shorter, and therefore the [1,7] B shift is faster than [1,3] B shift.

Conclusion

The study of the dynamic behavior of **14** allow us to propose the following general rules controlling [1,*j*] B sigmatropic migrations:

1) [1,3] and [1,7] boron shifts are allowed and [1,5] B shifts are prohibited.
2) The reaction proceeds with the inversion at the migrating center.
3) Among the allowed sigmatropic shifts the fastest one is that requiring the least motion of the boryl group.

To obtain further support for these conclusions, the dynamic behavior of a noncoordinated cycloheptatrienylborane is currently being studied.

Experimental Section

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

[1–4-η^4-*exo*-7-(Pr_2B)-cyclohepta-1,3,5-triene]tricarbonyliron (14): A solution of $C_7H_7Fe(CO)_3$ (6.0 g, 25.85 mmol) in THF (5 mL) was added dropwise to a suspension of KH (1.07 g, 26.85 mmol) in THF (30 mL). The mixture was stirred for 1 h, and excess KH was then filtered off. The resulting dark red solution of

$[C_7H_7Fe(CO)_3]K^+$ was cooled to −40 °C, and Pr_2BCl (3.42 g, 25.8 mmol) was added dropwise within 10 min. The mixture was allowed to warm to room temperature and stirred for an additional 20 min. The precipitate was filtered off, and the solvent removed under vacuum. The residue was dissolved in hexane (15 mL), and the solvent was stored in the refrigerator overnight. The solution was then filtered, and hexane was removed under vacuum to give 7.81 g (92%) of **14** as a greenish-brown oil.

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[1] a) R. B. Woodward, R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim, **1970**; b) C. W. Spangler, *Chem. Rev.* **1976**, *76*, 187; c) V. K. N. Houk, Y. Li, J. D. Evanseck, *Angew. Chem.* **1992**, *104*, 711; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 682.

[2] a) R. B. Larrabee, *J. Am. Chem. Soc.* **1971**, *93*, 1510; b) M. D. Curtis, R. Fink, *J. Organomet. Chem.* **1972**, *38*, 299; c) B. E. Mann, B. F. Taylor, N. A. Taylor, R. Wood, *ibid.* **1978**, *162*, 137.

[3] D. M. Heinekey, W. A. G. Graham, *J. Am. Chem. Soc.* **1979**, *101*, 6115.

[4] D. M. Heinekey, W. A. G. Graham, *J. Am. Chem. Soc.* **1982**, *104*, 915.

[5] A. J. Ashe, III, *J. Org. Chem.* **1972**, *37*, 2053.

[6] R. B. Larabee, *J. Organomet. Chem.* **1974**, *74*, 313.

[7] R. Benn, K. Cibura, P. Hofmann, K. Jonas, A. Rufinska, *Organometallics* **1985**, *4*, 2214.

[8] L. K. K. LiShingMan, J. G. A. Reuvers, J. Takats, G. Deganello, *Organometallics* **1983**, *2*, 28.

[9] a) M. Kobayashi, N. Kobayashi, *Chem. Lett.* **1986**, 385; b) H. Kwart, T. Slutsky, *J. Am. Chem. Soc.* **1972**, **94**, 2515.

[10] L. K. K. LiShingMan, J. Takats, *J. Organomet. Chem.* **1976**, *117*, C104–110.

[11] a) B. M. Mikhailov, Y. N. Bubnov, *Organoboron Compounds in Organic Synthesis*, Harwood, London, **1984**; b) Y. N. Bubnov, M. E. Gurskii, I. D. Gridnev, A. V. Ignatenko, Y. A. Ustynyuk, V. I. Mstislavsky, *J. Organomet. Chem.* **1992**, *424*, 127; c) M. E. Gurskii, I. D. Gridnev, A. V. Geiderich, A. V. Ignatenko, V. I. Mstislavsky, Y. A. Ustynyuk, *Organometallics* **1992**, *11*, 4056; d) M. E. Gurskii, I. D. Gridnev, Y. V. Il'ichev, A. V. Ignatenko, Y. N. Bubnov, *Angew. Chem.* **1992**, *104*, 762; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 781; e) I. D. Gridnev, M. E. Gurskii, A. V. Ignatenko, Y. N. Bubnov, Y. V. Il'ichev, *Organometallics* **1993**, *12* 2487; f) I. D. Gridnev, M. E. Gurskii, Y. N. Bubnov in *Current Topics in the Chemistry of Boron*, Royal Society of Chemistry, Cambridge, **1994**, pp. 56–59; g) M. E. Gurskii, I. D. Gridnev, A. V. Buevich, Y. N. Bubnov, *Organometallics* **1994**, *13*, 4658.

[12] The reaction of $Fe(CO)_5$ with organoboranes was found to give complex mixtures of products (see R. Köster, M. Yalpani, *Angew. Chem.*, **1985**, *97*, 600; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 572). Apparently, a similar reaction takes place here: one equivalent of **14** acts as a carbonylation reagent and another equivalent as organoborane.

[13] P. L. Pauson, G. H. Smith, J. H. Valentine, *J. Chem. Soc. C* **1967**, 1061.

[14] H. Günther, R. Wenzl, W. Grimme, *J. Am. Chem. Soc.* **1969**, *91*, 3808.

[15] H. Günther, R. Wenzl, *Z. Naturforsch.* **1967**, *22B*, 389.

[16] H. Günther, M. Gorlitz, H.-H. Hinrichs, *Tetrahedron* **1968**, *24*, 5665.

[17] H. Günther, *NMR Spectroscopy. An Introduction*, Wiley, New York, **1980**.

[18] L. A. Paquette, *Acc. Chem. Res.* **1993**, *26*, 57.

[19] R. R. Ernst, G. Bodenhausen, A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, Clarendon, Oxford, **1987**.

[20] C. L. Perrin, T. J. Dwyer, *Chem. Rev.* **1990**, *90*, 935.

[21] a) C. A. Hoeger, A. D. Johnston, W. H. Okamura, *J. Am. Chem. Soc.* **1987**, *109*, 4690; b) J. D. Enas, G. Y. Shen, W. H. Okamura, *ibid.* **1991**, *113*, 3873; c) J. E. Baldwin, V. P. Reddy, *ibid.* **1988**, *110*, 8223.

[22] B. C. Carpenter, *J. Am. Chem. Soc.* **1995**, *117*, 6336.

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