NMR study of the sigmatropic [1,3]-B shift in 7,8-dipropyl-7-borabicyclo[4.2.2]deca-2,4,9-triene

*I. D. Gridnev,[a] M. E. Gurskii,[b] A. O. Krasavin,[c] and Yu. N. Bubnov[b]**

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: 007 (095) 135 5085*

[b]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: 007 (095) 135 5328. E-mail: bor@cacr.ioc.ac.ru*

[c]*The Higher Chemical Colledge of the Russian Academy of Sciences, 9 Miusskaya pl., 125047 Moscow, Russian Federation*

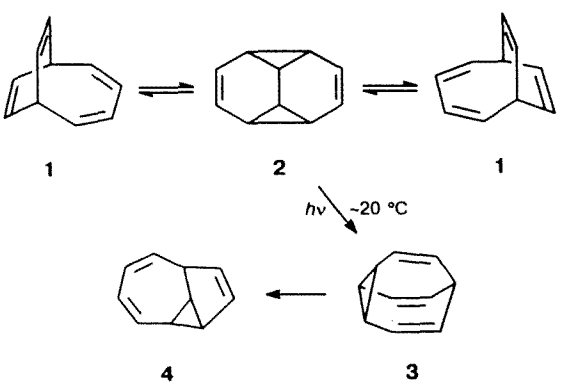
Activation parameters of the interconversion of geometric isomers **6a** and **6b** were determined by a complete lineshape analysis of the temperature-dependent ^{13}C NMR spectra of 7,8-dipropyl-7-borabicyclo[4.2.2]deca-2,4,9-triene (**6**). For the reaction **6a** → **6b**, $\Delta G^{\neq}_{298}$ = 52.2±0.1 kJ mol^{-1}, $\Delta H^{\neq}$ = 27.9±0.5 kJ mol^{-1}, $\Delta S^{\neq}$ = −82±8 J mol^{-1} K^{-1}; For the reaction **6b** → **6a**, $\Delta G^{\neq}_{298}$ = 52.6±0.1 kJ mol^{-1}, $\Delta H^{\neq}$ = 24.7±0.5 kJ mol^{-1}, $\Delta S^{\neq}$ = −93±10 J mol^{-1} K^{-1}. The interconversion of deuteropyridine complexes **9a** and **9b** proceeds *via* their dissociation, which indicates that the rearrangement of borane **6** occurs according to the [1,3]-B shift mechanism.

Key words: allylboranes, [1,3]-B shift; dynamic NMR; activation parameters.

Numerous thermal and photochemical rearrangements of hydrocarbons of the group $(CH)_{10}$ were studied in detail about 20 years ago.[1] Thus, the degenerate rearrangement occurring *via* tetracyclic compound **2** (Scheme 1) is characteristic of bicyclo[4.2.2]deca-2,4,7,9-tetraene (**1**) at high temperatures (see Ref. 2). Photolysis of tetraene **1** at room temperature results in bullvalene **3** which can be transformed into isobullvalene **4** (see Scheme 1) under certain conditions.[1] The chemoselectivity of reactions of this type[3] is in good agreement with the conservation rules of orbital symmetry.

Recently[4–6] we established that the main product of the rearrangement of cyclononatetraenyl(dipropyl)borane (**5**) at room temperature is 7,8-dipropyl-7-borabicyclo[4.2.2]deca-2,4,9-triene (**6**), which can be considered to be a boron-containing analog of hydrocarbon **1** (Scheme 2). This analogy was unambiguously confirmed[6] in studies on the chemical transformations of compound **6**. Treatment of the latter with methanol or acetone gave products *considerably differing in the structure of the carbon framework*. This work is dedicated to studying the dynamic properties of triene **6**.

Scheme 1



Scheme 2

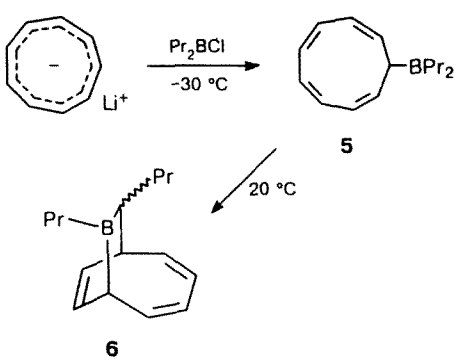


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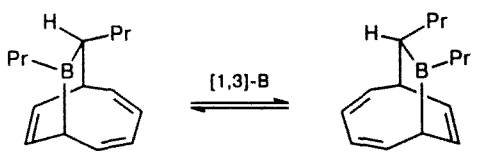
Table 1. Parameters of the NMR spectra (δ) of compounds **6a,b** and **9a,b**

Atom	6a		6b		9a		9b	
	δ ^{1}H	δ ^{13}C	δ ^{1}H	δ ^{13}C	δ ^{1}H	δ ^{13}C	δ ^{1}H	δ ^{13}C
C(1), H(1)	2.51	35.9	2.87	34.5	2.95	39.21	2.51	44.25
C(2), H(2)	6.02	142.1	5.83	140.9	5.98	137.19	6.42	142.20
C(3), H(3)	5.42	122.4	5.46	123.3	5.65	127.23	5.70	123.75
C(4), H(4)	5.72	128.4	5.66	128.5	5.65	126.82	5.60	127.15
C(5), H(5)	5.60	133.4	5.71	133.7	6.40	144.68	6.15	145.55
C(6), H(6)	2.79	36.8	2.77	36.3	2.23	36.07	2.25	36.95
C(8), H(8)	0.89	43.1	1.37	38.4	0.89	31.90	1.86	38.09
C(9), H(9)	5.65	128.3	5.95	130.8	6.12	128.64	6.22	130.63
C(10), H(10)	5.45	123.5	5.49	123.9	6.51	131.38	5.65	126.94

The temperature dependences of the ^{1}H and ^{13}C NMR spectra of compound **6** (Figs. 1 and 2) are evidence that this compound has dynamic properties. However, the exchange mechanism can not be drawn directly from temperature dependences. To this end, low-temperature two-dimensional NMR spectroscopy experiments were needed. The assignment of signals in the NMR spectra of both isomers (Table 1) was based on their two-dimensional ^{1}H–^{1}H COSY spectra and the ^{1}H–^{13}C correlation obtained at −70 °C. The cross-peaks observed in the two-dimensional ^{13}C–^{13}C EXSY spectra of compound **6** at the same temperature (Fig. 3) unambiguously correspond to the reversible interconversion of two geometric isomers **6a** and **6b** (Scheme 3).

Scheme 3



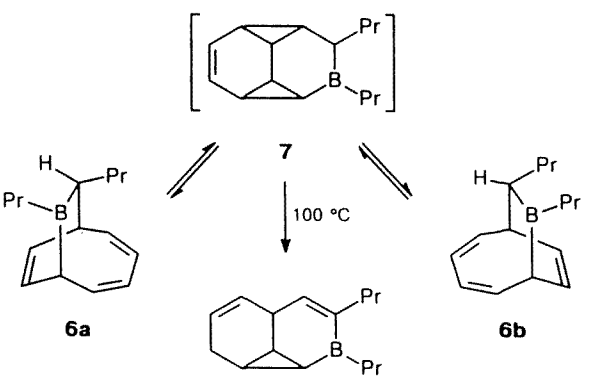
6a **6b**

To determine the activation parameters of the **6a** ⇌ **6b** rearrangement, we carried out a complete lineshape analysis for 15 temperature-dependent ^{13}C NMR spectra following the previously described procedure[7] of iterating all experimental spectra. In principle, all 15 pairs of signals can be used in calculations. However, for several reasons (strong temperature dependence of the line width, overlapping of several signals, a limited number of points) only the five most appropriate pairs of signals were chosen. Experimental and calculated spectra are presented in Fig. 4.

The following activation parameters of the rearrangement were obtained: for the reaction **6a** → **6b**, $\Delta G^{\neq}_{298}$ = 52.2±0.1 kJ mol^{-1}, $\Delta H^{\neq}$ = 27.9±0.5 kJ mol^{-1}, $\Delta S^{\neq}$ = −82±8 J mol^{-1} K^{-1}; for the reaction **6b** → **6a**, $\Delta G^{\neq}_{298}$ = 52.6±0.1 kJ mol^{-1}, $\Delta H^{\neq}$ = 24.7±0.5 kJ mol^{-1}, $\Delta S^{\neq}$ = −93±10 J mol^{-1} K^{-1}.

Two possible mechanisms of the rearrangement observed can be considered. The most evident path of the **6a** ⇌ **6b** interconversion is the [1,3]-B shift which is always observed for allylic type triorganoboranes.[8] The first [1,3]-B shift transforms compound **6a** into **6b** while the second one leads to the reverse reaction (see Scheme 2). However, the above-mentioned similarity between borane **6** and hydrocarbon **1** allows one to assume that the interconversion of isomers **6a** and **6b** proceeds analogously to the degenerate rearrangement in compound **1** (see Scheme 1), which includes the intermediate formation of tetracyclic borane **7** (Scheme 4). This mechanism is supported by the appearance of vinyl borane **8** when compound **6** is heated to 100 °C for 1 h.[4,6] The latter reaction likely proceeds *via* the intermediate formation of tetracycle **7**. Compound **8** can also be obtained after prolonged ageing of borane **6** at room temperature, which is evidence for the presence of a small equilibrium amount of tetracyclic product **7** (see Scheme 4).

Scheme 4



6a **6b**

8

To choose between the two possible mechanisms of the interconversion of isomers **6a** and **6b**, we studied the NMR spectra of **6** in deuteropyridine. As is known,

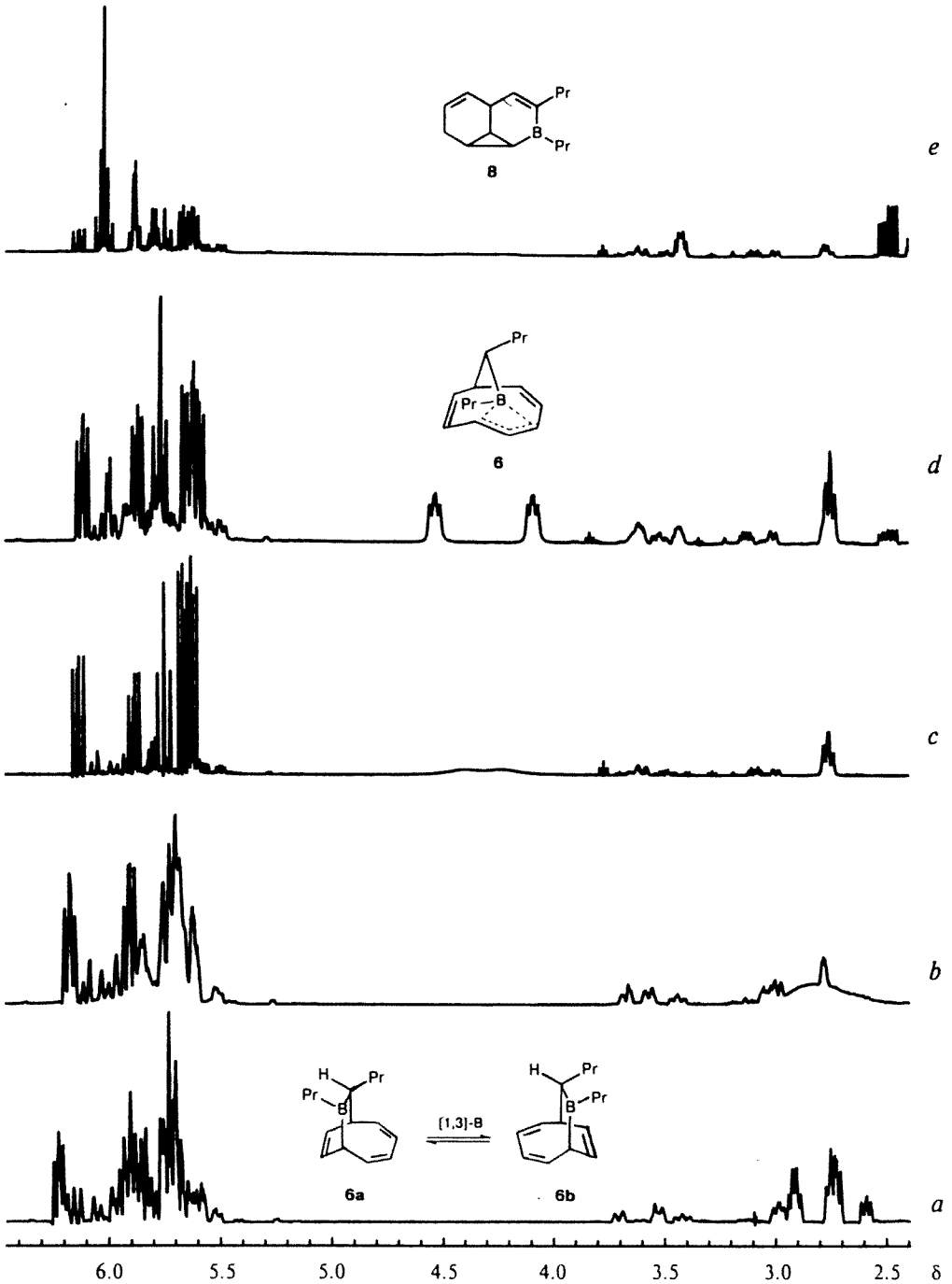


Fig. 1. ^{1}H NMR spectra (400 MHz, CD_2Cl_2) of compound **6** at various temperatures: T/K = 183 (*a*), 243 (*b*), 303 (*c*), 343 (*d*), and 298 (*e*) after heating at 373 K for 1 h (mainly contains the signals of the thermolysis product **8**).

the boron atom is coordinated by amines saturating its 2p-atomic orbitals which makes the [1,3]-B shift impossible.[8] The experiments showed that two sets of signals corresponding to two different complexes with deuteropyridine, **9a** and **9b**, are observed in the ^{1}H and ^{13}C NMR spectra of compound **6** in deuteropyridine. At the same time, four isomers, **9a—d**, can be formed (Scheme 5) because of the fact that the boron atom in complexes **9** is tetracoordinated. Using two-dimensional correlation NMR spectroscopy, we carried out the complete assignment of the signals in the spectra of two isomeric complexes **9a,b** (see Table 1). ^{1}H—^{1}H EXSY experiments at 298 K (Fig. 5) showed that an equilibrium exists between isomers **9a** and **9b** analogous to that observed for free boranes **6a,b** at low temperatures, *i.e.*, complexes **9a** and **9b** differ in the configura-

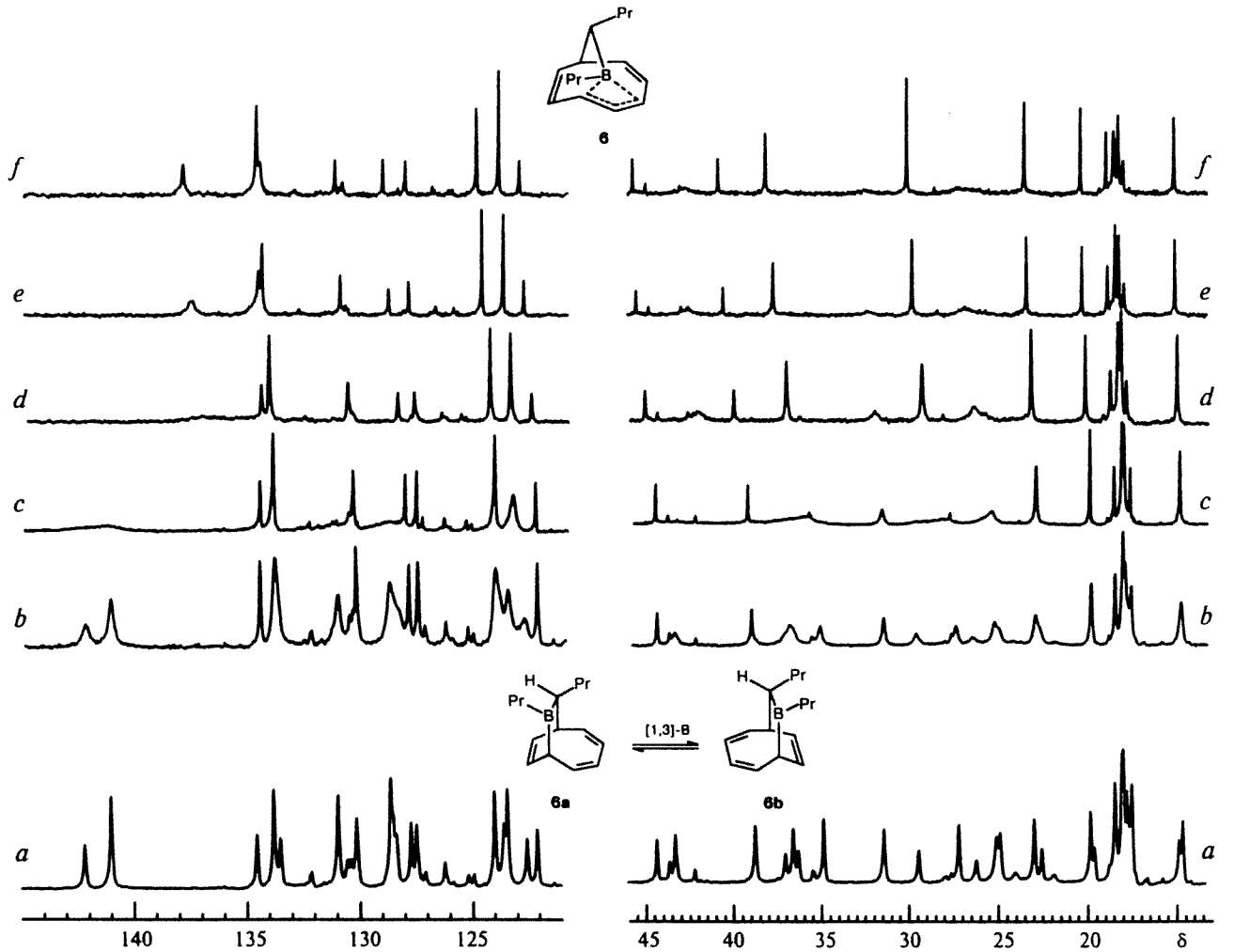
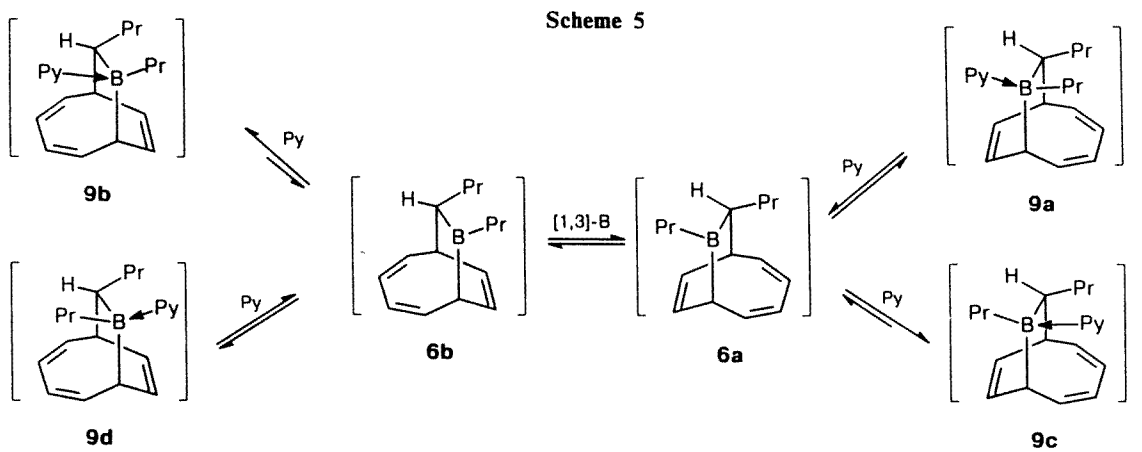


Fig. 2. ^{13}C NMR spectra (50 MHz, CD_2Cl_2) of compound **6** at various temperatures: T/K = 203 (*a*), 223 (*b*), 243 (*c*), 273 (*d*), 303 (*e*), and 323 (*f*).

tion of the C(8) atom (the numeration of atoms is given in Figs. 3—5).

The fact that only signals of complexes **9a** and **9b** (but not **9c** and **9d**) are observed in the NMR spectra is likely associated with the relative thermodynamic instability of the complexes **9c** and **9d**, which is due to steric interaction between the pyridine cycle and the propyl group at the C(8) atom.

Scheme 5



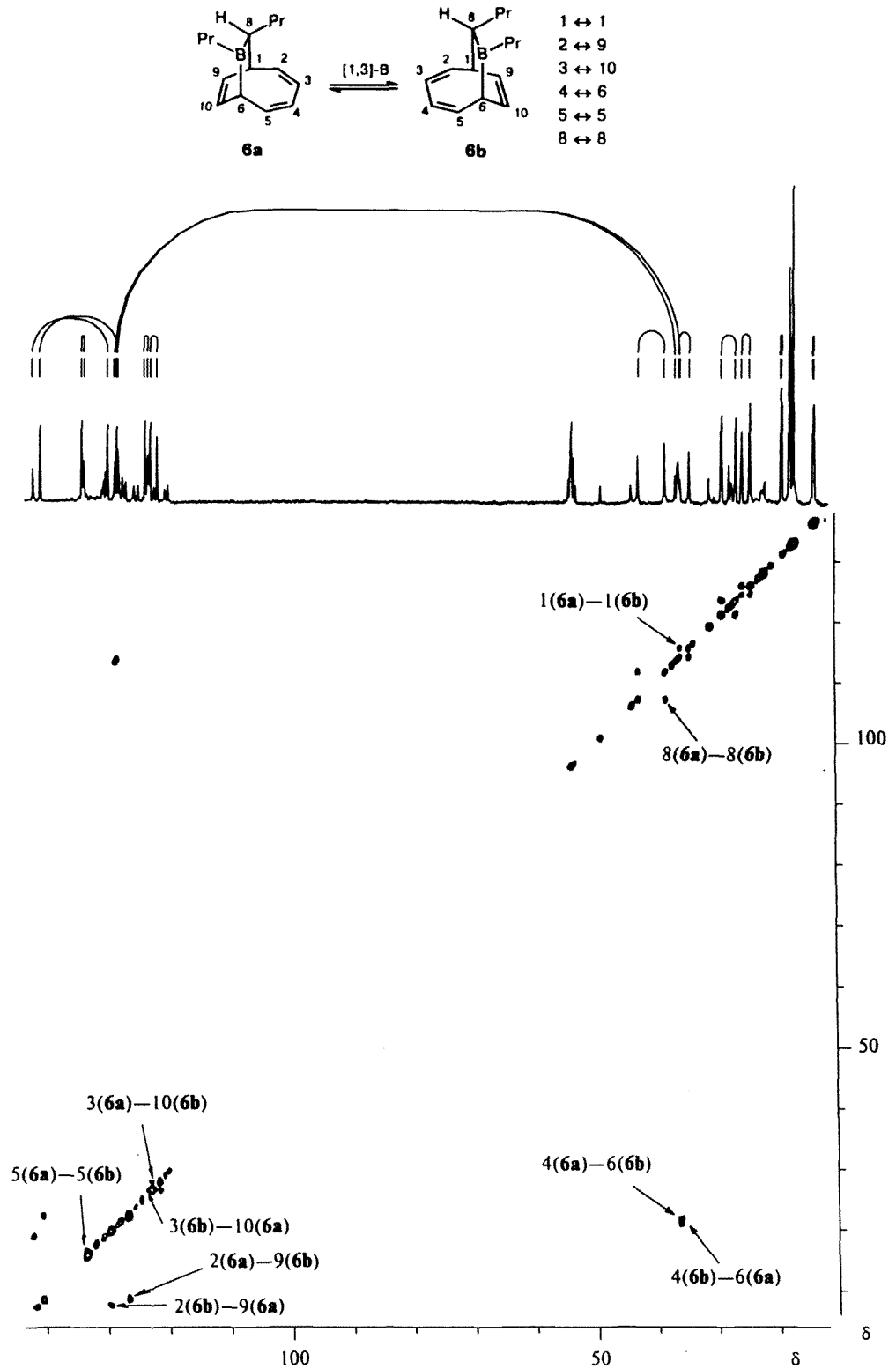


Fig. 3. $^{13}C-^{13}C$ EXSY NMR spectrum (100 MHz, CD_2Cl_2) of compound **6** at 203 K. The size of the experimental spectrum is 1024×512; after Fourier transformation it is 1024×1024; mixing duration is 0.3 s. Cross-peaks 5(**6a**)—5(**6b**) and 3(**6b**)—10(**6a**) as well as certain cross-peaks between the propyl group signals of **6a** and **6b** are not resolved from the diagonal peaks. Upfield cross-peaks not mentioned above are related to intersignal exchange between the propyl groups in isomers **6a** and **6b**.

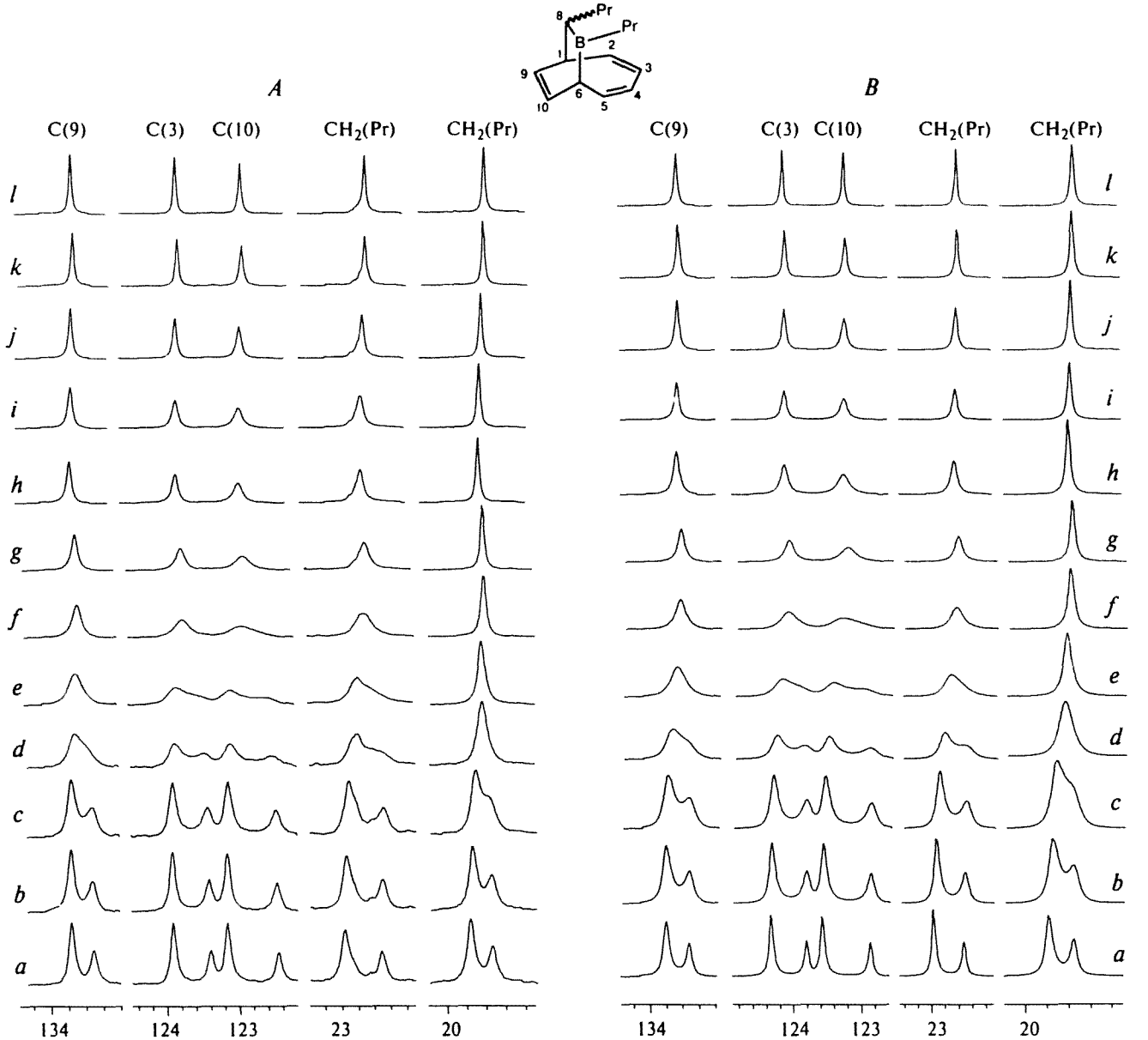


Fig. 4. Experimental (*A*) and calculated (*B*) line shapes of the signals in the ^{13}C NMR spectra of compound **6** at various temperatures: T/K = 190 (*a*), 198 (*b*), 203 (*c*), 210 (*d*), 217 (*e*), 222 (*f*), 229 (*g*), 232 (*h*), 238 (*i*), 242 (*j*), 247 (*k*), and 257 (*l*).

The **9a** → **9b** transformation (as well as the reverse reaction) proceeds *via* three successive steps: dissociation of the complex with isolation of the corresponding free borane **6a**, the **6a** → **6b** rearrangement, and finally, formation of complex **9b**. It is obvious that the rate of the whole transformation is limited by the first step (dissociation of complex **9a** with the formation of **6a**), since the rate of the second step at 298 K must be fairly high as it results in the appearance of an averaged NMR spectrum (see above). At the same time, the rate of the third step is much higher than the dissociation rate (at least by a factor of several tens since no signals of compound **6** are observed in the NMR spectra, and taking into account the sensitivity of the method, the constant of the complex stability $K = k_1/k_3 \geq 20$).

Thus, one can draw the conclusion that the rearrangement that changes the configuration of the C(8) atom proceeds only in the case of free borane **6** and is not observed for the pyridine complex **9**. Therefore, the presence of an unoccupied orbital at the boron atom is of fundamental importance in the interconversion of isomers, which points to the fact that the rearrangement of compound **6** follows the [1,3]-B shift mechanism.

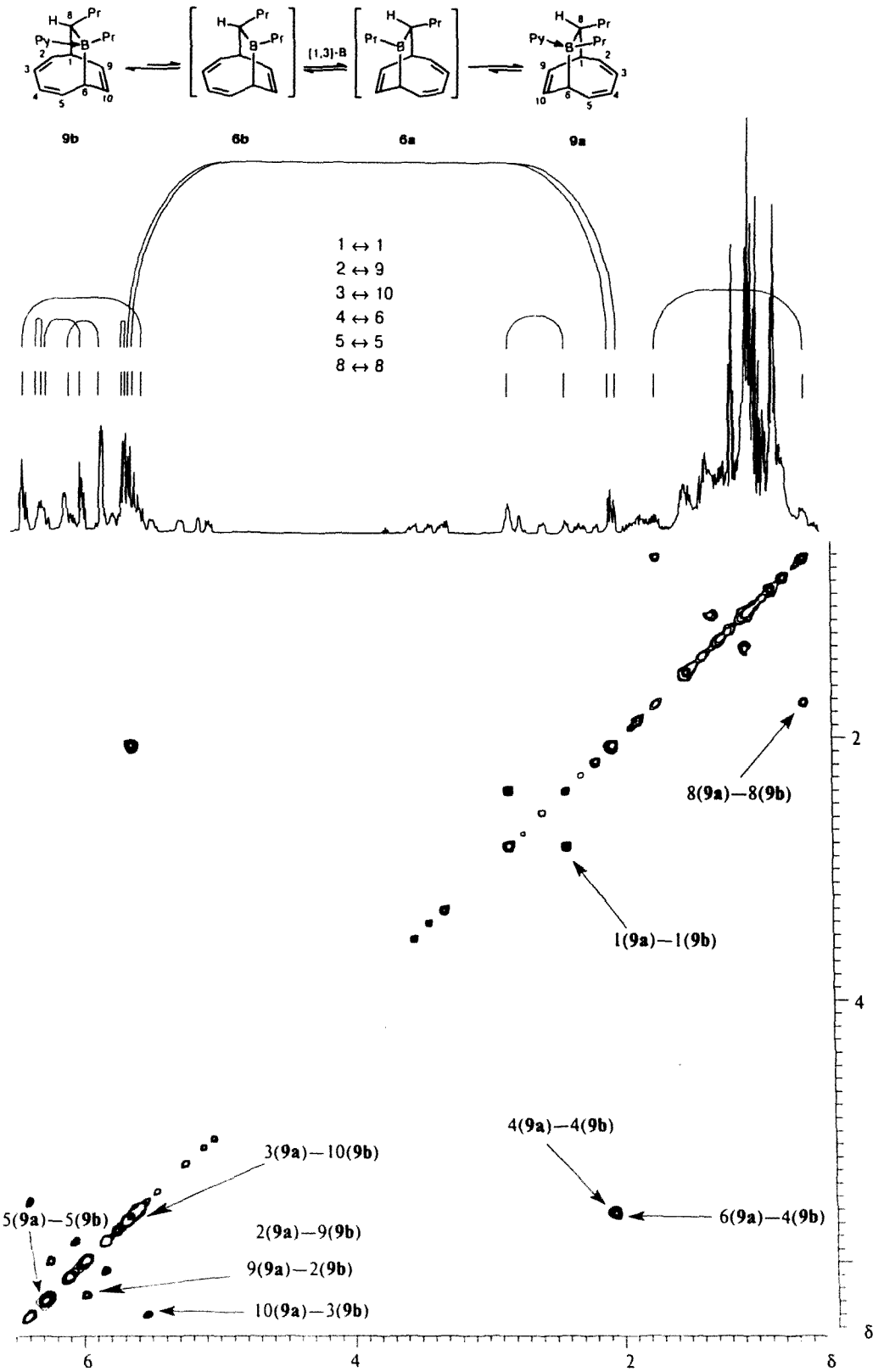
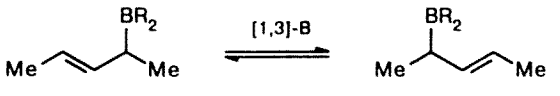


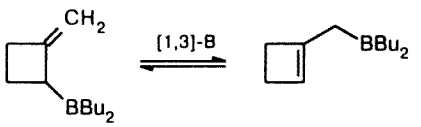
Fig. 5. $^1H-^1H$ EXSY NMR spectrum (400 MHz, pyridine-d_5) of complex **9** at 298 K. The size of the experimental spectrum is 1024×512; after Fourier transformation it is 1024×1024; mixing duration is 1 s. Cross-peaks 5(**9a**)—5(**9b**) and 3(**9a**)—10(**9b**) are not resolved from the diagonal peaks. Upfield cross-peaks not mentioned above are related to the intersignal exchange between the propyl groups in isomers **9a** and **9b**.

Scheme 6



10a **10b**

$\Delta G^{\ddagger}_{298}$ = 54.6 kJ mol^{-1}



11a **11b**

$\Delta G^{\ddagger}_{298}$ (**11a** → **11b**) = 53.8 kJ mol^{-1}
$\Delta G^{\ddagger}_{298}$ (**11b** → **11a**) = 52.8 kJ mol^{-1}

6a $\overset{[1,3]\text{-B}}{\rightleftharpoons}$ **6b**

$\Delta G^{\ddagger}_{298}$ (**6a** → **6b**) = 52.6 kJ mol^{-1}
$\Delta G^{\ddagger}_{298}$ (**6b** → **6a**) = 52.2 kJ mol^{-1}

It is of interest that the activation barrier of the [1,3]-B shift in the bicyclic allylic type triorganoborane **6** (measured in the present work) virtually coincides with the activation barriers of [1,3]-B shift in molecules **10** and **11**, which also contain an α-alkyl substituent[9,10] (Scheme 6). The activation barriers for all three compounds (**6**, **10**, and **11**) are substantially lower than those for nonbranched (at the α-position) allylboranes ($\Delta G^{\ddagger}_{298}$ = 52 to 54 kJ mol^{-1} and 62 to 77 kJ mol^{-1},[9] respectively). Therefore, one can state that the presence of an alkyl substituent at the α-position of an allylic type triorganoborane leads to an appreciable acceleration of the [1,3]-B shift.

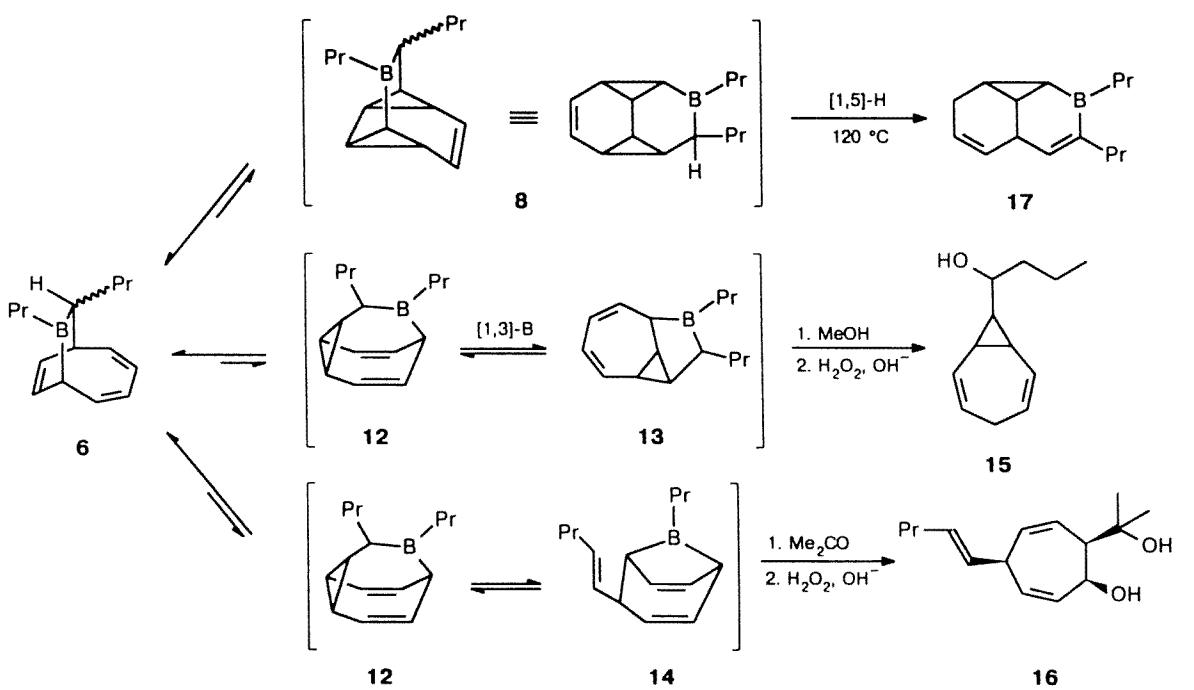
It should be noted that the [1,3]-B shift is not the only dynamic process proceeding in the molecule of borane **6**. The chemical reactions of this compound are evidence that it has much more complicated dynamic properties. The selective formation of products fundamentally differing in their carbon frameworks in reactions of the triene **6** with methanol (*only* carbinol **15** is obtained) and acetone (diol **16** is *the only* product) as well as in thermolysis (*only* compound **17** is obtained) points to the fact that borane **6** reversibly coexists with the minor tautomeric forms **8**, **12**—**14** (Scheme 7).[6] However, our attempts at direct detection of these compounds in the NMR spectra of borane **6** failed. This might be explained by a relatively high thermodynamic stability of compound **6** (which was already mentioned above) as compared to other valent tautomers.

Experimental

All experiments were carried out under an atmosphere of dry argon using absolute solvents. The synthesis of compound **6** has been described previously.[4,5] The NMR spectra were recorded on Bruker AC-200P and AMX-400 spectrometers.

To analyze the lineshape, the corresponding intervals were chosen from the experimental ^{13}C NMR spectra of compound **6** at various temperatures, and the number of points was reduced in such a way that each spectrum used in calculations contained no more than 1K points.

Scheme 7



A standard NOESYPH procedure modified for proton decoupling spectra was used to obtain the $^{13}C-^{13}C$ EXSY NMR spectra.

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References

1. L. T. Scott and M. J. Jones, *Chem. Rev.*, 1972, **72**, 181.
2. (a) M. Jones, Jr., S. D. Reich, and L. T. Scott, *J. Am. Chem. Soc.*, 1970, **92**, 3118; (b) M. Jones, Jr., S. D. Reich, L. T. Scott, and L. E. Sullivan, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 644.
3. (a) R. B. Woodward and R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 781; (b) C. W. Spangler, *Chem. Rev.*, 1976, **76**, 187.
4. M. E. Gurskii, I. D. Gridnev, A. V Buevich, and Yu. N. Bubnov, *Organometallics*, 1994, **13**, 465.
5. I. D. Gridnev, M. E. Gurskii, A. V. Buevich, and Yu. N. Bubnov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 117 [*Russ. Chem. Bull.*, 1996, **45**, 107 (Engl. Transl.)].
6. I. D. Gridnev, M. E. Gurskii, A. V. Buevich, T. V. Potapova, and Yu. N. Bubnov, *J. Org. Chem.*, 1996, **61**, 3514.
7. R. Laatikainen, *J. Magn. Reson.*, 1985, **64**, 375.
8. I. D. Gridnev, M. E. Gurskii, and Yu. N. Bubnov, in *Current Topics in the Chemistry of Boron*, Royal Society of Chemistry, Cambridge, 1994, 56.
9. V. S. Bogdanov, Yu. N. Bubnov, M. N. Bochkareva, and B. M. Mikhailov, *Dokl. Akad. Nauk SSSR*, 1971, **201**, 605 [*Dokl. Chem.*, 1971, **201** (Engl. Transl.)].
10. I. D. Gridnev, M. E. Gurskii, and Yu. N. Bubnov, *Organometallics*, 1996, **14**, 3696.

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