Chemical Behavior of 9-Cyclopentyl-9-borabarbaralane. Diverse Chemoselectivity in the Reactions with Methanol and Other Nucleophiles†

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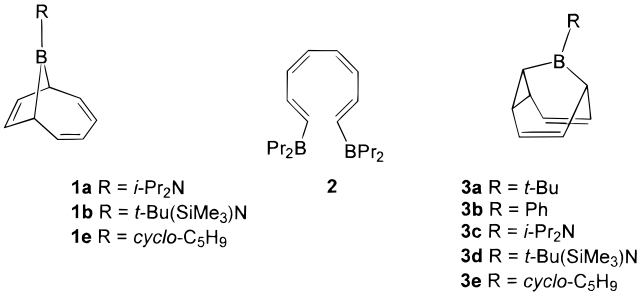
The 9-cyclopentyl-9-borabarbaralane (**3e**) was obtained by the reaction of $K_2C_8H_8$ with *cyclo*-C_5H_9-BCl_2. Upon reaction of **3e** with acetone, acetaldehyde, ethoxyacetylene, trideuterioacetonitrile, and acetic acid, only products derived from 9-cyclopentyl-9-borabicyclo[4.2.1]nona-2,4,7-triene (**1e**) were obtained. On the other hand, by methanolysis of **3e**, the boronic ester **17** was formed. The tetracyclic borane **18** is proposed as the intermediate. Possible reasons for this unusual chemical behavior are discussed.

Introduction

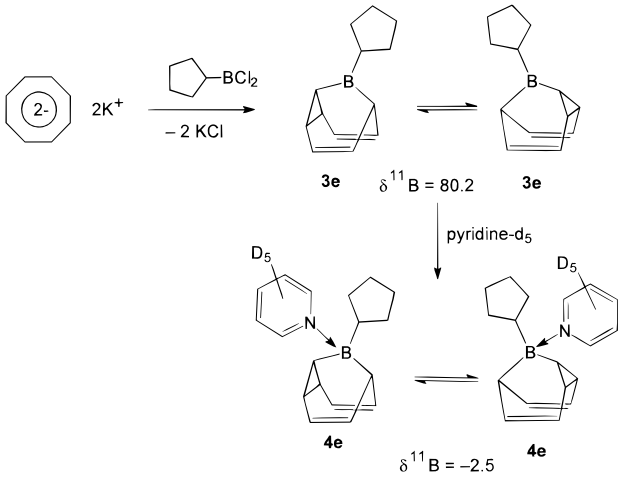
Products with different carbon frameworks have been recently obtained by treatment of the cyclooctatetraenide dianione with boron halides. The bicycle **1a** was obtained by the reaction of $K_2C_8H_8$ with *i*-Pr_2NBCl_2 and characterized by X-ray diffraction.[1] On the other hand, the reaction of $K_2C_8H_8$ with 2 equiv of Pr_2BCl by electrocyclic ring opening gave compound **2** in quantitative yield.[2] Furthermore, it was shown that reactions of MgC_8H_8 with several organyldihaloboranes and (diorganylamino)dihaloboranes, RBX_2, led to borabarbaralanes **3** as the thermodynamically stable products. Borabarbaralanes are formed either directly (R = Ph, X = Cl (**3b**) or R = *t*-Bu, X = F (**3a**)) or obtained either by photolysis or thermolysis of the initially formed bicycles **1a,b** (**3c** and **3d**, respectively) (Scheme 1).[3]

We report here the borabarbaralane **3e** (R = cyclopentyl), which in the reactions with acetone, acetaldehyde, acetonitrile, ethoxyacetylene, and acetic acid gives products apparently formed from the 9-cyclopentyl-9-borabicyclo[3.2.1]nona-2,4,7-triene (**1e**, R = cyclopentyl). In the reaction of **3e** with methanol, however, the structure of the product **17** requires the formation of another intermediate.

Scheme 1. Compounds 1−3



Scheme 2. Synthesis of 3e and 4e



Results

Synthesis and NMR spectra of 3e. The compound **3e** was prepared by the reaction of $K_2C_8H_8$ with *cyclo*-$C_5H_9BCl_2$ in hexane at −50 °C (Scheme 2). The NMR analysis of the reaction mixture obtained after filtration and removal of the solvents indicated the clean formation of **3e** (a small amount of cyclooctatetraene was present as the only impurity). Distillation afforded pure **3e** in a 58% yield. The structure of borabarbalane **3e** was easily deduced from its characteristic ^1H and ^{13}C spectra (C_{2v} symmetry at room temperature due to fast Cope rearrangements).[3]

Slow-exchange ^1H and ^{13}C NMR spectra were obtained at 198 K. Figure 1 depicts the ^1H 2D EXSY spectrum of **3e** taken at 208 K, showing the intramolecular Cope rearrangement resulting in the exchange between H-4 and H-8, as well as between H-1,7 and H-3,5. The rate constant of the Cope rearrangement of **3e** at 208 K is

† Dedicated to Professor Dr. Heinrich Nöth on the occasion of his 70th birthday.

(1) Maringgele, W.; Stalke, D.; Heine, A.; Meller, A.; Sheldrick, G. M. *Chem. Ber.* **1990**, *123*, 489−490.

(2) Gurskii, M. E.; Geiderikh, A. V.; Ignatenko, A. V.; Bubnov, Yu. N. *Metalloorg. Khim.* **1991**, *4*, 202−203.

(3) Herberich, G. E.; Marx, H.-W.; Moss, S.; Schleyer, P. v. R.; Wagner, T. *Chem. Eur. J.* **1996**, *2*, 458−461.

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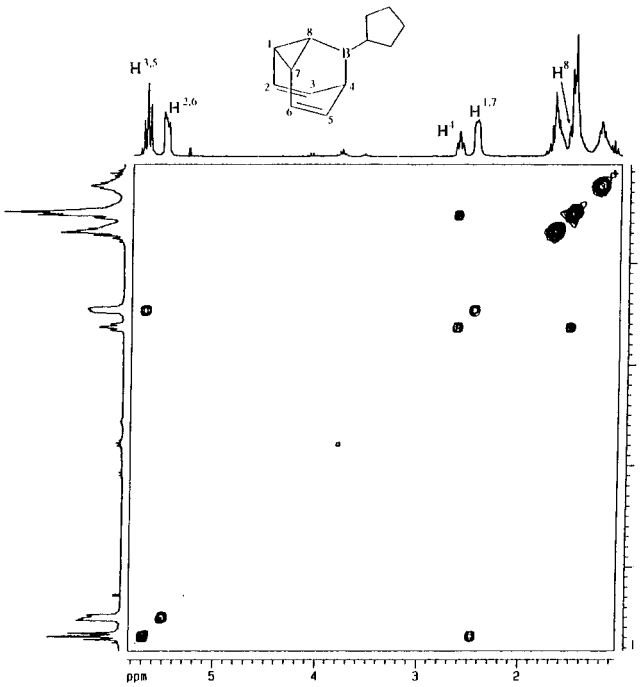
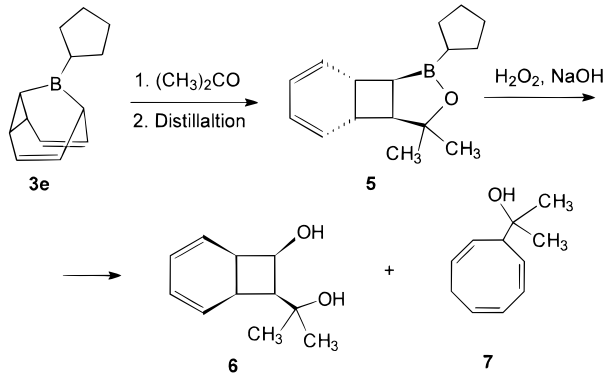


Figure 1. 2D $^1H-^1H$ EXSY spectrum of compound **3e** (250 MHz, $CDCl_3-CD_2Cl_2-CCl_4$, 208 K), mixing time 0.5 s, initial delay 1s.

Scheme 3. Reaction of 3e with Acetone

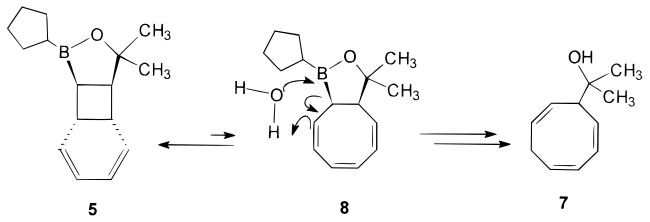


1.1 s^{-1} ($\Delta G^{\ddagger}(208) = 50.2 \pm 0.5$ kJ mol^{-1}); it was obtained by the volume integration of the diagonal and cross-peaks between H-1,7 and H-3,5.[4] In the deuteriopyridine complex **4**, the tetracoordination at the 9-B atom leads to considerable acceleration of the Cope rearrangement;[3,5] thus, all signals in the averaged ^1H and ^{13}C NMR spectra were observed at room temperature.

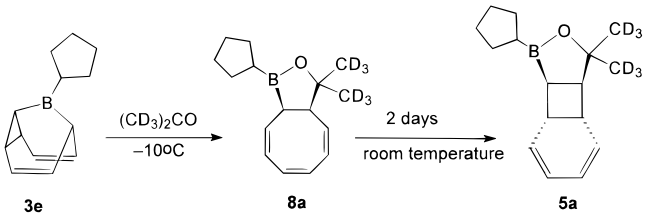
Reactions of 3e with Carbonyl Compounds and Acetic Acid. The reaction of **3e** with acetone proceeds readily at −10 °C. After distillation, the boronic ester **5** (Scheme 3) was the only product. The structure of **5** was unambiguously assigned by 2D correlation NMR spectroscopy. The oxidation of **5** with alkaline H_2O_2 afforded a mixture of the two compounds **6** and **7** in a 5:1 ratio (see the stereochemical assignment below).

The diol **6** is the expected product of the oxidation of **5**, whereas the alcohol **7** cannot be formed directly from

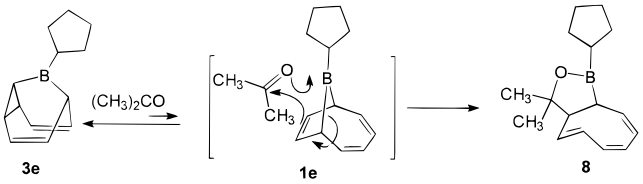
Scheme 4. Mechanism of the Formation of 7



Scheme 5. Reaction of 3e with Deuterioacetone



Scheme 6. Mechanism of the Formation of 8



5. Its presence in the reaction mixture after oxidation indicates the existence of two valence tautomers: the bicyclooctadiene **5** and the cyclooctatriene **8** (Scheme 4). Due to the presence of an allylboron fragment in **8**, its hydrolysis (to the alcohol **7)** proceeds much faster than its oxidation. Compound **5**, without an allylboron fragment, is stable to basic hydrolysis and exclusively gives the oxidation product **6**.

The structure of the carbon skeleton of **5** differs remarkably from that of the starting borane **3e**. To clarify the mechanism of the formation of **5** in the reaction of the borabarbaralane **3e** with acetone, we reacted **3e** with deuterioacetone. The NMR spectra proved that upon addition of deuterioacetone (in excess) to **3e** at −10 °C, the boronic ester **8a** is the only reaction product. However, **8a** rearranges completely to **5a** within 2 days at ambient temperature (Scheme 5).

Since the allylboration of carbonyl compounds proceeds with an allylic rearrangement,[6] it can be concluded that the direct precursor of **8** is 9-cyclopentyl-9-borabicyclo-[4.2.0]nona-2,4,7-triene (**1e**) (Scheme 6).

Reactions of the borabarbaralane **3e** with acetaldehyde, ethoxyacetylene, trideuterioacetonitrile, and tetradeuterioacetic acid proceed analogously to give only products derived from the bicyclic borane **1e** (Scheme 7).

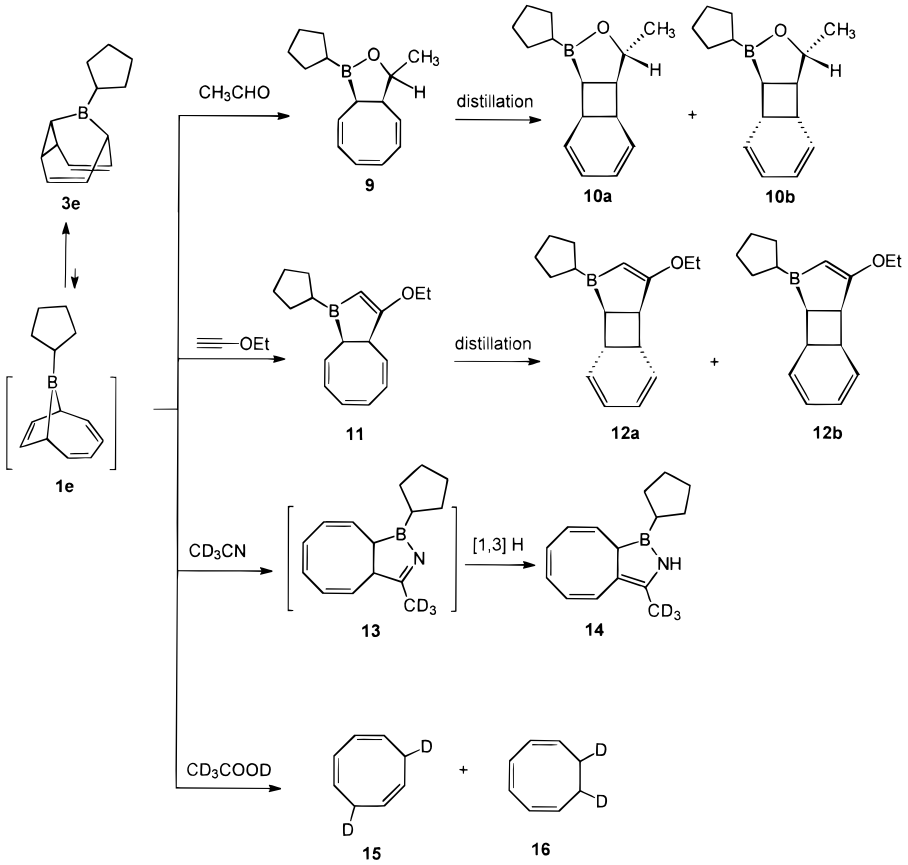
In the reactions of **3e** with acetaldehyde and ethoxyacetylene, the initial formation of the cyclooctatrienes **9** and **11** is detected by NMR. After distillation or prolonged storage at room temperature, the boronic ester **9** converts to an equilibrium mixture of the compounds **9**, **10a**, and **10b** in a ratio of 1:15:3. The borane **11** under the same conditions gives a mixture of the isomers **12a,b** in 4:1 ratio.

The reaction of **3e** with trideuterioacetonitrile readily proceeds at −30 °C, yielding the bicyclic compound **14**,

(4) Perrin, C. L.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935−967.
(5) (a) Anastassien, A. G.; Reichmanis, E.; Winston, A. E. *Angew. Chem.* **1976**, *88*, 382−383. (b) Paquette, L. A.; Jacobsson, U.; Oku, M. *J. Chem. Soc., Chem. Commun.* **1975**, 115−116. (c) Märkl, G.; Alig, B. *Tetrahedron Lett.* **1983**, *24*, 3981−3984.

(6) Mikhailov, B. M.; Bubnov, Y. N. *Organoboron Compounds in Organic Synthesis*; Harwood: Chur, London, New York, 1984.

Scheme 7. Reactions of 3e with Acetaldehyde, Ethoxyacetylene, Trideuterioacetonitrile, and Tetradeuterioacetic Acid



which apparently results from a [1,3] H shift in the intermediate **13**. However, all attempts to detect the initial formation of **13** failed. The driving force for the rearrangement of **13** into **14** probably is the increased thermodynamic stability of the latter due to a more favorable donor−acceptor interaction between the nitrogen and boron atoms.

The reaction of **3e** with tetradeuterioacetic acid carried out at 0 °C gave a mixture of the deuterated cyclooctatrienes **15** and **16** in a 4:1 ratio. These hydrocarbons must be formed also via **1e** as the intermediate, as the expected products of the acidolysis of **3e** itself, viz. bicyclo[5.1.0]octadienes, rearrange into cyclooctatrienes only at temperatures above 200 °C.[7]

Attempts To Detect 1e in the NMR Spectra. Due to the results described previously, it must be concluded that **1e** is a minor valence tautomer of **3e**, as assumed in similar cases;[8] therefore, we attempted to detect **1e** in equilibrium with **3e** in the NMR spectra.

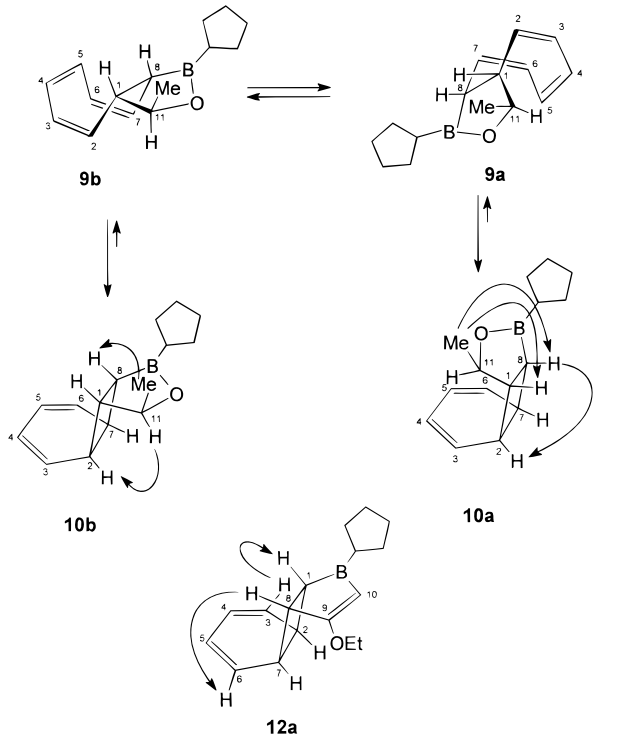
An upper limit for the concentration of **1e** in the equilibrium with **3e** could be estimated from a detailed analysis of the 2D EXSY spectra at low temperatures and the line shape of the temperature-dependent ^{13}C NMR spectra. Even at low temperatures, the equilibrium between **3e** and **1e** must be established rapidly so that the observed chemoselectivity results. Therefore, the exchange cross-peaks in the 2D EXSY spectra must appear if the concentration of **1e** is sufficient. Previously, we have observed intensive exchange cross-peaks for two tautomers with the concentration of the minor tautomer as low as 4%.[9] However, no indication of the presence of **1e** was found in the ^{1}H 2D EXSY spectra of **3e** from 198 to 225 K, the mixing time varying between 0.2 and 1 s. Thus, it can be concluded that the equilibrium concentration of **1e** at low temperatures does not exceed 1%. On the other hand, the equilibrium concentration of **1e** might increase at high temperatures due to a more favorable entropy factor. In this case, the positions of the averaged signals in the ^{13}C NMR spectra should differ from the mean values of the low-temperature chemical shifts of the exchanging atoms. However, our experimental findings indicate that this is not the case. The chemical shifts of the carbons C(1,7) and C(3,5) at 208 K are 36.1 and 129.5 ppm, respectively (in toluene-d_8). The chemical shift of the averaged signal at 343 K is 82.4 ppm, which corresponds to the calculated mean value (82.8). This signal would exhibit a significant low-field shift if an appreciable concentration of **1e** were in equilibrium with **3e** at high temperatures. Thus, it can be concluded that in the temperature interval between 198 and 343 K less than 1% of **1e** is present in the equilibrium with **3e**.

Stereochemistry of the Tricyclic Boron Heterocycles 5, 10, and 12. The cyclooctatrienes **8**, **9**, and **11** are *cis*-isomers, as deduced from the structure of the

(7) Doering, W. v. E.; Roth, W. R. *Tetrahedron* **1963**, *19*, 715−737.
(8) (a) Paquette, L. A. *Tetrahedron* **1975**, *31*, 2855−2894. (b) Lewis, C. P.; Brookhart, M. *J. Am. Chem. Soc.* **1975**, *97*, 651−664. (c) Larrabee, R. B.; Dowden, B. F. *Tetrahedron Lett.* **1970**, 915−918. (d) Asche III, A. J. *Ibid.* **1970**, 2105−2108. (e) Rigby, S. S.; Gupta, H. K.; Werstiuk, N. H.; Bain, A. D.; McGlinchey, M. J. *Polyhedron* **1995**, *14*, 2787−2800.

(9) Gridnev, I. D.; Gurskii, M. E.; Bubnov, Yu. N. *Organometallics* **1996**, *15*, 3696−3702.
(10) Cotton, F. A.; Deganello, G. *J. Am. Chem. Soc.* **1973**, *95*, 396−402.

Scheme 8. Conformational and Tautomeric Equilibria for 9a,b and 10a,b and the Results of NOE Experiments



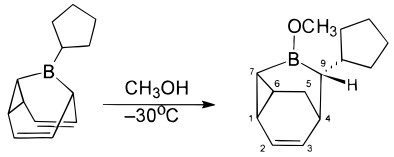
initial bicyclic borane **1e** (e.g., Scheme 6). Electrocyclic ring closure leading to the tricyclic compounds **5**, **10**, and **12** can also result only in products with *cis*-conjugated cyclohexadiene and cyclobutane rings. However, depending on the conformation of the starting cyclooctatriene, either exo or endo isomers of the compounds **5**, **10**, and **12** can appear (e.g., Scheme 8).

The stereochemistry of both isomers **10a** and **10b** was established by the 2D NOESYTP spectrum of their mixture. The long-range NOE's observed in this experiment sufficient for the stereochemical assignment are shown in Scheme 8. Since a minor amount of **9** is also detected in the reaction mixture after distillation, an equilibrium between **9**, **10a**, and **10b** is observed, and the concentrations of **10a** and **10b** accordingly reflect their relative thermodynamic stabilities. The endo isomer **10a** appears to be more stable than the exo isomer **10b**. Two other isomers with the alternative orientation of the methyl group are not observed; therefore, the reaction of **1e** with acetaldehyde proceeds stereoselectively.

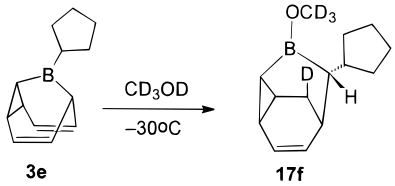
Unfortunately, three of the four signals of the cyclobutane protons in the ^{1}H NMR spectrum of compound **5** overlap strongly and the stereochemical assignment by NOESY experiments is hampered. Nevertheless, as only one isomer of **5** is observed in the NMR spectra, and the obvious sterical hindrance in the endo isomer is caused by the second methyl group (as compared to **10a**), **5** must be the exo isomer.

The configuration of the diol **6** was assigned on the basis of the existence (confirmed by a COSY spectrum) of the long-range couplings, ^4J(H-1,H-7) = 1.4 Hz and ^4J(H-6,H-8) = 1.2 Hz, and NOE data. The configurations of the boronic ester **5** and the product of its oxidation **6** are different. This can be explained, however, by the

Scheme 9. Reaction of 3e with Methanol



Scheme 10. Reaction of 3e with Deuteriomethanol



cyclooctatriene−bicyclooctadiene and the conformational equilibria discussed earlier.

The structure of the main isomer **12a** was deduced from the long-range NOE's between H-1 and H-3 and between H-6 and H-8 (Scheme 8).

Bicyclo[4.2.0]diene tautomers strongly predominate in all three organoboron compounds **5**(**8**), **9**(**10**), and **11**(**12**). This is in accord with the previous observation of the stabilizing effect of the five-membered ring fusion on the diene tautomer in the cyclooctatriene−bicyclooctadiene equilibrium.[10,11]

Reactions of 3e with Methanol and Deuteriomethanol. By treatment of **3e** with an excess of methanol at −30 °C, the compound **17e** was obtained as the only product (Scheme 9).

The structure of the boronic ester **17e** was unambiguously proved by 2D NMR correlation experiments. Figure 2 shows a phase-sensitive double-quantum filtered ^{1}H−^{1}H COSY spectrum of **17e** at 500 MHz. The HMQC spectrum shows that the two high-field doublets of doublets at 0.43 and 0.79 ppm both originate from the carbons adjacent to the boron atom (broad resonances in the ^{13}C NMR spectrum). The proton δ 0.43 ppm together with both its coupling partners (δ 1.54 and 1.64 ppm) correspond to three CH units of a cyclopropane. This can be seen from the multiplicity and the characteristic values of the $^1J_{C-H}$ observed for the signals of the corresponding carbon atoms in the undecoupled ^{13}C NMR spectrum (~150 Hz for C−B, 168.7 and 165.3 Hz, respectively). These additional facts are sufficient for the unambiguous elucidation of the structure of **17e** from the spectrum depicted in Figure 2. The orientation of the proton H-9 follows from its long-range coupling with exo-H-5. Furthermore, this conclusion is supported by the unusually low chemical shift of H-9 (δ 0.5), which is explained by the orientation of H-9 across the shielding zone of the double bond.

The second proton at C-5 originates from methanol, as proved by the reaction of **3e** with deuteriomethanol, which gave **17f** (Scheme 10).

To explain the clean formation of **17e** from **3e** and methanol, it is necessary to assume that **18e** with a *cis*-bishomobenzene framework can be formed from **3e**

(11) Graham, C. R.; Scholes, G.; Brookhart, M. *J. Am. Chem. Soc.* **1977**, *99*, 1180−1188.

(12) (a) Gurskii, M. E.; Gridnev, I. D.; Buevich, A. V.; Bubnov, Yu, N. *Organometallics* **1994**, *13*, 4658−4660. (b) Gridnev, I. D.; Gurskii, M. E.; Bubnov, Yu. N. *Russ. Chem. Bull.* **1996**, *45*, 107−114.

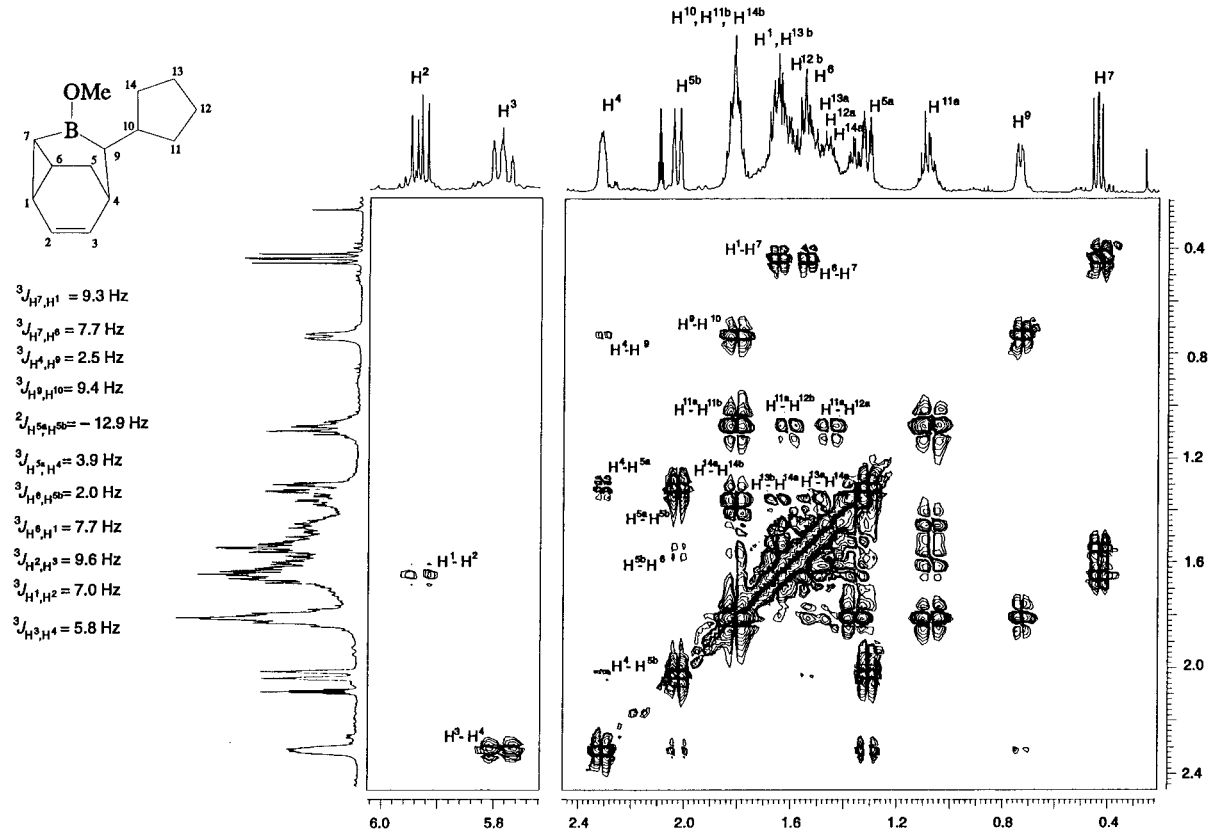
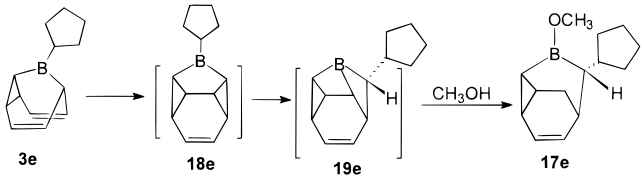


Figure 2. $^1H-^1H$ COSYDQ spectrum of compound **17** (500 MHz, CDCl3, 297 K).

Scheme 11. Proposed Mechanism for the Formation of 17



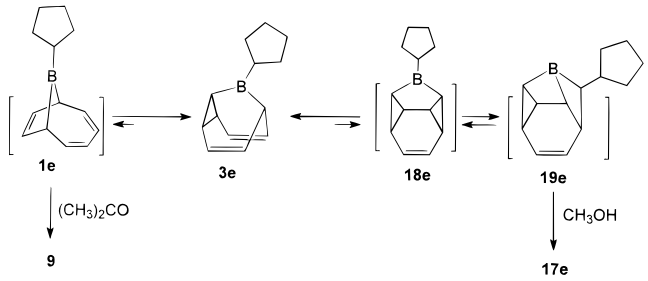
(Scheme 11). The direct precursor of **17e** should be **19e**. The rearrangement of a borylcyclopropyl moiety into a boracyclobutane, accompanied by the migration of the alkyl group from the boron atom to the α-carbon atom (as in the transformation **18e** → **19e**), has been recently documented.[12]

Discussion

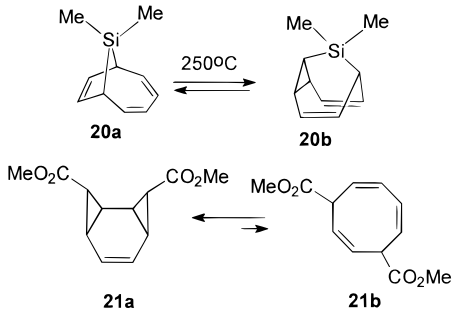
The salient feature in the chemical behavior of 9-cyclopentyl-9-borabarbaralane **3e** is the formation of products with frameworks that differ strikingly from those in the starting compound. This phenomenon is explained by the existence of minor valence tautomers not detectable in the spectra but present in small amounts in the equilibrium with the starting compound.[8] In the case of the compound **3e**, apparently *two different tautomers* are trapped upon treatment with various reagents. This implies an equilibrium between at least four compounds: **1e**, **3e**, **18e**, and **19e** (Scheme 12).

Direct analogies can be found for both parts of this equilibrium. For example, the silicon derivatives **20a,b** were found to equilibrate at 250 °C,[13] whereas **21a** in solution is in equilibrium with 10% of the monocyclic isomer **21b**[14] (Scheme 13).

Scheme 12. Selective Reactions of the Minor Valence Tautomers 1e and 19e with Acetone and Methanol



Scheme 13. Examples of the Valence Tautomerism in Cyclooctatrienes

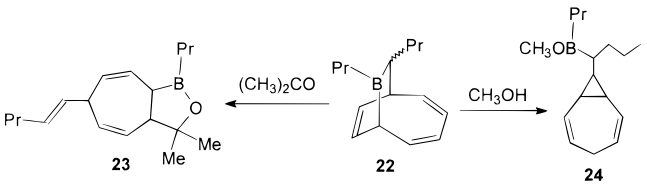


Taking into account the equilibrium displayed in Scheme 12, it is still difficult to explain why **3e** does not

(13) Barton, T. J.; Juvet, M. *Tetrahedron Lett.* **1975**, 2561−2564.

(14) Kerber, R. C.; Müller, H. *J. Organomet. Chem.* **1987**, *329*, 357−367.

Scheme 14. Diverse Chemoselectivity in the Reactions of 22



react rapidly with acetone and methanol directly, since triorganoboranes of allylic type (as **3e**) usually are highly reactive toward nucleophiles.

Previously, a comparable behavior was observed only for the bicyclic borane **22**,[15] which gave selectively the boronic esters **23** and **24** in the reactions with methanol and acetone, respectively (Scheme 14).

One might conclude that the formation of products with different frameworks in reactions with nucleophiles appears to be typical for polycyclic unsaturated triorganoboranes. Studies to elucidate mechanisms of the observed processes will continue.

Experimental Section

General. Methods. All manipulations were carried out under an atmosphere of dry nitrogen by standard Schlenk techniques. $C_5H_9BCl_2$ was prepared as described previously.[16] The structure of all new compounds was established by homo- and heteronuclear 2D NMR correlation experiments, using the standard procedures COSY, XHCORR, HMQC, and NOESYTP.

9-Cyclopentyl-9-borabarbaralane (3e). Cyclopentylborondichloride (6.04 g, 40 mmol) was added to a suspension of $K_2C_8H_8$ (7.28 g, 40 mmol) in hexane (100 mL) at −50 °C. After being stirred for 1 h at −50 °C, the reaction mixture was allowed to warm to room temperature and was stirred for 3 h. The precipitate was filtered off, the solvent removed in a vacuum, and the residue distilled to give 4.3 g (58%) of **3e** as a yellow oil, bp 72 °C (1 mbar); ^{1}H NMR (250 MHz, $CDCl_3$, 297 K) δ 1.3−1.8 (m, 9H, cyclopentyl), 2.17 (t, 2H, ^3J = 7.0 Hz), 4.1 (br, 4H), 5.55 (t, 2H, H-5, ^3J = 7.2 Hz); ^{1}H NMR (250 MHz, CD_2Cl_2−$CDCl_3$−CCl_4, 208 K) δ 1.24 (m, 2H of C_5H_9), 1.50 (m, 5H of C_5H_9), 1.55 (m, 1H, H-8), 1.72 (m, 2H of C_5H_9), 2.46 (dm, 2H, H-1,7 5.7 Hz), 2.63 (dd, 1H, H-4, ^3J = 6.2, 7.9 Hz), 5.50 (dm, 2H, H-2,6, ^3J = 7.9 Hz), 5.69 (br t, 2H, H-3,5, ^3J = 7.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 297 K) δ 121.8 (C-3,C-7), 28, 29, 30 (cyclopentyl); ^{13}C NMR (62.5 MHz, CD_2Cl_2−$CDCl_3$−CCl_4, 208 K) δ 18.5 (C-8), 26.4, 27.2 ($2CH_2$ of C_5H_9), 34.1 (C-1,7), 34.4 (CH of C_5H_9), 36.5 (C-4), 121.6 (C-2,6), 128.6 (C-3,5); ^{11}B NMR (80 MHz, $CDCl_3$, 297 K) δ 80.2; MS (EI, 70 eV) *m*/*z* 184 (8, M^+), 104 (100, C_8H_8); HRMS (M^+) 184.1423, calcd for $C_{13}H_{17}B$ 184.1423. When **3e** was dissolved in deuteriopyridine, **9-cyclopentyl-9-borabarbaralane pyridine-*d*$_5$ (4)** was formed in the solution: ^{1}H NMR (250 MHz, $CDCl_3$, 297 K) δ 1.2−1.7 (m, 9H cyclopentyl), 1.69 (t, 2H, H-1/H-5, ^3J = 7.6 Hz), 3.98 (td, 2H, H-2/H-4, ^3J = 7.6 Hz, ^4J = 2.9 Hz), 4.28 (td, 2H, H-6/H-8, ^3J = 7.6 Hz, ^4J = 2.9 Hz), 5.51 (t, 1H, H-3, ^3J = 7.5 Hz), 5.70 (t, 1H, H-7, ^3J = 7.5 Hz); ^{11}B NMR (80 MHz, $CDCl_3$, 297 K) δ −2.9. ^{13}C NMR (100 MHz, pyridine-*d*$_5$, 297 K) δ 24.55 (br, C-1/C-5), 26.97 ($2CH_2$, cyclopentyl), 31.49 ($2CH_2$, cyclopentyl), 35.81 (br. CHB cyclopentyl), 78.22 (br C-2/C-4), 79.20 (br C-6/C-8), 122.36 and 122.96 (C-3 and C-7), 124.62 (t, $^1J_{CD}$ = 24.7 Hz), 139.18 (t, $^1J_{CD}$ = 25.0 Hz), 145.76 (t, $^1J_{CD}$ = 28.0 Hz).

***exo*-9-Cyclopentyl-11,11-dimethyl-9-bora-10-oxatricyclo-[6.3.0.0^{2,7}]undeca-3,5-diene (5).** Acetone (2.3 g, 40 mmol) was added with stirring to a solution of 1.6 g (8.6 mmol) of **3e** in 10 mL of diethyl ether at −10 °C. The reaction mixture was allowed to warm to room temperature, the excess of acetone removed in a vacuum, and the residue distilled to give 1.4 g (67%) of **5** as a colorless oil: bp 85 °C (1 mbar); ^{1}H NMR (250 MHz, $CDCl_3$, 297 K) δ 1.11 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.4−1.8 (m, 9H, cyclopentyl), 2.50 (dd, 1H, H-8, ^3J = 3.3, 7.8 Hz, ^4J = 0.9 Hz), 2.82 (H-1), 2.84 (H-2), 2.90 (H-7), 5.46 (m, 1H, H-6), 5.67 (H-5), 5.68 (H-3), 5.73 (H-4); ^{13}C NMR (100 MHz, $CDCl_3$ 297 K) δ 23.10 (CH_3), 26.88, 26.90, 28.38, 28.46 ($4CH_2$ cyclopentyl), 28.5 (br, CHB of cyclopentyl), 29.07 (CH_3), 30.89 (C-2), 33.13 (C-7), 45.51 (br, C-8), 56.70 (C-1), 88.03 (C quart.), 121.24 (C-4), 121.96 (C-3), 125.97 (C-6), 130.04 (C-5); ^{11}B NMR (80 MHz, 297 K) δ 54.2. MS *m*/*z* 242 (18, M^+), 164 (20, $M^+ - C_6H_6$), 78 (100, C_6H_6); HRMS (M^+) 242.1835, calcd for $C_{16}H_{23}$-BO 242.1841.

Oxidation of 5. A solution of NaOH (0.5 g) in 5 mL of H_2O was added with stirring to a solution of **5** (0.9 g, 3.7 mmol) in 10 mL of Et_2O at −10 °C. In due course, 1.5 mL of 30% H_2O_2 was added dropwise at 0 °C. The reaction mixture was stirred at room temperature overnight. The organic layer was separated, washed with water, and dried over Na_2SO_4. The oily residue was chromatographed on SiO_2 in hexane−acetone (4:1) to give 0.28 g (43%) of **6** (R_f = 0.2) and 0.06 g of **7** (R_f = 0.4).

7-Hydroxy-8-(dimethylhydroxymethyl)bicyclo[4.2.0]-octa-2,4-diene (6): ^{1}H NMR (250 MHz, $CDCl_3$, 297 K) δ 1.10 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 2.60 (ddd, 1H, H-8, ^3J = 8.4, 7.3 Hz, ^4J = 1.4 Hz), 2.77 (dm, H-6, ^3J = 12.0 Hz), 3.22 (dddd, 1H, H-1, ^3J = 12.0, 8.4, 4.9 Hz, ^4J = 1.2 Hz), 4.46 (dd, 1H, H-7, ^3J = 7.3, 2.3 Hz), 5.15 (m, 3H, H-2, H-3, H-5), 5.25 (m, 1H, H-4);^{13}C NMR (100 MHz, $CDCl_3$, 297 K) δ 28.23 (CH_3), 28.33 (CH_3), 29.82 (C-1), 41.63 (C-6), 60.02 (C-8), 72.75 (CH), 73.87 (C quart.), 79.7 (C-7), 121.2 (C-3), 122.3 (C-4), 124.8 (C-5), 127.95 (C-2); MS (EI, 70 eV) *m*/*z* 180 (0.3, M^+), 165 (1, $M^+ - CH_3$), 162 (2, $M^+ - H_2O$), 102 (30, $M^+ - C_6H_6$), 78 (45, C_6H_6).

8-(Dimethylhydroxymethyl)cycloocta-1,3,6-triene (7): ^{1}H NMR (400 MHz, $CDCl_3$, 297 K) δ 1.23 (s, 6H, $2CH_3$), 1.5 (br, 1H, OH), 2.65 (dm, H-8a, ^2J = 16.2 Hz), 2.86 (dt, 1H, H-8b, ^2J = 16.2 Hz, ^3J = 7.0 Hz), 3.19 (dm, 1H, H-7, ^3J = 7.0 Hz), 5.43 dd, 1H, ^3J = 10.3, 6.9 Hz), 5.46 (dd, 1H, ^3J = 10.4, 7.6 Hz), 5.63 (dddd, 1H, ^3J = 10.9, 7.6 Hz, ^4J = 3.4, 2.5 Hz), 5.70 (ddd, ^3J = 10.9, 4.0 Hz, ^4J = 2.3 Hz), 6.06 (ddm, 1H, ^3J = 10.7, 3.4 Hz), 6.13 (ddm, 1H, ^3J = 10.7, 3.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 297K): δ = 26.94 (CH_3), 27.75 (CH_3), 28.39 (CH_2), 48.18 (CH), 72.19 (C quart.), 125.78, 126.75, 127.81, 127.97, 128.49, 129.39 (6CH); MS (EI, 70 eV) *m*/*z* 164 (M^+), 149 ($M^+ - CH_3$), 146 ($M^+ - H_2O$), 121 ($M^+ - CH_3CO$), 120 ($M^+ - CH_3$-COH), 106 ($M^+ - (CH_3)_2CO$); MS (FI) 164 (M^+, 100).

Reaction of 3e with Deuterioacetone. $(CD_3)_2CO$ (0.4 mL) cooled to −20 °C was added to 0.1 g (0.54 mmol) of **3e**. Immediately recorded NMR spectra indicated the quantitative formation of **9-bora-10-oxa-9-cyclopentyl-11,11-bis(trideuteriomethyl)bicyclo[6.3.0]undeca-2,4,6-triene (8a):** ^{1}H NMR (300 MHz, acetone-*d*$_6$, 297 K) δ 0.9−1.5 (m, 9H, *cyclo*-C_5H_9), 2.15 (dd, 1H, H-8, ^3J = 6.6, 5.6 Hz), 2.46 (ddd, 1H, H-1, ^3J = 6.6, 5.0 Hz, ^4J = 2.2 Hz), 5.34 (dd, 1H, H-2, ^3J = 11.8, 5.0 Hz), 5.42 (close AB, 2H, H-4, H-5), 5.45 (br d, 1H, H-6, ^3J = 11.8 Hz), 5.52 (br d, 1H, H-6, ^3J = 10.6 Hz), 5.59 (dd, 1H, H-7, ^3J = 10.6, 5.6 Hz); ^{13}C NMR (75 MHz, $(CD_3)_2CO$, 297 K) δ 26.03, 26.10, 27.25, 27.63 (4 CH_2 of cyclopentyl), 26.8 (br, CH of cyclopentyl), 35.45 (br, C-8), 50.63 (C-1), 86.45 (C quart.), 127.09, 127.26, 127.28, 128.15, 130.55, 131.13 (6 CH); ^{11}B NMR (64 MHz, $(CD_3)_2CO$, 297 K) δ 54.2; MS (EI, 70 eV) *m*/*z* 248 (2, M^+), 170 (18, M^+-C_6H_6), 78 (100, C_6H_6); HRMS 248.2209 (M^+), calcd for $C_{16}H_{17}D_6OB$ 248.2219. After storage of the sample for 48 h at room temperature, NMR analysis showed that **8a** had completely rearranged into **5a**, whose NMR spectra were the same as for **5**, excluding the signals of the two methyl groups, absent in the ^{1}H NMR spectrum of **5a** and appearing as two septets at δ = 23.1 and 29.1 in the ^{13}C NMR.

Reaction of 3e with Acetaldehyde. Acetaldehhyde (1.0 g, 22.7 mmol) cooled to −30 °C was added to 0.6 g (3.3 mmol) of **3e** at −30 °C. The NMR analysis of the reaction mixture showed the clean formation of **9-cyclopentyl-11-methyl-9-bora-10-oxabicyclo[6.3.0]undeca-2,4,6-triene (9):** ^{1}H NMR

(15) Gridnev, I. D.; Gurskii, M. E.; Buevich, A. V.; Potapova, T. V.; Bubnov, Yu. N. *J. Org. Chem.* **1996**, *61*, 3514−3519.

(16) Brown, H. C.; Ravindran, N. *J. Am. Chem. Soc.* **1973**, *95*, 2396−2397.

(300 MHz, $CDCl_3$, 297 K) δ 1.28 (d, 3H, CH_3, ^3J = 6.6 Hz), 2.11 (m, 1H, H-8), 3.20 (td, 1H, H-1, ^3J = 4.1, 2 × 7.1 Hz), 4.26 (qd, 1H, H-11, ^3J = 4.1, 6.6 Hz), 5.44 (m, 1H, H-2), 5.60−5.73 (m, 2H, H-4, H-5), 5.81 (m, 1H, H-6), 6.22 (dm, 1H, H-7, ^3J = 12.5 Hz), 6.6 (dd, 1H, H-3, ^3J = 4.6, 12.3 Hz);^{13}C NMR (75 MHz, $CDCl_3$, 297 K) δ 16.8 (CH_3), 26.7,26.8, 27.6, 28.0 ($4CH_2$ of cyclopentyl), 27.0 (br, CH of C_5H_9), 40.6 (br, C-8), 45.3 (C-1), 80.6 (C-11), 125.5 (C-2), 126.4, 128.5 (C-4, C-5), 129.6 (C-7), 130.9 (C-2), 131.5 (C-6).

The reaction mixture was allowed to warm to room temperature, the excess of acetaldehyde was removed in a vacuum, and the residue was distilled to give 0.55 g (73%) of a mixture of the isomeric boronic esters **9**, **10a**, and **10b** in a 1:15:3 ratio (pale yellow oil): bp 75 °C (1 mbar); MS (EI, 70 eV), *m*/*z* 228 (0.5, M^+), 150 (32, $M^+ - C_6H_6$), 78 (100, C_6H_6); ^{11}B NMR (64 MHz, $(CD_3)_2CO$, 297 K) δ 55.1.

***endo*-9-Cyclopentyl-11-methyl-9-bora-10-oxatricyclo-[6.3.0.0^{2,7}]undeca-3,5-diene (10a):** ^{1}H NMR (300 MHz, $CDCl_3$, 297 K): δ = 1.24 (d, 3H, CH_3 ^3J = 6.4 Hz), 2.34 (dd, 1H, H-8, ^3J = 3.6, 8.0 Hz), 2.79 (ddd, 1H, H-7, ^3J = 3.2, 4.1, 10.2 Hz), 2.89 (dd, 1H, H-2, ^3J = 5.6, 6.0, 8.0 Hz), 4.47 (dq, ^3J = 6.0, 6.4 Hz), 5.36 (m, 1H, H-3), 5.57−5.70 (m, 3H, H-4, H-5, H-6);^{13}C NMR (75 MHz, $CDCl_3$, 297 K) δ 17.3 (CH_3), 26.9 (2 CH_2 of C_5H_9), 27.8 (br, CH), 28.6 (CH_2), 29.1 (CH_2), 31.2 (C-2), 31.9 (C-7), 45.9 (br., C-8), 52.0 (C-1), 82.6 (C-11), 121.2, 122.0 (C5, C-6), 126.0 (C-3), 129.8 (C-4).

***exo*-9-Cyclopentyl-11-methyl-9-bora-10-oxatricyclo-[6.3.0.0^{2,7}]undeca-3,5-diene (10b):** ^{1}H NMR (300 MHz, $CDCl_3$, 297 K) δ 1.02 (d, 3H, CH_3 ^3J = 6.4 Hz), 2.46 (dd, 1H, H-8, ^3J = 4.2, 8.2 Hz), 2.58 (dd, 1H, H-1, ^3J = 5.0, 8.2 Hz), 2.73 (dt, 1H, H-2, ^3J = 5.0, 11.0 Hz), 2.85 (m, 1H, H-7), 4.49 (br q, ^3J = 6.4 Hz), 5.46 (m, 1H, H-3), 5.5−5.75 (m, 3H, H-4, H-5, H-6);^{13}C NMR (75 MHz, $CDCl_3$, 297 K) δ 22.9 (CH_3), 26.9 ($2CH_2$ of C_5H_9), 27.8 (br, CH of C_5H_9), 28.3, 28.6 ($2CH_2$ of C_5H_9), 32.0 (C-2), 37.3 (C-7), 44.3 (br, C-8), 52.9 (C-1), 86.4 (C-11), 120.9, 121.6 (C-5, C-6), 125.7 (C-3), 129.6 (C-4).

Reaction of 3e with Ethoxyacetylene. A 50% solution of ethoxyacetylene in hexane (10 mL) was added to the stirred solution of **3e** (0.70 g, 3.8 mmol) in 10 mL of hexane at −20 °C. The reaction mixture was allowed to warm to room temperature, and the solvent was removed. The NMR analysis of the reaction mixture showed the presence of three products, **11**, **12a**, and **12b**, in a 10:4:1 ratio. After distillation at 100 °C (1 mbar), 0.32 g (33%) of yellow oil was obtained, which contained a mixture of the two isomers **12a** and **12b** in a 4:1 ratio of about 90% purity: ^{11}B NMR (64 MHz, $CDCl_3$, 297 K) δ 73.4. MS (EI, 70 eV) *m*/*z* 176 (4, $M^+ - C_6H_6$), 78 (100, C_6H_6).

9-Ethoxy-11-cyclopentyl-11-borabicyclo[6.3.0]undeca-2,4,6,9-tetraene (11): ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ 1.22 (m, 1H), 1.60 (m, 4H), 1.75 (m, 3H), 1.91 (m, 1H) − 9H of C_5H_9, 1.37 (t, 3H, CH_3, ^3J = 7.0 Hz), 2.36 (t, 1H, H-1, ^3J = 6.5 Hz), 3.58 (t, 1H, H-8, ^3J = 6.5 Hz), 4.11 (q, 2H, CH_2, ^3J = 7.0 Hz), 5.04 (br s, 1H, H-10), 5.76 (close AB, 2H, H-4, H-5), 5.80 (dm, 1H, H-3, ^3J = 12.5 Hz), 5.91 (dd, 1H, H-7, ^3J = 6.7, 11.7 Hz), 6.00 (dm, 1H, H-6, ^3J = 11.7 Hz), 6.05 (dd, 1H, H-2, ^3J = 6.6, 12.5 Hz);^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ 14.1 (CH_3), 26.3, 29.9, 30.0 ($4CH_2$ of C_5H_9), 28.0 (br, CH of C_5H_9), 39.2 (br, C-1), 49.2 (C-8), 74.2 (CH_2), 100.8 (br, C-10), 127.7, 129.7 (C-4, C-5), 127.8 (C-3), 130.1 (C-6), 131.3 (C-2), 132.3 (C-7).

***exo*-9-Ethoxy-11-cyclopentyl-11-cyclopentylboratricyclo[6.3.0^{1,8}]undeca-3,5,9-triene (12a):** ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ 1.41 (t, 3H, CH_3, ^3J = 7.1 Hz), 1.5−1.9 (m, 9H, C_5H_9), 2.61 (t, 1H, H-1, ^3J = 5.7 Hz), 2.69 (dd, 1H, H-2, ^3J = 3.8, 5.7 Hz), 2.74 (m, 1H, H-7), 3.19 (dd, 1H, H-8, ^3J = 3.5, 6.0 Hz), 4.08 (m, 2H, CH_2O), 5.30 (s, 1H, H-10), 5.68 (dd, 1H, H-6, ^3J = 4.2, 9.3 Hz), 5.75 (m, 2H, H-3, H-4), 5.82 (m, 1H, H-5); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ 14.3 (CH_3), 26.9, 28.2 ($4CH_2$ of C_5H_9), 28.8 (br, CH of C_5H_9), 30.4 (C-2), 35.2 (C-7), 46.0 (br, C-1), 56.4 (C-8), 65.1 (OCH_2), 104.7 (br, C-10), 120.1 (C-3), 121.6 (C-5), 126.6 (C-6), 128.8 (C-4), 196.1 (C-11).

***endo*-9-Ethoxy-11-cyclopentyl-11-cyclopentylboratricyclo[6.3.0^{1,8}]undeca-3,5,9-triene (12b):** (only signals identified by COSY and XHCORR spectra are given); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ 2.69 (m, 1H, H-1), 2.72 (m, 1H), 3.49 (m, 1H), 5.40, 5.49, 5.53, 5.55 (each m, 4H), 5.50 (s, 1H, H-10); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ 14.5 (CH_3), 29.7, 29.9 ($4CH_2$ of C_5H_9, CH not found), 30.5 (C-2), 34.3 (C-7), 55.0 (C-8), C-1 not found, 65.1 (OCH_2), 108.8 (br, C-10), 120.7, 122.9, 125.5, 128.8 (C-3−6), 196.0 (C-11).

Reaction of 3e with Deuterioacetonitrile. Trideuterioacetonitrile (1.0 g, 22.7 mmol) cooled to −30 °C was added to 0.8 g (4.3 mmol) of **3e**. The NMR analysis of the reaction mixture showed the clean formation o f **10**. Distillation at 90 °C (1 mbar) gave 0.79 g (81%) of **9-cyclopentyl-11-(trideuteriomethyl)-9-bora-10-azabicyclo[6.3.0]undeca-2,4,6,11-tetraene (10):** pale yellow oil; ^{1}H NMR (300 MHz, $CD_3CN-CDCl_3$, 298 K) δ 1.3−1.8 (m, 9H, C_5H_9), 3.35 (br d, 1H, H-8, ^3J = 8.2 Hz), 5.48 (ddd, 1H, H-3, ^3J = 6.4, 12.8 Hz, ^5J = 1.0 Hz), 5.75 (dd, 1H, H-5, ^3J = 4.1, 12.3 Hz), 5.82 (dd, 1H, H-4, ^3J = 6.4, 12.3 Hz), 5.90 (dd, 1H, H-7, ^3J = 8.4, 10.7 Hz), 6.25 (dddd, 1H, H-6, ^3J = 4.1, 10.7 Hz, ^4J = 1.3 Hz, ^5J = 1.0 Hz), 6.44 (d, 1H, H-2, ^3J = 12.8 Hz), 6.63 (br s, 1H, NH); ^{13}C NMR (75 MHz, $CD_3CN-CDCl_3$, 298 K) δ 25.6, 25.8, 28.5, 28.7 ($4CH_2$ of C_5H_9), 27.7 (br, CH of C_5H_9), 37.9 (br, C-8), 117.1 (C-3), 120.7 (C-1), 125.0 (C-5), 126.7 (C-2), 127.7 (C-5), 129.0 (C-4), 130.6 (C-6), 143.8 (C-11); ^{11}B NMR (64 MHz, $CD_3CN-CDCl_3$, 297 K) δ 52.8; MS (EI) *m*/*z* 228 (3, M^+), 159 (6, $M^+ - C_5H_9$), 125 (12, C_5H_9-BN=$CHCD_3^+$), 73 (100), 45 (58, CD_3CNH^+); MS (FI) *m*/*z* 228 (100, M^+); HRMS (M^+) 228.1874, calcd for $C_{15}H_{17}D_3BN$ 228.1877.

Reaction of 3e with Tetradeuterioacetic Acid. 3e (0.1 g, 0.54 mmol) was dissolved in 0.4 mL of $CDCl_3$ and the solution cooled to −20 °C. Then, a solution of 0.1 g (1.5 mmol) of CD_3COOD in 0.2 mL of $CDCl_3$ was added dropwise. The NMR analysis (including COSY and HMQC experiments) of the reaction mixture indicated the formation **of 5,8-dideuterio-1,3,6-cyclooctatriene (15)** and **7,8-dideuterio-1,3,5-cyclooctatriene (16)** in a 4:1 ratio.

15: ^{1}H NMR (300 MHz, $CD_3CCOOD-CDCl_3$, 298 K) δ 2.39 (m, 2H, H-5,8), 5.69 (m, 2H, H-1,4), 5.91 (m, 4H, H-2,3,7,6); ^{13}C NMR (75 MHz, $CD_3CN-CDCl_3$, 298 K) δ 27.5 (t, C-5,8, $^1J_{CD}$ = 19.7 Hz), 126.0, 126.7, 135.2.

16: ^{1}H NMR (300 MHz, $CD_3CCOOD-CDCl_3$, 298 K) δ = 1.80 (m, 2H, H-7,8), 5.12 (dd, 2H, H-1,6, ^3J = 6.0, 8.7 Hz), 6.09 (br d, 2H, H-3,4, ^3J = 8.7 Hz), 6.65 (m, 2H, H-2,5); ^{13}C NMR (75 MHz, $CD_3CN-CDCl_3$, 298 K) δ 123.8, 128.9, 130.8 (C-7,8 not found).

NMR spectra of both cyclooctatrienes[17] and of **16**[17b] (recorded at lower frequency) were previously described.

Reaction of 3e with Methanol. 3e (1.0 g, 5.4 mmol) was added to 10 mL of methanol cooled to −20 °C. The reaction mixture was allowed to warm to room temperature; two layers formed. All volatiles were removed under high vacuum to give 1.0 g (87%) of **8-methoxy-9-cyclopentyl-8-boratricyclo-[4.1.2^{4,7}0^{1,6}]non-2-ene (17e)** (yellow oil) of approximately 95% purity. Compound **17** can be distilled at 79−82 °C (1 mbar), but the purity of thus obtained samples is less, due to partial decomposition of **17**: ^{1}H NMR (500 MHz, toluene-d_8, 298 K) δ 0.43 (dd, 1H, H-7, ^3J = 9.3, 7.7 Hz), 0.73 (dd, 1H, H-9, ^3J = 9.4, 2.5 Hz), 1.07 (m, 1H, H-11a), 1.31 (ddd, 1H, H-5a, ^2J = −12.9 Hz, ^3J = 3.9, 2.1 Hz), 1.36 (td, 1H, H-14a, ^2J = −11.2 Hz, ^3J = 11.2, 2.9 Hz), 1.46 (m, 1H, H-13a), 1.52 (m, 1H, H-12a), 1.54 (td, 1H, H-6, ^3J = 2 m~ 7.7, 2.0 Hz), 1.59 (m, 1H, H-13b), 1,64 (m, 2H, H-1, H-12b), 1.80 (m, 3H, H-10, H-11b, H-12b), 2.02 (dm, 1H, H-5b, ^2J = −12.9 Hz), 2.30 (m, 1H, H-4), 3.47 (s, 3H, OCH_3), 5.79 (dddd, 1H, ^3J = 9.6, 7.0 Hz, ^4J = 1.2, 0.8 Hz), 5.94 (dd, 1H, H-3, ^3J = 9.6, 5.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 297 K) δ 12.8 (br, C-7), 18.7 (C-6), 19.9 (C-1), 21.3 (C-5), 25.4 (C-12), 26.3 (C-13), 33.6 (C-11), 34.1 (C-4), 34.2 (C-14), 39.3 (C-10), 43.0 (br, C-9), 53.5 (OCH_3), 126.8 (C-2), 132.5 (C-3); ^{11}B NMR (64 MHz, $CDCl_3$, 298 K) δ 50.3. MS (EI, 70 eV) *m*/*z* 216 (5, M^+), 111 (35), 43 (100); HRMS (M^+) 216.1694, calcd for $C_{14}H_{21}{}^{11}BO$ 216.1685; (M^+) 215.1710, calcd for $C_{14}H_{21}$-^{10}BO 215.1722.

Under the same conditions, the reaction of **3e** with tetradeuteriomethanol gave **17f**: ^{1}H NMR (300 MHz, $CDCl_3-C_6D_6$

(17) (a) Echter, T.; Meier, H. *Chem. Ber.* **1985**, *118*, 182−197. (b) Jacques, M. S.; Prud'homme, R. *Tetrahedron Lett.* **1970**, 4833−4836.

3:1, 297 K) δ 0.51 (dd, 1H, H-7, ^3J = 7.7, 9.6 Hz), 0.58 (br d, 1H, H-9, ^3J = 9.6 Hz), 1.0 (m, 1H of C_5H_9), 1.20 (m, 1H, H-5), 1.35−1.80 (m, 9H, 8H of C_5H_9, H-9), 1.57 (tt, 1H, H-6, ^3J = 2.4, 2 × 7.7 Hz, ^4J = 2.4 Hz), 1.71 (dddd, 1H, H-1, ^3J = 5.7, 7.7, 9.6 Hz, ^4J = 1.2 Hz), 2.26 (m, 1H, H-4), 5.70 (ddt, 1H, H-3, ^3J = 8.5, 9.4 Hz, ^4J = 2 × 1.4 Hz), 5.88 (ddd, 1H, H-2, ^3J = 5.7, 9.4, ^4J = 1.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$−C_6D_6 3:1, 297 K) δ 10.7 (br, C-7), 17.4 (C-6), 18.7 (C-1), 19.7 (t, C-5, $^1J_{C-D}$ = 20.4 Hz), 24.2 (C-12), 25.1 (C-13), 32.4 (C-11), 32.6 (C-4), 33.1 (C-14), 38.0 (C-10), 42.0 (br, C-9), 125.9 (C-2), 131.6 (C-3); ^{11}B NMR (64 MHz, $CDCl_3$, 298 K) δ 50.2; MS (EI, 70 eV), *m*/*z* 220 (6, M^+), 140 (45), 79 (100); HRMS (M^+) 220.1935, calcd for $C_{14}H_{17}D_4BO$ 220.1937.

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Supporting Information Available: ^{13}C NMR spectra of compounds **3e**, **5**, **5a**, **6**, **7**, **8a**, **9**, **9** + **10a** + **10b**, **12a** + **12b**, **14**, **17**, and **17a** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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