A Convenient Method for the Generation of Allylic Dihaloboranes and Diallyl(chloro)borane and Their Application in the Allylboration of Alkenes and Acetylenes

Yuri N. Bubnov,*[a] Nikolai Y. Kuznetsov,[a] Fedor V. Pastukhov,[a] and Vadim V. Kublitsky[a]

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A convenient approach to the highly reactive allylic dihaloboranes and diallyl(chloro)borane based on exchange reactions between $BHal_3$ (Hal = Cl, Br) and allylic triorganoboranes (allyl, cinnamyl and 2-methylenecyclobutane derivatives) has been developed. The compounds thus generated readily react with terminal alkenes and acetylenes to form the corresponding *cis*-1,2-allylboration products. These products were isolated by standard techniques and transformed into boronates (boron amides). Deboronation of these products led to 1,4-pentadiene derivatives or unsaturated alcohols. 2-Substituted 1,4-pentadienyl(dichloro)boranes obtained from acetylenes underwent intramolecular chloroboration at a moderate temperature to form 5-chloro-2-borinene derivatives.

Introduction

The 1,2-allylboration of organic compounds containing multiple bonds (C=O, C=S, C=N, C=C, N=O, C≡C, C≡N) is a general reaction that proceeds with allylic transposition via a cyclic six-membered transition state.[1–3] The more the multiple bond is polarized or strained the easier the allylboration.[2] 1,2-Addition reactions of allylic triorganylboranes, such as triallyl-, trimethallyl- and tricrotylboranes, or allyl(diorganyl)boranes to certain olefins, cyclopropenes and terminal acetylenes have successfully been used in the preparation of various 1,4-dienes,[1c,2,4] cyclopropanes,[1c,5] tri- and tetravinylmethanes,[6] allyl methyl ketone derivatives,[7] 1,4-enynes,[8] as well as cyclohexane and cyclohexene compounds.[1c] In the case of $RC{\equiv}C{-}MR'_3$ (M = Si, Sn, Ge), a competition between 1,1- and 1,2-allylboration takes place, 1,1-allylboration proceeding with retention of configuration of the allylic group.[9]

As expected, highly electrophilic allyldichloro- and allyldibromoboranes possess high reactivity and selectivity in the 1,2-addition to alkenes, certain 1,3-dienes and alkynes.[10] No 1,4-addition to cyclic and linear 1,3-dienes has been observed.

Allylic dihaloboranes are unstable and should be used for further transformations as quickly as possible. The half-life of these compounds in dilute $CDCl_3$ ranges from several days (allylic difluoroboranes) to 3–7 minutes (allylic dibromoboranes).[11a] A general approach to the synthesis of allyldihaloboranes involves a transmetallation reaction between allylic tin compounds and $BHal_3$ (Hal = F, Cl, Br).[10,11] Wardell and co-workers have shown through a NMR study that exchange between allylic tin derivatives and haloboron compounds proceeds with retention of the configuration of the allylic group.[12] However, transfer of allylic groups from tin to boron also occurs with allylic transposition, presumably via a six-membered cyclic transition state.[11b,c,13] α-Methylated allylic boranes formed initially from crotyl- or prenylstannanes rearrange to the thermodynamically more stable crotyl and prenylboranes.[11,13] The disadvantage of this method is the use of toxic organotin derivatives. Therefore we have developed an environmentally friendly method based on the exchange reaction between the corresponding allylic triorganoboranes and BCl_3 or BBr_3. The principle of this process has been known since 1975 when the reactions of triallyl- and tricrotylborane with an excess of BCl_3 were investigated by NMR spectroscopy.[14]

Results and Discussion

Allyl(dichloro)borane (**1a**, ^{11}B NMR: δ = 61.4 ppm)[11a] and diallyl(chloro)borane (**1c**, ^{11}B NMR: δ = 73.8 ppm) are cleanly obtained in situ by adding of triallylborane to a cooled (–10 °C) solution of 1 M BCl_3 in hexane in a ratio of 1:2 and 2:1, respectively. Monitoring the reactions with NMR spectroscopy shows that they are complete within 5 min. Allyl(dibromo)borane (**1b**, solution in hexane) can be generated from triallylborane and BBr_3 (1:2) at –40 °C in hexane (Scheme 1).

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[a] A. N. Nesmeyanov Institute of Organoelement Compounds,
Russian Academy of Sciences,
Vavilov 28, 119991, Moscow, Russia

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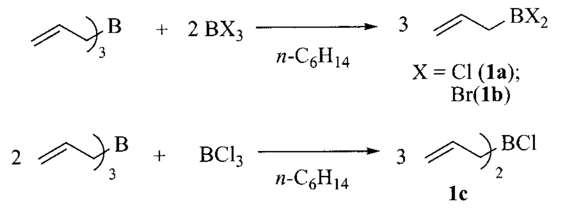
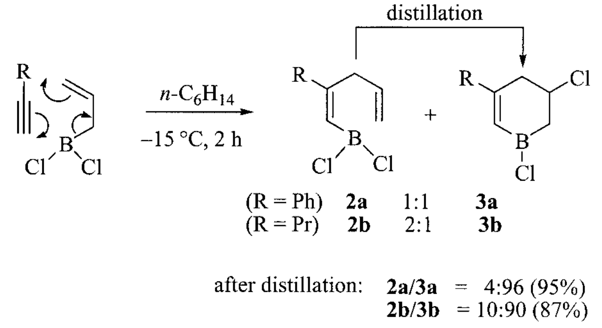


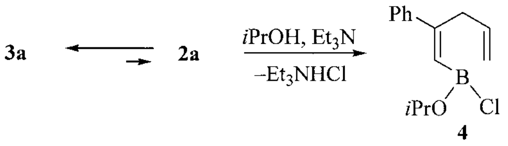
Scheme 1.

Allyl(dichloro)borane (**1a**) generated as above was then allowed to react with phenylacetylene or 1-pentyne in hexane at –15 °C (Scheme 2). After evaporation of the solvent, two pairs of compounds were detected by NMR spectroscopy in the each case: the corresponding products of the *cis*-allylboration of the acetylene triple bond, **2a** (^{11}B NMR: δ = 52.5 ppm) or **2b** (^{11}B NMR: δ = 51.1 ppm), and **3a** or **3b**, which result from intramolecular chloroboration of the terminal C=C bond in **2a** or **2b**. Refluxing the mixture of **2** and **3** in hexane for 2 h or distillation gives rise to 2-borinene derivatives **3a** (^{11}B NMR: δ = 62.3 ppm) or **3b** (^{11}B NMR: δ = 64.8 ppm) with 90–96% purity. The 2-borinenes seem to be in equilibrium (cyclization ↔ β-elimination) with the acyclic form **2** (≤4–10%) (Scheme 2).



Scheme 2.

Nucleophilic reagents were found to open the cyclic system of **3a** (β-elimination), leading to the recovery of the 1,4-diene-type structure. Thus treatment of "pure" **3a** with 1 equiv. of 2-propanol in the presence of 1 equiv. of Et_3N (–20 °C → room temp., 2 h) produces monochloroborane **4** and Et_3NHCl (Scheme 3).

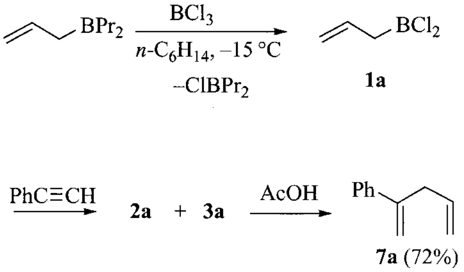


Scheme 3.

The reactions of 2-borinenes (**3a** or **3b**) with 2 equiv. of *i*PrOH and Et_3N produce diisopropyl 1,4-pentadienylboronates **5** in approximately 80% yield while treatment with lithium diethylamide affords the corresponding bis(diethylamino)boranes **6** (Scheme 4).

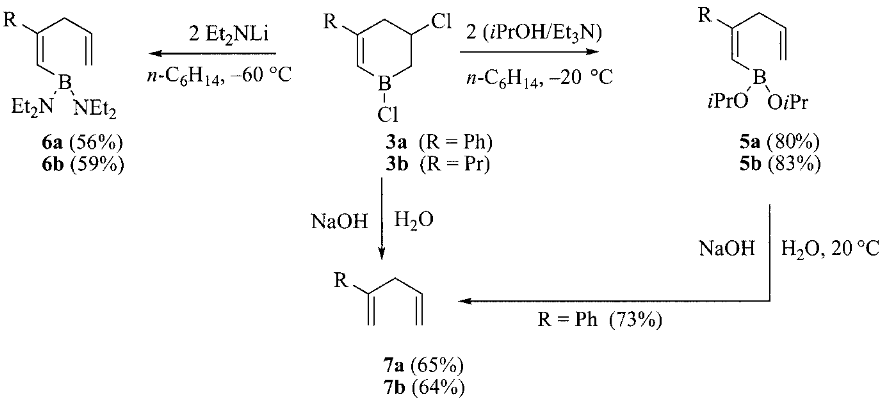
All the allylboration products (**2**, **3** and **5**) undergo deboronation with base (5 N NaOH, 20 °C) to furnish 2-phenyl- (**7a**) or 2-propyl-1,4-pentadiene (**7b**), respectively.

We found that allyl(dichloro)borane is also generated by the interaction between allyl(dipropyl)borane and BCl_3. Further treatment of the mixture with phenylacetylene produces a mixture of **2a** and **3a** (^{1}H NMR spectroscopy). Diene **7a** (72%) was obtained after deboronation of the reaction mixture with acetic acid (Scheme 5).

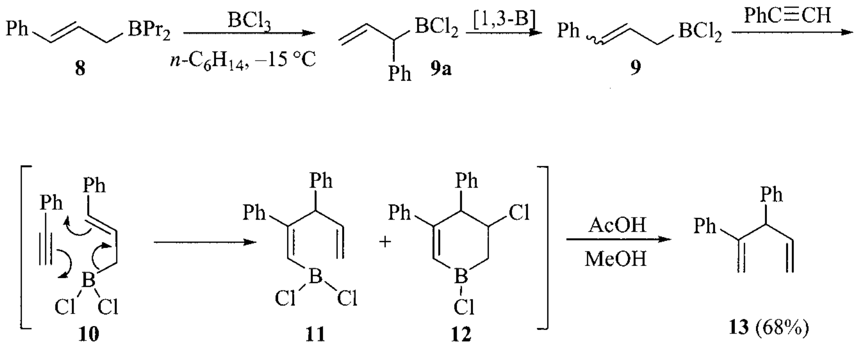


Scheme 5.

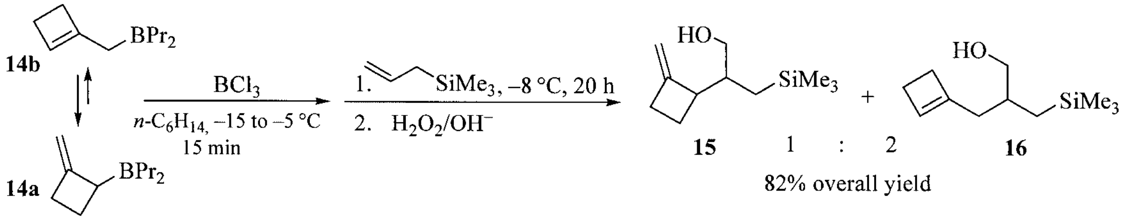
This approach is equally suitable for the generation of more complicated allylic dihaloboranes. Thus, cinnamyl(dipropyl)borane (**8**) (prepared as only the *trans* isomer from cinnamyllithium and Pr_2BOMe) when mixed with BCl_3 affords cinnamyl(dichloro)borane (**9**) (Scheme 6). It should be stressed that transfer of allylic groups from one boron atom to another in these exchange reactions proceeds with



Scheme 4.



Scheme 6.



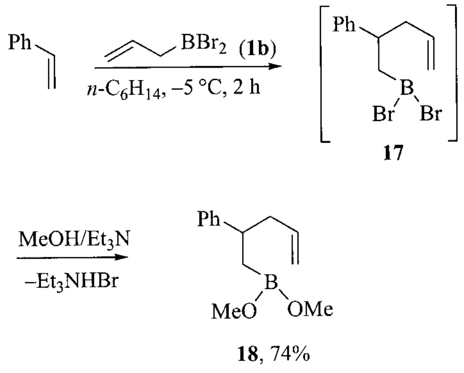
Scheme 7.

allylic transpositions, probably via a six-membered cyclic transition state. However, initially formed 1-phenylallyl(dichloro)borane (**9a**) rearranges to the thermodynamically preferred cinnamyl derivative **9**, the isomer with less substituents on the α-carbon atom.[14] The latter allylborates phenylacetylene with rearrangement (**10**) to form the product(s) **11** and/or **12**, which undergo protolytic deboronation to give 2,3-diphenyl-1,4-pentadiene (**13**).

It was previously reported by Singleton et al.[10a] that the allylboration of allylic silanes with borane **1a** is a facile process that leads to the corresponding adducts in high yields (up to 93%). We have investigated a similar reaction with a mixture of isomeric dichloroboranes generated from BCl_3 and a dynamic mixture of 2-methylenecyclobutyl- (**14a**) and 1-cyclobutenylmethyl(dipropyl)borane (**14b**)[15] (Scheme 7). Further oxidation of the mixture with alkaline hydrogen peroxide led to two silylated carbinols **15** and **16** in a 1:2 ratio. Again, addition to the double bond of allylsilane occurs with allylic rearrangement. The predominant product **16** is obtained from the thermodynamically more stable 2-methylenecyclobutyl(dichloro)borane.

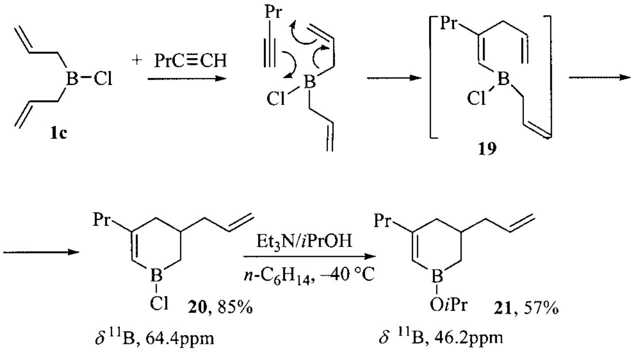
Allyldibromoborane (**1b**) is much more reactive than the corresponding dichloride **1a** and adds to alkenes and 1,3-dienes.[10] We tested **1b** generated from BBr_3 and triallylborane in the reaction with styrene (Scheme 8). 1,2-Addition (hexane, –5 °C) is complete within 2 h. The dibromoborane **17** formed was transformed (without isolation) into boronate **18** by treatment with a MeOH/Et_3N mixture. Vacuum distillation affords pure **18** in 74% yield.

Our attempts to allylborate internal acetylenes (octyne or tolane) with **1a** or **1b** failed.



Scheme 8.

Diallyl(chloro)borane (**1c**) also readily allylborates 1-pentyne (Scheme 9) to form the borane **19** which is transformed by distillation into the cyclic product **20** (85%) through intramolecular allylboration of the terminal double bond. The latter was transformed into borinate **21** by treatment with a mixture of 2-propanol and triethylamine.



Scheme 9.

Conclusions

A convenient method for the generation of various highly reactive allylic dihaloboranes and diallyl(halo)boranes involves facile exchange reactions between allylic triorganoboranes and BCl_3 or BBr_3. Allylic haloboranes thus generated readily allyborate terminal acetylenes and alkenes. Allylboration products can be transformed into different organoboron compounds (esters, amides, boracyclanes) or their deboronation products, such as unsaturated alcohols and 1,4-dienes.

Experimental Section

General: All reactions were performed in dry argon. The solvents were purified by standard techniques. Tetrahydrofuran (THF), diethyl ether and toluene were distilled from sodium-benzophenone ketyl. Hexane was distilled and stored over sodium. NMR spectra were recorded with Bruker AMX-400, Avance-300 and WP-200SY instruments. Chemical shifts are given in δ (ppm) and J values in Hz. Mass spectra were recorded with a Finnigan Polaris Q Ion Trap spectrometer. Column chromatography was carried out on silica gel (Merck), 60–230 mesh. Allyltrimethylsilane and phenylacetylene were obtained from Aldrich. Triallylborane was prepared in a multigram scale following a procedure described in the literature.[16]

Allyldichloroborane (1a): Triallylborane (4.5 mL, 0.025 mol) was added to a solution of BCl_3 in hexane (1 M, 50 mL, 0.05 mol) at –10 °C and the mixture was stirred for 15 min at this temperature. ^{11}B NMR (64 MHz): δ = 61.4 (s, $Cl_2B–R$) ppm.

Allyldibromoborane (1b): Triallylborane (3.48 g, 4.53 mL, 0.026 mol) was added to a solution of BBr_3 (13 g, 5 mL, 52 mmol) in hexane (100 mL) at –70 °C with stirring. The reaction mixture was warmed to –40 °C for 10 min and immediately used in allylboration reactions.

Diallylchloroborane (1c): Triallylborane (8.7 mL, 0.05 mol) was added to a solution of BCl_3 in hexane (1 M, 25 mL, 0.025 mol) at –10 °C and stirred for 30 min. ^{11}B NMR (64 MHz): δ = 73.8 (s, $ClBR_2$) ppm.

Dichloro[(1*E*)-2-phenyl-1,4-pentadienyl]borane (2a) and 1,5-Dichloro-3-phenyl-2-borinene (3a): Phenylacetylene (8.2 mL, 0.075 mol) was rapidly added at –15 °C to a solution of **1a** (0.075 mol) in hexane (prepared as indicated above). After addition was complete the reaction mixture was allowed to warm to 0 °C and stirred for 1 h. Then all volatiles were removed in vacuo at ambient temperature and the residue was analyzed by ^1H NMR spectroscopy; two products **2a** and **3a** were detected in a ratio of 1:1. Distillation of the mixture in vacuo gave compounds **2a** and **3a** in a 4:96 ratio (13.4 g, 95%), as a colorless liquid, b.p. 98–99 °C (0.5 Torr).

2a: ^1H NMR (200 MHz, $CDCl_3$): δ = 3.9 (d, J = 6.1 Hz, 2 H), 5.08 (dd, J = 9.9, 1.4 Hz, 1 H), 5.25 (dd, J = 15.7, 1.4 Hz, 1 H), 5.91 (ddt, J = 15.7, 9.9, 6.1 Hz, 1 H), 6.48 (s, 1 H,), 7.3–7.6 (m, 5 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 37.05 (CH_2), 116.82 (CH_2=), 126.27 (2 CH_{Ph}), 128.38 (CH_{Ph}), 128.5 (2 CH_{Ph}), 129.63 (C_{Ph}), 135.27 (CH=), 167.0 (CPh) ppm. ^{11}B NMR (64 MHz, $CDCl_3$): δ = 52.5 (s, BCl_2) ppm.

3a: ^1H NMR (200 MHz, C_6D_6): δ = 1.59 (dd, J = 17.6, 11.2 Hz, 1 H); 1.98 (dd, J = 17.6, 4.6 Hz, 1 H), 2.6 (ddd, J = 17.2, 9.5, 1.4 Hz, 1 H), 2.8 (dd, J = 17.2, 4.5 Hz, 1 H), 3.91 (m, 1 H), 6.44 (d, J = 1.4 Hz, 1 H), 7.3–7.6 (m, 5 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 36.28 (br. CH_2B), 41.8 (CH_2), 58.14 (CHCl), 126.99 (CH_{Ph}), 129.2 (2 CH_{Ph}), 129.0 (2 CH_{Ph}), 130.20 (C_{Ph}), 168.7 (CPh=) ppm. ^{11}B NMR (64 MHz, $CDCl_3$): δ = 62.3 (s, $ClBR_2$) ppm.

Dichloro[(1*E*)-2-propyl-1,4-pentadienyl]borane (2b) and 1,5-Dichloro-3-propyl-2-borinene (3b): Compounds **2b** and **3b** were prepared from 1-pentyne (2.04 g, 0.03 mol) and a solution of **1a** (0.03 mol) in hexane according to the above procedure. Compounds **2b** and **3b** were initially formed in a ratio of 2:1. Distillation of the mixture in vacuo gave compounds **2b** and **3b** in a 10:90 ratio (5.0 g, 87%) as a colorless liquid, b.p. 88–89 °C (1 Torr).

2b: ^1H NMR (200 MHz, $CDCl_3$): δ = 0.94 (t, J = 7.3 Hz, 3 H), 1.6 (tq, J = 7.6, 7.3 Hz, 2 H), 2.25 (t, J = 7.6 Hz, 2 H), 3.38 (d, J = 6.6 Hz, 2 H), 5.08 (dd, J = 8.2, 1.5 Hz, 1 H), 5.15 (dd, J = 14.8, 1.5 Hz, 1 H), 5.72 (ddt, J = 14.8, 8.2, 6.6 Hz, 1 H), 5.96 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.72, 20.90, 38.72, 42.86, 116.87, 127.08, 134.94, 174.65 ppm. ^{11}B NMR (64 MHz, $CDCl_3$): δ = 51.09 (s, Cl_2BR) ppm.

3b: ^1H NMR (200 MHz, $CDCl_3$): δ = 0.94 (t, J = 7.3 Hz, 3 H), 1.59 (m, 2 H), 1.6 (dd, J = 17.6, 11.0 Hz, 1 H), 2.10 (dd, J = 17.6, 4.6 Hz, 1 H), 2.34 (t, J = 7.5 Hz, 2 H), 2.57 (dd, J = 17.3, 7.0 Hz, 1 H), 2.75 (dd, J = 17.3, 4.7 Hz, 1 H), 4.35 (m, 1 H), 5.99 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.62, 20.10, 35.61, 43.03, 42.7, 57.37, 128.05, 175.80 ppm. ^{11}B NMR (64 MHz, $CDCl_3$): δ = 64.84 (s, $ClBR_2$) ppm.

1-Isopropoxy(chloro)boryl-2-phenyl-1,4-pentadiene (4): A mixture of *i*PrOH (1.64 g, 2.1 mL, 27.4 mmol) and Et_3N (2.76 g, 3.8 mL, 27.4 mmol) in hexane (10 mL) was slowly added with rigorous stirring to a solution of **3a** (96% purity) (6.17 g, 27.4 mmol) in hexane (40 mL) at –40 °C. An abundant precipitation of Et_3NHCl was observed. After complete addition the reaction mixture was stirred for 2 h, the precipitate was filtered and washed with hexane (2 × 10 mL). Evaporation of the filtrate under reduced pressure and vacuum distillation of the residue yielded **4** (5.5 g, 82%) as a yellow liquid; b.p. 110–112 °C (1 Torr). ^1H NMR (200 MHz, $CDCl_3$): δ = 1.3 (d, J = 6.6 Hz, 6 H), 3.61 (d, J = 6.1 Hz, 2 H), 4.6 (sept, J = 6.6 Hz, 1 H), 5.03 (dd, J = 9.8, 1.4 Hz, 1 H), 5.15 (dd, J = 17.0, 1.4 Hz, 1 H), 5.8–6.03 (m, 1 H), 5.90 (s, 1 H), 7.30–7.60 (m, 5 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.57, 38.29, 65.69, 115.42, 126.33, 127.35, 128.38, 137.2, 144.32, 154.33 ppm. ^{11}B NMR (64 MHz, C_6D_6): δ = 30.79 ppm. MS (70 eV, EI): 249 $[M]^+$, 214 (27), 188 (23), 172 (56), 155 (20), 144 (58), 130 (53), 129 (84), 105 (70), 91 (46), 87 (66), 77 (62), 66 (42), 59 (50), 43 (100). $C_{14}H_{18}BClO$ (248.6): calcd. C 67.65, H 7.30, B 4.35, Cl 14.26; found C 67.51, H 7.24, B 4.33, Cl 14.15.

Diisopropyl (1*E*)-2-Phenyl-1,4-pentadienylboronate (5a): A mixture of isopropyl alcohol (3.8 g, 4.9 mL, 64 mmol) and Et_3N (6.4 g, 8.9 mL, 64 mmol) was slowly added dropwise with rigorous stirring to a solution of the mixture **2a** and **3a** (4:96) (6.75 g, 0.03 mol) in hexane (80 mL) at –20 °C. Et_3NHCl was formed as a precipitate. The reaction mixture was stirred for 2 h at room temperature, filtered and the precipitate was washed with hexane (2 × 10 mL). The filtrate was evaporated and the residue distilled in vacuo. This provided the boronate **5a** (6.5 g, 80%) as a colorless liquid, b.p. 132–133 °C (5 Torr). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, J = 7.2 Hz, 2 H), 7.35 (t, J = 7.2 Hz, 2 H), 7.28 (t, J = 7.2 Hz, 1 H), 5.9 (ddt, J = 17, 9.0, 6.5 Hz, 1 H), 5.86 (sept, 1 H), 5.13 (dd, J = 17.1, 1.2 Hz, 1 H), 4.99 (dd, J = 9.0, 1.2 Hz, 1 H), 4.54 (sept, J = 6.0 Hz, 2 H_{OCHMe}), 3.59 (d, J = 6.5 Hz, 2 H), 1.25 (d, $J_{CH,Me}$ = 6.2 Hz, 12 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 154.73 C, 143.49 (C_{Ph}), 137.01 (CH=), 127.81 (2 CH_{Ph}), 127.10 (CH_{Ph}), 126.03 (2 CH_{Ph}), 120.09 (br. CH_B), 115.44 (CH_2=), 65.29 (2 CH_{OiPr}), 38.03 (CH_2), 24.33 (2 $CH_{3,OiPr}$) ppm. ^{11}B NMR

(64 MHz, $CDCl_3$): δ = 26.0 [s, R-B(O*i*Pr)$_2$] ppm. MS (70 eV, EI): *m*/*z* (%) = 272 $[M]^+$, 188 (15), 170 (55), 143 (70), 129 (90), 105 (70), 87 (80), 77 (50), 69 (40), 59 (50), 43 (100). $C_{17}H_{25}BO_2$ (272.2): calcd. C 75.01, H 9.26, B 3.97; found C 75.00, H 9.24, B 3.83.

Diisopropyl (1*Z*)-2-Propyl-1,4-pentadienylboronate (5b): Compound **5b** was obtained from **3b** (90% purity, 5.70 g, 0.03 mol) and a mixture of *i*PrOH (3.43 g, 0.06 mol) and NEt_3 (5.76 g, 0.06 mol) according to the procedure described above for the preparation of **5a**. Distillation gave the boronate **5b** (5.9 g, 83%) as a colorless liquid, b.p. 58–60 °C (1 Torr). ^1H NMR (200 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.9 Hz, 3 H), 1.17 (d, *J* = 6.3 Hz, 12 H), 1.45 (qt, *J* = 7.9, 7.4 Hz, 2 H), 2.05 (t, *J* = 7.4 Hz, 2 H), 3.03 (d, *J* = 6.9 Hz, 2 H), 4.42 (sept, *J* = 6.3 Hz, 2 H), 4.95 (d, *J* = 11.6 Hz, 1 H), 5.03 (d, *J* = 18.5 Hz, 1 H), 5.21 (s, 1 H), 5.70–5.90 (m, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.73, 20.78, 24.42, 30.78, 39.71, 65.24, 117.0, 130.0, 137.37, 157.25 ppm. ^{11}B NMR (64 MHz, $CDCl_3$): δ = 24.77 [s, -B(O*i*Pr)$_2$] ppm. $C_{14}H_{27}BO_2$ (238.2): calcd. C 70.6, H 11.43, B 4.54; found C 69.64, H 11.67, B 4.44.

(1*E*)-1-Bis(diethylamino)boryl-2-phenyl-1,4-pentadiene (6a): A suspension of lithium diethylamide (0.065 mol) [freshly prepared from Et_2NH (4.75 g, 6.73 mL, 0.065 mol) and BuLi (1.6 M, 40.6 mL, 0.065 mol) in hexane (50 mL)] was slowly added to a solution of the mixture of **2a** and **3a** (4:96) (7.0 g, 0.031 mol) in hexane (50 mL) at –20 °C. The mixture was stirred for 15 min at –20 °C and then for 2 h at ambient temperature. The precipitate was filtered off and the filtrate was evaporated under reduced pressure. The residue was distilled in vacuo to yield **6a** (5.2 g 56%) as a yellow oil, b.p. 155–157 °C (2 Torr). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 7.5 Hz, 2 H), 7.36 (t, *J* = 7.5 Hz, 2 H), 7.26 (t, *J* = 7.5 Hz, 1 H), 6.13 (s, 1 H), 5.82 (ddt, *J* = 17.1, 10.0, 6.5 Hz, 1 H), 5.06 (dd, *J* = 17.1, 1.6 Hz, 1 H), 4.97 (d, *J* = 10.0 Hz, 1 H), 3.40 (d, *J* = 6.5 Hz, 2 H), 3.08 (q, *J* = 6.8 Hz, 8 H), 1.09 (t, *J* = 6.9 Hz, 12 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 144.28 (C), 143.42 (C_{Ph}), 136.1 (CH=), 128.04 (CH_{Ph}), 126.15 and 126.44 (2 CH_{Ph}), 115.43 (CH_2=), 42.66 (4 $CH_{2,Et}$), 38.22 (CH_2), 15.75 (4 $CH_{3,Et}$) ppm. ^{11}B NMR (64 MHz, $CDCl_3$): δ = 34.4 [s, R-B(NEt_2)$_2$] ppm. MS (70 eV, EI): *m*/*z* (%) = 298 (4) $[M]^+$, 225 (20), 210 (90), 155 (10), 127 (20), 105 (15), 84 (50), 77 (15), 72 (30), 58 (100), 44 (50). $C_{19}H_{31}BN_2$ (298.3): calcd. C 76.51, H 10.48, B 3.62, N 9.39; found C 76.75, H 10.25, N 9.30.

(1*Z*)-1-Bis(diethylamino)boryl-2-propyl-1,4-pentadiene (6b): Compound **6b** (4.6 g, 59%), b.p. 131–132 °C (1 Torr) was obtained according to the above procedure from **3b** (90% purity) (5.70 g, 0.03 mol) and $LiNEt_2$ (0.06 mol). ^1H NMR (200 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.9 Hz, 3 H), 1.0 (t, *J* = 9.8 Hz, 12 H), 1.46 (qt, *J* = 7.9, 7.6 Hz, 2 H), 2.02 (t, *J* = 7.6 Hz, 2 H), 2.82 (d, *J* = 8.0 Hz, 2 H), 2.98 (q, *J* = 9.8 Hz, 8 H), 4.98 (dd, *J* = 9.0, 1.8 Hz, 1 H), 5.02 (dd, *J* = 14.5, 1.8 Hz, 1 H), 5.35 (s, 1 H), 5.79 (ddt, *J* = 14.5, 9.0, 8.0 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.87, 15.68, 21.02, 39.59, 39.71, 42.51, 115.0, 127.0, 137.49, 145.87 ppm. ^{11}B NMR (64 MHz, $CDCl_3$): δ = 30.75 ppm.

2-Phenyl-1,4-pentadiene (7a). Method A: An aqueous solution NaOH (5 M, 50 mL, 0.25 mol) was added with stirring to a solution of **5a** (12 g, 0.056 mol) in hexane (30 mL). The reaction mixture was stirred at room temperature until complete deboronation (negative green-flame test of organic layer). Then the organic layer was separated and the aqueous layer was extracted with hexane (3 × 15 mL). The combined extracts were dried with K_2CO_3 and the solvents evaporated. Vacuum distillation of the residue gave **7a** (5.8 g, 73%) as a colorless liquid, b.p. 101–102 °C (10 Torr). ^1H NMR (200 MHz, $CDCl_3$): δ = 7.3–7.50 (m, 5 H), 5.85–6.10 (m, 1 H), 5.44 (s, 2 H), 5.09–5.21 (m, 2 H), 3.30 (d, *J* = 6.5 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 146.22 C, 140.83 (C_{Ph}), 136.08 (CH=), 128.16 (2 CH_{Ph}), 127.35 (2 CH_{Ph}), 125.9 (CH_{Ph}), 116.35 (CH_2=), 113.02 (CH_2=), 39.43 (CH_2) ppm.[17a]

Method B: Deboronation of the mixture of **2a** and **3a** (7.0 g, 0.03 mol) under alkaline conditions following the above procedure (Method A) also provided **7a** (2.8 g, 65%).

Method C: A solution of allyl(dipropyl)borane (0.52 g, 0.68 mL, 3.8 mmol) in hexane (1.5 mL) was added at –15 °C to a solution of BCl_3 (0.63 M, 6.0 mL, 3.8 mmol) in hexane. The mixture was stirred for 20 min at –10 to –5 °C, and then phenylacetylene (0.3 g, 0.33 mL, 3.0 mmol) in hexane (2 mL) was rapidly added. The reaction mixture was stirred for 1 h at 0 °C, and then all volatiles were removed under reduced pressure. The resulting light-yellow liquid was treated with AcONa (1.55 g, 19 mmol) in AcOH (4 mL) and refluxed for 1 h. After cooling the mixture was made alkaline with NaOH (5 N, 20 mL) and extracted with hexane (3 × 10 mL). The extracts were washed twice with a solution of $NaHCO_3$ (10%), dried with Na_2SO_4, evaporated. Flash chromatography in hexane on silica gel furnished **7a** (0.33 g, 72%).

2-Propyl-1,4-pentadiene (7b): A solution of NaOH (5 N, 60 mL, 0.3 mol) was added with stirring to a solution of a mixture **2b** and **3b** (9.5 g, 0.05 mol) in hexane (50 mL). The reaction mixture was stirred for 1 h until complete deboronation (green-flame test). The organic layer was separated and the aqueous one was extracted with hexane (3 × 15 mL) and the combined extracts dried with K_2CO_3. Distillation of the residue gave **7b** (3.5 g, 64%) as a colorless liquid, b.p. 115–116 °C (760 Torr). ^1H NMR (200 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 8.1 Hz, 3 H), 1.48 (tq, *J* = 8.1, 8.4 Hz, 2 H), 2.03 (t, *J* = 8.4 Hz, 2 H), 2.75 (d, *J* = 7.4 Hz, 2 H), 4.71 (s, 2 H), 5.01 (s, 1 H), 5.07 (d, *J* = 5.9 Hz, 1 H), 5.70–6.00 (m, 1 H) ppm.[17b]

***trans*-Cinnamyl(dipropyl)borane (8):** *t*BuLi (1.83 M, 23.5 mL, 43 mmol) was added to a stirred solution of allylbenzene (5.31 g, 6 mL, 45 mmol) in THF (40 mL) at –70 to –60 °C and stirring was continued for 10 min and then for 40 min at –20 to –10 °C. The reaction mixture was cooled to –70 °C and Pr_2BOCH_3 (5 g, 43 mmol) was injected, the red color of the mixture being rapidly discharged. The reaction mixture was then allowed to warm to room temperature and quenched with TMSCl (6.1 mL, 48 mmol). The solvents were removed under reduced pressure; the oily residue was stirred with hexane (20 mL) and supernatant was separated from the precipitate of LiCl. The hexane solution was concentrated and vacuum distillation of the residue gave borane **8** (6.6 g, 73%) as a colorless liquid, b.p. 99–100 °C (0.5 Torr). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.28 (m, 4 H), 7.20 (t, *J* = 7.2 Hz, 1 H), 7.41 (dt, *J* = 7.8, 15.6 Hz, 1 H), 6.32 (d, *J* = 15.6 Hz, 1 H), 2.34 (d, *J* = 7.8 Hz, 2 H), 1.54 (sext., *J* = 6.7 Hz, 4 H), 1.32 (t, *J* = 8.0 Hz, 4 H), 0.97 (t, *J* = 7.6 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.30 (C), 129.49 (CH=), 128.26 (2 CH_{Ph}), 127.76 (CH=), 126.20 (CH_{Ph}), 125.50 (2 CH_{Ph}), 33.60 (br., 2 CH_2B), 30.86 (br., CH_2B), 17.77 (2 CH_3), 17.35 (2 CH_2) ppm. ^{11}B NMR (64 MHz, $CDCl_3$): δ = 86.14 (s) ppm.

2,3-Diphenyl-1,4-pentadiene (13): Borane **8** (1 g, 5 mmol) at –15 °C was added to a solution of BCl_3 in hexane (0.8 M, 6.4 mL, 5.1 mmol). The solution was stirred at 0 °C for 15 min. The mixture was then cooled to –30 °C and a solution of phenylacetylene (0.52 g, 5.1 mmol) in hexane (1 mL) was rapidly added through a syringe. The reaction was allowed to warm to 0 °C for 1 h and stirred for 30 min. The reaction was quenched by addition of AcONa (melted) (1.64 g, 20 mmol) in AcOH (4 mL) and refluxed for 1 h. The hexane layer was washed with water, $NaHCO_3$ (10%), dried with Na_2SO_4 and the solvents evaporated. Flash chromatography of the residue with hexane furnished diene **13** (0.76 g, 68%) as a yellowish oil (R_f = 0.21). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (m, 2 H), 7.33–7.20 (m, 8 H), 6.22 (ddd, J = 7.2, 10.2, 17.1 Hz, 1 H), 5.60 (s, 1 H), 5.21 (dt, J = 10.2, 1.2 Hz, 1 H), 5.18 (s, 1 H), 4.99 (dt, J = 17.1, 1.6 Hz, 1 H), 4.67 (d, J = 6.5 Hz, 1 H) ppm.[18] ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.78 (C), 141.61 (C), 141.54 (C), 140.25 (CH), 128.69 (2 CH), 128.41 (2 CH), 128.16 (2 CH), 127.32 (CH), 126.58 (2 CH), 126.46 (CH), 116.28 (CH_2=), 115.54 (CH_2=), 54.07 (CH) ppm. MS (70 eV, EI): m/z (%) = 220 (3) $[M]^+$, 205 (4) $[M - CH_3]^+$, 179 (15) $[M - C_3H_5]^+$, 129 (15), 117 (35), 115 (30), 105 (100), 91 (70), 77 (98), 51 (65), 43 (30). $C_{17}H_{16}$ (220.3): calcd. C 92.68, H 7.32; found C 92.55, H 7.14.

2-(2-Methylenecyclobutyl)-3-(trimethylsilyl)-1-propanol (15) and 3-(1-Cyclobutenyl)-2-[(trimethylsilyl)methyl]-1-propanol (16): A mixture of isomeric boranes **14a** and **14b**[15] (0.5 g, 3.0 mmol) was added to a solution of BCl_3 (0.82 M, 3.7 mL, 3.0 mmol) at –15 °C. The solution was stirred for 15 min at –15 to –5 °C and then the reaction mixture was cooled to –15 °C and allyltrimethylsilane (0.25 g, 0.35 mL, 2.2 mmol) was rapidly added. The reaction mixture was kept for 20 h at –8 °C. After that, NaOH (3 M, 6 mL, 18 mmol), THF (5 mL) and H_2O_2 (30%, 3 mL) were added to the cooled reaction mixture, which was then stirred overnight at ambient temperature. The organic layer was separated, dried with Na_2SO_4 and the solvent evaporated. Flash chromatography of the residue with n-C_6H_{14}/EtOAc (9:1) on silica gel furnished a mixture of isomeric alcohols **15** and **16** (0.36 g, 82%) as a viscous oil (R_f = 0.16) in a ratio of 1:2. ^{1}H NMR (400 MHz, $CDCl_3$) [the bolded subscripts **15** and **16** show that the proton indicated belong to compounds **15** and **16**, respectively]: δ = 5.71 (s, 1 $H_{\mathbf{16}}$), 4.82 (q, J = 2.4 Hz, 1 $H_{\mathbf{15}}$), 4.76 (q, J = 2.4 Hz, 1 $H_{\mathbf{15}}$), 3.65 (dd, J = 5.6, 10.4 Hz, 1 $H_{\mathbf{15}}$, $C\mathit{H}_a\mathrm{H}_b\mathrm{OH}$), 3.53 (t, J = 5.6 Hz, 1 $H_{\mathbf{15}}$, $C\mathrm{H}_a\mathit{H}_b\mathrm{OH}$), 3.51 (t, J = 5.6 Hz, 1 $H_{\mathbf{16}}$, $C\mathit{H}_a\mathrm{H}_b\mathrm{OH}$), 3.47 (dd, J = 6.4, 10.8 Hz, 1 $H_{\mathbf{16}}$, $C\mathrm{H}_a\mathit{H}_b\mathrm{OH}$), 3.07 (dtt, J = 6.5, 10.2, 2.6 Hz, 1 $H_{\mathbf{15}}$), 2.60–2.50 (m, 2 H), 2.42 (m, 2 $H_{\mathbf{16}}$), 2.34 (m, 2 $H_{\mathbf{16}}$), 2.10 (dd, J = 7.2, 16.4 Hz, 1 $H_{\mathbf{16}}$), 2.02–1.95 (m, 1 $H_{\mathbf{16}}$, 1 $H_{\mathbf{15}}$), 1.84 (sept, J = 6.0 Hz, 1 $H_{\mathbf{16}}$), 1.80–1.72 (m, 3 H), 0.59 (dd, J = 6.4, 0.8 Hz, 2 $H_{\mathbf{15}}$), 0.55 (d, J = 6.8 Hz, 2 $H_{\mathbf{16}}$), 0.02 (s, 9 $H_{\mathbf{15}}$), 0.01 (s, 9 $H_{\mathbf{16}}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): compound **15**: δ = 149.22 ($C_{\mathbf{15}}$), 104.90 ($CH_2{=}_{\mathbf{15}}$), 65.63 ($CH_{2,\mathbf{15}}$), 47.95 ($CH_{\mathbf{15}}$), 35.53 ($CH_{\mathbf{15}}$), 28.97 ($CH_{2(\mathrm{cycle})\mathbf{15}}$), 20.18 ($CH_{2(\mathrm{cycle})\mathbf{15}}$), 16.12 ($CH_2Si_{\mathbf{15}}$), –0.86 (3 $CH_{3,\mathbf{15}}$) ppm; compound **16**: δ = 153.12 ($C_{\mathbf{16}}$), 128.73 ($CH{=}_{\mathbf{16}}$), 68.01 ($CH_{2,\mathbf{16}}$), 39.45 ($CH_{\mathbf{16}}$), 35.83 ($CH_{2,\mathbf{16}}$), 31.76 ($CH_{2(\mathrm{cycle})\mathbf{16}}$), 26.69 ($CH_{2(\mathrm{cycle})\mathbf{16}}$), 18.66 ($CH_2Si_{\mathbf{16}}$), –0.68 (3 $CH_{3,\mathbf{16}}$) ppm. MS (70 eV, EI): m/z (%) = 198 $[M]^+$, 197 $[M - H]^+$, 157 (40) $[M - C_3H_5]^+$, 147 (18), 129 (51) $[M - H_2O]^+$, 83 (40), 75 (90), 73 (100), 59 (40), 55 (50), 43 (80). $C_{11}H_{22}OSi$ (198.4): calcd. C 66.60, H 11.18; found C 66.04, H 10.92.

Dimethyl 2-Phenyl-4-pentenylboronate (18): Styrene (4.06 g, 4.5 mL, 39 mmol) was added at –40 °C to a solution of allyl(dibromo)borane **1b** (78 mmol, prepared as described above) in hexane (100 mL). The mixture was allowed to warm to 0 °C and stirred at this temperature for 2 h. Then a mixture of Et_3N (16.2 g, 22.3 mL, 160 mmol) and MeOH (5.1 g, 6.5 mL, 160 mmol) was added at –60 °C with rigorous stirring. When the mixture reached room temperature, a precipitate of Et_3NHBr was filtered off and thoroughly washed with hexane. The filtrate was evaporated under reduced pressure and the residue was subjected to vacuum distillation, which provided boronate **18** (6.2 g, 74%) as a colorless liquid, b.p. 80–84 °C (2 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.19 (m, 5 H), 5.74 (m, 1 H), 5.02 (d, J = 17.12 Hz, 1 H), 4.98 (d, J = 9.96 Hz, 1 H), 3.51 (s, 6 H), 3.02 (m, 1 H), 2.44 (t, J = 7.16 Hz, 2 H), 1.25 (dd, J = 7.48, 15.56 Hz, 1 H), 1.12 (dd, J = 7.48, 15.56 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 147.40 (C_{Ph}), 137.31 (CH=), 128.06 (2 CH_{Ph}), 127.06 (2 CH_{Ph}), 125.67 (CH_{Ph}), 115.66 (CH_2=), 51.04 (2 CH_3O), 43.00 (CH), 41.04 (CH_2), 21.05 (br., CH_2B) ppm. ^{11}B NMR (64 MHz, $CDCl_3$): δ = 31.03 [s, R-$B(OMe)_2$] ppm. MS (70 eV, EI): m/z (%) = 218 (<3) $[M]^+$, 131 (40), 105 (70), 91 (100), 79 (20), 77 (20), 67 (15), 58 (20), 41 (70). $C_{13}H_{19}BO_2$ (218.1): calcd. C 71.59, H 8.78, B 4.96; found C 71.61, H 8.83, B 4.90.

5-Allyl-1-chloro-3-propyl-2-borinene (20): 1-Pentyne (7.4 mL, 0.075 mol) was added to a solution of **1c** (0.075 mol, prepared as indicated above) in hexane (25 mL) at –15 °C. The reaction mixture was stirred for 1 h at 20 °C, and the solvent evaporated under reduced pressure. The residue was distilled in vacuo to give borane **20** (12.5 g, 85%) as a colorless liquid, b.p. 64–65 °C (1 Torr). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (dd, J = 12.67, 3.0 Hz, 1 H), 0.94 (t, J = 7.4 Hz, 3 H), 1.54 (m, 2 H), 1.60 (dd, J = 12.67, 6.5 Hz, 1 H), 1.19–2.25 (m, 2 H), 2.21 (m, 2 H), 2.21 (t, J = 7.54 Hz, 2 H), 2.95 (d, J = 13.5 Hz, 1 H), 5.01 (d, J = 2.9 Hz, 1 H), 5.05 (s, 1 H), 5.7–5.86 (m, 1 H), 5.92 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.69, 20.27, 29.96, 35.61, 39.13, 42.46, 42.99, 116.05, 127.38, 136.26, 177.03 ppm. ^{11}B NMR (64 MHz, $CDCl_3$): δ = 64.40 (s) ppm. MS (70 eV, EI): m/z (%) = 195 (7) $[M - 1]^+$, 182 (10) $[M - 14]^+$, 167 (25) $[M - C_2H_5]^+$, 153 (20) $[M - Pr]^+$, 107 (46), 95 (53), 91 (69), 79 (78), 67 (100) $[C_5H_7]^+$, 55 (25), 41 (33). $C_{11}H_{18}BCl$ (196.5): calcd. C 67.23, H 9.23, B 5.50; found C 66.47, H 9.76, B 4.97.

5-Allyl-1-isopropoxy-3-propyl-2-borinene (21): A mixture of isopropyl alcohol (1.1 mL, 0.014 mol) and Et_3N (1.94 mL, 0.014 mol) was added with rigorous stirring to a solution of **20** (2.8 g, 0.014 mol) in hexane (40 mL) at –40 °C. The mixture was stirred for 2 h at room temperature. A precipitate of Et_3NHCl was filtered off and washed with hexane (2 × 10 mL); the filtrate was evaporated under reduced pressure. Distillation of the residue gave **21** (1.75 g, 57%) as a yellow liquid, b.p. 95–96 °C (2 Torr). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.50 (dd, J = 15.8, 11.6 Hz, 1 H), 0.90 (t, J = 7.3 Hz, 3 H), 1.28 (dd, J = 15.8, 6.3 Hz, 1 H), 1.23 (d, J = 6.8 Hz, 6 H), 1.47 (tq, J = 7.7, 7.3 Hz, 2 H), 1.83 (d, J = 12.2 Hz, 1 H), 1.70–1.90 (m, 1 H), 2.05–2.15 (m, 3 H), 2.12 (t, J = 7.7 Hz, 2 H), 4.47 (sept, J = 6.8 Hz, 1 H), 4.94 (s, 1 H), 5.02 (d, J = 4.2 Hz, 1 H), 5.53 (s, 1 H), 5.70–5.90 (m, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.84, 20.76, 24.55, 25.00, 35.96, 39.77, 40.86, 43.28, 68.15, 115.29, 125.68, 137.27, 170.66 ppm. ^{11}B NMR (64 MHz, $CDCl_3$): δ = 46.16 (s, iPrOB<). MS (70 eV, EI): m/z (%) = 220 $[M]^+$, 191 (30) $[M - C_2H_5]^+$, 179 (15), 177 (20), 161 (22), 150 (56), 121 (45), 109 (36), 94 (58), 91 (72), 79 (73), 67 (100) $[C_5H_7]^+$, 55 (40), 41 (37). $C_{14}H_{25}BO$ (196.5): calcd. C 76.38, H 11.45, B 4.91; found C 76.47, H 11.44, B 4.88.

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[1] a) D. S. Matteson, *Stereodirected Synthesis with Organoboranes*, Springer, Berlin, **1995**; b) A. Pelter, K. Smith, H. C. Brown, *Borane reagents*, Academic Press, London, **1988**; c) B. M. Mikhailov, Y. N. Bubnov, *Organoboron compounds in organic synthesis*, Harwood Academic Scientific Publishers, London, New York, **1984**.

[2] a) Y. N. Bubnov, *Pure Appl. Chem.* **1987**, *59*, 895–906; b) Y. N. Bubnov in *Science of Synthesis Houben-Weyl Methods of molecular Transformation* (Eds.: D. E. Kaufmann, D. S. Matteson), Georg Thieme Verlag, Stuttgart, **2005**, vol. 6, ch. 35, pp. 942–1072.

[3] P. V. Ramachadran, *Aldrichimica Acta* **2002**, *35*, 23–35.

[4] a) Y. N. Bubnov, M. S. Grigorian, A. V. Tsyban′, B. M. Mikhailov, *Synthesis* **1980**, 902–904; b) . Y. N. Bubnov, M. Y. Etinger, *Tetrahedron Lett.* **1985**, *26*, 2797–2800; c) Y. N. Bubnov, L. I. Lavrinovich, *Tetrahedron Lett.* **1985**, *26*, 4551–4554; d) Y. N. Bubnov, V. I. Zheludeva, *Izv. Acad. Nauk SSSR, Ser. Khim.* **1987**, 235–236; e) Y. N. Bubnov, L. I. Lavrinovich, *Izv. Acad. Nauk SSSR, Ser. Khim.* **1988**, 420–425; f) Y. N. Bubnov, M. E. Gurskii, D. G. Pershin, *Izv. Acad. Nauk SSSR, Ser. Khim.* **1987**, 1193–1194; g) Y. N. Bubnov, V. I. Zheludeva, T. C. Kuznetsova, *Izv. Acad. Nauk SSSR, Ser. Khim.* **1987**, 2632–2633; h) Y. N. Bubnov, M. Y. Etinger, A. V. Ignatenko, *Izv. Acad. Nauk SSSR, Ser. Khim.* **1989**, 1343–1351; i) Y. N. Bubnov, V. I. Zheludeva, A. V. Ignatenko, *Izv. Acad. Nauk SSSR, Ser. Khim.* **1989**, 420–426; j) Y. N. Bubnov, V. I. Zheludeva, A. V. Ignatenko, *J. Organomet. Chem.* **1989**, *359*, 151–158.

[5] a) Y. N. Bubnov, O. A. Nesmeyanova, T. Y. Rudashevskaya, B. M. Mikhailov, B. A. Kazansky, *Tetrahedron Lett.* **1971**, *12*, 2153–2156; b) Y. N. Bubnov, B. A. Kazansky, O. A. Nesmeyanova, T. Y. Rudashevskaya, B. M. Mikhailov, *Izv. Acad. Nauk SSSR, Ser. Khim.* **1977**, 2545 and references cited therein.

[6] Y. N. Bubnov, A. V. Geiderich, A. V. Ignatenko, P. Y. Meleshkin, M. E. Gursii, *Mendeleev Commun.* **1994**, 214–215.

[7] B. M. Mikhailov, Y. N. Bubnov, M. S. Grigorian, *Zh. Obshch. Khim.* **1974**, *44*, 2465 and references cited therein.

[8] Y. N. Bubnov, A. V. Tsyban′, V. M. Mikhailov, *Synthesis* **1980**, 904–905.

[9] a) B. Wrackmeyer, O. L. Tok, Y. N. Bubnov, *Angew. Chem. Int. Ed.* **1999**, *38*, 124–126; b) B. Wrackmeyer, O. L. Tok, E. V. Klimkina, Y. N. Bubnov, *Inorg. Chim. Acta* **2000**, *300–302*, 169–174; c) B. Wrackmeyer, M. H. Bhatti, S. Ali, O. L. Tok, Y. N. Bubnov, *J. Organomet. Chem.* **2002**, *657*, 146–154; d) B. Wrackmeyer, O. L. Tok, Y. N. Bubnov, *Appl. Organomet. Chem.* **2004**, *18*, 43–50 and references cited therein.

[10] a) D. A. Singleton, S. C. Waller, Z. Zhang, D. E. Frantz, S.-W. Leung, *J. Am. Chem. Soc.* **1996**, *118*, 9986–9987; b) D. E. Frantz, D. A. Singleton, *Org. Lett.* **1999**, *1*, 485–486.

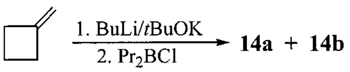
[11] a) S. L. Serre, J.-C. Guillemin, *Organometallics* **1997**, *16*, 5844–5848; b) K. M. Depew, S. J. Danishefsky, N. Rosen, L. Sepp-Lorenzino, *J. Am. Chem. Soc.* **1996**, *118*, 12463–12464; c) J. M. Sohkeryanz, J. C. G. Woo, P. Siliphaivanh, K. M. Depew, S. J. Danishefsky, *J. Am. Chem. Soc.* **1999**, *121*, 11964–11975; d) Y. Tanigawa, I. Moritani, S. Nishida, *J. Organomet. Chem.* **1971**, *28*, 73–79.

[12] P. Harston, J. L. Wardell, D. Marton, G. Tagliavini, P. Smith, *Inorg. Chim. Acta* **1989**, *162*, 245–250.

[13] R. W. Hoffmann, G. Feussner, H. J. Zeiss, S. Schulz, *J. Organomet. Chem.* **1980**, *187*, 321–329.

[14] a) B. M. Mikhailov, Y. N. Bubnov, B. S. Bogdanov, *Zh. Org. Chim.* **1975**, *45*, 324–332; b) B. M. Mikhailov, Y. N. Bubnov, B. S. Bogdanov, *Zh. Org. Chim.* **1975**, *45*, 333–338 (*Chem. Abstr.* **1975**, 82, 111345d).

[15] A mixture of dynamic isomers **14a** and **14b** was synthesized in 37% yield by metallation of methylenecyclobutane followed by treatment with Pr_2BCl.



a) Y. N. Bubnov, M. E. Gurskii, L. I. Lavrinovich, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 1918–1919; b) I. D. Gridnev, M. E. Gurskii, Y. N. Bubnov, *Organometallics* **1996**, *15*, 3696–3702.

[16] L. I. Zakharkin, V. I. Stanko, *Izv. Acad. Nauk SSSR, Ser. Khim.* **1960**, 1896–1898 (*Chem. Abstr.* **1961**, 55, 15337d).

[17] a) K. Lee, J. Lee, P. H. Lee, *J. Org. Chem.* **2002**, *67*, 8265–8268; b) Y. Naruta, Y. Nishigaichi, K. Maruyama, *J. Org. Chem.* **1991**, *56*, 2011–2017.

[18] S. Araki, A. Imai, K. Shimizu, M. Yamada, A. Mori, Y. Butsugan, *J. Org. Chem.* **1995**, *60*, 1841–1847.

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