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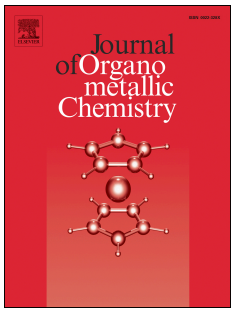

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New boron reagents for cycloboration of α-olefins into boriranes under Cp_2TiCl_2 catalysis

Liliya I. Khusainova, Leila O. Khafizova,* Tatyana V. Tyumkina,

Kirill S. Ryazanov, Natalya R. Popodko, Usein M. Dzhemilev

Institute of Petrochemistry and Catalysis of Russian Academy of Sciences,

141 Prospekt Oktyabrya, Ufa 450075, Russian Federation

Abstract

The one-pot cycloboration of α-olefins (oct-1-ene, dec-1-ene) for a facile access to substituted boriranes has been carried out with the use of alkyl, arylalkyl, and cycloalkyl boron dichlorides ($EtBCl_2$, n-$PentBCl_2$, n-$HexBCl_2$, $Ph(CH_2)_2BCl_2$, cyclo-$OctBCl_2$, 2-norbornylBCl_2) under Cp_2TiCl_2 catalysis.

Keywords

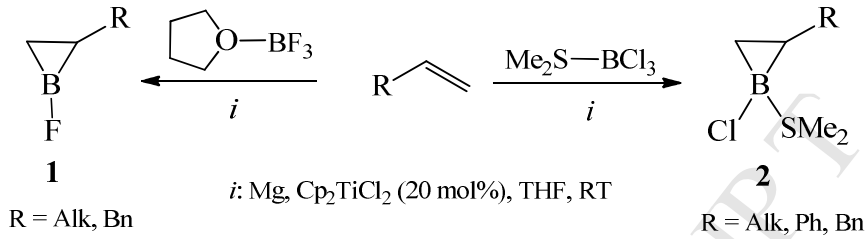
Boriranes, *α*-olefins, cycloboration, catalysis, titanacyclopropane, dichloroboranes

1. Introduction

The three-membered heterocycles such as azacyclopropanes (aziridines) [1], oxacyclopropanes (oxiranes) [2], thiacyclopropanes (thiiranes) [3], silacyclopropanes (siliranes) [4] are readily available and have a rich chemistry. In contrast, boron analogs of cyclopropanes (boracyclopropanes, or boriranes) are more rare [5], presumably because they combine two features − ring strain and Lewis acidity − that often impart reactivity. For the first time, Berndt A. and Klusik H. have synthesized boriranes in 1983 [6]. Later, Denmark has synthesized pyridine complexes of boriranes [7], and Braunschweig [8] and Wang [9] have recently prepared a number of stable NHC-substituted boriranes. In 2017, D. Curran has reported a direct synthesis of NHC-boriranes by reactions of dimethyl acetylenedicarboxylate with NHC-boranes [10]. However, before our investigations, catalytic methods for producing boriranes via cycloboration of unsaturated compounds have not been discussed.

* Corresponding author. Fax: +73472842750;
e-mail: khafizovaleila@gmail.com (L.O. Khafizova).

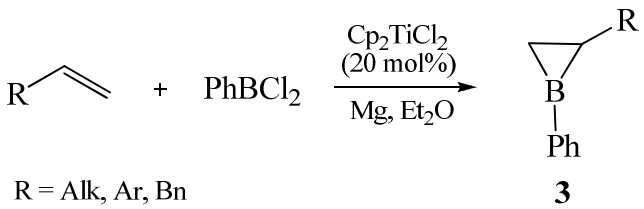
Recently, for the first time, we have carried out direct cycloboration of *α*-olefins with complexes of boron trihalides ($BCl_3 \cdot SMe_2$ and $BF_3 \cdot THF$) in the presence of Mg and Cp_2TiCl_2 catalyst [11] (Scheme 1) to afford appropriate 1-fluoro(chloro)-2-substituted boriranes **1** and **2**.



Scheme 1. Synthesis of 1-flouro(chloro)-2-substituted boriranes from α-olefins and $BF_3 \cdot THF$ (or $BCl_3 \cdot SMe_2$) in the presence of Cp_2TiCl_2.

The experimental data on the preparation of 1-chloroboriranes [11a] are in good agreement with the results of our theoretical modeling of the mechanism of the one-pot formation of boriranes from α-olefins and BCl_3, the key step of which is the replacement of the transition metal atom by the boron atom in the titanacyclopropane intermediate [12]. The identification of boriranes using multinuclear ^1H, ^{13}C and ^{11}B NMR spectroscopy is difficult due to the lack of signals of *endo*-cyclic carbon and hydrogen atoms. In addition, chemical shift values of boron atoms in ^{11}B NMR spectra described in the literature for boriranes vary in a wide range from -1 to +38 ppm [6, 11]. Mass-spectrometry analysis is often unsuitable for the identification because of the low stability of many boriranes.

Based on the results of the quantum-chemical DFT investigations we have predicted that along with BCl_3, aryl(alkyl) boron dichlorides may also serve as transmetallating reagents [12]. Later, we have successfully implemented reactions of α-olefins with $PhBCl_2$ in the presence of metallic magnesium and catalytic amounts of Cp_2TiCl_2 producing 1-phenyl-2-substituted borirans **3** (Scheme 2) [13].



Scheme 2. Cp_2TiCl_2-catalyzed cycloboration of α-olefins with $PhBCl_2$.

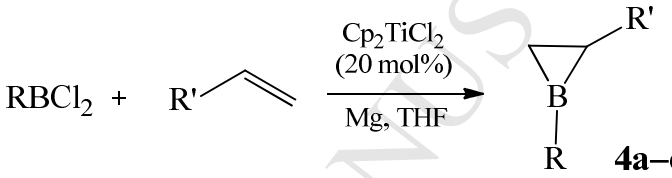
In this paper, we report the results of our further investigations into the structure of initial R-substituted boron dichlorides and the cycloboration reaction with the participation of α-olefins under Cp_2TiCl_2 catalysis.

2. Results and discussion

In order to study the effect of structure of the starting boron dichlorides on the yield and selectivity of the formation of the three-membered organoboron compounds, we have studied the reaction of diverse boron dichlorides with acyclic and cyclic olefins in the presence of Cp_2TiCl_2 catalyst.

Alkyl boron dichlorides ($EtBCl_2$, $PentBCl_2$, $HexBCl_2$) and arylalkyl boron dichlorides ($Ph(CH_2)_2BCl_2$, $Naphth(CH_2)_2BCl_2$) have been selected as the objects of study.

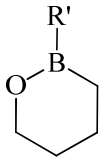
Thus, the reaction of α-olefins (oct-1-ene, dec-1-ene) with alkyl boron dichlorides under the reaction conditions (olefin: [B]: [Mg]: [Ti] = 1 : 1.2 : 2 : 0.2, THF, 50 ºC for 5h, then ~ 22-25 ºC for 16 h) afforded 1,2-dialkyl boriranes **4a-e** in 67–82% yield, which have been isolated and identified by spectral and chemical methods (Scheme 3).



a: R = Et, R' = Hex (82%) **b**: R = Et, R' = Oct (80%)
c: R = Pent, R' = Hex (77%) **d**: R = R' = Hex (67%)
e: R = Pent, R' = Oct (74%)

Scheme 3. Alkyldichloroboranes in the cycloboration reaction of *α*-olefins.

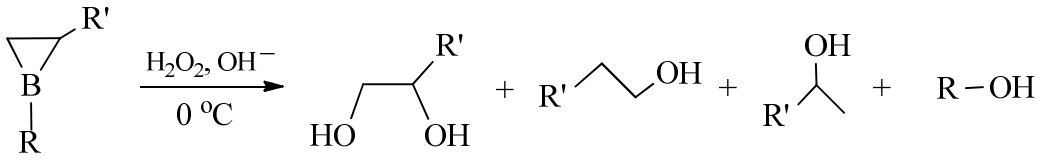
Along with borirans **4a-e**, under this reaction conditions, small amounts of 2-alkyl-1,2-oxaborinanes **5a,b** (10-12%) have been detected. Formation of **5a,b**, apparently, occurs with the participation of THF, which is used in the reaction as a solvent.



a: R' = Oct
b: R' = Dec

5a,b

The oxidation of 1,2-dialkylboriranes **4a-d** (H_2O_2, NaOH) [11–14] led to the corresponding diols **6a–e** and monools **7–9** in a ratio of 1:1:1:1 (Scheme 4).



4a–e **6a–e** **7a–e** **8a–e** **9a–e**

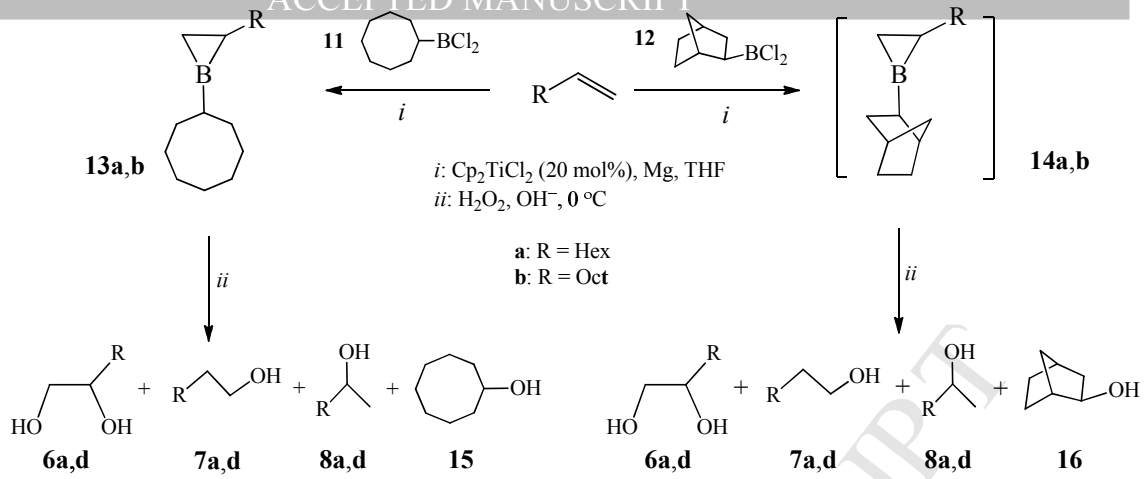
a: R = Et, R' = Hex **b**: R = Et, R' = Oct
c: R = Pent, R' = Hex **d**: R = R' = Hex
e: R = Pent, R' = Oct

Scheme 4. Oxidation of 1,2-dialkylboriranes.

It should be noted that in contrast to the Cp_2TiCl_2-catalyzed cycloboration reactions of α-olefins with $PhBCl_2$, $BCl_3{\cdot}SMe_2$ or $BF_3{\cdot}THF$, which occur at room temperature, the reactions involving alkyldichloroboranes occur only when heated to 50 °C. Experiments have shown that dichloro[(2-phenyl)ethyl]borane ($Ph(CH_2)_2BCl_2$), hardly reacts with α-olefins in the cycloboration reaction even at elevated temperatures (50–100 °C). The formation 1-(2-phenylethyl)-2-hexylborirane was confirmed only by the oxidation products (octane-1,2-diol **6a**, octan-1-ol **7a**, octan-2-ol **8a**, 2-phenylethanol **10**). Dichloro[2-(2-naphthyl)ethyl]borane ($Naphth(CH_2)_2BCl_2$) does not give rise to the desired boriranes under selected reaction conditions.

Apparently, the low reactivity of arylalkyldichloroboranes is associated with ~~an increase in the energy barrier at the intramolecular cyclization stage compared with that calculated for BCl3 [12]. The calculated energy barrier (or energy of activation, Ea) is ~20 kcal /mol for the reactions, which occur at room temperature.~~ high-energy barriers (more than 20 kcal /mol) at the stages of borirane formation. We have performed a series of DFT calculations for the cycloboration reaction according to the proposed mechanism [12] including the insertion of the boron-containing compound ($BnBCl_2$ and $PhBCl_2$) into the cyclopropane intermediate and subsequent intramolecular cyclization to give the corresponding borirane. It turned out that the experiment is in good agreement with the theoretical data about the lack of reactivity of alkyldichloroboranes as compared to $PhBCl_2$ (see *Support. inform*. pp. 19), although, it is difficult to analyze different reactivity of alkyldichloroborane and $Ph(CH_2CH_2)BCl_2$ in the direct cycloboration reaction of α-olefins with organoboron reagents.

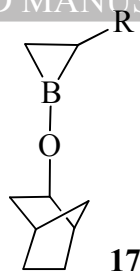
Along with alkyl boron dichlorides and arylalkyl boron dichlorides, we have synthesized aliphatic cycloalkyldichloroboranes, namely, cyclooctyldichloroborane **11** and *exo*-norbornyldichloroborane **12**, which have been successfully involved in the Cp_2TiCl_2-catalyzed cycloboration reaction of α-olefins giving rise to 2-alkyl-1-cyclooctyl(norbornyl)boriranes **13a**,**b** and **14a**,**b** (Scheme 5). Oxidation of boriranes **13a**,**b** and **14a**,**b** under basic conditions (H_2O_2/NaOH) led to the expected diols **6a**,**d** and monools **7a**,**d**, **8a**,**d**, **15** and **16.**



Scheme 5. Cyclooctyl- and *exo*-norbornyldichloroboranes in the cycloboration reaction of α-olefins.

The structures of boriranes **4a–e** and **13a**,**b** obtained by vacuum distillation have been confirmed by multinuclear (^{1}H, ^{13}C, ^{11}B) NMR spectroscopy. In ^{1}H and ^{13}C NMR spectra of boriranes **4a–e** and **13a**,**b** signals of carbon and hydrogen atoms, which occupy α-position, i.e. adjacent to the boron atom, do not occur, obviously, due to quadrupole broadening effects of the boron nuclei [15], which is characteristic for three-membered boracyclanes [6,11b,13,16]. The ^{11}B NMR spectra ($CDCl_3$) demonstrate expected broadened signals at δ ~31 ppm, which agrees well with the spectral data for alkyl substituted boriranes in $CDCl_3$ described in the literature [6,12,13]. The resulting boriranes was analyzed by GC-MS. So, for example, mass spectrum of borirane **4d** displayed mass peaks, which were exhibited at 240 ($C_{14}H_{29}BO_2$), 112 [M^+–H_2O] ($C_8H_{18}O$ – octan-1-ol and octan-2-ol) and 84 [M^+–H_2O] (hexan-1-ol). All these peaks are consistent with oxidation and hydrolysis products, arising from **4d** in the mass spectrometer. Similar results have been obtained for the whole series of the synthesized boriranes.

However, the NMR spectra of the expected boriranes **14a**,**b**, along with the signals attributed to the alkyl substituent and the norbornyl moiety, show the signals of the tertiary carbon atom of the norbornane skeleton at δ_C 74 ppm thus indicating the incorporation of an oxygen atom through the B–C bond with retention of the boracyclopropane fragment. Obviously, 1-norbornyl-2-alkylboriranes **14a**,**b** being formed under the reaction conditions are very sensitive to even trace amounts of air oxygen, and therefore 1-(bicyclo[2.2.1]hept-2-yloxy)-2-alkylboriranes **17a**,**b** have been identified as final products after isolation of the desired product by distillation.



17a,**b**

3. Conclusion

In summary, we have successfully carried out direct cycloboration of a-olefins with new boron reagents, namely, ethyl-, *n*-pentyl-, *n*-hexyl-, phenylethyl-, cyclooctyl-, and *exo*-norbornyl boron dichlorides in THF in the presence of metallic magnesium and Cp_2TiCl_2 as the catalyst. For the first time, 1-alkyl(cycloalkyl)-2-alkyl substituted boriranes have been synthesized from available and commonly used monomers with good yields.

4. Experimental section

All reactions were carried out using standard Schlenk techniques. Commercially available olefins, $HBCl_2 \cdot SMe_2$, BCl_3 (1 M solution in hexane), Et_3B and Cp_2TiCl_2 (Aldrich) were used. THF employed were pre-dried over KOH, refluxed over sodium-wire for 2 h and distilled from $LiAlH_4$ in a stream of argon. Reactions with organometallic compounds were performed in a dry argon flow.

The ^1H, ^{13}C, ^{11}B and 2D homo- (COSY) and heteronuclear (HSQC, HMBC) NMR spectra were measured in $CDCl_3$ on a Bruker Avance-400 spectrometer [400.13 (^1H), 100.62 (^{13}C), 128.33 (^{11}B) MHz]. Chemical shifts (δ) are given in ppm relative to TMS, and the coupling constants (*J*) in Hz. ^1H and ^{13}C NMR shifts were referenced to internal solvent resonances and reported in parts per million (ppm) relative to Me_4Si. ^{11}B NMR spectra were referenced to an external standard of $BF_3 \cdot Et_2O$.

Mass spectra were obtained on Shimadzu GCMS-QP2010 Ultra, capillary column Supelco PTE-5 (60 m × 0.25 mm, carrier gas helium, ramp from 40 to 280°C at a rate 8 deg/min, ionizing electrons energy 70 eV, injector temperature 260°C, ion source temperature 200°C).

The H_2O_2 oxidation of boriranes was done under alkaline conditions as described in Refs. [11–14]. Spectral and physical characteristics of compounds (**6**, **7**, **8**, **9**, **15**, **16**) have been reported [17].

*4.1. Synthesis of n-PentBCl_2, n-HexBCl_2, Ph$(CH_2)_2BCl_2$, Naphth$(CH_2)_2BCl_2$, cyclo-OctBCl_2 (**11**), exo-2-norbornylBCl_2 (**12**) as complexes with SMe_2.*

4.1.1. General procedure.

Boron dichlorides, $RBCl_2$ (R = *n*-Pent, *n*-Hex, $Ph(CH_2)_2$, $Naphth(CH_2)_2$, cyclo-Oct, *exo*-norbornyl) were synthesized as complexes with SMe_2 according to the method as described in Ref. [18]. Spectral assignments for dichloroborane–dimethyl sulfides reagent have been made for the first time.

4.1.1.1. Spectral data for n-pentyldichloroborane-dimethyl sulfide. Colorless steaming liquid, bp 161 ºC. IR spectrum, ν, cm^{-1}: 2958, 2928, 2871, 2861, 1459, 1383, 1220, 1180, 1038, 908, 824, 733, 649. ^{1}H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ = 0.84−0.94 (m, 5H, B–CH_2, CH_3), 1.25−1.36 (m, 4H, $2CH_2$), 1.37–1.48 (m, 2H, CH_2), 2.38 (br.s, 6H, Me_2S). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ = 13.97, 19.58 (br, Me_2S), 22.44, 24.90, 26.06 (br, B−CH_2), 34.61. ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): δ = 11.66.

4.1.1.2. Spectral data for n-hexyldichloroborane-dimethyl sulfide. Colorless steaming liquid, bp 169 ºC. IR spectrum, ν, cm^{-1}: 2960, 2935, 2927, 2870, 2861, 1455, 1458, 1380, 1210, 1221, 1185, 1050, 900, 833, 820, 730, 699. ^{1}H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ = 0.86−0.94 (m, 5H, B–CH_2, CH_3), 1.25−1.38 (m, 6H, $3CH_2$), 1.40–1.48 (m, 2H, CH_2), 2.38 (br.s, 6H, Me_2S). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ = 14.12, 19.48 (br, Me_2S), 22.62, 25.29, 25.77 (br, B−CH_2), 31.76, 32.17. ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): δ = 10.87.

4.1.1.3. Spectral data for cyclooctyldichloroborane-dimethyl sulfide ***11***. Colorless steaming liquid, bp 90 ºC (10 mm). IR spectrum, ν, cm^{-1}: 2870, 2848, 2350, 2218, 2111, 1461, 1401, 1355, 1248, 1211, 1209, 1180, 1135, 1039, 960, 850, 801, 730, 621. ^{1}H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ = 0.90–1.02 (m, 1H, B–CH), 1.41–1.67 (m, 10H, $2CH^A$, $4CH_2$), 1.67−1.84 (m, 4H, $2CH^B$, CH_2), 2.40 (br.s, 6H, Me_2S). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ = 19.66 (br, Me_2S), 26.47, 27.23, 27.35, 29.50, 30.03 (br, B–CH). ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): δ = 13.30.

4.1.1.4. Spectral data for exo-2-norbornyldichloroborane-dimethyl sulfide ***12***. Pale yellow steaming liquid, bp 112 ºC (40 mm). IR spectrum, ν, cm^{-1}: 2951, 2869, 2359, 2253, 1454, 1372, 1265, 1219, 1199, 1149, 1108, 1033, 950, 908, 834, 735, 650, 546. ^{1}H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ = 0.86 (t, 1H, B–C^2H, J = 8.2 Hz), 1.06 (d, 1H, C^7H^A, ^2J = 9.5 Hz), 1.16−1.19 (m, 2H, C^5H^A, C^6H^A), 1.29–1.36 (m, 1H, C^3H^A), 1.46−1.57 (m, 3H, C^3H^B, C^5H^B, C^6H^B), 1.70 (dt,

1H, C^7H^B, ^4J = 1.9 Hz), 2.25 (br.s, 1H, C^4H), 2.26 (br.s, 1H, C^1H), 2.36 (br.s, 6H, Me_2S). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ = 20.25 (br, Me_2S), 28.68 (C^5), 33.67 (C^6), 34.38 (C^3), 36.42 (br, B–C^2H), 36.73 (C^4), 36.89 (C^7), 39.36 (C^1). ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): δ = 12.15.

*4.2. Synthesis of 1-ethyl-2-hexylborirane (**4a**), 1-ethyl-2-octylborirane (**4b**), 2-octyl-1,2-oxaborinane (**5a**), 2-decyl-1,2-oxaborinane (**5b**)*

4.2.1. General procedure.

A glass reactor (50 mL), under a dry argon atmosphere at 0 °C, was charged under stirring with Cp_2TiCl_2 (2 mmol, 0.498 g), magnesium (powder) (20 mmol, 0.486 g), THF (30 mL), the corresponding α-olefin (10 mmol) and $EtBCl_2$ (12 mmol). $EtBCl_2$ was synthesized according to the methods as described in Refs. [19]. The temperature was raised to 55–60 °C and the mixture was stirred 5 h. Then reaction mixture was cooled to room temperature (~ 20–22 ºC) and was stirred for additional 16 h. Then the reaction mixture was centrifuged, the excess of magnesium was filtered off, the solvent was evaporated and the residue was distilled under reduced pressure in a stream of argon.

*4.2.1.1. Spectral date for 1-ethyl-2-hexylborirane **4a***. Yield: 82% (1.25 g, 8.2 mmol). Pale yellow liquid, bp 72 ºC (10 mm). IR spectrum, ν, cm-1: 2960, 2901, 2855, 1490, 1410, 1350, 1211, 1101, 1050, 980, 905, 890, 765, 725, 693. ^1H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ = 0.85−0.98 (m, 6H, CH_3, B-CH_2-C$\underline{H}_3$), 1.22−1.52 (m, 8H, $4CH_2$). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ = 7.92 (B-CH_2-$\underline{C}H_3$), 14.06, 22.63, 29.25, 29.34, 31.80. ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): δ = 31.34. [In the ^1H and ^{13}C spectra signals of protons and carbon atoms directly attached to the boron atom (B-C^2H, B-C^3H_2 (cycle), B-CH_2) and C^4H_2 were not detected].

*4.2.1.2. Spectral date for 1-ethyl-2-octylborirane **4b***. Yield: 80% (1.44 g, 8.0 mmol). Pale yellow liquid, bp 86 ºC (10 mm). IR spectrum, ν, cm^{-1}: 2955, 2854, 1481, 1460, 1415, 1333, 1219, 1119, 1076, 1051, 968, 910, 895, 793, 762, 722, 665. ^1H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ = 0.87−0.95 (m, 6H, CH_3, B-CH_2-C$\underline{H}_3$), 1.20–1.46 (m, 12H, $6CH_2$). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ = 7.83 (B-CH_2-$\underline{C}H_3$), 14.06, 22.69, [(29.38, 29.62, 29.67) 4C], 31.94. ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): δ = 31.36. [In the ^1H and ^{13}C spectra signals of protons and carbon atoms directly attached to the boron atom (B-C^2H, B-C^3H_2 (cycle), B-CH_2) and C^4H_2 were not detected].

4.2.1.3. Spectral date for 2-octyl-1,2-oxaborinane ***5a***. Yellow oil liquid, bp 75 ºC (1 mm). Yield: 10% (0.20 g, 1.0 mmol). IR spectrum, ν, cm^{-1}: 2925, 2855, 1458, 1416, 1332, 1296, 1209, 1180, 1077, 1049, 893, 793, 722. ^{1}H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ = 0.74 (t, 2H, B-CH_2, cycle, *J* = 7.8 Hz), 0.88 (t, 3H, CH_3, *J* = 6.2 Hz), 0.97 (t, 2H, B-CH_2, alkyl, *J* = 7.8 Hz), 1.26 (m, 12H, 6CH_2, alkyl), 1.55 (m, 2H, CH_2, cycle), 1.64 (m, 2H, CH_2, cycle), 4.04 (t, 2H, O-CH_2, *J* = 5.8 Hz). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ = 14.27, 16.09 (br, B-CH_2, cycle), 19.42, 22.21 (br, B-CH_2, alkyl), 22.92, 24.24, 28.23, 29.56, 29.81, 32.20, 32.98, 66.48. ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): δ = 52.73. MS *m/z*: 196 $[M]^+$.

4.2.1.4. Spectral date for 2-decyl-1,2-oxaborinane ***5b***. Yellow oil liquid, bp 88 ºC (1 mm). Yield: 12% (0.27 g, 1.2 mmol). IR spectrum, ν, cm^{-1}: 2918, 2835, 1460, 1425, 1415, 1341, 1300, 1211, 1155, 1089, 1040, 888, 795, 730, 702, 695. ^{1}HMR ($CDCl_3$, in ppm, 400.13 MHz): δ = 0.75 (t, 2H, B-CH_2, cycle, *J* = 7.8 Hz), 0.89 (t, 3H, CH_3, *J* = 6.5 Hz), 0.98 (t, 2H, B-CH_2, alkyl, *J* = 7.0 Hz), 1.27 (m, 16H, 8CH_2, alkyl), 1.56 (m, 2H, CH_2, cycle), 1.64 (m, 2H, CH_2, cycle), 4.06 (t, 2H, O-CH_2, *J* = 5.4 Hz). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ = 14.11, 15.92 (br, B-CH_2, cycle), 19.18, 21.89 (br, B-CH_2, alkyl), 22.70, 24.05, 27.98, 29.32, 29.58, 29.66, 29.69, 31.96, 32.76, 66.34. ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): δ = 52.76. MS *m/z*: 224 $[M]^+$.

*4.3. Synthesis of 1-pentyl-2-hexylborirane (****4c****), 1,2-dihexylborirane (****4d****), 1-pentyl-2-octylborirane (****4e****), 1-cyclooctyl-2-hexylborirane (****13a****), 1-cyclooctyl-2-octylborirane (****13b****), 1-(bicyclo[2.2.1]hept-2-yloxy)-2-hexylborirane (****17a****), 1-(bicyclo[2.2.1]hept-2-yloxy)-2-octylborirane (****17b****)*

4.3.1. General procedure

A glass reactor (50 mL), under a dry argon atmosphere at 0 °C, was charged under stirring with Cp_2TiCl_2 (2 mmol, 0.498 g), magnesium (powder) (20 mmol, 0.486 g), THF (30 mL), the corresponding *α*-olefin (10 mmol) and $RBCl_2 \cdot SMe_2$ [†] (12 mmol). The temperature was raised to 55–60 °C and the mixture was stirred 5 h. Then reaction mixture was cooled to room temperature (~ 20–22 ºC) and was stirred for additional 16 h. Then the reaction mixture was centrifuged, the excess of magnesium was filtered off, the solvent was evaporated and the residue was distilled under reduced pressure in a stream of argon.

[†] Initial boron dichlorides were involved in the reaction as complexes with SMe_2 [18] because they are more stable and resistant to oxidation. The isolated in vacuum boriranes did not contain SMe_2 in their structure as in the case with individual $RBCl_2$.

4.3.1.3. Spectral date for 1-pentyl-2-hexylborirane ***4c***. Yield: 77% (1.50 g, 7.7 mmol). Pale yellow liquid, bp 107 ºC (10 mm). IR spectrum, ν, cm^{-1}: 2940, 2920, 2833, 2801, 1501, 1490, 1315, 1310, 1056, 1015, 1009, 932, 850, 724, 650. ^{1}H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ = 0.90 (t, 6H, $2CH_3$, J = 6.4 Hz), 1.10−1.50 (m, 12H, $6CH_2$), 1.50−1.70 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ = 14.29 (2C), 22.68, 22.87, [(29.50, 29.59) 3C], 32.05, 32.14. ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): δ = 31.70. [In the ^{1}H and ^{13}C spectra signals of protons and carbon atoms directly attached to the boron atom (B-C^2H, B-C^3H_2 (cycle), B-CH_2) and C^4H_2 were not detected].

4.3.1.4. Spectral date for 1,2-dihexylborirane ***4d***. Yield: 67% (1.40 g, 6.7 mmol). Pale yellow liquid, bp 80 ºC (2 mm). IR spectrum, ν, cm^{-1}: 2955, 2924, 2855, 1458, 1415, 1332, 1077, 1055, 1029, 909, 892, 800, 723, 665. ^{1}H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ = 0.84–0.90 (m, 6H, $2CH_3$), 1.27–1.42 (m, 14H, $7CH_2$), 1.50–1.65 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ = 14.02, 14.08, 22.64 (2C), [(29.27, 29.38) 3C], 31.62, 31.83, 31.94. ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): δ = 31.25. [In the ^{1}H and ^{13}C spectra signals of protons and carbon atoms directly attached to the boron atom (B-C^2H, B-C^3H_2 (cycle), B-CH_2) and C^4H_2 were not detected].

4.3.1.5. Spectral date for 1-pentyl-2-octylborirane ***4e***. Yield: 74% (1.64 g, 7.4 mmol). Pale yellow liquid, bp 85 ºC (2 mm). IR spectrum, ν, cm^{-1}: 2947, 2935, 2923, 2855, 1460, 1458, 1450, 1330, 1081, 1054, 1033, 1032, 990, 908, 892, 810, 727, 631. ^{1}H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ = 0.85–0.95 (m, 6H, $2CH_3$), 1.23–1.60 (m, 18H, $9CH_2$). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ = 14.09 (2C), 22.46, 22.67, [(29.29, 29.35, 29.61, 29.65) 5C], 31.90 (2C). ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): δ = 30.66. [In the ^{1}H and ^{13}C spectra signals of protons and carbon atoms directly attached to the boron atom (B-C^2H, B-C^3H_2 (cycle), B-CH_2) and C^4H_2 were not detected].

4.3.1.6. Spectral date for 1-cyclooctyl-2-hexylborirane ***13a***. Pale yellow liquid, bp 110 ºC (1 mm). Yield: 70% (1.64 g, 7.0 mmol). ^{1}H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ = 0.90 (t, 3H, CH_3, J = 6.2 Hz), 1.20−1.80 [m, 22H, $4CH_2$ (alkyl), $7CH_2$ (cyclooctyl)]. ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ = 14.11, 22.68, 25.54 (cyclooctyl), 26.65 (cyclooctyl), 26.83 (cyclooctyl), 29.37, 29.70, 30.78 (cyclooctyl), 31.92. ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): δ = 32.01. [In the ^{1}H and ^{13}C spectra signals of protons and carbon atoms directly attached to the boron atom (2 B-CH, B-CH_2) and C^4H_2 were not detected].

4.3.1.7. Spectral date for 1-cyclooctyl-2-octylborirane ***13b***. Pale yellow liquid, bp 120 ºC (1 mm). Yield: 68% (1.78 g, 6.8 mmol). ^{1}H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ = 0.89 (t, 3H, CH_3, J = 6.4 Hz), 1.22−1.89 [m, 26H, $6CH_2$ (alkyl), $7CH_2$ (cyclooctyl)]. ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ = 14.09, 22.65, 25.40 (cyclooctyl), 26.71 (cyclooctyl), 26.91 (cyclooctyl), [29.25, 29.37, 29.70 (4C)], 31.05 (cyclooctyl), 31.86. ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): δ = 32.38. [In the ^{1}H and ^{13}C spectra signals of protons and carbon atoms directly attached to the boron atom (2 B-CH, B-CH_2) and C^4H_2 were not detected].

4.3.1.8. Spectral date for 1-(bicyclo[2.2.1]hept-2-yloxy)-2-hexylborirane ***17a***. Yellow oil liquid, bp 103 ºC (1 mm). Yield: 75% 1.76 g, 7.5 mmol). ^{1}H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ = 0.90 (t, 3H, CH_3, J = 6.2 Hz), 1.00–1.19 (m, 3H, 3CH), 1.20–1.75 (m, 15H, 3CH, $6CH_2$), 2.15 (m, 1H, CH), 2.23 (m, 1H, CH), 4.02 (m, 1H, O–CH). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ = 14.08 (alkyl), 22.65 (alkyl), 24.36, 28.35, 29.28 (alkyl), 29.36 (alkyl), 31.83 (alkyl), 31.90 (alkyl), 34.82, 35.38, 42.13, 43.64, 75.25. ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): δ = 30.92. [In the ^{1}H and ^{13}C spectra signals of protons and carbon atoms directly attached to the boron atom (B-C^2H, B-C^3H_2 (cycle)) were not detected].

4.3.1.9. Spectral date for 1-(bicyclo[2.2.1]hept-2-yloxy)-2-octylborirane ***17b***. Yellow oil liquid, bp 120 ºC (1 mm). Yield: 72% 1.89 g, 7.2 mmol). ^{1}H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ = 0.80–0.95 (m, 3H, CH_3), 1.00–1.80 (m, 24H, 2CH, $11CH_2$), 4.02 (m, 1H, 2CH–O). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ = 14.08 (alkyl), 22.65 (alkyl), 24.27, 28.40, [29.21, 29.62 (4C, alkyl)], 31.83 (alkyl), 32.60 (alkyl), 34.80, 35.37, 42.20, 43.74, 74.95. ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): δ = 30.91. [In the ^{1}H and ^{13}C spectra signals of protons and carbon atoms directly attached to the boron atom (B-C^2H, B-C^3H_2 (cycle)) were not detected].

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Highlights

- Cp_2TiCl_2 catalyzes cycloboration of α-olefins with $RBCl_2$
- Alkyl, arylalryl, cycloalkyldichloroboranes act as transmetallating agents
- Disubstituted boriranes are the final products