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First Example of Borirane Synthesis by α-Olefins Reaction with $BCl_3 \cdot SMe_2$ Catalyzed with $(\eta^5\text{-}C_5H_5)_2TiCl_2$

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Abstract—New method was developed of the synthesis of 2-phenyl(alkyl, benzyl, phenoxy)-1-chloroboriranes via reaction of α-olefins with $BCl_3 \cdot SMe_2$ catalyzed by Cp_2TiCl_2. The method is based on the boracyclopropanes (boriranes) formation resulting from transmetallation of titanacyclopropanes arising from the reaction of α-olefins with Cp_2TiCl_2. The calculations were fulfilled of thermodynamic and activation parameters of possible reaction routes.

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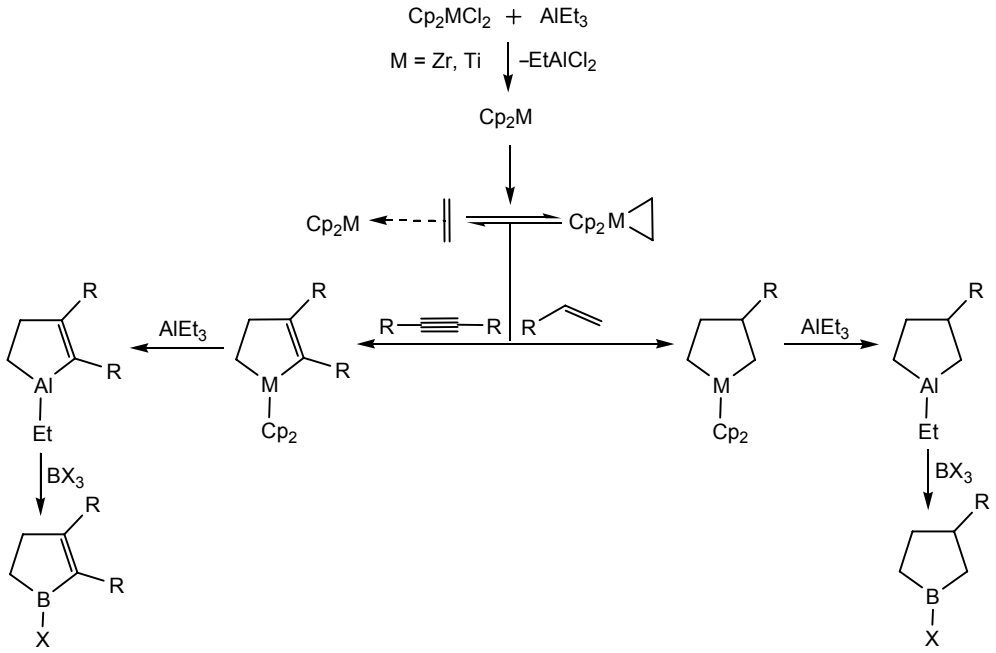
In the preparative synthesis of alumina(magnesa) cyclopentan(en)es and aluminacyclopropan(en)es reactions are widely used of catalytic cyclometallation of olefins and acetylenes with trialkylaluminum and alkylaluminum halides as well as with Grignard reagents under the catalysis with titanium and zirconium complexes. The catalytic cycloalumination of unsaturated compounds (α-olefins, 1,2-dienes, acetylenes, vinylcycloalkanes) proceeds through a stage of formation of intermediate three- and five-membered metallacarbocycles including transition metals (Ti, Zr). The subsequent transmetallation with excess of alkyl- and alkynylaluminum halides or alkylmagnesium derivatives leads to the formation of the corresponding metallacycles of non transition metals (Mg, Al) [1–5].

Scheme 1.



R = alkyl, X = Cl, F, Br.

Aluminacyclopentanes and aluminacyclopentenes synthesized *in situ* by cycloalumination of α-olefins or disubstituted acetylenes applying $AlEt_3$ in the presence of catalyst Cp_2ZrCl_2 fairly easily undergo transmetallation with BX_3 (X = F, Cl, Br) affording 1-halosubstituted borolanes and 2,3-dihydro-1*H*-boroles [6–8] (Scheme 1).

The developed method of converting aluminocyclanes in borolanes and 2,3-dihydro-1*H*-boroles is one of efficient one-pot methods of preparation of five-membered organoboron compounds [6–8].

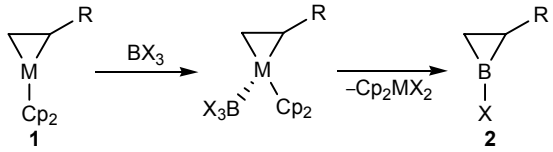
Taking into consideration the studies in this field, the acquired experimental practice, and aiming at the development of a one-pot procedure for the synthesis of difficultly available and practically important three-membered cyclic organoboron compounds, boriranes, we attempted to carry out the reaction of direct cycloboration of α-olefin with the help of BX_3 (X = Cl, F) using complex catalysts of titanium.

The key intermediates in the formtion of five-membered organoaluminum and organoboron cycles are titana- or zirconacyclopropanes. We presumed that under chosen conditions we would perform the transmetallation of small metallacycles with boron halides (BCl_3, BF_3) into the corresponding boriranes.

The boron halides chosen for the reaction possessing electron-acceptor properties would according to our assumption coordinate to the central Ti or Zr atom thus assisting the stabilization of small metallacycles formed by the transition metal. Further interaction of the stabilized titana- or zirconacyclopropanes **1** with excess BCl_3 or BF_3 may lead to the formation of the target boriranes 2 (Scheme 2).

At the moment when we started these studies no published information existed on the possibility of direct cycloboration of unsaturated compounds with the formation of difficultly accessible boriranes. Nowadays a special interest of researchers is addressed to the strained three-membered cyclic organoboron compounds [9, 10], since the number of synthesized saturated three-membered cyclic organoboron compounds is very limited. A synthesis is described of 1-*tert*-butyl-3-(*tert*-butylborilene)-2,2-bis(trimethylsilyl)-borirane [11] by heating 1-bis(*tert*-butylchloroboryl)-2,2-bis(trimethylsilyl)ethylene with K or Na. *trans*-1,1,2,3-Tetraphenylborirane formed under isomerization conditions from triphenylborate tetramethylammonium salt under UV irradiation [12].

Scheme 2.

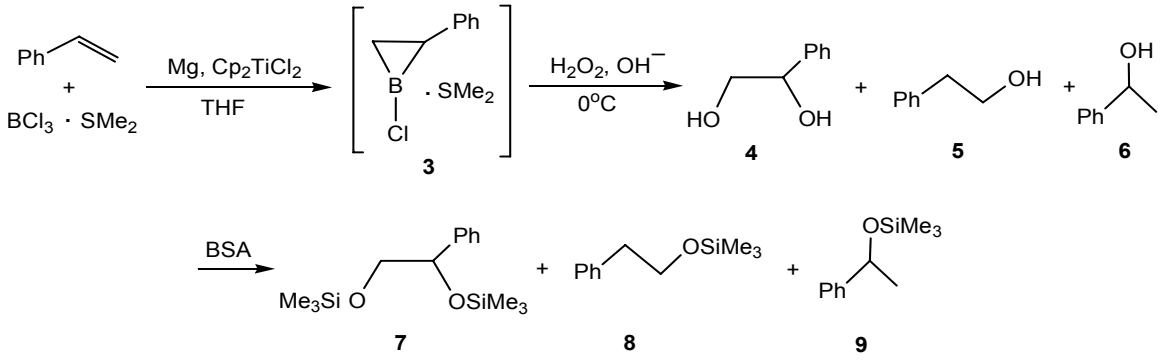


M = Ti, Zr; R = alkyl, X = Cl, F.

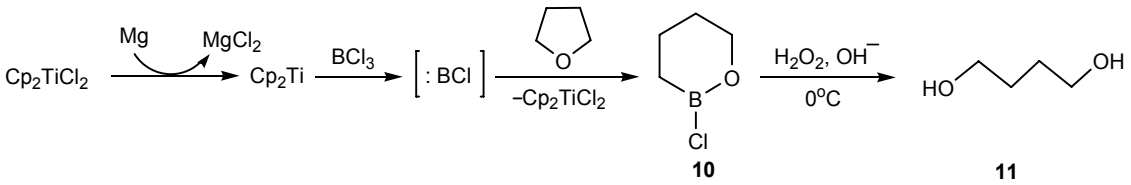
Aiming to develop a universal method of boriranes preparation we selected as a model reaction styrene interaction with $BCl_3{\cdot}SMe_2$ in the presence of metal Mg (chlorine ions acceptor) and a catalyst Cp_2TiCl_2. In the reaction of styrene with $BCl_3{\cdot}SMe_2$ (styrene–$BCl_3{\cdot}SMe_2$–Mg–[Ti], 1 : 2 : 4 : 0.1; THF, ~20°C, 14 h) 2-phenyl-1-chloroborirane **3** formed in 75% yield (Scheme 3). The best catalyst for this reaction is Cp_2TiCl_2.

2-Phenyl-1-chloroborirane **3** was identified by multinuclear ^1H, ^{13}C, ^{11}B NMR spectroscopy. The cycloboration occurred with a complete conversion of initial styrene that resulted in the selective formation of borirane **3**. The presence of a three-membered ring with one asymmetric center is indicated by the *ABC* system characteristic of such molecular structures. Methylene protons of boracyclopropane are diastere-

Scheme 3.



Scheme 4.



otopic, and the difference in the chemical shifts attains 1.01 ppm [$\delta(C^3H^A)$ –0.39, $\delta(C^3H^B)$ 0.62 ppm]. In the HSQC spectrum they correlate with the signal of the carbon atom at 17.36 ppm, and in the homonuclear COSY experiment the coupling is observed between protons H^A of the methylene fragment and vicinal methine proton of the ring (C^2H) at δ 1.05 ppm [$\delta(\underline{C}^2H)$ 25.0 ppm]. Thus with the help of the 2D correlation NMR spectroscopy (COSY, HSQC, HMBC) at the room temperature we assigned the signals of the cyclic core and the aromatic substituent and confirmed the structure of 2-phenyl-1-chloroborirane **3**. The obtained borirane exists in the complex with dimethyl sulfide whose signals are present at δ_C 18.74 and δ_H 1.26 ppm. In the ^{11}B NMR spectrum the signal δ_B 2 ppm in the region of tetracoordinated boron atom [13] we assigned to the complex of compound **3** with SMe_2.

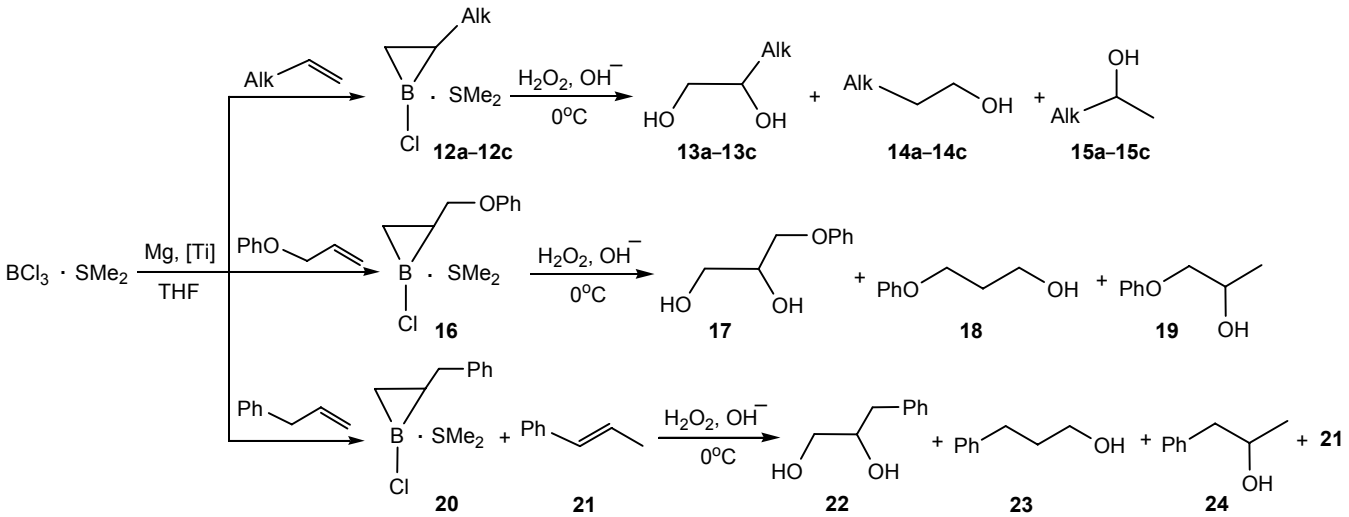
The ^{11}B NMR spectrum contains another more downfield signal demonstrating the presence of the other organoboron compound. The chemical shift value (30.0 ppm) suggests the presence in the molecule of a B–O fragment [13]. Applying the analysis of 2D spectra we concluded on the formation of 2-chloro-1,2-oxaborinane **10** [δ, ppm: 15.1 ($B\underline{C}H_2$), 23.5 and 30.6 ($\underline{C}H_2\underline{C}H_2$), 62.7 ($O\underline{C}H_2$)]. Compound **10** evidently is not a product of styrene cycloboration, but formed as a result of a side reaction between tetrahydrofuran and BCl_3 catalyzed by Cp_2TiCl_2 (Scheme 4).

The insertion of a low-coordinated organoboron compound into the C-O bond of the tetrahydofuran molecule under UV irradiation was described in [14, 15].

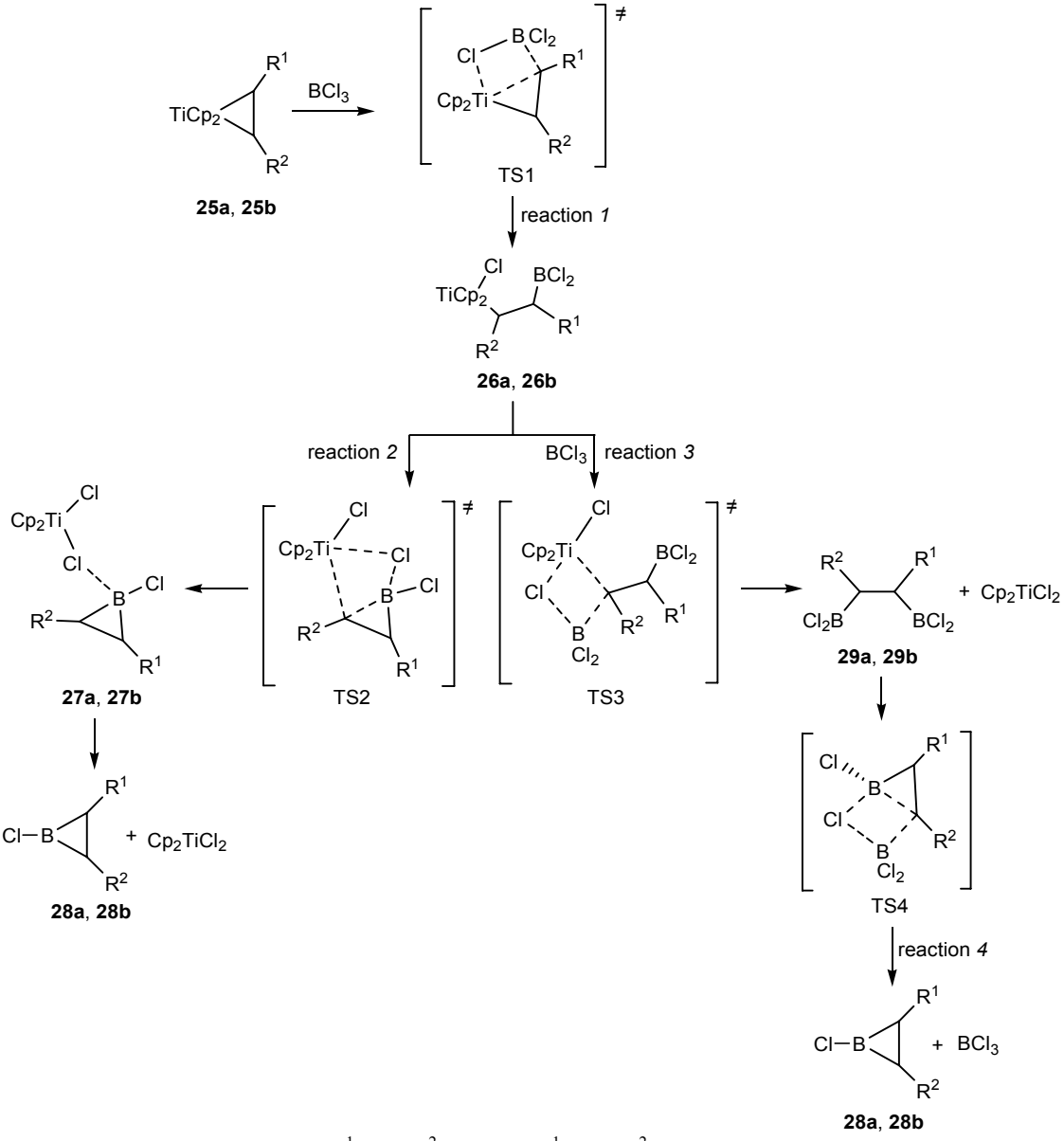
The oxidation of the obtained reaction mixture with H_2O_2 in alkaline environment [6, 7, 16] led to the formation of alcohols **5** and **6** and diol **4** in a ratio 1 : 1 : 1 (Scheme 2). The overall yield of compounds **4**–**6** was ~75%. Alongside alcohols **4**–**6** butan-1,4-diol **11** was obtained, oxidation product of 2-chloro-1,2-oxaborinane **10**. To perform the identification of the alcohols by means of GLC we converted them into the corresponding ethers **7**–**9** by treating the reaction mixture with bis(trimethylsilyl)acetamide (BSA) [16] (Scheme 3).

Alcohols **4**–**6** isolated by column chromatography were identified by spectral methods. The detection of diol **4** and alcohols **5** and **6** confirms the formation of the target 2-phenyl-1-chloroborirane **3**.

Scheme 5.



Scheme 6.



R^1 = H, R^2 = Et (**a**); R^1 = Et, R^2 = H (**b**).

The obtained data of ^{1}H, ^{13}C, ^{11}B NMR spectra, 2D experiments (COSY, HMBS, HSQS) with compound **3**, and also the structure of oxidation products permit a conclusion that in reaction of styrene with $BCl_3{\cdot}SMe_2$ in THF in the presence of the catalyst Cp_2TiCl_2 2-phenyl-1-chloroborirane formed as a complex with SMe_2.

To show the general character of this process we investigated the reaction of $BCl_3{\cdot}SMe_2$ with 1-hexene, 1-octene, 1-decene, allylbenzene, and allyl phenyl ether in above described conditions in the presence of the catalyst Cp_2TiCl_2. In each experiment 1-chloro-boriranes **12a–12c**, **16**, and **20** were obtained in fair yields (Scheme 5). Unlike the aliphatic α-olefins and allyl phenyl ether the allylbenzene in reaction with $BCl_3{\cdot}SMe_2$ along with the target 2-benzyl-1-chloroborirane **20** affords a product of initial allylbenzene isomerization, 1-phenylpropene **21** in a ratio 2 : 3 (Scheme 5). The oxidation of 1-chloro-boriranes **12a–12c**, **16**, and **20** with hydrogen peroxide furnished 1,2-diols **13a–13c**, **17**, and **22** and alcohols **14a–14c**, **15a–15c**, **18**, **19**, **23**, and **24**. The ratio of diol and alcohols in each case was ~1 : 1 : 1.

Thermodynamic and activation parameters of catalytic cycloboration of 1-butene with BCl_3·SMe_2, in a gas phase at 298.15 K (PBE/3z, PRIRODA 6.0)

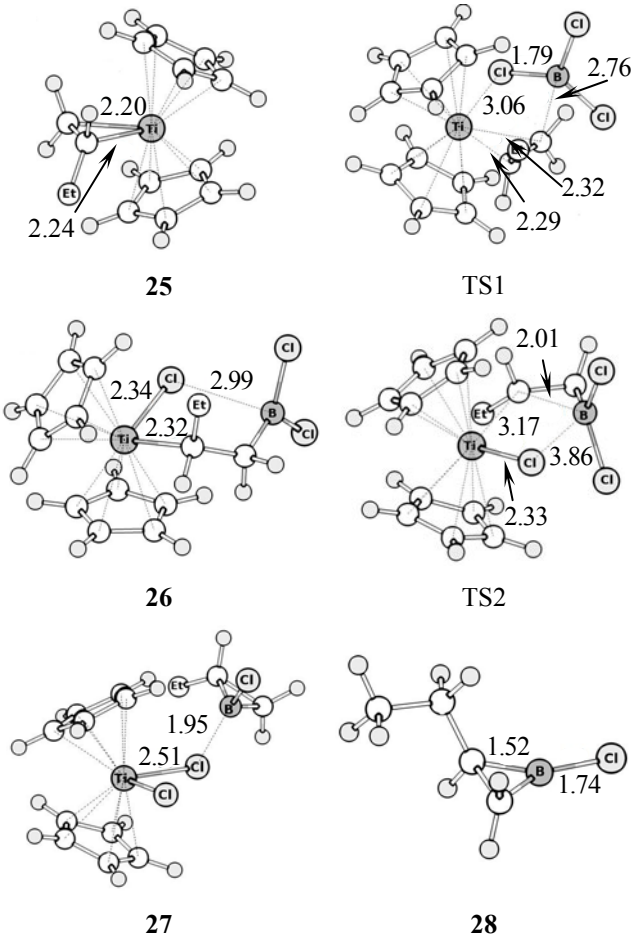
Reactions	ΔH^0, kcal mol^{-1}	ΔG^0, kcal mol^{-1}	ΔS^0, cal mol^{-1} K^{-1}	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta G^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}$, cal mol^{-1} K^{-1}
25a + BCl_3 → **26a**	–15.8	–2.4	–44.9	6.61	20.2	–45.4
25b + BCl_3 → **26b**	–18.7	–6.2	–42.1	0.9	24.1	–44.4
26a → **27a**	–1.1	–2.4	4.4	19.4	19.4	–0.1
26b → **27b**	1.0	0.1	2.8	16.1	17.4	–4.4
27a → **28a** + Cp_2TiCl_2	5.7	–7.6	44.5			
27b → **28b** + Cp_2TiCl_2	6.6	–6.4	43.3			
26a + BCl_3 → **29a** + Cp_2TiCl_2	–36.0	–39.2	10.5	32.6	48.0	–51.6
26b + BCl_3 → **29b** + Cp_2TiCl_2	–33.1	–35.4	7.7	9.7	22.3	–42.4
29a → **28a** + BCl_3	40.6	29.1	38.4	46.5	47.8	–4.5
29b → **28b** + BCl_3	40.6	29.1	38.4	46.4	47.7	–4.3

Hence we for the first time fulfilled the direct cycloboration of α-olefins of diverse structures using BCl_3·SMe_2 in THF in the presence of metal magnesium and catalyst Cp_2TiCl_2 and obtained difficultly accessible 1-chloro-boriranes. The reaction has a general character and can be successfully used for preparation of substituted boriranes of various structures.

In order to find the theoretical justification of the assumed transmetallation mechanism of the formed *in situ* titanacyclopropane into the corresponding boriranes we performed calculations of the thermodynamic and activation parameters of the possible reaction routes (method PBE/3z, program PRIRODA 6.0 [17]). Titanacyclopropane forms in ether solvents [18, 19], yet the mechanism of the exchange of Ti atoms for boron in cyclic systems has not yet been considered.

We first considered two possible routes of BCl_3 reaction with titanacyclopropane with the formation of an "open" structure of organoboron intermediate **26a** and **26b** (Scheme 6, reaction *1*).

Further either an intramolecular transformation is possible with the simultaneous formation of 3-alkylborirane **28** (reaction *2*), or the formation of diboron derivative **29** via the ligand exchange between titanocenaalkyl chloride **26** and the second molecule of BCl_3 (reaction *3*). The last version of the process we considered as an alternative route that requires an addition cyclization stage (reaction *4*).



Optimized structures formed in key stages of catalytic cycloboration of 1-butene with BCl_3·SMe_2.

The analysis of the obtained calculation data for reactions *1–4* (see the table) showed that at room temperature the process can occur including successive reactions *1* and *2*, since the maximum energy barrier of

this route was ~20 kcal mol^{-1}. The optimized structures of all found extrema are presented in the figure.

As seen from the table, the barriers to the formation of 1-chloro-2-ethylborirane **28a** involving two BCl_3 molecules via intermediate diboron derivative are fairly high. Even the cyclization process (reaction *4*) requires 48 kcal mol^{-1} and is unfavorable by energy (ΔG^{298} 29.1 kcal mol^{-1}). The same amount of energy is required for the stage of replacement of titanium atom for the second boron atom.

We concluded from the results obtained that the rection of titanacenacyclopropane with boron chloride included a stage of the metallacycle cleavage with the formation of monoboron substituted intermediate whose subsequent intramolecular transformation led to 1-chloro-2-ethyl-borirane **28a**.

EXPERIMENTAL

All reactions were carried out in an argon atmosphere. $BCl_3{\cdot}SMe_2$ and Cp_2TiCl_2 were commercial products. Tetrahydrofuran was dried by boiling over metal sodium and was used just after distillation.

1D (^{1}H, ^{13}C, ^{11}B) and 2D homo- (COSY) and heteronuclear (HSQC, HMBC) NMR spectra were registered on a spectrometer Bruker Avance 400 with operating frequencies 400.13 (^{1}H), 100.62 (^{13}C), 128.33 (^{11}B) MHz from solutions in $CDCl_3$. At registering ^{1}H and ^{13}C NMR spectra Me_4Si served as reference, for ^{11}B spectra, $BF_3{\cdot}Et_2O$. Oxidation of boriranes was done with hydrogen peroxide in alkaline environment by procedures [6, 7, 16]. GC-MS measurements were carried out on an instrument 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 calculations were performed using PRIRODA 6.0 software [17, 20]. The geometry parameters optimization, oscillation analysis, and the corrections for the total energy of compound were done on the level of DFT by PBE method (basis 3ζ). The method was previously successfully used for the calculation of thermodynamic an activation parameters of Ti-containing systems [21]. The thermodynamic parameters and activation energy were calculated for 298.15 K. The visualization of the quantum-chemical results was performed using Chemcraft program. Spectral data and physical characteristics of compounds **4–6**, **11**, **13–15**, **17–19**, and **21–24** are known [22-36].

Reactions of α-olefins with $BCl_3{\cdot}SMe_2$ in the presence of catalyst Cp_2TiCl_2. General procedure. Into a glass reactor (50 mL) in an atmosphere of dry argon at stirring with a magnetic stirrer was charged in succession while cooling to 0°C 5 mL of THF, 4 mg at of Mg powder, 1 mmol of α-olefin, 0.2 mmol of catalyst Cp_2TiCl_2, and 2 mmol of $BCl_3{\cdot}SMe_2$. The excess of magnesium was filtered off, the solvent was evaporated, and 1-chloro-2-R-borirane was analyzed by NMR.

1-Chloro-2-phenylborirane (4). Yield 75%. ^{1}H NMR spectrum, δ, ppm: –0.39 br.m (1H, H^{3A}), 0.62 br.m (1H, H^{3B}), 1.15–1.26 m [7H, H^2, $S(CH_3)_2$], 7.00-7.20 m ($5H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 17.36 (C^3, $W_{1/2}$ 27.9 Hz), 18.74 [$S(CH_3)_2$], 25.90 (C^2), 126.50, 127.57, 128.04, 144.10. ^{11}B NMR spectrum, δ, ppm: 2.78.

2-Butyl-1-chloroborirane (14a). Yield 75%. ^{1}H NMR spectrum, δ, ppm: –0.51 br.m (1H, H^{3A}), 0.40 br.m (1H, H^{3B}), 0.55–0.62 m (3H, C^9H_3), 0.80–1.05 m (7H, H^2, $C^{4-6}H_2$), 1.27 br.s [6H, $S(CH_3)_2$]. ^{13}C NMR spectrum, δ, ppm: 13.43, 16.91 (C^3, $W_{1/2}$ 28.1 Hz), 18.80 [$S(CH_3)_2$], 22.90, 25.05 (C^2), 29.94, 32.20. ^{11}B NMR spectrum, δ, ppm: 2.95.

2-Hexyl-1-chloroborirane (14b). Yield 80%. ^{1}H NMR spectrum, δ, ppm: –0.58 br.m (1H, H^{3A}), 0.39 br.m (1H, H^{3B}), 0.51–0.58 m (3H, C^9H_3), 0.85–1.10 m (11H, H^2, $C^{4-8}H_2$), 1.28 br.s [6H, $S(CH_3)_2$]. ^{13}C NMR spectrum, δ, ppm: 13.67, 16.62 (C^3, $W_{1/2}$ 30.6 Hz), 17.40 [$S(CH_3)_2$], 22.33, 24.50 (C^2), 28.96, 29.90, 31.19, 32.20. ^{11}B NMR spectrum, δ, ppm: 2.54.

1-Chloro-2-octylborirane (14c). Yield 55%. ^{1}H NMR spectrum, δ, ppm: –0.42 br.m (1H, H^{3A}), 0.59 br.m (1H, H^{3B}), 0.65–0.70 m (3H, $C^{11}H_3$), 1.00–1.40 m (15H, H^2, $C^{4-10}H_2$), 1.26 br.s [6H, $S(CH_3)_2$]. ^{13}C NMR spectrum, δ, ppm: 13.67, 17.26 (C^3, $W_{1/2}$ 30.1 Hz), 18.10 [$S(CH_3)_2$], 22.42, 25.50 (C^2), 28.90, 29.1, 29.40, 29.50, 31.05, 32.11. ^{11}B NMR spectrum, δ, ppm: 2.75.

1-Chloro-2-(phenoxymethyl)borirane (18). Yield 85%. ^{1}H NMR spectrum, δ, ppm: –0.55 br.m (1H, H^{3A}), 0.44 br.m (1H, H^{3B}), 1.10 br.m (1H, H^2), 1.20 br.s [6H, $S(CH_3)_2$], 2.80 m (1H, H^{4A}), 3.25 m (1H, H^{4B}), 6.40 m, 6.63 m, 6.77 m ($5H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 17.10 (C^3, $W_{1/2}$ 19.6 Hz), 18.30

[$S(CH_3)_2$], 24.55 (C^2), 68.50 (C^4O), 117.16, 120.27, 127.90, 161.10. ^{11}B NMR spectrum, δ, ppm: 2.67.

2-Benzyl-1-chloroborirane (22). Yield 40%. ^1H NMR spectrum, δ, ppm: –0.38 br.m (1H, H^{3A}), 0.62 br.m (1H, H^{3B}), 1.20–1.29 br.m [7H, H^2, $S(CH_3)_2$], 2.48 m (2H, H_2^4), 7.04–7.17 m ($5H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 17.79 (C^3, $W_{1/2}$ 30.8 Hz), 18.50 (SMe_2), 24.30 (C^2), 37.71 (C^4), 125.30, 127.60, 127.80, 144.10. ^{11}B NMR spectrum, δ, ppm: 2.84.

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REFERENCES

1. Dzhemilev, U.M. and Ibragimov, A.G., *J. Organometal. Chem*., 2010, vol. 695, p. 1085.
2. D'yakonov, V.A. and Dzhemilev, U.M., *Reactions in Organic and Organometallic Synthesis*, New York: NOVA Sci. Publ., 2010.
3. Dzhemilev, U.M. and Ibragimov, A.G., *Russ. Chem. Rev*., 2000, vol. 69, p. 121.
4. Dzhemilev, U.M. and Ibragimov, A.G., *Russ. Chem. Rev*., 2005, vol. 74, p. 807.
5. Dzhemilev, U.M. and Ibragimov, A.G., *J. Organometal. Chem*., 1994, vol. 466, p. 1.
6. Khafizova, L.O., Khusainova, L.I., Tyumkina, T.V., and Dzhemilev, U.M., *Russ. J. Org. Chem*., 2012, vol. 48, p. 755.
7. Khafizova, L.O., Khusainova, L.I., Tyumkina, T.V., and Dzhemilev, U.M., *Russ. J. Org. Chem*., 2012, vol. 48, p. 761.
8. Khusainova, L.I., Khafizova, L.O., Tyumkina, T.V., and Dzhemilev, U.M., *Russ. J. Org. Chem*., 2014, vol. 50, p. 309.
9. Braunschweig, H., Damme, A., Dewhurst, R.D., Ghosh, S., Kramer, T., Pfaffinger, B., Radacki, K., and Vargas, A., *J. Am. Chem. Soc*., 2013, vol. 135, p. 1903.
10. Braunschweig, H., Herbst, T., Rais, D., Ghosh, S., Kupfer, T., and Radacki, K., *J. Am. Chem. Soc*., 2009, vol. 131, p. 8989.
11. Klusik, H. and Berndt, A., *Angew. Chem., Int. Ed*., 1983, vol. 22, p. 877.
12. Kropp, M., Bhamidapaty, K., and Schuster, G.B., *J. Am. Chem. Soc*., 1988, vol. 110, p. 6252.
13. Wrackmeyer, B., *Annu. Rep. NMR Spectr*., 1988, vol. 20, p. 61.
14. Eisch, J.J., Shafii, B., and Boleslawski, M.P., *Pure Appl. Chem*., 1991, vol. 63, p. 365.
15. Pachaly, B. and West, R., *Angew. Chem., Int. Ed*., 1984, vol. 23, p. 454.
16. Brown, H.C. and Zaidlewicz, M., *J. Am. Chem. Soc*., 1976, vol. 98, p. 4917.
17. Laikov, D.L., *Chem. Phys. Lett*., 1997, vol. 281, p. 151.
18. Kulinkovich, O.G., *Pure Appl. Chem*., 2000, vol. 72, p. 1715.
19. Eisch, J.J., Gitua, J.N., Otieno, P.O., and Shi, X., *J. Organometal. Chem*., 2001, vol. 624, p. 229.
20. Laikov, D.N. and Ustynyuk, Yu.A., *Russ. Chem. Bull*., 2005, vol. 54, p. 820.
21. Ustynyuk, L.Yu., Ustynyuk, Yu.A., Laikov, D.N., and Lunin, V.V., *Russ. Chem. Bull*., 2001, vol. 50, p. 376.
22. Han, Zh., Rong, L., Wu, J., Zhang, L. Wang, Zh., and Ding, K., *Angew. Chem., Int. Ed*., 2012, vol. 51, p. 13041.
23. Szostak, M., Spain, M., Eberhart, A.J., and Procter, D.J., *J. Am. Chem. Soc*., 2014, vol. 136, p. 2268.
24. Cao, L., Ding, J., Gao, M., Wang, Z., Li, J., and Wu, A., *Org. Lett*., 2009, vol. 11, p. 3810.
25. Denney, D.B., Denney, D.Z., and Gigantino, J.J., *J. Org. Chem*., 1984, vol. 49, p. 2831.
26. Monguchi, Y., Wakayama, F., Takada, H., Sawama, Y., and Sajiki, H., *Synlett*., 2015, vol. 26, p. 700.
27. Ejchart, A., *Org. Magn. Res*., 1981, vol. 15, p. 22.
28. Shao, P., Shen, L., and Ye, S., *Chin. J. Chem*., 2012, vol. 30, p. 2688.
29. Shaikh, N.S., Junge, K., and Beller, M., *Org. Lett*., 2007, vol. 9, p. 5429.
30. Kim, J.W., Koike, T., Kotani, M., Yamaguchi, K., and Mizuno, N., *Chem. Eur. J*., 2008, vol. 14, p. 4109.
31. Prat, I., Font, D., Company, A., Junge, K., Ribas, X., Beller, M., and Costas, M., *Adv. Synth. Catal*., 2013, vol. 355, p. 947.
32. Fernandez-Mateos, E., Macia, B., and Yus, M., *Adv. Synth. Catal*., 2013, vol. 355, p. 1249.
33. Liu, Y., Park, S.K., Xiao, Y., and Chae, J., *Org. Biomol. Chem*., 2014, vol. 12, p. 4747.
34. Talwar, D., Wu, X., Saidi, O., Salguero, N.P., and Jianliang, X., *Chem. Eur. J*., 2014, vol. 20, p. 1.
35. Johnson, C.R. and Elliot, R., *J. Am. Chem. Soc*., 1982, vol. 104, p. 7041.
36. Zhao, Y. and Weix, D., *J. Am. Chem. Soc*., 2014, vol. 136, p. 480.