ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 7, pp. 1330–1338. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © E.G. Gordeev, A.Yu. Shkulipa, A.D. Kirilin, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 7, pp. 1134–1142.

Reactions of Dichlorocarbene, Dichlorosilylene, and Dichlorogermylene with Carboranes(12). A Theoretical Study

E. G. Gordeev, A. Yu. Shkulipa, and A. D. Kirilin

Lomonosov Moscow State University of Fine Chemical Technologies, Vernadskii pr. 86, Moscow, 119571 Russia
e-mail: mp2sdtq@gmail.com

Received November 21, 2013

Abstract—Insertion of CCl_2, $SiCl_2$, and $GeCl_2$ into the B–H and C–H bonds of the carborane(12) molecules as well as into the B–Hal, C–Hal bonds of some halogen-substituted *ortho*-carboranes are studied at the B3LYP/6-311+G(d,p) and M06-2X/6-311+G(d,p) levels of theory. Thermodynamic parameters of the reactions are calculated and their variation for the isomeric carboranes(12) and for a series of carbenoid species is shown. For several insertion reactions the energies of activation are calculated based on the model of three-center synchronous transition state. The energy barriers are regularly varied depending on the position of the B–H bond in the carborane molecule.

Keywords: carboranes(12), carbenes, sylilenes, germylenes, insertion reactions

DOI: 10.1134/S1070363214070147

The chemistry of carbenes and carbenoids provides a wide spectrum of efficient procedures for preparation of new organic and organoelementalal compounds [1–3] like reactions of insertion into σ-bonds [4], addition to multiple bonds with the formation of cyclic products [5, 6], dimerization and polymerization (the latter is more characteristic of the Ge and Sn analogs of carbenes) [7], complexation [8], intramolecular rearrangements [9, 10]. The ability to insert into σ-bonds is a typical general feature of carbenes and their analogs whose activity in these reactions is determined, first of all, by the substituents at the carbene atom [4, 11].

Reactions of carbenes [12, 13] and silylenes [14, 15] with various types of chemical compounds are well studied, whereas there is much less information available concerning the processes with participation of their more heavy analogs since the chemistry of these compounds is much younger. Thus, the first communication on the experimental preparation of the products of insertion of diorganogermylene into the C–Ge bond appeared in 1984 [16], and the first insertion into the C–H bond was mentioned in 1987 [17]. The first systematic theoretical investigation of the thermodynamics and kinetics of the insertion of a series of germylenes into the C–H bonds refers to 1999 [18], although theoretical studies of the molecular and electronic structure of the isolated molecules of silylenes and germylenes have been performed much earlier [7, 19]. In spite of the relatively short story, the chemistry of heavy analogs of carbenes is one of most dynamically developing fields of organoelemental chemistry. The majority of investigations concerning the insertion of carbenoid species concern the insertion into the C–H and C–Hal bonds, whereas much less studies correspond to the interaction with the X–H bonds of other elements.

Insertion of carbenes and their analogs into the B–H bonds can be an efficient method for preparation of the carboranes(12) derivatives. Carboranes(12) are stable polyhedral molecules of composition $C_2B_{10}H_{12}$, where the backbone bonds and the terminal B–H and C–H bonds can be discriminated (Fig. 1). The boron-carbon carborane scaffold is highly stable due to the strong delocalization of the electrons of its bonds [20], therefore the scaffold bonds will remain likely intact under the action of carbenoid species and the insertion reactions will proceed at the terminal bonds.

The insertion of the silylene molecule (RR'Si) into the B–H bond results in the formation of the B–

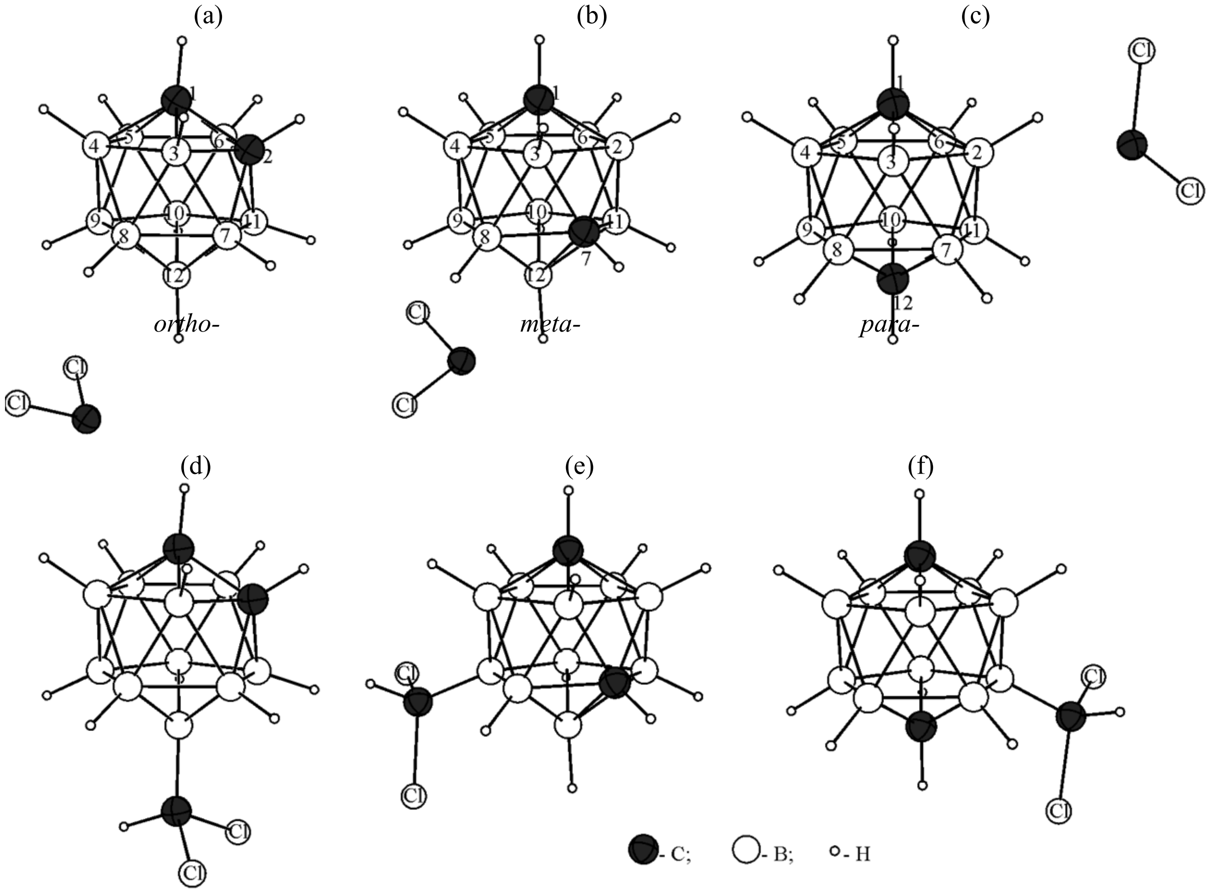


Fig. 1. Molecular structure of prereaction complexes (a–c) and some products (d–f) of insertion of dichlorocarbene into the B–H bonds of the molecules of *ortho*-, *meta*-, and *para*-carboranes, M06-2X/6-311+G(d,p) (boron atom numbers are given).

SiRR'H group, with the hydrogen atom at silicon, which can further be used in the reaction of hydrosilylation in order to prepare the derivatives of carboranes(12) with more complex organosilicon substituents. Similarly, the insertion of germylene leads to the B–GeRR'H group capable of the reaction of hydrogermylation.

The insertion of dichlorosilylene into the B–H bonds allows the preparation of carborane-containing chlorosilanes, whose hydrolytic condensation can lead to new carborane-containing siloxane oligomers, polymers or scaffold molecules.

The insertion of silylenes into the B–H, B–Cl, and B–F bonds of simplest boranes and their halogen-derivatives was mentioned in the literature [21]. Recently the insertion of carbenes into the B–H bonds catalyzed by the Rh salts was described [22]. However, we failed to find any reports on the insertion of heavy analogs of carbenes (SiR_2, GeR_2) into the B–H bond of polyhedron boron compounds.

So far, there were only two publications describing the investigation of the insertion of carbenes into the B–H bond of carboranes(12) [23, 24], although their results were, to some extent, contradictory. Thus, in [23] it is stated that *meta*- and *para*-carboranes do not enter the reaction with carbenes, whereas in [24] the insertion of carbene into the terminal bonds of *para*-carboranes has been successfully realized.

Modern methods of quantum chemistry are a powerful instrument for investigation of the mechanism of many reactions, especially with participation of active short-living species, for which the experimental study is complicated. In the present work, the insertion of CCl_2, $SiCl_2$, and $GeCl_2$ into the terminal B–H and C–H bonds of *ortho*-, *meta*-, and *para*-carboranes were studied using the methods of quantum chemistry.

Thermodynamics of insertion reactions of CCl_2, $SiCl_2$, $GeCl_2$ into the terminal bonds of carboranes(12) and their chloro-substituted derivatives. The

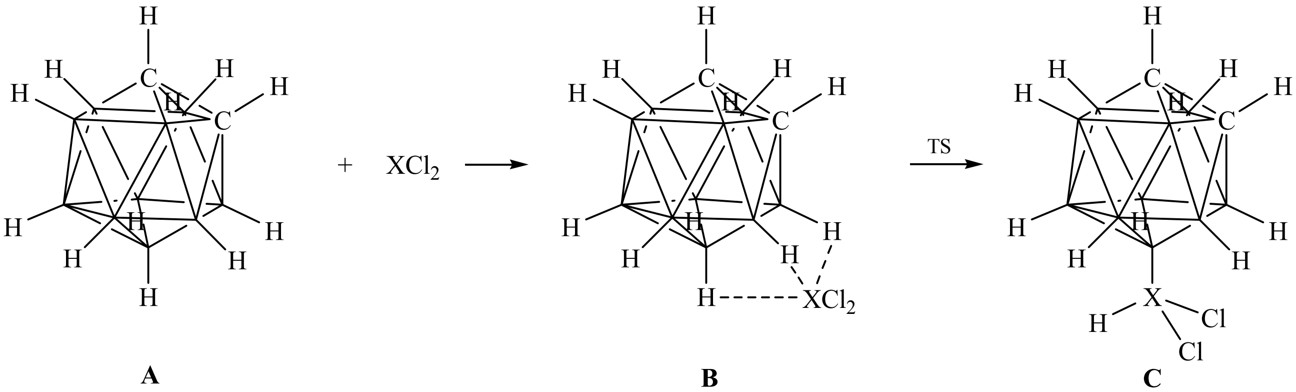
Table 1. Energy Δ*E*, enthalpy Δ*H*, and Gibbs energy Δ*G* (kcal/mol) for insertion of CCl_2, $SiCl_2$, $GeCl_2$ into the B–H, C–H bonds of the carborane(12) molecules

Parameter	B3LYP/6-311+G(d,p)				
	$CCl_2/SiCl_2/GeCl_2$	$CCl_2/SiCl_2/GeCl_2$	$CCl_2/SiCl_2/GeCl_2$	$CCl_2/SiCl_2/GeCl_2$	$CCl_2/SiCl_2/GeCl_2$
ortho	$BH^{9,12}$	$BH^{8,10}$	$BH^{4,5,7,11}$	$BH^{3,6}$	$CH^{1,2}$
Δ*E*	–75.1/–28.7/–4.8	–74.7/–28.5/–5.4	–74.9/–27.8/–4.6	–74.6/–26.6/–3.2	–60.5/–24.4/+5.0
Δ*H*	–71.2/–27.7/–4.4	–70.8/–27.5/–5.6	–71.0/–26.8/–4.2	–70.8/–25.6/–2.8	–57.6/–24.7/+4.1
Δ*G*	–59.1/–16.2/+6.9	–58.7/–16.1/+7.7	–58.7/–15.2/+7.4	–58.5/–13.8/+8.8	–44.8/–12.4/+16.2
meta	$BH^{9,10}$	$BH^{5,12}$	$BH^{4,6,8,11}$	$BH^{2,3}$	$CH^{1,7}$
Δ*E*	–73.9/–28.0/–4.6	–72.7/–26.0/–2.3	–74.7/–26.0/–4.3	–72.9/–24.9/–0.8	–59.1/–23.5/+5.4
Δ*H*	–70.1/–27.0/–4.3	–69.1/–25.3/–2.2	–70.9/–25.2/–4.0	–69.8/–24.7/–1.2	–56.3/–23.9/+3.6
Δ*G*	–59.0/–15.8/+5.7	–57.7/–14.5/+8.5	–59.2/–14.5/+7.2	–56.2/–11.6/+11.7	–44.1/–12.8/+16.9
para	BH	–	–	–	$CH^{1,12}$
Δ*E*	–74.5/–27.5/–4.0	–	–	–	–59.6/–23.7/+5.6
Δ*H*	–70.6/–26.5/–3.6	–	–	–	–56.7/–24.6/+4.6
Δ*G*	–60.1/–16.2/+6.6	–	–	–	–45.5/–12.0/+14.1
	M06-2X/6-311+G(d,p)				
ortho	$BH^{9,12}$	$BH^{8,10}$	$BH^{4,5,7,11}$	$BH^{3,6}$	$CH^{1,2}$
Δ*E*	–86.8/–38.0/–18.2	–85.6/–37.8/–18.9	–86.6/–37.0/–18.0	–86.1/–35.8/–16.6	–73.5/–35.6/–11.8
Δ*H*	–82.4/–37.2/–17.5	–81.4/–37.2/–18.3	–82.5/–35.9/–18.0	–82.1/–34.5/–15.9	–70.3/–35.4/–12.2
Δ*G*	–70.1/–23.6/–6.3	–69.4/–23.5/–7.7	–70.3/–24.6/–4.3	–70.0/–22.2/–4.0	–57.4/–22.7/+0.4
meta	$BH^{9,10}$	$BH^{5,12}$	$BH^{4,6,8,11}$	$BH^{2,3}$	$CH^{1,7}$
Δ*E*	–85.3/–37.0/–18.1	–84.3/–34.9/–15.4	–83.9/–34.8/–17.6	–84.2/–33.5/–13.6	–72.0/–34.7/–10.7
Δ*H*	–81.5/–36.7/–17.7	–80.7/–34.3/–15.2	–80.1/–34.1/–17.8	–81.1/–33.4/–14.0	–69.2/–34.9/–12.2
Δ*G*	–69.9/–23.5/–6.2	–68.7/–23.6/–4.2	–68.2/–23.0/–4.5	–67.6/–20.0/–0.7	–56.8/–23.3/+1.6
para	BH	–	–	–	$CH^{1,12}$
Δ*E*	–86.1/–36.5/–17.3	–	–	–	–72.7/–34.9/–11.2
Δ*H*	–82.4/–36.5/–17.8	–	–	–	–70.0/–36.1/–12.0
Δ*G*	–71.9/–24.0/–5.4	–	–	–	–58.5/–23.2/–1.0

insertion of carbenoid species into the terminal bonds of carboranes(12) molecules can be represented by the example of *ortho*-carborane by Scheme 1, where **A** is the isolated reagents; **B** is the prereaction intermolecular complex of the carborane molecule and carbenoid species (examples of complexes are shown in Figs. 1a–1c); **C** is the product of insertion. The results of calculations are presented in Table 1.

In the prereaction complexes with participation of the *ortho* and *meta*-carboranes the carbenoid species is coordinated predominantly with atoms, which are the

Scheme 1.



most distant from the carbon atoms, since these very regions of the molecules of these isomers of carboranes(12) have enhanced electron density [25, 26].

As follows from Table 1, for all three isomers of carboranes(12) the insertion of CCl_2, $SiCl_2$, $GeCl_2$ into the C–H bonds is less exothermic than into the B–H bonds. For example, for insertion of CCl_2 into *ortho*-carborane molecule, $\Delta G(B_{9;12}–H) = –70.1$ kcal/mol and $\Delta G(C–H) = –57.4$ kcal/mol [M06-2X/6-311+G(d,p)]. A similar picture is observed for insertion of $SiCl_2$ and $GeCl_2$: for $GeCl_2$ and *ortho*-carborane $\Delta G(B_{9;12}–H) = –6.3$ kcal/mol, whereas the insertion into the C–H bond is virtually thermoneutral, $\Delta G(C–H) = +0.4$ kcal/mol [M06-2X/6-311+G(d,p)].

For comparison: ΔH for the insertion of $GeCl_2$ into the C–H bond of the methane molecule calculated at the B3LYP/6-311G(d) level is –0.08 kcal/mol [18], whereas ΔH for insertion of $GeCl_2$ into the C–H bonds of *ortho*, *meta,* and *para*-carboranes, calculated in the same work using the B3LYP/6-311+G(d,p) method, is +4.1, +3.6, and +4.6 kcal/mol, respectively [18].

Note, that there are no principal differences in the thermodynamics of the insertion for the *ortho*, *meta* and *para*-isomers within the framework of the chosen approximations. As should be expected, in the series $CCl_2 > SiCl_2 > GeCl_2$ the thermodynamic probability of insertion is decreased.

At the B3LYP/6-311+G(d,p) level, the value of ΔG is positive for insertion of $GeCl_2$ into all C–H bonds of all isomers, meaning that this process cannot occur spontaneously. M06-2X method with the same basis set gives for this reaction the ΔG values close to zero, as distinct from large negative ΔG values for insertion of $GeCl_2$ into the B–H bonds. This is in compliance with the experimentally observed inertness of the C–H bonds with respect to insertion of dihalogenogermylenes [1, 7].

The obtained thermodynamic parameters for the insertion are in agreement with the experimental data [23, 24], according to which the products of insertion of CCl_2 into the C–H bonds of carboranes(12) are not formed. However, the insertion of CCl_2 into all bonds of all isomers (including C–H bonds) in both approximations are characterized by substantial negative ΔG values, consequently, the course of insertion into the molecules of carboranes(12) can be governed not only by thermodynamic but also by kinetic factors.

Association of the carbenoid species with the molecule of substrate leading to the formation of the prereaction complex **B** (Scheme 1) is usually considered as a separate stage of the insertion reaction [27, 28] resulting in a small decrease of the total energy of the system. In the series $CCl_2 < SiCl_2 < GeCl_2$ the energy gain for the formation of intermediate **B** is regularly increased. Thus, for *ortho*-carborane at the B3LYP/6-311+G(d,p) level, the value of ΔE for the formation of complex **B** is –0.6, –1.5, –2.1 kcal/mol for CCl_2, $SiCl_2$, $GeCl_2$, respectively, and at the M06-2X/6-311+G(d,p) level in the same rank it equals –4.4, –5.8, and –6.2 kcal/mol. However, the energy of formation of complex **B** and the value of the hydride ion affinity of carbenoid species ($XCl_2 + H^- \rightarrow XHCl_2^-$; X = C, Si, Ge) do not vary in the same direction. In particular, the hydride ion affinities at the M06-2X/6-311+G(d,p) level are equal to –128.2, –109.5, and –107.9 kcal/mol for X = C, Si, Ge, respectively, therefore the character of coordination of the XCl_2 molecule with the spatially bulky carborane molecule is complex and depends not only on electron-acceptor properties of the central atom X, but also on its size and orientation relative to the carborane

Table 2. Energy ΔE, enthalpy ΔH, and Gibbs energy ΔG (kcal/mol) for insertion reactions of CCl_2, $SiCl_2$, $GeCl_2$ into the B–Cl, B–Br, C–Cl, and C–Br haloderivatives

Parameter	B^9–Cl	B^9–Br	C–Cl	C–Br
B3LYP/6-311+G(d,p)				
	CCl_2/$SiCl_2$/$GeCl_2$	CCl_2/$SiCl_2$/$GeCl_2$	CCl_2/$SiCl_2$/$GeCl_2$	CCl_2/$SiCl_2$/$GeCl_2$
ΔE	–40.5/–36.9/–11.0	–41.9/–37.9/–14.6	–55.3/–64.7/–31.2	–54.3/–62.9/–32.4
ΔH	–38.7/–35.8/–10.2	–39.5/–36.0/–13.1	–52.7/–62.8/–29.7	–51.6/–60.9/–30.8
ΔG	–24.1/–22.1/+3.1	–27.0/–24.3/–2.1	–39.6/–50.5/–18.0	–38.5/–48.7/–18.9
M06-2X/6-311+G(d,p)				
	CCl_2/$SiCl_2$/$GeCl_2$	CCl_2/$SiCl_2$/$GeCl_2$	CCl_2/$SiCl_2$/$GeCl_2$	CCl_2/$SiCl_2$/$GeCl_2$
ΔE	–53.2/–47.2/–25.6	–54.1/–48.8/–28.6	–69.1/–76.7/–49.3	–67.7/–75.3/–50.7
ΔH	–51.3/–46.0/–24.7	–52.1/–46.3/–27.5	–66.3/–74.8/–47.9	–65.8/–74.0/–49.2
ΔG	–36.6/–31.9/–11.1	–37.4/–32.1/–13.9	–53.0/–62.0/–36.1	–50.8/–59.2/–37.8

molecule, while for the binding the hydride ion the size of atom X, apparently, is much less important.

To analyze the binding of the carbenoid species with the molecule of *ortho*-carborane we performed topological analysis of the total electron density functions in complexes **B** using the M06-2X/6-311+G(d,p) method within the framework of the Beider's Atoms-in-Molecules theory [29, 30]. In complex **B** with CCl_2 the carbon atom of dichlorocarbene is bound with one of the carborane hydrogen atoms via one bonding path with the potential energy density $V(r)$ in the bond critical point equal to –0.005 a.u. A similar picture is observed in the case of $SiCl_2$ but the corresponding value of $V(r)$ in the critical point of the corresponding bond is equal to –0.01 a.u. In the complex with $GeCl_2$, the germanium atom is bound via two bonding paths with the hydrogen atoms in the 9 and 12 positions of the *ortho*-carborane molecule [the values of $V(r)$ in the (3; –1) bcp for these paths are –0.007 and –0.004 a.u.]. Since the bond energy determined by a specific bonding path, according to the Espinosa–Molins–Lecomte correlation [31] is proportional to the potential energy density in the bond critical point for this path [$E = 0.5V(r)$], the bonding energy between atom X in XCl_2 and the carborane molecule increases in the order $CCl_2 < SiCl_2 < GeCl_2$, which is in agreement with the calculated above energy of formation of complexes **B**. It is worth to mention that not only the X atom but also the chlorine atoms of the XCl_2 molecule participate in coordination between the carbenoid species and the carborane molecule (there are bonding paths having small values of the potential energy density between the Cl atoms and the hydrogen atoms of the *ortho*-carborane molecule).

Thermodynamics of the insertion into the B–Hal, C–Hal bonds we studied by the example of halogenated *ortho*-carboranes, in particular, 1-chloro-*ortho*-carborane, 1-bromo-*ortho*-carborane, 9-chloro-*ortho*-carborane, and 9-bromo-*ortho*-carborane (Table 2).

In both methods, all insertion reactions into the C(B)–Hal bonds are thermodinamically allowed and only for insertion of $GeCl_2$ into the B–Cl bond the value of ΔG at the B3LYP/6-311+G(d,p) level is positive.

The insertion into the B–Br bond in all cases is thermodinamically more probable than into the B–Cl bond, whereas for the C–Br and C–Cl bonds the situation is reversed.

For the insertion into the B–Cl and B–Br the value ΔG is increasing in $CCl_2 > SiCl_2 > GeCl_2$ series. For example, for insertion into the B(9)–Cl bond it amounts to –36.6, –31.9, and –11.1 kcal/mol for CCl_2, $SiCl_2$, and $GeCl_2$ respectively, the former two values being rather close while the value for $GeCl_2$ is much less negative. For insertion into the C–Hal bonds, in

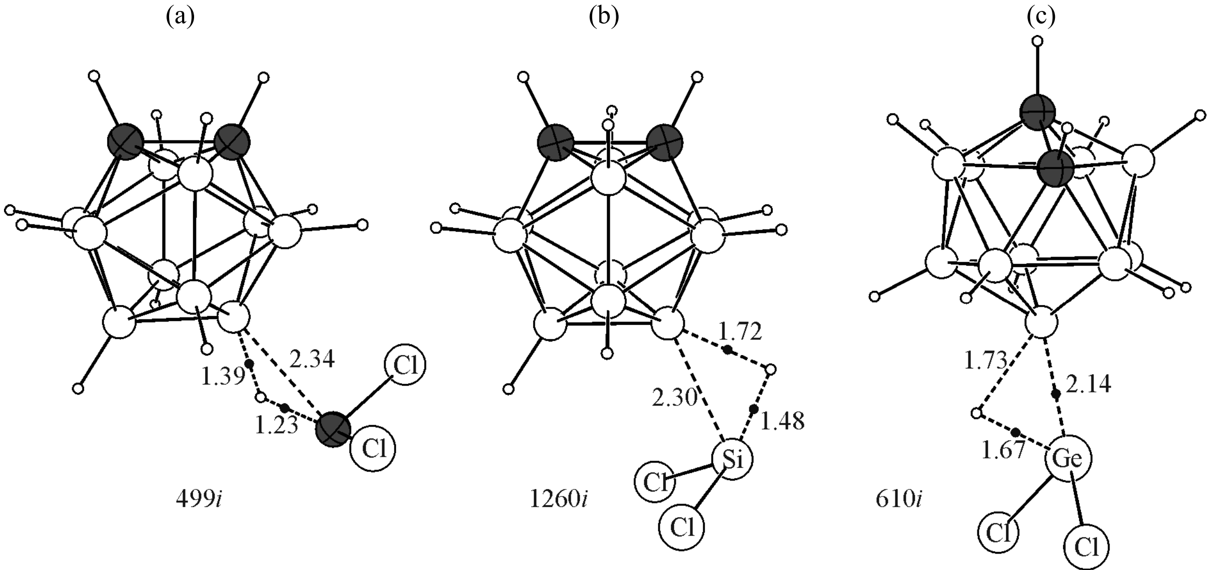


Fig. 2. Molecular structure of TSs for insertion of (a) CCl_2, (b) $SiCl_2$, and (c) $GeCl_2$ into the B^9–H bond of *ortho*-carborane. Interatomic distances (Å) in the reaction node and imaginary frequencies (cm^{-1}) for each TS are given. Black dots refer to the bond critical points [M06-2X/6-311+G(d,p)].

both approximations, the most negative values of ΔG are observed for $SiCl_2$. Note that the differences in the thermodynamics of the insertion of CCl_2 and $SiCl_2$ into the X–Hal bonds are much less than for insertion into the X–H bonds.

The thermodynamic factor is more favorable for insertion of the carbenoid species under consideration into the C–Hal than into the B–Hal bonds.

Analysis of activation energies for insertion of CCl_2, $SiCl_2$, $GeCl_2$ into the terminal bonds of carboranes(12) and their chloro-derivatives. The experimental data on the insertion of methylene and a series of its derivatives are indicative of a substantial selectivity of this reaction with respect to the position of the B–H bond in the carborane molecule. For example, it was shown that the yields of the products of insertion of CCl_2 into the B–H bonds of *ortho*-carborane are distributed as follows: 33% of the products of insertion in the 4, 5, 7, 11 positions (see numeration of atoms in Fig. 1); 24%, in positions 9, 12; 25%, in positions 8, 10; 8%, in positions 3, 6; no products of insertion into the C–H bonds were found [23]. A similar ratio of the products was observed for the insertion of CF_2. In the later work [24] the products of insertion of methylene and carbethoxycarbene into the B–H bonds of *para*-carborane were obtained and, as in the case of the *ortho*-isomer, it was shown that the insertion into the C–H bonds did not occur.

As can be seen from Table 1, in both approximations (B3LYP and M06-2X) the thermodynamics favors the insertion of CCl_2 into all B–H bonds as well as the C–H bonds of all three isomers of carboranes(12). With this in mind, we performed the analysis of the energies of activation of this process in order to explain the observed selectivity for different positions of the terminal bonds of the carborane molecules.

Since the ground electronic state of XCl_2 is singlet, the search for the TS was performed using the model of synchronous three-membered TS (Fig. 2).

The differences in the molecular structure of the TSs of the insertion in the series CCl_2, $SiCl_2$, $GeCl_2$ can serve an illustration to the Hammond–Leffler principle [32, 33], according to which for more endothermic reactions the structure of the TS is more close to the structure of the reaction products, whereas for more exothermic reactions it is closer to the reagents. Based on the topological analysis of the total electron density function in TS structures it was shown (Fig. 2) that for insertion of CCl_2 and $SiCl_2$ the central atom of the carbenoid species is not directly connected with the boron atom of the carborane scaffold (there is no bond critical point between the pairs of atoms C–B and Si–B), whereas the hydrogen atom eliminated from the boron atom retains the H–B bond in the TS. Thus, the structure of TS for insertion of CCl_2 and $SiCl_2$ in this sense is similar to the structure of the

Table 3. Activation energy $\Delta E^{\neq}$, enthalpy $\Delta H^{\neq}$, and Gibbs energy $\Delta G^{\neq}$ (kcal/mol) for insertion of CCl_2 into the B–H, C–H bonds of the carboranes(12) molecules

Parameter	B3LYP/6-311+G(d,p) // M06-2X/6-311+G(d,p)				
ortho	$BH^{9;12}$	$BH^{8;10}$	$BH^{4;5;7;11}$	$BH^{3;6}$	$CH^{1;2}$
$\Delta E^{\neq}$	11.2//3.8	12.1//5.4	12.8//8.5	13.7//6.7	21.4//19.1
$\Delta H^{\neq}$	11.3//3.9	12.0//5.7	12.7//7.7	13.4//6.6	20.1//17.4
$\Delta G^{\neq}$	22.2//15.2	22.7//17.2	23.9//21.2	24.5//18.6	30.6//30.5
meta	$BH^{9;10}$	$BH^{5;12}$	$BH^{4;6;8;11}$	$BH^{2;3}$	$CH^{1;7}$
$\Delta E^{\neq}$	12.4//5.1	12.4//7.4	13.5//8.3	15.8//9.0	22.2//19.4
$\Delta H^{\neq}$	12.3//4.9	12.1//6.5	13.3//7.2	15.5//8.5	20.2//17.3
$\Delta G^{\neq}$	23.1//16.3	23.0//19.6	24.3//20.3	26.2//19.8	32.5//30.2
para	BH	–	–	–	$CH^{1;12}$
$\Delta E^{\neq}$	13.2//8.1	–	–	–	21.7//18.4
$\Delta H^{\neq}$	13.2//6.9	–	–	–	20.4//16.3
$\Delta G^{\neq}$	23.3//19.1	–	–	–	29.6//28.3

reagents. In the TS of more endothermic insertion of $GeCl_2$, there is a bonding path between the germanium and the boron atoms, whereas the leaving hydrogen atom loses bonding with boron. Thus, the structure of TS for insertion of $GeCl_2$ is closer to the product of the reaction.

In all three cases presented in Fig. 2, two bond critical points were found in the reaction node. According to the AIM theory, the presence of the critical point of the type (3; –1) between a pair of atoms is a necessary condition for the existence of the chemical bond between this pair of atoms. Therefore, the reaction nodes of the TSs of the insertion reactions within the method [M06-2X/6-311+G(d,p)] used for the topological analysis are not cyclic structures, as one could assume based on the so-called “chemical reasonings.”

Potential barriers for the insertion reactions were calculated by the formula $\Delta E^{\neq} = E(\mathrm{TS}) - E(\mathbf{A})$ (Scheme 1). As clear from Table 3, on going from the $B^{9/12}$–H bonds to the C–H bonds of the *ortho*-carborane the potential barrier of the reaction increases, and the largest increase is observed for the C–H bonds. A similar pattern is observed for *meta*-carborane. Apparently, the difference in the activation energies causes the observed selectivity of the insertion of dichlorocarbene into the *ortho*-carborane bonds.

We have obtained qualitatively similar results using the semiempirical method PM6 [34]. For example, for *ortho*-carborane, $\Delta G^{\neq}$ for the insertion of CCl_2 is 10.9; 11.2; 12.7; 14.2, and 36.3 kcal/mol for positions 9(12); 8(10); 4(5,7,11); 3(6), and CH, respectively.

The transition from the *ortho*- to the *para*-isomer is followed by a small increase in the barrier to insertion into the B–H bond, but the barriers for different isomers still are comparable. Thus, there are neither thermodynamic nor kinetic constraint for insertion of CCl_2 into the B–H bonds in the *meta* and *para*-carboranes.

The activation energy ($\Delta E^{\neq}$) for insertion of $SiCl_2$ in the case of *ortho*-carborane is 44.4 kcal/mol into the B^9–H bond and 53.2 kcal/mol into the C–H bond at the B3LYP/6-311+G(d,p) level; 36.7 kcal/mol into the B^9–H bond and 46.8 kcal/mol into the C–H bond at the M06-2X/6-311+G(d,p) level. For insertion of $GeCl_2$ into the terminal bonds of *ortho*-carborane $\Delta E^{\neq}$ is 52.1 kcal/mol into the B^9–H bond and 92.5 kcal/mol into the C–H bond at the B3LYP/6-311+G(d,p) level; 43.6 kcal/mol into the B^9–H bond and 85.9 kcal/mol into the C–H bond at the M06-2X/6-311+G(d,p) level. As follows from these values, potential barriers to insertion of $SiCl_2$ and $GeCl_2$ are much higher than for CCl_2, but remain at the acceptable level for the insertion into the B-H bond, especially in the M06-2X/6-311+G(d,p) approximation. The barriers to insertion of $GeCl_2$ into the C–H bond are extremely high at both theoretical levels, therefore, this process seems unlikely for the considered model of TS.

Higher potential barriers for the insertion of $SiCl_2$ and $GeCl_2$ imply more rigid conditions for their realization as compared to the insertion of CCl_2, although this is not a limiting factor, since the molecules of carboranes(12) are highly thermally stable and start to rearrange at the temperatures above 400°C, with retention of the scaffold structure up to 700°C.

The activation energy $\Delta E^{\neq}$ for the insertion of $GeCl_2$ into the B–Cl bond is notably smaller than into the B-H bond, being for the molecule of 9-chloro-*ortho*-carborane 41.2 kcal/mol at the B3LYP/6-311+G (d,p) approximation and 35.4 kcal/mol at the M06-2X/6-311+G(d,p) approximation.

EXPERIMENTAL

Molecular structures of the reagents, products and transition states (TS) were fully optimized at the DFT level of theory using the hybrid functional B3LYP [35, 36] and hybrid *meta*-functional M06-2X [37, 38] in the 6-311+G(d,p) basis set [39, 40]. For TS, the validity of assignment of the found stationary points on the potential energy surface was proved by vibration frequencies calculations (the presence of only one imaginary frequency corresponding to the vibration along the reaction coordinate). In most cases the validity of the found TSs was also proved by IRC calculations [41, 42].

Carbenoid species were calculated in the singlet state which is the ground state for CCl_2, $SiCl_2$ and $GeCl_2$ [1].

Thermodynamic parameters were calculated at the temperature 273.15 K and pressure 1 atm. All calculations were performed with Gaussian 09 program package [43].

REFERENCES

1. Nefedov, O.M., Ioffe, A.I., and Menchikov, L.G., *Khimiya karbenov* (Chemistry of Carbenes), Khimiya, Moscow, 1990.
2. Bourissou, D., Guerret, O., Gabbai, F.P., and Bertrand, G., *Chem. Rev.*, 2000, vol. 100, p. 39. DOI: 10.1021/cr940472u.
3. Mizuhata, Y., Sasamori, T., and Tokitoh, N., *Chem. Rev.*, 2009, vol. 109, p. 3479. DOI: 10.1021/cr900093s.
4. Vignolle, J., Cattoën, X., and Bourissou, D., *Chem. Rev.*, 2009, vol. 109, p. 3333. DOI: 10.1021/cr800549j.
5. Mendez, F. and Garcia-Garibay, M.A., *J. Org. Chem.*, 1999, vol. 64, p. 7061. DOI: 10.1021/jo990584r.
6. Lebel, H., Marcoux, J.-F., Molinaro, C., and Charette, A.B., *Chem. Rev.*, 2003, vol. 103, p. 977. DOI: 10.1021/cr010007e.
7. Neumann, W.P., *Chem. Rev.*, 1991, vol. 91, p. 311. DOI: 10.1021/cr00003a002.
8. Öfele, K., Tosh, E., Taubman, C., and Herrmann, W.A., *Chem. Rev.*, 2009, vol. 109, p. 3408. DOI: 10.1021/cr800516g.
9. Moss, R.A., *Pure Appl. Chem.*, 1995, vol. 67, p. 741. DOI: 10.1351/pac199567050741.
10. Baird, M.S., *Chem. Rev.*, 2003, vol. 103, p. 1271. DOI: 10.1021/cr010021r.
11. Hirai, K., Itoh, T., and Tomioka, H., *Chem. Rev.*, 2009, vol. 109, p. 3275. DOI: 10.1021/cr800518t.
12. *Carbene Chemistry. From Fleeting Intermediates to Powerful Reagents*, Bertrand, G., Ed., Lausanne: FontisMedia S.A., Marcel Dekker Inc., 2002.
13. *Advances in Carbene Chemistry*, Brinker, U.H., Ed., Amsterdam: Elsevier, 2001, vol. 3.
14. Chernyshev, E.A., Komalenkova, N.G., and Bashkirova, S.A., *Russ. Chem. Rev.*, 1976, vol. 45, p. 913. DOI: 10.1070/RC1976v045n10ABEH002739.
15. Chernyshev, E.A. and Komalenkova, N.G., *Russ. Chem. Rev.*, 1990, vol. 59, p. 531. DOI: 10.1070/RC1990v059n06ABEH003541.
16. Bleckmann, P., Minkwitz, R., Neumann, W.P., Schriewer, M., Thibud, M., and Watta, B., *Tetrahedron Lett.*, 1984, vol. 25, p. 2467. DOI: 10.1016/S0040-4039(01)81206-5.
17. Lange, L., Meyer, B., and DuMont, W.-W., *J. Organomet. Chem.*, 1987, vol. 329, p. C17. DOI: 10.1016/S0022-328X(00)99800-0.
18. Su, M.-D. and Chu, S.-Y., *J. Am. Chem. Soc.*, 1999, vol. 121, p. 4229. DOI: 10.1021/ja983763j.
19. Boehme C. and Frenking G., *J. Am. Chem. Soc.*, 1996, vol. 118, p. 2039. DOI: 10.1021/ja9527075.
20. Grimes, R.N., *Carboranes*, London: Academic Press, 2011.
21. Kajiwara, T., Takeda, N., Sasamori, T., and Tokitoh, N., *Organometallics*, 2004, vol. 23, p. 4723. DOI: 10.1021/om049558w.
22. Li, X. and Curran, D.P., *J. Am. Chem. Soc.*, 2013, vol. 135, p. 12076. DOI: 10.1021/ja4056245.
23. Sung, D.D., Lee, J.D., and Choi, S.K., *Bull. Korean Chem. Soc.*, 1987, vol. 8, p. 63.

24. Yuan, K. and Jones, M., Jr., *Tetrahedron Lett.*, 1992, vol. 33, p. 7481. DOI: 10.1016/S0040-4039(00)60801-8.
25. Potenza, J.A., Lipscomb, W.N., Vickers, G.D., and Schroeder, H., *J. Am. Chem. Soc.*, 1966, vol. 88, p. 628. DOI: 10.1021/ja00955a059.
26. Knyazev, S.P., Gordeev, E.G., and Chernyshev, E.A., *Russ. Chem. Bull.*, 2006, vol. 55, no. 12, p. 2154. DOI: 10.1007/s11172-006-0567-6.
27. Abronin, I.A., Avdyukhina, N.A., and Chernyshev, E.A., *Russ. Chem. Bull.*, 1994, vol. 43, no. 5, p. 751. DOI: 10.1007/BF00717332.
28. Bach, R.D., Su, M.-D., Aldabbagh, E., Andres, J.L., and Schlegel, H.B., *J. Am. Chem. Soc.*, 1993, vol. 115, p. 10237. DOI: 10.1021/ja00075a045.
29. Bader, R.F.W., *Atoms in Molecules. A Quantum Theory*, Oxford: Clarendon Press, 1994.
30. Keith, T.A. *AIMAll 09.10.24.* (*http://aim.tkgristmill.com*).
31. Espinosa, E., Molins, E., and Lecomte, C., *Chem. Phys. Lett.*, 1998, vol. 285, p. 170. DOI: 10.1016/S0009-2614(98)00036-0.
32. Hammond, G.S., *J. Am. Chem. Soc.*, 1955, vol. 77, p. 334. DOI: 10.1021/ja01607a027.
33. Leffler, J.E., *Science*, 1953, vol. 117, p. 340. DOI: 10.1126/science.117.3039.340.
34. Stewar,t J.J.P., *J. Mol. Model.*, 2007, vol. 13, p. 1173. DOI: 10.1007/s00894-007-0233-4.
35. Becke, A.D., *J. Chem. Phys.*, 1993, vol. 98, p. 5648. DOI: 10.1063/1.464913.
36. Stephens, P.J., Devlin, F.J., Chabalowski, C.F., and Frisch, M.J., *J. Phys. Chem.*, 1994, vol. 98, p. 11623. DOI: 10.1021/j100096a001.
37. Zhao, Y. and Truhlar, D.G., *Acc. Chem. Res.*, 2008, vol. 41, p. 157. DOI: 10.1021/ar700111a.
38. Zhao, Y. and Truhlar, D.G., *J. Chem. Theory Comput.*, 2008, vol. 4, p. 1849. DOI: 10.1021/ct800246v.
39. Krishnan, R., Binkley, J.S., Seeger, R., and Pople, J.A., *J. Chem. Phys.*, 1980, vol. 72, p. 650. DOI: 10.1063/1.438955.
40. Clark, T., Chandrasekhar, J., Spitznagel, G.W., and Schleyer, P.v.R., *J. Comp. Chem.*, 1983, vol. 4, p. 294. DOI: 10.1002/jcc. 540040303.
41. Hratchian, H.P. and Schlegel, H.B., *J. Chem. Phys.*, 2004, vol. 120, p. 9918. DOI: 10.1063/1.1724823.
42. Hratchian, H.P. and Schlegel, H.B., *J. Chem. Theory Comput.*, 2005, vol. 1, p. 61. DOI: 10.1021/ct0499783.
43. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G.A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H.P., Izmaylov, A.F., Bloino, J., Zheng, G., Sonnenberg, J.L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J.A., Jr., Peralta, J.E., Ogliaro, F., Bearpark, M., Heyd, J.J., Brothers, E., Kudin, K.N., Staroverov, V.N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J.C., Iyengar, S.S., Tomasi, J., Cossi, M., Rega, N., Millam, J.M., Klene, M., Knox, J.E., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Martin, R.L., Morokuma, K., Zakrzewski, V.G., Voth, G.A., Salvador, P., Dannenberg, J.J., Dapprich, S., Daniels, A.D., Farkas, O., Foresman, J.B., Ortiz, J.V., Cioslowski, J., and Fox, D.J., *GAUSSIAN 09*, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.