Full Articles

Quantum chemical study of interactions of carbenes and their analogs of the EH_2 and EHX types (E = Si, Ge, Sn; X = F, Cl, Br) with HX and H_2, respectively: the insertion and substituent exchange reactions

S. E. Boganov, V. M. Promyslov, V. I. Faustov,† M. P. Egorov, and O. M. Nefedov*

N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (499) 135 8941. E-mail: bog@ioc.ac.ru

Interactions of carbenes and carbene analogs EH_2 and EHX with HX and H_2 (E = C, Si, Ge, Sn; X = F, Cl, Br), respectively, were studied by quantum chemical methods. Theoretical analysis of the carbene and silylene systems was carried out at the G3 level of theory using the MP2(full)/6-31G(d) calculated geometries and vibrational frequencies. The stannylene systems were examined at the MP2 level using a modified LANL2DZ basis set for the Sn atoms and the 6-31+G(d,p) basis sets for other atoms. Transformations in the germylene systems were studied within the framework of both approaches, which gave similar results. This allowed one to compare the reaction pathways and their energy profiles for the whole series of systems. In addition to the insertions into the H—X and H—H bonds, the exchange reactions resulting in interconversions of EH_2 and EHX can proceed in the systems under consideration. The effects of the nature of the E and X atoms on the reaction barriers and exothermicity of both the insertion and exchange reactions are analyzed. Possible role of radical processes in these systems is assessed.

Keywords: carbenes, carbene analogs, hydrogen halides, hydrogen, insertion reaction, substituent exchange, quantum chemical calculations, G3 and MP2 methods.

Short-lived carbene analogs, derivatives of the dicoordinate Group 14 elements, *viz.*, silylenes (SiR_2), germylenes (GeR_2) and stannylenes (SnR_2), are an important type of highly reactive intermediates of chemical transformations of compounds containing these elements.[1—5] Except several triplet silylenes,[6—8] all carbene analogs are singlet in their ground electronic state.[9,10] The most characteristic reactions of singlet carbene analogs are insertions into single bonds and additions to multiple bonds.[4,5,11] The simplest reagents, whose single bonds can be attacked by carbene analogs, are molecular hydrogen[12—15] and hydrogen halides HX.[14,16—22]

† Deceased.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2107—2119, November, 2011.

1066-5285/11/6011-2147

The insertion reactions of silylenes and germylenes into the H—H and H—X bonds, as well as the corresponding reverse reactions are certain steps of various CVD processes, such as production of amorphous silicon films,[23] silicon-germanium alloys,[24] and silicon carbide.[25—28] Reactions of surface silylenes and free chlorinated germylenes with HCl are parts of the mechanisms of direct syntheses of chlorosilanes and chlorogermanes from elemental silicon and germanium.[29—31] Studies of these reactions provide necessary data for modelling of the listed and related processes.[32]

Some of these reactions have been analysed theoretically. Those are the reactions $EH_2 + H_2$, E = Si,[15,32—42] Ge,[15,38] Sn,[38] Pb;[38] $SiHF + H_2$;[40,41,43] $SiF_2 + H_2$;[40,41] $SiHCl + H_2$;[22,32,39,44—46] $SiCl_2 + H_2$;[32,39,42,44—47] $SiH_2 + HF$;[40,48—50] $SiHF + HF$;[40,49] $SiF_2 + HF$;[40] $SiH_2 + HCl$;[22,32,39,50,51] $SiHCl + HCl$;[32,39,42,44—47] $SiCl_2 + HCl$;[32,39,44—46,51] $GeMe_2$ + HF and HCl;[52,53] reactions of several silylenes bearing organic substituents with H_2,[33] and also silylsilylenes and fluoro(silyl)silylenes with H_2 and HF.[54] It was shown that these reactions are usually not straightforward, but often represent two-step processes involving a barrierless formation of various types of complexes and their further rearrangements into the final insertion products proceeding with activation barriers.

Most studies on the subject are devoted to the reactions of silylenes with HF and HCl. Therefore, general trends in the course of these reactions are not ascertained yet. In particular, effects of the nature of the central atom in carbene analogs and halogen atoms have not been elucidated.

Quantum chemical calculations of some silylene and germylene insertion reactions revealed additional unusual pathways leading to exchange of the substrate substituents by the carbene analog substituents:

$$SiH_2 + HCl \rightleftharpoons SiHCl + H_2,^{22} \quad (1)$$

$$SiHCl + HCl \rightleftharpoons SiCl_2 + H_2,^{44—46} \quad (2)$$

$$SiH_2 + SiH_nCl_{4-n} \rightleftharpoons SiHCl + SiH_{n+1}Cl_{3-n} \quad (3)$$

(n = 0—3),[55]

$$SiHCl + SiH_nCl_{4-n} \rightleftharpoons SiCl_2 + SiH_{n+1}Cl_{3-n} \quad (4)$$

(n = 0—3),[55]

$$SiH_2 + ROH \rightleftharpoons Si(OR)H + H_2 \quad (5)$$

(R = H,[56—59] Me,[56—58] Et, CF_3[56,57]),

$$GeH_2 + ROH \rightleftharpoons Ge(OR)H + H_2 \quad (6)$$

(R = H, Me[56,57]),

$$SiHCl + Me_nSiH_{4-n} \rightleftharpoons SiHCl + Me_nSiH_{4-n} \quad (7)$$

(n = 1, 3[60]).

Those are Cl/H (reactions (1)—(4)), RO/H (reactions (5) and (6)), and degenerate H/H (reaction (7)) exchange processes. Not all of them can compete with the insertion processes occurring in these systems. Only the barriers to reactions (1) (in the forward direction), (2) (in both directions), (5) (for R = CF_3, in the forward direction), (6) (in the forward direction), and (7) (in both directions) are lower than the barriers to the corresponding insertion reactions, and thus the insertion processes in these systems should be accompanied by fast exchange processes. The forward reactions (5) for R = H, Me, Et and the corresponding insertion reactions have comparable barriers.

Although the exchange processes in the chemistry of stannylenes have not been reported yet, the above data suggest that the existence of the exchange channels should be quite typical of the systems in which insertion reactions of carbene analogs proceed. It is also important that an exchange reaction was revealed[61] in the following carbene system:

$$CHF + HF \rightleftharpoons CF_2 + H_2. \quad (8)$$

However, in this case, the barriers to the exchange reactions in both directions are considerably higher than the barriers to the corresponding insertion reactions.

Here we report the results of a systematic quantum chemical study of the interactions of the parent carbene analogs EH_2 (E = Si, Ge, Sn) with HX (X = F, Cl, Br) and the complementary interactions of EHX with molecular hydrogen. Analogous reactions of singlet CH_2 and CHX are also considered for comparison. As a result, a detailed description of the potential energy surfaces (PESs) for these prototype systems was obtained, the effects of the nature of the central atoms in carbene analogs and halogen atoms on the insertion and exchange reactions were elucidated for the first time, the role of the exchange processes in these systems was determined, and the possibility for competing radical processes to occur was assessed.

Calculation Procedure

Electronic structure calculations were performed with the Gaussian 03, Revision-C.02 software package.[62] For the systems EH_3X (E = C, Si, Ge, X = F, Cl, Br), a conventional G3 approach[63] was used with the following modifications. Geometry optimizations and normal vibrational frequency calculations were performed at the MP2(full)/6-31G(d) level of theory since preliminary calculations of the $CH_2 + HCl$ and $SiH_2 + HCl$ reactions showed that geometry optimization by the HF/6-31G(d) method led to loss of some stationary points. The basis sets recommended for application in the G3 calculations[63,64] were used for all atoms. The MP2(full)/6-31G(d) calculated vibrational

frequencies were used in calculations of thermodynamic functions after scaling by a factor of 0.9646 (see Refs. 65, 66). Higher-level corrections were obtained as is indicated in the routine G3 method. These calculations are denoted below as the G3(MP2 freq) calculations.

Because some basis sets required for G3 calculations are not defined for the Sn atom, the SnH_3X systems were studied at the MP2 level of theory using the 6-31+G(d,p) basis sets for the H, F, Cl, and Br atoms and the quasi-relativistic effective core potential LANL2DZ basis set[67] supplemented with polarization d-functions ($\alpha_d = 0.183$) and diffuse sp-functions ($\alpha_{sp} = 0.0231$)[21] for the Sn atom. These calculations are denoted below as MP2/LANL2DZ(suppl). For comparison, the stationary points on the PESs of the GeH_3X systems (X = F, Cl, Br) were also optimized by the MP2/LANL2DZ(suppl) method. The LANL2DZ basis set for the Ge atom[67] was supplemented with polarization d-functions ($\alpha_d = 0.246$)[68] and diffuse sp-functions ($\alpha_{sp} = 0.0222$)*. Based on good agreement between the results of the MP2/LANL2DZ(suppl) and G3(MP2 freq) calculations of the GeH_3X systems, the MP2/LANL2DZ(suppl) level of theory was used to estimate the energies of the SnH_3X systems and to directly compare the calculated values for all the systems studied.

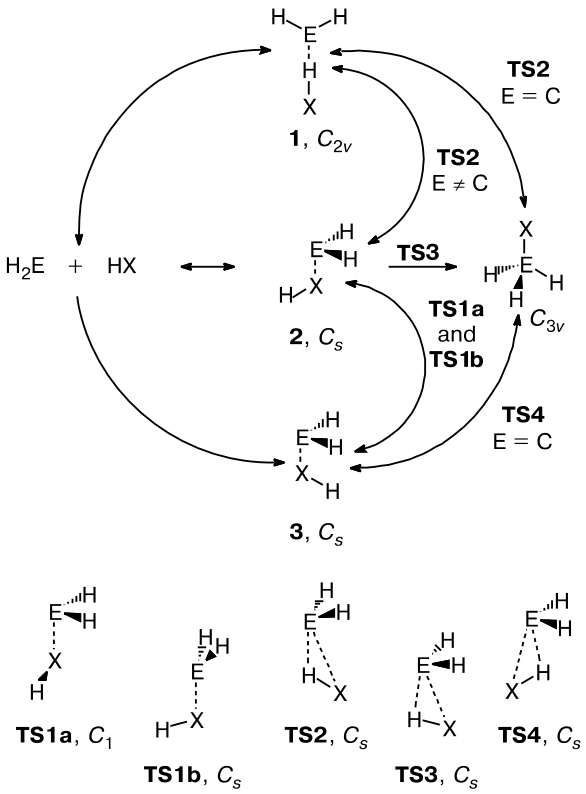
All geometries were fully optimized without imposing any symmetry constraints, although the resulting structures often exhibited certain symmetry elements. The character of the stationary points (a minimum or a first-order saddle point) was determined by calculating the eigenvalues of the Hessian matrices. To ascertain the PES topology, mass-weighted intrinsic reaction coordinate (IRC) calculations[70,71] were carried out for all of the transition-state structures.

Results and Discussion

The EH_2 + HX (E = C, Si, Ge, Sn, X = F, Cl, Br) insertion reactions

The first step of the reactions of singlet EH_2 (E = C, Si, Ge, Sn) with HX (X = F, Cl, Br) consists in the formation of pre-reaction complexes. Three types of complexes were revealed in these systems. These are complexes **1**, in which EH_2 acts as a Lewis base and the H atom of hydrogen halide is coordinated to the E atom, and complexes **2** and **3**, in which EH_2 acts as a Lewis acid and the X atom is coordinated to the E atom (Scheme 1). In the case of the CH_2 + HF system, only complex **1** was found. Apparently, large negative charge on the F atom (the Mulliken charge is −0.517) precludes its coordination to the negative charged C atom (−0.282) and prevents formation of complexes **2** and **3**. The formation of complexes between SiH_2 and HF of unknown structure was observed earlier by matrix IR spectroscopy[49].

Scheme 1



Except complexes **3** in the systems CH_2 + HCl and CH_2 + HBr where the H—C—H angles are ~13° larger than in free singlet methylene, the formation of the other complexes is accompanied by minor changes in the geometries of the reacting molecules. This fact indicates weakness of the complexes. Indeed, the formation of the most of the complexes leads to a slight decrease in the energies of the systems, whereas the Gibbs free energies (ΔG°) mainly increase (Table 1), *i.e.*, the running concentrations of the complexes under normal conditions are very low. Despite the low values of the complexation energies, there are some regularities in their dependence on the nature of the E and X atoms.

The energy gain upon formation of complexes **1** decreases on going from HF to HCl and then remains almost unchanged on going to HBr; this trend agrees with the decrease in the positive charge on the H atoms in hydrogen halides.[72] It also decreases on going from carbene to stannylene, thus showing weakening of the Lewis basicity of EH_2 in this series. Complexes **2** are slightly less stable or comparable in stability with the corresponding complexes **3** in all the systems. According to the G3(MP2 freq) calculations, the energy gain in the formation of complexes **2** and **3** in the systems involving CH_2, SiH_2, and GeH_2 increases on going from HF to HBr (Table 1), thus reflecting the increase in the Lewis basicity of hydrogen ha-

* This value was optimized by Ted Packwood at NDSU using ROHF method with a flexible ECP basis set.[69]

Table 1. Relative energies[a,b] (ΔE_0/kcal mol^{-1}) and Gibbs free energies[a,c] ($\Delta G°$/kcal mol^{-1}, in brackets) of the structures corresponding to the stationary points in the PES regions corresponding to the reactions of insertion of EH_2 into HX

System	Method[d]	**1**	**2**	**3**	**TS1a**	**TS1b**	**TS2**	**TS3**	**TS4**	EH_3X
CH_2 + HF	A	−7.7	—	—	—	—	−4.9	—	23.8	−91.0
		[−1.7]					[1.6]		[30.9]	[−83.0]
CH_2 + HCl	A	−4.0	−3.8	−5.6	−1.6	0.3	−4.3	−3.6	5.2	−97.1
		[2.3]	[2.6]	[1.8]	[4.8]	[7.8]	[2.5]	[2.9]	[12.4]	[−89.0]
CH_2 + HBr	A	−3.3	−6.9	−10.3	−3.5	—	−3.3	−4.3	0.7	−100.0
		[3.0]	[0.0]	[−2.8]	[3.2]		[3.4]	[2.3]	[7.9]	[−92.5]
SiH_2 + HF	A	−3.1	−2.2	−3.3	−2.3	—	−2.1	8.5	—	−80.4
		[2.5]	[4.5]	[3.3]	[4.8]		[3.5]	[15.9]		[−72.1]
SiH_2 + HCl	A	−1.7	−4.4	−4.5	−3.8	43.4	−1.2	0.7	—	−71.8
		[3.7]	[1.9]	[1.9]	[2.9]	[51.1]	[4.2]	[8.0]		[−63.3]
SiH_2 + HBr	A	−1.7	−5.8	−5.7	−4.9	—	−1.3	−2.3	—	−71.4
		[3.8]	[0.8]	[1.0]	[2.0]		[4.1]	[4.8]		[−63.5]
GeH_2 + HF	A	−3.1	−2.2	−3.4	—	—	−2.4	16.9	—	−46.6
		[2.2]	[4.9]	[3.5]			[3.5]	[24.9]		[−37.8]
GeH_2 + HF	B	−2.5	−3.3	−4.1	—	—	−1.2	13.1	—	−56.3
		[3.2]	[2.9]	[2.3]			[4.6]	[20.6]		[−48.5]
GeH_2 + HCl	A	−1.7	−4.4	−4.6	—	—	−1.2	4.7	—	−50.6
		[4.1]	[2.4]	[2.4]			[4.5]	[12.7]		[−42.2]
GeH_2 + HCl	B	−1.5	−3.0	−3.3	—	—	−0.8	8.9	—	−55.3
		[3.9]	[3.4]	[3.3]			[4.5]	[16.5]		[−47.3]
GeH_2 + HBr	A	−1.7	−5.7	−5.7	−5.1	—	−1.3	−0.7	—	−53.2
		[4.1]	[1.3]	[1.5]	[2.4]		[4.4]	[7.3]		[−44.7]
GeH_2 + HBr	B	−1.6	−4.4	−4.4	—	—	−1.1	2.2	—	−58.2
		[3.8]	[2.2]	[2.3]			[4.3]	[9.8]		[−50.1]
SnH_2 + HF	B	−1.9	−3.5	−4.9	—	—	−1.0	19.1	—	−42.3
		[4.1]	[2.7]	[1.8]			[5.0]	[27.1]		[−34.1]
SnH_2 + HCl	B	−1.1	−2.6	−3.3	−2.5	—	−0.7	16.2	—	−40.9
		[4.5]	[3.8]	[3.4]	[4.7]		[4.8]	[24.3]		[−32.6]
SnH_2 + HBr	B	−1.3	−3.8	−4.2	−3.5	—	−0.9	8.2	—	−45.9
		[4.3]	[2.9]	[2.7]	[3.9]		[4.7]	[16.4]		[−37.5]

[a] Relative to noninteracting EH_2 and HX.
[b] ΔE_0 are the relative energies obtained by the G3(MP2 freq) method or by the MP2/LANL2DZ(suppl) method with ZPE corrections.
[c] At T = 298 K and p = 1 atm.
[d] A denotes the G3(MP2 freq) method, B denotes the MP2/LANL2DZ(suppl) method.

lides.[73] The MP2/LANL2DZ(suppl) calculations of the systems with GeH_2 and SnH_2 do not predict this trend probably due to the lower accuracy of this computational method and the close relative energies of the complexes. Among carbene analogs, the relative energies of complexes **2** and **3** with the same hydrogen halide are close for each type of the complexes, whereas singlet CH_2 forms stronger complexes **2** and **3** with HBr and complex **3** with HCl than do other EH_2 species.

The effect of the nature of the central atom in carbene analogs on the energy of their complexation with Lewis bases was investigated in several studies. Based on the results of MP2/CEP-31+G(2d,1p) calculations, it was concluded that the relative stabilities of the EH_2 complexes (E = Si, Ge, Sn) with AH_3 (A = N, P, As, Sb, Bi) and AH_2 (A = O, S, Se, Te) increase from stannylene to silylene.[74] The same trend was obtained for the complexes of EH_2, EHMe, and EHCl (E = Si, Ge) with NH_3 and PH_3 in the B3LYP/6-311+G(d,p) calculations.[75] However, the results obtained for the complexes of EF_2 and ECl_2 (E = Si, Ge) with NH_3 and PH_3 show the opposite trend.[75] The opposite order of stability was also found for the complexes between EX_2 (E = Si, Ge, Sn, Pb; X = F, Cl) and N_2 in experiment.[76,77] Thus, the ability of carbene analogs to form complexes with Lewis bases strongly depends on the types of their substituents and on the nature of the Lewis base.

Complexes **2** and **3** easily interconvert by relative rotation of their fragments around the dative bond axis *via* transition states **TS1a** (Scheme 1). Although purposeful search for such transition states was not undertaken, they have been found for several systems (Table 1). The ener-

gies of these transition states are close to those of the complexes; hence, the rotation around the E-X dative bond is almost free. However, it should be noted that under normal conditions, interconversions of these complexes *via* dissociation into the reactants are somewhat more thermodynamically favourable because $\Delta G^\circ > 0$ for all **TS1a**. The third pathway of interconversions of complexes **2** and **3** consists in inversion of the EH_2 group *via* **TS1b** (Scheme 1). The energies of two optimized transition states **TS1b** indicate that this pathway is energetically much less favourable than the pathway *via* **TS1a** (Table 1).

In the carbene analog systems, complexes **1** and **2** also readily interconvert *via* **TS2** (Scheme 1). According to the G3(MP2 freq) calculations, the energy of **TS2** in the GeH_2 + HF system is lower than that of **2**; therefore the formation of complex **2** in this system is impossible. No pathway for transformation of **1** into **3** was found in all systems. The obvious reason is that this transformation requires simultaneous coordination of both atoms, H and X, of hydrogen halide on the E atom of carbene analog involving the lone electron pair and the vacant p-orbital of the atom E, respectively; this implies a mutual orientation of the EH_2 and HX species corresponding to the structure of complex **2** rather than complex **3**.

There is no pathway for interconversions of complexes **1** and **2** in the CH_2 systems. Instead, the transition states **TS2** lead from **1** to the insertion products CH_3X. In the CH_2 + HCl and CH_2 + HBr systems, the G3(MP2 freq) energies of **TS2** are lower than the energies of complexes **1** (Table 1); however, low barriers on the Gibbs free energy surfaces correspond to these transition states at room temperature. CH_3X molecules are also formed from complexes **2** and **3** *via* transition states **TS3** and **TS4**, respectively (Scheme 1). The structures of **TS3** resemble those of **TS2**. The major differences between them consist in that the X—H—C angle in **TS3** is close to 90°, whereas it varies in **TS2** from 135 to 171° on going from HF to HBr and the distance between the C atom and the H atom of HX in **TS2** is about 1.5 times shorter than in **TS3**. The energies of these transition states are also very close and lower than the sums of the energies of the corresponding free compounds CH_2 and HX. Therefore, the insertion pathways *via* complexes **1** and **2** and transition states **TS2** and **TS3** are virtually barrierless.

The energies of transition states **TS4** corresponding to the insertion processes starting from complexes **3** are higher than those of the initial free reactants; therefore, these processes are energetically less favourable. The transition state **TS4** was also found in the CH_2 + HF system, despite the fact that there is no complex **3** in this system. This transition state is responsible for the degenerate isomerization of CH_3F molecule. This type of isomerization of alkyl halides has not been reported before. The reaction barrier corresponding to **TS4** is high (Table 1); consequently, this isomerisation is kinetically highly unfavourable.

The only pathway leading to the insertion products, EH_3X, in the systems involving SiH_2, GeH_2, and SnH_2 starts at complexes **2** and goes *via* **TS3**. It can be considered as a nucleophilic attack of the EH_2 fragment on the H atom of the HX fragment in the complexes.[13] Unlike complexes **2**, the E atom in **TS3** is located closer to the H atom than to the X atom of hydrogen halide. The E—H bonds in the EH_2 fragment of **TS3** are much shorter than in free EH_2, and their lengths are closer to the values typical of EH_3X, the H—E—H angles are remarkably increased as compared to free EH_2, the H—X bonds are strongly elongated in comparison with free HX. The barrier heights determined by **TS3** systematically increase on going from SiH_2 to SnH_2 (actually, from CH_2 to SnH_2, *i.e.*, this regularity is valid for the whole series of the systems) and decrease from HF to HBr. The former trend indicates a decrease in nucleophilicity on going from SiH_2 to SnH_2, while the latter is to a great extent caused by weakening of the H—X bonds in the series HF > HCl > HBr.

Previous B3LYP/6-311G(d) and MP2/6-311G(d) calculations[52,53] showed that $GeMe_2$ insertion into HCl proceeds easier than into HF. This result agrees with the tendency revealed for our systems and demonstrates similarity in the behaviour of EH_2 and carbene analogs with organic substituents.

One can expect very fast insertion reactions (even at room temperature) between SiH_2 and HCl (HBr) and between GeH_2 and HBr because the transition state energies in these systems are close to or lower than the energies of the initial free reactants.

The formation of the insertion products, EH_3X, is thermodynamically very favourable, although the exothermicity of these reactions is approximately halved on going from CH_2 to SnH_2 (Table 1) due to a decrease in the total energy of the E—H and E—X bonds formed in the reactions. This is an illustration of the inert lone pair effect:[78] the energies of the divalent states decrease relative to those of the tetravalent states on going down Group 14.

Based on the experimental enthalpies for formation[79—83] of the species involved in the reactions under study, one can obtain the enthalpies for all of the CH_2 and SiH_2 insertion reactions, as well as for two reactions with participation of GeH_2. The enthalpies obtained in this way are compared with the calculated values in Table 2. Better agreement between two sets of values is observed for the CH_2 rather than SiH_2 reactions. This largely relates to lower accuracy of the experimental enthalpies of formation of silicon-containing compounds. Indeed, for the reaction of SiH_2 with HF characterized by the largest difference between the values obtained on the basis of experimental data and from calculations, the uncertainty of the former value based on the uncertainties for $\Delta H_f^\circ(SiH_2)$

Table 2. Enthalpies of reactions $EH_2 + HX \rightarrow EH_3X$

Reaction	$\Delta H°_{calc}$[a]	$\Delta H°_{exp}$[b]	References[c]
	kcal mol^{-1}		
$CH_2 + HF \rightarrow MeF$	−93.0	−92.2	80
$CH_2 + HCl \rightarrow MeCl$	−99.1	−99.3	80
$CH_2 + HBr \rightarrow MeBr$	−101.9	−101	79, 80
$SiH_2 + HF \rightarrow SiH_3F$	−82.3	−90	80, 81
$SiH_2 + HCl \rightarrow SiH_3Cl$	−73.5	−76	80, 81
$SiH_2 + HBr \rightarrow SiH_3Br$	−73.1	−75	80, 81
$GeH_2 + HF \rightarrow GeH_3F$	−48.4; −58.0[d]	−46	80, 82, 83
$GeH_2 + HCl \rightarrow GeH_3Cl$	−52.2; −56.9[d]	−49	80, 82, 83

[a] Obtained from G3(MP2 freq) calculations.
[b] Obtained from experimental enthalpies of formation of the involved molecules.
[c] Sources of experimental enthalpies of formation.
[d] Obtained by the MP2/LANL2DZ(suppl) method.

and $\Delta H_f°(SiH_3F)$[81] equals 10 kcal mol^{-1}. This figure exceeds the indicated difference.

The CH_2 + HF (see Refs 48, 61, 84—87) and CH_2 + HCl (see Ref. 86) systems were studied by quantum chemical methods earlier. As in our calculations, only complex **1** was located in the CH_2 + HF system. For the CH_2 + HCl system, only complexes **1** and **3** were reported. Although the geometric parameters of these species and the transition states separating them from the insertion products to some extent vary depending on computational method and basis sets used, the reported relative energies are in good agreement with our values. Particularly, in the system CH_2 + HF, the relative energies of **1** (relative to free CH_2 and HF) obtained at the CBS-Q,[87] CCSD(T)/DZP,[61] and QCISD/6-311G(d,p)[61] levels of theory are equal to −8.6, −11.1, and −9.6 kcal mol^{-1}, respectively, the corresponding energies of **TS2** are −5.8, −8.3, and −6.5 kcal mol^{-1}, and those of CH_3F are equal to −93.8, −97.5 and −96.2 kcal mol^{-1}, respectively. The values obtained with the use of the CBS-Q composite method are the closest to our values obtained using an alternative composite method G3. In the system CH_2 + HCl, the relative energies of **1**, **3**, **TS2**, **TS4**, and CH_3Cl obtained at the MP4/6-311G(df,p)//MP2/6-31G(d) level are −5.7, −4,3, −6.0, 7.6, and −106.4 kcal mol^{-1} (see Ref. 86).

Previous theoretical studies of the system SiH_2 + HF revealed complexes **1**,[48—50] **2**,[50] **3**,[40] and transition state **TS3**.[40,50] For the system SiH_2 + HCl, complexes **1**,[50] **2**,[22,50,51] **3**,[22,39] and transition states **TS1a**[22] and **TS3**[22,32,39,50,51] were found. It was reported[39,40] that in the systems SiH_2 + HF and SiH_2 + HCl the transition states **TS3** connect complexes **3** with EH_3X, whereas our IRC calculations predict that the pathway *via* **TS3** starts from complexes **2**. However, this discrepancy has no principal meaning because interconversions of **2** and **3** are practically barrierless. The relative energies of the stationary points obtained for the SiH_2 insertion into HF at the MP2/6-311++G(d,p) level of theory[48] and into HCl by the MP2/6-311++G(3df,3pd)//MP2/6-31G(d,p) (see Ref. 39) and G3 methods (see Ref. 22) are very close to those obtained by us. The MP4(SDTQ)/6-31G(d,p)//HF/6-31G(d) calculations predict[40] an additional stabilization of complex **3** and a decrease in the energy of **TS3** in the SiH_2 + HF system by the same value of 6 kcal mol^{-1}. The CCSD(T)/a-cc-pVNZ//CASSCF/cc-pVDZ (N = D, T) calculations with subsequent approximation to the complete basis set predict[32] lowering of the **TS3** energy to −1.2 kcal mol^{-1} in the SiH_2 + HCl system. Although this value is more precise, it differs insignificantly from our value. An additional weak van-der-Waals complex between HF and SiH_2 with the H atom of HF coordinated to an H atom of SiH_2 was located in the HF/STO-3G calculations.[49] We did not look for this type of complexes because they should be even weaker, if exist, and most probably, their formation does not lead to opening new reaction pathways.

The EHX + H_2 insertion reactions (E = C, Si, Ge, Sn; X = F, Cl, Br). Degenerate H/H exchange

The energies of noninteracting pairs CHX + H_2 and CH_2 + HX (X = F, Cl, Br) are close to each other, whereas noninteracting pairs EHX + H_2 (E = Si, Ge, Sn) are stabilized by 20—40 kcal mol^{-1} in comparison with the corresponding pairs EH_2 + HX (Table 3). This indicates that the differences D(E—X) − D(E—H) depend slightly on the nature of the E atoms in carbene analogs, but noticeably differ from the corresponding differences for carbenes. Also, this suggests that the E—X bonds in EHX (E = C, Si, Ge, Sn) weaken in parallel with the H—X bonds in hydrogen halides on going from F to Br.

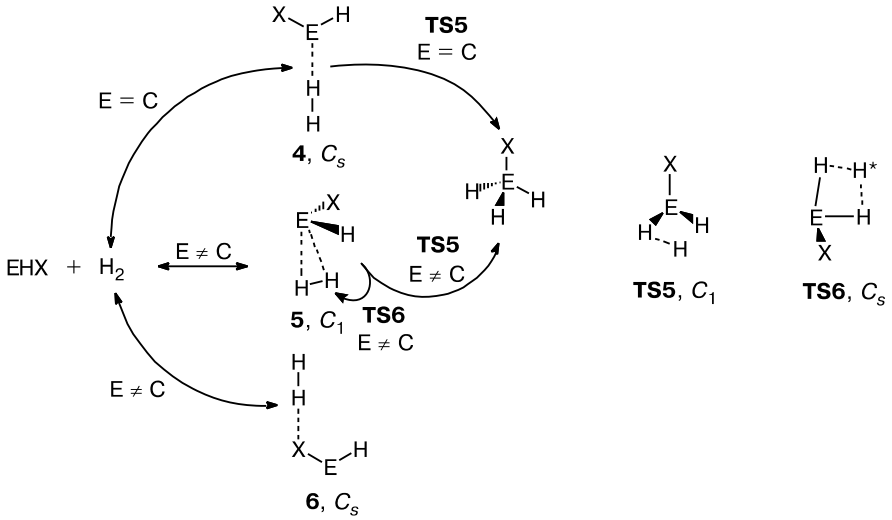
Structures corresponding to complexes between reactants with almost unchanged EHX and H_2 geometries were located for all systems (Scheme 2). In the CHX + H_2 systems, those are complexes **4**. A similar complex was located previously in the CHF + H_2 system in the MP2/6-31G(d) calculations,[87] and by the CCSD(T) and QCISD methods using extended basis sets.[61] In the case of the carbene analog systems, complexes **5** instead of complexes **4** were located (Scheme 2). Previous theoretical studies of the reactions of SiHF with H_2 at the MP4(SDTQ)/6-31G(d,p)//HF/6-31G(d) level[40,41] and SiHCl with H_2 at the MP2/6-311++G(3df,3pd)//MP2/6-31G(d,p) level[39] also revealed only complexes **5**. Our calculations of some systems involving carbene analogs also revealed unusual, previously non-reported complexes **6** (Scheme 2). Undoubtedly, this type of complexes can also exist in other systems.

Table 3. Relative energies[a,b] (ΔE_0/kcal mol^{-1}) and Gibbs free energies[a,c] ($\Delta G°$/kcal mol^{-1}, in brackets) of the structures corresponding to the stationary points in the PES regions corresponding to the reactions of EHX insertion into H_2

System	Method[d]	EHX+H_2	**4**	**5**	**6**	**TS5**	**TS6**
CHF + H_2	A	0.0 (−2.0)	0.9 (−1.1)	—	—	7.1 (5.0)	—
		[0.0 (−1.4)]	[4.0 (2.6)]			[13.5 (12.1)]	
CHCl + H_2	A	0.0 (−4.2)	0.7 (−3.5)	—	—	7.3 (3.1)	—
		[0.0 (−3.4)]	[4.0 (0.6)]			[13.7 (10.3)]	
CHBr + H_2	A	0.0 (−5.2)	0.7 (−4.5)	—	—	6.6 (1.4)	—
		[0.0 (−4.3)]	[4.1 (−0.2)]			[13.0 (8.7)]	
SiHF + H_2	A	0.0 (−35.8)	—	0.2 (−35.6)	0.6 (−35.1)	21.2 (−14.6)	16.1 (−19.7)
		[0.0 (−34.9)]		[3.8 (−31.0)]	[3.9 (−31.0)]	[27.9 (−7.0)]	[22.8 (−12.1)]
SiHCl + H_2	A	0.0 (−28.7)	—	0.1 (−28.6)	0.3 (−28.4)	19.1 (−9.5)	16.0 (−12.7)
		[0.0 (−27.6)]		[3.5 (−24.2)]	[1.7 (−26.0)]	[25.9 (−1.8)]	[22.7 (−5.0)]
SiHBr + H_2	A	0.0 (−29.2)	—	0.0 (−29.2)	—	18.7 (−10.6)	15.6 (−13.6)
		[0.0 (−28.1)]		[3.5 (−24.7)]		[25.4 (−2.7)]	[22.3 (−5.8)]
GeHF + H_2	A	0.0 (−23.0)	—	0.0 (−22.9)	0.7 (−22.3)	32.8 (9.8)	20.1 (−2.9)
		[0.0 (−21.6)]		[4.0 (−17.7)]	[4.2 (−17.4)]	[39.5 (17.9)]	[26.7 (5.1)]
GeHF + H_2	B	0.0 (−29.7)	—	0.6 (−29.0)	0.4 (−29.2)	40.0 (10.3)	24.9 (−4.8)
		[0.0 (−28.7)]		[5.0 (−23.7)]	[4.4 (−24.3)]	[46.7 (18.0)]	[31.5 (2.8)]
GeHCl + H_2	A	0.0 (−27.0)	—	0.0 (−27.0)	—	30.4 (3.5)	20.2 (−6.8)
		[0.0 (−25.4)]		[3.6 (−21.8)]		[37.2 (11.7)]	[26.9 (1.4)]
GeHCl + H_2	B	0.0 (−28.7)	—	0.6 (−28.1)	—	36.8 (8.2)	25.2 (−3.5)
		[0.0 (−27.6)]		[4.8 (−22.8)]		[43.6 (16.0)]	[31.9 (4.3)]
GeHBr + H_2	A	0.0 (−30.0)	—	0.0 (−30.0)	—	29.8 (−0.2)	20.1 (−9.9)
		[0.0 (−28.3)]		[3.6 (−24.7)]		[36.5 (8.2)]	[26.7 (−1.6)]
GeHBr + H_2	B	0.0 (−32.5)	—	0.5 (−32.0)	—	36.4 (3.9)	24.9 (−7.7)
		[0.0 (−31.3)]		[4.7 (−26.6)]		[43.2 (11.9)]	[31.6 (0.2)]
SnHF + H_2	B	0.0 (−34.4)	—	0.4 (−33.9)	0.4 (−33.9)	56.0 (21.7)	28.2 (−6.2)
		[0.0 (−33.0)]		[4.4 (−28.6)]	[4.2 (−28.8)]	[62.7 (29.7)]	[34.8 (1.8)[
SnHCl + H_2	B	0.0 (−33.1)	—	0.5 (−32.6)	—	53.5 (20.4)	28.8 (−4.3)
		[0.0 (−31.6)]		[4.8 (−26.8)]		[60.2 (28.7)]	[35.4 (3.9)]
SnHBr + H_2	B	0.0 (−38.9)	—	0.5 (−38.4)	—	53.2 (14.3)	28.8 (−10.1)
		[0.0 (−37.2)]		[4.7 (−32.5)]		[59.9 (22.7)]	[35.4 (−1.8)]

[a] Relative to noninteracting EHX and H_2 or EH_2 and HX (in parentheses).
[b] ΔE_0 are the relative energies obtained by the G3(MP2 freq) method or by the MP2/LANL2DZ(suppl) method with ZPE corrections.
[c] At $T = 298$ K and $p = 1$ atm.
[d] A denotes the G3(MP2 freq) method, B denotes the MP2/LANL2DZ(suppl) method.

Scheme 2



Both our and previous calculations show that the energies of complexes **4**—**6** essentially coincide with the energies of the initial free reactants. Therefore, the formation of these complexes is insignificant for the transformations under consideration. Moreover, according to our calculations, their energies obtained either upon inclusion of the ZPE corrections or in accordance with the G3 procedure are higher than the energies of free reactants (Table 3). This means that it is possible that these complexes can probably not be located at higher levels of theory.

According to our IRC calculations, the insertion products, EH_3X, are connected to complexes **4** (E = C) or **5** (E = Si, Ge, Sn) *via* structurally similar transition states **TS5** (Scheme 2). Compared to free H_2, the H—H bonds in **TS5** are approximately 1.1 times longer for E = C and 1.6 — 2 times longer in other systems. In other words, the H—H bonds in the systems with E = Si, Ge, Sn are practically broken. The lengths of the E—X bonds in **TS5** are close to the values typical of the insertion products. In the systems with E = Si, Ge, Sn, the retained and one of the forming E—H bonds in **TS5** are approximately equal in their lengths to the E—H bonds in EH_3X, thus indicating that the formation of one of the new E—H bonds is practically completed. However, the second H atom of the H_2 fragment remains at a long distance from E atom. In addition, to complete the insertion processes, the configuration of the formed EH_2X fragments in **TS5** should be inverted because all H atoms and the X atom are located in the same half-space relative to the E atom. As a whole, the geometric parameters of **TS5** are closer to the corresponding parameters of the insertion products in the carbene analog systems than in the carbene systems.

The barrier heights determined by the transition states **TS5** increase with increasing the atomic number of E and depend only slightly on the nature of the atom X. The observed trends indicate a decrease in nucleophilicity on going from carbenes to stannylenes and a rather weak influence of the electronic effects of substituents on the nucleophilicity of these species. The previously reported theoretical values of insertion barriers to the reactions of CHF (see Refs 41, 61, 87, 88), SiHF (see Refs 40, 41, 43) and SiHCl (see Refs 22, 32, 39, 45) with H_2 are in good agreement with our values. Particularly, the barriers predicted for the CHF reaction by the QCISD/6-311G(d,p) method,[61] for the SiHF reaction by the QCISD(T)/6-311G(2df,pd)//MP2/6-31G(d,p) method,[43] and for the SiHCl reaction by the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVDZ method[45] are 6.7 (without ZPE), 18.0, and 19.0 kcal mol^{-1}, respectively. From the experimental enthalpies of formation available in the literature,[80] it is possible to determine enthalpies of the CHF and CHCl reactions with H_2. They are equal to −86.0 and −100.0 kcal mol^{-1}, respectively. These values are in reasonable agreement with the values of −90.9 and −94.9 kcal mol^{-1} obtained in the G3(MP2 freq) calculations.

Additional transition states, **TS6**, were located in all of the carbene analog systems. These transition states are responsible for H/H exchange between EHX and H_2 fragments in complexes **5** (Scheme 2). No such transition state was revealed in the carbene systems. Main geometric parameters of **TS6** are given in Table 4 (the calculated geometric parameters of the reactants and products, EH_3X, are shown in Tables 5 and 6 for comparison purposes). The E—X bond and two symmetric E—H bonds in **TS6** are somewhat stretched as compared to free EHX mole-

Table 4. Bond lengths (Å) and angles (deg) in transition states **TS6** of investigated systems*

System	E—H /Å	H—E—H /deg	E—X /Å	H—E—X /deg	H—H* /Å	E—H—H*	H—E—H—H*
						deg	
			MP2(Full)/6-31G(d) method				
SiH_3F	1.628	76.48	1.633	99.12	1.096	74.00	7.29
SiH_3Cl	1.609	77.99	2.106	97.52	1.104	73.51	7.77
SiH_3Br	1.607	78.30	2.288	97.08	1.106	73.42	7.70
GeH_3F	1.761	70.95	1.759	96.48	1.090	74.53	4.45
GeH_3Cl	1.741	72.21	2.207	95.10	1.098	74.38	4.38
GeH_3Br	1.737	72.49	2.372	95.10	1.100	74.37	4.32
			MP2/LANL2DZ(suppl) method				
GeH_3F	1.736	70.65	1.780	94.17	1.066	73.89	10.21
GeH_3Cl	1.722	71.43	2.214	94.56	1.069	73.86	4.19
GeH_3Br	1.718	71.70	2.398	93.92	1.071	73.82	4.01
SnH_3F	1.956	62.40	1.917	92.89	1.053	74.43	2.53
SnH_3Cl	1.945	62.81	2.382	93.11	1.055	74.51	2.34
SnH_3Br	1.943	62.90	2.552	93.00	1.055	74.52	2.26

* The migrating H atom is marked with asterisk.

Table 5. Bond lengths (Å) and angles (deg) in EH_2, HX, and H_2 obtained by MP2(Full)/6-31G(d) and MP2/LANL2DZ(suppl) (in parentheses) methods

Molecule	E—H /Å	H—E—H /deg	Molecule	H—X /Å
CH_2	1.109	102.07	H_2	0.738 (0.734)
SiH_2	1.519	92.49	HF	0.934 (0.926)
GeH_2	1.593	91.48	HCl	1.280 (1.270)
	(1.583)	(91.64)		
SnH_2	(1.761)	(91.29)	HBr	1.428 (1.411)

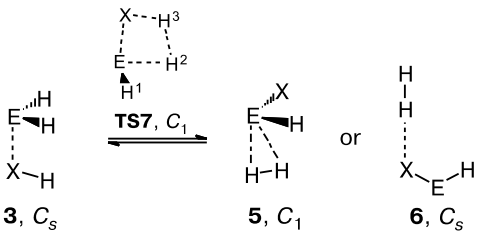
cules. The migrating H atom lies close to the plane defined by the bound H atoms and the E atom. The distance from the migrating H atom to each of the other H atoms is ca. 1.5 times longer than H—H distance in free H_2 molecule.

The barriers to these H/H exchange reactions are almost independent on the nature of the X substituents and considerably increase on going from silylenes to stannylenes. For all systems, the barriers to the exchange reactions are lower than the barriers to the insertion reactions. The difference between the exchange and insertion barrier heights is small for the silylene systems and substantial in the stannylene systems. Thus, fast exchange reactions should accompany the insertion reactions in all the systems, if the experimental conditions are suitable for the latter reactions to proceed at all. Previously, analogous H/H exchange reactions were revealed in our study[60] of the $SiHCl + Me_nSiH_{4-n}$ systems ($n = 1, 3$) by the G2MP2B3 and G3B3 methods. Barriers to these exchange processes are lower than the barriers to the corresponding insertion reactions.[60] Interestingly, no H/H exchange was revealed for the reactions of EH_2 (E = Si, Ge, Sn) with HX considered above. A possible reason consists in the presence of charges of different sign on the H atoms of HX and EH_2 fragments.

The H/X exchange

The studied PES regions of the systems under consideration are connected by the regions including global minima corresponding to the insertion products, EH_3X. Along with this channel, there is an additional channel connecting two regions of PESs in all the carbene analog systems. It corresponds to H/X exchange reactions proceeding *via* **TS7** (Scheme 3). According to the IRC calculations, transition states **TS7** connect complexes **3** to complexes **6** in the SiH_3F system and in the GeH_3F system at the MP2/LANL2DZ(suppl) level of theory, but to complexes **5** in all other systems. Since complexes **5** and **6** are extremely weak (or even energetically unfavourable), this difference in the results of the IRC calculations should not be considered as having physical significance.

Scheme 3



Transition states **TS7** are four-centred ones. The EH(2)H(3)X fragments in **TS7** are practically planar, and

Table 6. Bond lengths (Å) and bond angles (deg) in EHX and EH_3X obtained by the MP2(Full)/6-31G(d) and MP2/LANL2DZ(suppl) (in parentheses) methods

Molecule	E—H	E—X	H—E—H /deg	Molecule	E—H	E—X	H—E—H /deg
	Å				Å		
CHF	1.121	1.319	101.97	MeF	1.092	1.390	109.80
CHCl	1.109	1.695	102.97	MeCl	1.088	1.777	110.01
CHBr	1.109	1.858	101.61	MeBr	1.087	1.940	110.78
SiHF	1.530	1.626	97.69	SiH_3F	1.480	1.617	109.97
SiHCl	1.519	2.078	95.4	SiH_3Cl	1.479	2.058	110.29
SiHBr	1.518	2.249	94.75	SiH_3Br	1.479	2.227	110.44
GeHF	1.609	1.753	95.62	GeH_3F	1.538	1.743	111.68
	(1.593)	(1.770)	(94.43)		(1.527)	(1.752)	(112.12)
GeHCl	1.598	2.182	94.13	GeH_3Cl	1.535	2.157	111.62
	(1.585)	(2.188)	(94.07)		(1.526)	(2.160)	(111.50)
GeHBr	1.597	2.339	93.85	GeH_3Br	1.535	2.312	111.55
	(1.583)	(2.364)	(93.53)		(1.526)	(2.331)	(111.61)
SnHF	(1.770)	(1.917)	(93.77)	SnH_3F	(1.696)	(1.893)	(112.64)
SnHCl	(1.762)	(2.371)	(93.37)	SnH_3Cl	(1.694)	(2.331)	(112.14)
SnHBr	(1.762)	(2.538)	(93.21)	SnH_3Br	(1.694)	(2.491)	(112.06)

Table 7. Bond lengths (Å) and angles (deg) in transition states **TS7** of investigated systems*

System	E—H(1)	E—H(2)	E—X	H(2)—H(3)	H(3)—X	H(1)—E—H(2)	H(1)—E—X	H(3)—H(2)—E	H(3)—H(2)—E—X
	Å					deg			
MP2(Full)/6-31G(d) method									
SiH_3F	1.513	1.651	1.935	1.074	1.147	89.37	91.69	79.52	2.13
SiH_3Cl	1.511	1.604	2.456	1.148	1.487	89.53	88.82	84.44	4.65
SiH_3Br	1.512	1.587	2.642	1.236	1.595	90.05	88.17	86.06	5.67
GeH_3F	1.590	1.784	2.025	1.038	1.184	88.06	90.98	78.91	1.37
GeH_3Cl	1.587	1.711	2.548	1.133	1.506	87.98	88.21	85.46	2.85
GeH_3Br	1.588	1.684	2.721	1.228	1.606	88.51	87.76	87.01	3.65
MP2/LANL2DZ(suppl) method									
GeH_3F	1.576	1.757	2.091	1.017	1.173	87.96	89.43	81.05	1.49
GeH_3Cl	1.575	1.698	2.555	1.099	1.490	87.89	88.06	86.11	2.64
GeH_3Br	1.577	1.662	2.783	1.230	1.569	88.59	86.85	89.44	3.31
SnH_3F	1.754	1.943	2.258	1.056	1.135	87.81	88.71	82.21	1.08
SnH_3Cl	1.753	1.885	2.785	1.130	1.466	87.57	87.28	89.27	1.70
SnH_3Br	1.755	1.845	3.020	1.285	1.544	88.30	86.33	92.82	2.22

* Numbering of atoms is shown in Scheme 3.

the E—H(1) bonds are virtually normal to the EH(2)H(3)X planes (Table 7). The distances E—H(2), E—X, H(2)—H(3), and H(3)—X in **TS7** are 5—11, 16—19, 40—75, and 10—30% longer than in free EH_2, EHX, H_2, and HX, respectively. The relative elongation of the E—H(2) and H(3)—X distances decreases with the increase in the atomic number of halogen, while the H(2)—H(3) distances monotonically increase in this series. Thus, the fluorine-containing **TS7** are more similar to EHF and H_2 species, whereas the bromine-containing **TS7** are somewhat closer to the EH_2 and HBr species in their structure. No substantial dependence of these elongations on the nature of the E atom is observed.

The energies of **TS7** are collected in Table 8. Their dependence on the nature of the E or X atoms is not uniform. The barriers determined by **TS7** decrease on going from F to Br in the SiH_3X and GeH_3X systems. In the case of the SnH_3X systems, the barriers of the reverse processes ($SnHX + H_2 \rightarrow SnH_2 + HX$) increase on going from F to Br, but for the direct reactions, their dependence on the X atom is nonmonotonic. The exchange with H_2 is most difficult for SiHF. Among all EH_2 + HX pairs, the GeH_2 + HF pair of reactants is least prone to exchange. The transition state **TS7** in the SiH_3Cl system was located earlier in the G3 calculations.[22] Since the conventional G3 approach is very similar to our G3(MP2 freq) approach, the characteristics of **TS7** obtained in both studies are very close.

The barriers determined by **TS7** for the exchange reactions between EH_2 and HX do not exceed 8.5 kcal mol^{-1}; therefore, these processes are expected to proceed with at least moderate rates even at room temperature. Moreover, **TS7** lie in energy below or close (in the case of interactions of SiH_2 with HCl and HBr) to **TS3** (Tables 1 and 8); therefore, the exchange reactions should effectively compete with the insertion processes, and in the stannylene systems they represent the major channels of interactions. As a whole, the exchange processes between EH_2 and HX become increasingly more favorable compared with the insertion reactions with the increase in the atomic number of E and with the decrease in the atomic number of X; *i.e.*, the difference ΔE(**TS3**) — ΔE(**TS7**) increases in these series.

There is the only experimental evidence that the H/X exchange reactions between EH_2 and hydrogen halides take place. Weak dependence of the rate constants for the gas-phase interaction of SiH_2 with HCl on the total pressure in the range 1—100 Torr at temperatures between 296 and 611 K implies that the exchange reaction rather than insertion mainly proceeds under these conditions.[22] The exchange reaction may follow two pathways and proceed as a single-step and as a decomposition of vibrationally excited chlorosilane formed in the insertion reaction. However, the available data did not allow the authors[22] to estimate the contributions of each pathway to the overall process. It should also be noted that the interaction of SiH_2 with HCl is characterized by high rate constants of the order of about $5 \cdot 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} (see Ref. 22). These values qualitatively agree with the calculated reaction barriers determined by **TS3** and **TS7** (see Tables 1 and 8).

The significance of the exchange reactions in the interactions of EHX with H_2 also increases on going from silylenes to stannylenes (Tables 3 and 8). However, in this case only stannylenes are more prone to the exchange process rather than to the insertion one (the energies of **TS5** are higher than those of **TS7**). In the case of germylenes, both reactions require the overcoming of barriers

Table 8. Relative energies[a,b] (ΔE_0/kcal mol^{-1}) and Gibbs free energies[a,c] (ΔG°/kcal mol^{-1}, in brackets) of transition states **TS7** and pairs of free radicals

System	Method[d]	ΔE_0 [ΔG°]		
		TS7	EH_3 + X	EH_2X + H
CH_3F	A		19.5 (17.4) [19.5 (18.2)]	10.6 (8.6) [10.4 (9.0)]
CH_3Cl	A		−11.9 (−16.1) [−11.6 (−15.0)]	4.5 (0.3) [4.2 (0.8)]
CH_3Br	A		−26.3 (−31.5) [-26.0 (−30.3)]	3.9 (-1.3) [3.6 (-0.7)]
SiH_3F	A	41.6 (5.9) [48.3 (13.4)]	104.6 (68.8) [104.1 (69.2)]	48.0 (12.2) [47.9 (13.0)]
SiH_3Cl	A	29.9 (1.3) [36.5 (8.8)]	64.0 (35.3) [63.7 (36.1)]	47.1 (18.4) [47.0 (19.3)]
SiH_3Br	A	27.3 (−1.9) [33.8 (5.7)]	49.1 (19.9) [48.9 (20.8)]	47.2 (18.0) [47.1 (19.0)]
GeH_3F	A	31.5 (8.5) [38.1 (16.5)]	101.4 (78.4) [100.3 (78.6)]	60.3 (37.3) [60.2 (38.6)]
GeH_3F	B	35.6 (6.0) [42.2 (13.5)]	104.3 (74.7) [103.2 (74.5)]	51.1 (21.4) [51.0 (22.2)]
GeH_3Cl	A	28.7 (1.7) [35.2 (9.8)]	71.9 (44.9) [70.9 (45.5)]	58.8 (31.8) [58.7 (33.3)]
GeH_3Cl	B	34.5 (5.8) [41.1 (13.5)]	64.9 (36.2) [63.9 (36.4)]	49.6 (20.9) [49.5 (21.9)]
GeH_3Br	A	28.1 (−1.8) [34.7 (6.3)]	59.4 (29.5) [58.5 (30.2)]	58.6 (28.6) [58.5 (30.1)]
GeH_3Br	B	33.5 (1.0) [40.0 (8.7)]	58.2 (25.6) [57.3 (25.9)]	50.0 (17.4) [49.9 (18.5)]
SnH_3F	B	34.9 (0.6) [41.6 (8.6)]	120.1 (85.8) [119.0 (86.0)]	60.2 (25.9) [60.1 (27.1)]
SnH_3Cl	B	36.4 (3.3) [42.9 (11.4)]	80.4 (47.3) [79.4 (47.9)]	59.3 (26.2) [59.2 (27.6)]
SnH_3Br	B	38.1 (−0.8) [44.5 (7.3)]	75.6 (36.7) [74.6 (37.4)]	59.5 (20.6) [59.4 (22.2)]

[a] Relative to noninteracting EHX and H_2 or EH_2 and HX (in parentheses).

[b] ΔE_0 are the relative energies obtained by the G3(MP2 freq) method or by the MP2/LANL2DZ(suppl) method with ZPE corrections.

[c] At $T = 298$ K and $p = 1$ atm.

[d] A denotes the G3(MP2 freq) method, B denotes the MP2/LANL2DZ(suppl) method.

of comparable heights, while silylenes are reluctant to the exchange reactions. It should also be emphasized that the energies of **TS7** relative to free EHX + H_2 are quite high and, therefore, the exchange reactions can proceed at elevated temperatures only. The fastest reaction between EHX and H_2 is H/H exchange *via* **TS6** in all the systems (see previous Section).

The increasing role of the exchange reactions on going from silylenes to germylenes in the systems under consideration correlates with the finding made in the MP2/6-311++G(d,p) calculations of the EH_2 + ROH systems (E = Si, Ge; R = H, Me). Namely, H/RO exchange between GeH_2 and ROH (R = H, Me) is preferable to the insertion into the O—H bond, while both reactions have similar barriers in the case of SiH_2.[56,57] Analogously, our conclusion that the increasing electronegativity of the X atoms (from Br to F) favors the exchange process agrees with the finding[56,57] that the barrier to the H/RO exchange reaction of SiH_2 decreases relative to the barrier of the corresponding insertion reaction on going from MeOH to F_3COH. Thus, the regularities revealed for the interactions of EH_2 with HX seem to be applicable to a wider range of the carbene analog systems.

No exchange reaction pathways were found for the CH_3X systems in the present study. However, such a pathway was reported for the CH_2F_2 system.[61] The transition state for this H/F exchange lies in energy remarkably higher than the transition states for the insertion reactions of CHF with HF and CF_2 with H_2, and, therefore, it is not operative. Nevertheless, this fact shows that, in principle, the exchange channels can exist in some carbene systems. Clearly, the presence of strong electron-withdrawing substituents in carbenes is critical to an exchange pathway to emerge. Such substituents decreasing the negative charge on the carbene center make carbenes more similar to carbene analogs, whose central atoms usually bear a positive charge.

Radical reaction pathways

In addition to the closed-shell species, free radicals can in principle also be involved in chemical transformations in the EH_3X systems. The calculated relative energies of the EH_3 + X and EH_2X + H pairs of radicals are collected in Table 8. The energies of the E—H and E—X bonds in EH_3X obtained from the experimental enthalpies of formation of the involved species and in the G3(MP2 freq) calculations are compared in Table 9. As can be seen, the G3(MP2 freq) calculations satisfactorily reproduce the values based on the experimental data. According to the performed calculations, formation of both types of radical pairs is highly favourable in the CH_3Cl and CH_3Br systems in the course of interactions of both CH_2 with HX and CHX with H_2 because the energies of the pairs of radicals are lower or close to the energies of free reactants (Tables 1, 3, and 8). The formation of EH_2X and H radicals can also be a minor pathway during the interaction of CHF with H_2, as well as in the course of the interactions of SiH_2 and SnH_2 with HF under suitable conditions because the energies of these pairs of radicals are only slightly higher than the energies of some key transition states in these systems, *viz.*, **TS5** in the first and third systems and **TS3** in the second system. This conclusion regarding the SiH_3F system agrees with the results of previous calculations at the MP4(SDTQ)/6-31G(d,p)//HF/6-31G(d) level.[40] Transformations in other systems should not be complicated by radical reactions because of

Table 9. Enthalpies (kcal mol^{-1}) of the radical formation reactions

Reaction	$\Delta H°_{calc}$[a]	$\Delta H°_{exp}$[b]	References[c]
$MeF \rightarrow Me + F$	110.0	109.8	80
$MeCl \rightarrow Me + Cl$	82.6	83.8	80
$MeBr \rightarrow Me + Br$	70.0	70.7	79, 80
$MeF \rightarrow CH_2F + H$	101.1	100.1	79, 80
$MeCl \rightarrow CH_2Cl + H$	99.0	103.1	79, 80
$MeBr \rightarrow CH_2Br + H$	100.4	103.2	79, 80
$SiH_3F \rightarrow SiH_3 + F$	150.6	157.0	80, 81
$SiH_3Cl \rightarrow SiH_3 + Cl$	108.3	109.4	80, 81
$SiH_3Br \rightarrow SiH_3 + Br$	92.5	93.3	80, 81

[a] Obtained by the G3(MP2 freq) method.
[b] Obtained from experimental enthalpies of formation of the involved molecules.
[c] Sources of experimental enthalpies of formation.

high thermodynamic unfavourableness of formation of radicals. This conclusion regarding the SiH_3Cl system was already made earlier.[22,32,39]

The present study of the interactions between EH_2 and HX (E = C, Si, Ge, Sn, X = F, Cl, Br) and the complementary interactions between EHX and H_2 showed that the processes proceeding in these systems are quite complicated. According to calculations, the reactions start with the formation of several types of pre-reaction complexes, although such complexes between EHX and H_2, if exist, are practically isoenergetic to the reactants and thus have no influence on the overall processes. The complexes between EH_2 and HX are characterized by rather low stabilization energies and, as a rule, easily interconvert into each other. In the case of carbene analog systems, there is the only pathway leading from the complexes to EH_3X, the thermodynamically most stable products. At the same time, each complex between CH_2 and HX has its own channel of transformation into CH_3X.

The reaction barriers to the insertions of EH_2 into HX systematically increase on going from carbene to stannylene and from HBr to HF. The former trend indicates a decrease in the nucleophilicity of EH_2 in this series, while the latter one is related to the strengthening of the H—X bonds in hydrogen halides. The barriers on the pathways leading from EHX and H_2 to EH_3X also increase on going from carbenes to stannylenes, being only slightly affected by the nature of the X atoms. The exothermicity of EH_3X formation strongly decreases on going from E = C to E = Sn, thus reflecting a decrease in the total energy of the bonds being formed in the course of the insertion reaction.

In addition to the insertion reactions, two types of exchange reactions in the carbene analog systems were revealed. Those are the degenerate H/H exchange occurring upon interactions of EHX with H_2 and H/X exchange leading from EH_2 and HX to EHX and H_2 and backward. The barriers to the H/X exchange reactions between EH_2 and HX are quite low and, therefore, depending on the particular system, these reactions either compete with the insertion reactions or represent the only low-energy reaction channels. The barriers to the reverse X/H exchange reactions between EHX and H_2 are rather high. They are higher than the barriers to the insertion reactions in the silylene systems, comparable with the insertion barriers in the germylene systems, and lower than the latter in the stannylene systems. The lowest EHX and H_2 interaction barriers correspond to degenerate H/H exchange reactions. These barriers increase on going from silylenes to stannylenes and are practically independent on the nature of the X atom. Generally, the role playing by the exchange reactions in the overall interactions with H_2 increases for heavier carbene analogs. In addition to the closed-shell species, free radicals can be involved in chemical transformations in the CH_3Cl and CH_3Br systems. In several other systems, they can play a minor role only.

The authors thank S. S. Rynin for useful comments. This work was financially supported by the Russian Foundation for Basic Research (Project No 09-03-00475), the President of the Russian Federation (Presidential Program for Support of Leading Research Schools, Grant NSh-8242.2010.3), and the Russian Academy of Sciences (Program OKh-01).

References

1. O. M. Nefedov, M. N. Manakov, *Angew. Chem.*, *Int. Ed. Engl.*, 1966, **5**, 1021.
2. O. M. Nefedov, A. I. Ioffe, and L. G. Menchikov, *Khimiya karbenov* [*Chemistry of Carbenes*], Khimiya, Moscow, 1990, 304 pp. (in Russian).
3. O. M. Nefedov, *Pure Appl. Chem.*, 1991, **63**, 231.
4. W. P. Neumann, *Chem. Rev.*, 1991, **91**, 311.
5. P. P. Gaspar, R. West, in *The Chemistry of Organic Silicon Compounds*, Eds Z. Rappoport, Y. Apeloig, John Wiley and Sons, New York, 1998, **2** (chapter 43) 2463.
6. A. Sekiguchi, T. Tanaka, M. Ichinohe, K. Akiyama, P. P. Gaspar, *J. Am. Chem. Soc.*, 2008, **130**, 426.
7. A. Sekiguchi, T. Tanaka, M. Ichinohe, K. Akiyama, S. Tero-Kubota, *J. Am. Chem. Soc.*, 2003, **125**, 4962.
8. P. P. Gaspar, M. Xiao, D. H. Pae, D. J. Berger, T. Haile, T. Chen, D. Lei, W. R. Winchester, P. Jiang, *J. Organomet. Chem.*, 2002, **646**, 68.
9. O. M. Nefedov, M. P. Egorov, A. I. Ioffe, L. G. Menchikov, P. S. Zuev, V. I. Minkin, B. Y. Simkin, M. N. Glukhovtsev, *Pure Appl. Chem.*, 1992, **64**, 265.
10. S. E. Boganov, M. P. Egorov, V. I. Faustov, O. M. Nefedov, in *The Chemistry of Organic Germanium, Tin and Lead Compounds*, Ed. Z. Rappoport, Wiley, New York, 2002, **2** (part 1), 749.
11. Y. Mizuhata, T. Sasamori, N. Tokitoh, *Chem. Rev.*, 2009, **109**, 3479.
12. P. John, J. H. Purnell, *J. Chem. Soc.*, *Faraday Trans. 1*, 1973, **69**, 1455.

13. R. Becerra, R. Walsh, in *Research in Chemical Kinetics*, Eds R. G. Compton, G. Hancock, Elsevier, Amsterdam, 1995, **3** (chapter 6), 263.
14. K. L. Walker, R. E. Jardine, M. A. Ring, H. E. O´Neal, *Int. J. Chem. Kinet.*, 1998, **30**, 69.
15. R. Becerra, S. E. Boganov, M. P. Egorov, V. I. Faustov, O. M. Nefedov, R. Walsh, *Can. J. Chem.*, 2000, **78**, 1428.
16. P. W. Schenk, H. Bloching, *Z. Anorg. Allg. Chem.*, 1964, **334**, 57.
17. J. D. Cotton, P. J. Davidson, M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2275.
18. N. Takeda, T. Kajiwara, H. Suzuki, R. Okazaki, N. Tokitoh, *Chem.-Eur. J.*, 2003, **9**, 3530.
19. R. Becerra, S. E. Boganov, M. P. Egorov, I. V. Krylova, O. M. Nefedov, R. Walsh, *Chem. Phys. Lett.*, 2005, **413**, 194.
20. R. Becerra, C. R. Harrington, W. J. Leigh, L. A. Kefala, R. Walsh, *Organometallics*, 2006, **25**, 4439.
21. R. Becerra, S. E. Boganov, M. P. Egorov, V. I. Faustov, I. V. Krylova, O. M. Nefedov, R. Walsh, *J. Am. Chem. Soc.*, 2002, **124**, 7555.
22. R. Becerra, J. P. Cannady, R. Walsh, *J. Phys. Chem. A*, 2004, **108**, 3987.
23. R. D. Miller, in *Silicon Chemistry*, Eds. E. R. Corey, J. Y. Corey, P. P. Gaspar, Ellis Horwood, Chichester, 1988 (Chapter 35).
24. X. L. Yang, M. Tao, *J. Electrochem. Soc.*, 2007, **154**, H53 and references cited therein.
25. Ö. Danielsson, A. Henry, E. Janzén, *J. Cryst. Growth*, 2002, **243**, 170.
26. A. Veneroni, M. Masi, *Chem. Vapor Deposition*, 2006, **12**, 562.
27. R. Wang, R. Ma, *J. Cryst. Growth*, 2007, **308**, 189.
28. R. Wang, R. Ma, M. Dudley, *Ind. Eng. Chem. Res.*, 2009, **48**, 3860.
29. M. Okamoto, *Res. Chem. Intermed.*, 2006, **32**, 317.
30. M. P. Clarke, I. M. T. Davidson, *J. Organomet. Chem.*, 1991, **408**, 149.
31. L. A. Laukmanis, I. A. Feltin, *Neorg. mater.*, 1968, **4**, 1275 (in Russian).
32. S. P. Walch, C. E. Dateo, *J. Phys. Chem. A*, 2001, **105**, 2015.
33. Y. Wang, J. Ma, *J. Organomet. Chem.*, 2009, **694**, 2567.
34. A. Barbato, C. Seghi, C. Cavallotti, *J. Chem. Phys.*, 2009, **130**, 074108.
35. M. S. Gordon, D. R. Gano, J. S. Binkley, M. J. Frisch, *J. Am. Chem. Soc.*, 1986, **108**, 2191.
36. R. S. Grev, H. F. Schaefer, *J. Chem. Soc., Chem. Commun.*, 1983, 785.
37. M. S. Gordon, *J. Chem. Soc., Chem. Commun.*, 1981, 890.
38. G. Merino, S. Escalante, A. Vela, *J. Phys. Chem. A*, 2004, **108**, 4909.
39. M. D. Su, H. B. Schlegel, *J. Phys. Chem.*, 1993, **97**, 9981.
40. E. W. Ignacio, H. B. Schlegel, *J. Phys. Chem.*, 1992, **96**, 1620.
41. C. Sosa, H. B. Schlegel, *J. Am. Chem. Soc.*, 1984, **106**, 5847.
42. S. Koseki, A. Ishitani, *J. Appl. Phys.*, 1992, **72**, 5808.
43. C. Sosa, C. Lee, *J. Chem. Phys.*, 1993, **98**, 8004.
44. Y. Ge, M. S. Gordon, F. Battaglia, R. O. Fox, *J. Phys. Chem. A*, 2010, **114**, 2384.
45. Y. Ge, M. S. Gordon, F. Battaglia, R. O. Fox, *J. Phys. Chem. A*, 2007, **111**, 1475.
46. Y. Ge, M. S. Gordon, F. Battaglia, R. O. Fox, *J. Phys. Chem, A*, 2007, **111**, 1462.
47. J. M. Wittbrodt, H. B. Schlegel, *Chem. Phys. Lett.*, 1997, **265**, 527.
48. I. Alkorta, J. Elguero, *J. Phys. Chem.*, 1996, **100**, 19367.
49. T. C. McInnis, L. Andrews, *J. Phys. Chem.*, 1992, **96**, 5276.
50. K. Raghavachary, J. Chandrasekhar, M. S. Gordon, K. J. Dykema, *J. Am. Chem. Soc.*, 1984, **106**, 5853.
51. I. A. Abronin, N. A. Avdukhina, E. A. Chernyshev, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 810 [*Russ. Chem. Bull.* (*Engl. Transl.*), 1994, **43**, 751].
52. M. D. Su, S. Y. Chu, *J. Phys. Chem. A*, 1999, **103**, 11011.
53. M. D. Su, S. Y. Chu, *J. Chin. Chem. Soc.*, 2000, **47**, 135.
54. E. W. Ignacio, H. B. Schlegel, *J. Phys. Chem.*, 1992, **96**, 1758.
55. M. T. Swihart, R. W. Carr, *J. Phys. Chem. A*, 1997, **101**, 7434.
56. M. W. Heaven, G. F. Metha, M. A. Buntine, *J. Phys. Chem. A*, 2001, **105**, 1185.
57. M. W. Heaven, G. F. Metha, M. A. Buntine, *Aust. J. Chem.*, 2001, **54**, 185.
58. U. N. Alexander, K. D. King, W. D. Lawrance, *J. Phys. Chem. A*, 2002, **106**, 973.
59. R. Becerra, J. P. Cannady, R. Walsh, *J. Phys. Chem. A*, 2003, **107**, 11049.
60. R. Becerra, S. E. Boganov, M. P. Egorov, V. I. Faustov, I. V. Krylova, O. M. Nefedov, V. M. Promyslov, R. Walsh, *J. Phys. Chem. A*, 2009, **113**, 5512.
61. I. S. Ignatyev, H. F. Schaefer, *J. Am. Chem. Soc.*, 1997, **119**, 12306.
62. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, *Revision C.02*, Gaussian, Inc., Wallingford, CT, 2004.
63. L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, J. A. Pople, *J. Chem. Phys.*, 1998, **109**, 7764.
64. L. A. Curtiss, P. C. Redfern, V. Rassolov, G. Kedziora, J. A. Pople, *J. Chem. Phys.*, 2001, **114**, 9287.
65. J. A. Pople, A. P. Scott, M. W. Wong, L. Radom, *Isr. J. Chem.*, 1993, **33**, 345.
66. L. A. Curtiss, K. Raghavachari, J. A. Pople, *J. Chem. Phys.*, 1995, **103**, 4192.
67. W. R. Wadt, P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284.
68. J. Andzelm, S. Huzinaga, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, H. Tatewaki, in *Phys. Sci. Data*, *16*, *Gaussian basis sets for molecular calculations*, Ed. S. Huzinaga, Elsevier, Amsterdam–Oxford–New York–Tokyo, 1984.
69. *GAMESS User´s Guide*, Department of Chemistry, Iowa State University, Ames, IA 50011, http://www.msg.chem.iast-

ate.edu/GAMESS/GAMESS_Manual/refs.pdf (last visited on Oct. 22, 2010).
70. C. Gonzalez, H. B. Schlegel, *J. Chem. Phys.*, 1989, **90**, 2154.
71. C. Gonzalez, H. B. Schlegel, *J. Phys. Chem.*, 1990, **94**, 5523.
72. I. Alkorta, I. Rozas, O. Mó, M. Yáñez, J. Elguero, *J. Phys. Chem. A*, 2001, **105**, 7481.
73. E. P. L. Hunter, S. G. Lias, *J. Phys. Chem. Ref. Data*, 1998, **27**, 413.
74. W. W. Schoeller, R. Schneider, *Chem. Ber./Recl.*, 1997, **130**, 1013.
75. J. Oláh, F. De Proft, T. Veszprémi, P. Geerlings, *J. Phys. Chem. A*, 2005, **109**, 1608.
76. S. E. Boganov, V. I. Faustov, M. P. Egorov, O. M. Nefedov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2004, 920 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 960].
77. D. Tevault, K. Nakamoto, *Inorg. Chem.*, 1976, **15**, 1282.
78. N. V. Sidgwick, *The Electronic Theory of Valency*, Clarendon Press, Oxford, 1927.
79. S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, W. G. Mallard, *J. Phys. Chem. Ref. Data.*, 1988, **17**, Suppl. 1.
80. NIST Chemistry WebBook: http://webbook.nist.gov/chemistry (last visited on Oct. 22, 2010).
81. R. Becerra, R. Walsh, in *The Chemistry of Organic Silicon Compounds*, Eds Z. Rappoport, Y. Apeloig, John Wiley and Sons, New York, 1998, Vol. 2, Chapter 4, pp. 153-180.
82. V. V. Kafarov, V. N. Vetokhin, I. N. Dorokhov, L. P. Volkov, *Dokl. Akad. Nauk SSSR*, 1988, **298**, 394 [*Dokl. USSR*, 1988, **298**].
83. R. Becerra, S. E. Boganov, M. P. Egorov, V. I. Faustov, O. M. Nefedov, R. Walsh, *J. Am. Chem. Soc.*, 1998, **120**, 12657.
84. J. A. Pople, K. Raghavachari, M. J. Frisch, J. S. Binkley, P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1983, **105**, 6389.
85. J. A. Pople, *Chem. Phys. Lett.*, 1986, **132**, 144.
86. B. F. Yates, W. J. Bouma, L. Radom, *J. Am. Chem. Soc.*, 1987, **109**, 2250.
87. B. S. Jursic, *J. Mol. Struct.*, *THEOCHEM*, 1999, **467**, 103.
88. C.-K. Wong, W.-K. Li, J. Baker, *J. Mol. Struct.*, *THEOCHEM*, 1995, **357**, 75.

Received July 11, 2011