ELSEVIER

Journal of Organometallic Chemistry 499 (1995) 27–34

Journal of Organometallic Chemistry

Redox properties of dihalogermylenes, dihalostannylenes and their complexes with Lewis bases ☆

V.Ya. Lee [a], A.A. Basova [a], I.A. Matchkarovskaya [a], V.I. Faustov [a], M.P. Egorov [a], O.M. Nefedov [a,*], R.D. Rakhimov [b], K.P. Butin [b]

[a] *N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russia*
[b] *M.V. Lomonosov Moscow State University, Department of Chemistry, Leninskie Gory, 119889 Moscow, Russia*

Received 15 February 1995

Abstract

Reduction and oxidation potentials of GeI_2, $GeBr_2 \cdot B$ (B = dioxane, PPh_3), $GeCl_2 \cdot B$ (B = dioxane, PPh_3, $AsPh_3$, Py, dip), $SnCl_2 \cdot$ dioxane, SnX_2 (X = F, Cl Br, I) were measured in MeCN at 20 °C. The data obtained indicate that in many cases the EX_2 and $EX_2 \cdot B$ (E = Ge, Sn) can act not only as a good reducing agents, but also as strong oxidants. Examples of redox reactions in which EX_2 and $EX_2 \cdot B$ react as oxidizing agents were found. The variation of the redox potentials of the dihalogermylenes and dihalostannylenes with complexation and with the nature of the halogen substituent and the Lewis base is discussed. In some cases (GeI_2, $GeX_2 \cdot B$; X = Cl, Br, B = dioxane, PPh_3), the reduction or oxidation was found to be quasi-reversible, indicating the presence of relatively stable ion radicals. AM1 calculations on $GeCl_2 \cdot$ dioxane and $GeCl_2 \cdot PH_3$ complexes show that the complexation destabilizes both the highest occupied and the lowest unoccupied MOs of the carbene analogues. The complexation reduces the IP and lowers the oxidation potential; its influence on the electron affinity is not straightforward. Calculations of the ion radicals of $GeCl_2$ and $GeCl_2 \cdot B$ (B = dioxane, PH_3) show that in the ground state an unpaired electron occupies σ-MO in the cation and π-MO in anion radicals.

Keywords: Germanium; Tin; Germylenes; Stannylene; Electrochemistry; AM1 calculations

1. Introduction

The derivatives of two-coordinated silicon, germanium, tin – silylenes, germylenes, stannylenes are an important class of reactive intermediates from both theoretical and synthetic points of view [1,2]. The mechanisms of their reactions, particularly insertion reactions, are of great interest. Both concerted and non-concerted radical abstraction–recombination mechanisms have been discussed for these reactions [1–3].

Whereas redox processes in the chemistry of organic derivatives of tetracoordinated IVB group elements E(IV) (E = Si, Ge, Sn) [4] have been much studied, practically nothing is known about the role of electron transfer in the reactions of E(II) species. At the same time, the relatively low values of ionization potentials (IP) and the significant values of electron affinities (EA) known for a number of carbene analogues [5] suggest that they can participate in electron transfer interactions with a variety of electron acceptors/donors. Indeed, the formation of germylene cation and anion radicals as intermediates during germylene reactions has recently been suggested [6]. A correlation was observed between reduction potentials of halogen-containing substrates and their reactivity toward dimethylgermylene [6]. An ion-radical mechanism was suggested for these reactions in which an electron-transfer from dimethylgermylene to a substrate, with the formation of an ion radical pair, is the key step. Electron transfer from the stable stannylene $[(Me_3Si)_2N]_2Sn$ to organic halides has also been proposed as the first stage of the reaction between R_2Sn and R′X [7,8].

In the reactions discussed above the nucleophilic species Me_2Ge or $[(Me_3Si)_2N]_2Sn$ react as reducing agents. We have also found examples of reactions which can be rationalized in the terms of electron transfer from substrate to a germylene [6]. Thus, the reaction between

---

☆ Dedicated to Professor Hideki Sakurai on the occasion of his retirement from Tohoku University.

[*] Corresponding author.

0022-328X/95/$09.50
SSDI 0022-328X(95)00320-7

$GeCl_2 \cdot$ dioxane complex and the good reducing agent hexamethylditin (E_p(ox) = 1.28 V vs. Ag/AgCl [9]) does not result in germylene insertion into the Sn–Sn bond, but in cleavage of the Sn–Sn bond and quantitative formation of Me_3SnCl and oligomers $(GeCl)_x$ [6]. The Ge–Ge bond in the derivative of strained 1,1,2,2-tetramethyl-1,2-digermacyclobutene-3 is also cleaved by $GeCl_2 \cdot$ dioxane. These reactions were interpreted in terms of the ion radical mechanism with formation of the $GeCl_2 \cdot$ dioxane anion radical as the first step [6].

The suggestion that single electron transfers (SET) may be involved in the reactions of heavy carbene analogues has been recently confirmed by the first direct ESR detection of a germylene and a stannylene anion radical, $[(Me_3Si)_2CH]_2E^{\cdot -}Na^+$ (E = Ge, Sn) [10].

Further evidence of the existence of carbene analogue ion radicals can be obtained from electrochemical studies. This method has already proved its value in the study of carbene ion radicals [11]. However, information on the electrochemistry and redox properties of carbene analogues is still lacking.

We describe below the results of electrochemical, chemical and theoretical studies of dihalogermylenes, dihalostannylenes and their complexes with the Lewis bases. The work forms a part of our systematic study of electrochemistry of carbene analogues and their complexes.

2. Results and discussion

The electrochemistry of $EX_2 \cdot B$ (E = Ge, Sn; X = Cl, Br, I; B = dioxane, PPh_3, $AsPh_3$, pyridine), $2GeCl_2 \cdot$ dip (dip = α, α-dipyridyl) as well as GeI_2 and SnX_2 (X = F, Cl, Br, I) is rather simple. Cyclic voltammetry (in MeCN, platinum electrode, with Bu_4NBF_4 as supporting electrolyte, vs. Ag/AgCl/KCl (sat.)) revealed one reduction and one oxidation peak (both one-electron). The $E_{1/2}$ values are presented in Table 1.

Two electron waves were observed for the oxidation of $GeCl_2 \cdot PPh_3$ and $2GeCl_2 \cdot$ dip. The first is due to simultaneous oxidation of both $GeCl_2 \cdot PPh_3$ and a free ligand, PPh_3, at 1.14 V ($E^{ox}_{1/2}(PPh_3)$ = 1.10–1.20 V). Oxidation of the $2GeCl_2 \cdot$ dip complex needs two electrons simply because two $GeCl_2$ molecules are coordinated to one molecule of the ligand (dip). Two one-electron waves were detected in the reduction of SnX_2 (X = Cl, Br, I).

Table 1

Redox potentials and electrochemical gaps of dihalogermylenes (stannylene) and their complexes with Lewis bases in MeCN (platinum electrode, Bu_4NBF_4 as supporting electrolyte, vs. Ag/AgCl/KCl (sat.))

EX_2	B	$E_{1/2}$(ox) (V)	$-E_{1/2}$(red) (V)	G [a] (V)
$GeCl_2$	dioxane	1.46 [b]	0.41 [b]	1.87
$GeCl_2$	PPh_3	1.14	0.58	1.72
$GeCl_2$	$AsPh_3$	1.05	0.59	1.64
$GeCl_2$	Py	1.12 [b]	0.56	1.68
$GeCl_2$	dip	0.91	0.74	1.65
$GeBr_2$	dioxane	1.08 [b]	0.45	1.53
$GeBr_2$	PPh_3	0.72	0.38	1.10
GeI_2	–	no [c]	0.99 [b]	> 3.59
GeI_2	PPh_3	1.44	no [d]	> 3.15
SnF_2	–	no	0.94	> 3.54
$SnCl_2$	–	1.88	0.21, 1.20	2.09
$SnCl_2$	dioxane	1.67	0.78	2.45
$SnBr_2$	–	1.82	0.40, 1.31	2.22
SnI_2	–	1.16	0.02, 0.51	1.14

[a] Electrochemical gap, $G = E_{ox} - E_{red}$.

[b] Quasi-reversible.

[c] No wave was observed up to 2.60 V.

[d] No wave was observed up to −1.71 V. At this potential a 6e-reduction process occurs.

It is known that $GeX_2 \cdot B$ complexes dissociate in solutions [12], and so "free" GeX_2 molecules could be expected to participate in redox processes. The data presented in Table 1 show that the redox potentials of $GeX_2 \cdot B$ complexes vary significantly with the nature of a Lewis base B. This may be a result of differing stabilities of the $GeX_2 \cdot B$ complexes. We were able to determine the equilibrium formation constants, K, for $GeCl_2 \cdot PPh_3$ ($K = 7 \cdot 10^3$ mol l^{-1}, MeCN, 20 °C) and $GeCl_2 \cdot AsPh_3$ ($K = 2 \cdot 10^4$ mol l^{-1}, MeCN, 20 °C) using the standard method based on the $E_{1/2}$ shift with increasing PPh_3 or $AsPh_3$ concentration [13]. The electrochemically determined K value for $GeCl_2 \cdot PPh_3$ is close to that obtained earlier by UV spectroscopy ($K = 2 \cdot 10^3$ mol l^{-1}, 23 °C, n-Bu_2O) [12].

In the electrochemical experiments we used acetonitrile as a solvent. This can also act as a Lewis base towards GeX_2 because of the presence of a lone electron pair on nitrogen. Indeed, our AM1 calculations predict the existence of $GeX_2 \cdot$ MeCN complexes. But the strong dependence of the redox potential on the nature of ligand B indicates that there is no noticeable transcomplexation of $GeX_2 \cdot B$ in acetonitrile solutions.

Most of the reduction and oxidation waves of EX_2 and $EX_2 \cdot B$ were found to be irreversible, suggesting that the corresponding ion radicals are very unstable. Quasi-reversible oxidation waves were observed for $GeX_2 \cdot$ dioxane (X = Cl, Br) and $GeCl_2 \cdot$ Py complexes (Fig. 1). The cyclic voltammograms show that the reversibility of the processes increases in the order $GeCl_2 \cdot$ dioxane < $GeBr_2 \cdot$ dioxane < $GeCl_2 \cdot$ Py (see Fig. 1). The difference between oxidation potentials of a complex $GeX_2 \cdot B$ and a ligand B (0.33 V (X = Cl, B = dioxane), 0.71 V (X = Br, B = dioxane), 1.18 V (X = Cl, B = Py)) increases in the same direction. Thus, a ligand B must have a considerably more positive oxidation potential than $GeX_2 \cdot B$ if it is to stabilize effectively $GeX_2^{\cdot +}$ cation radicals. Such stabilization should be ineffective or impossible in the $GeCl_2 \cdot B$ complexes with the nucleophilic ligands having less

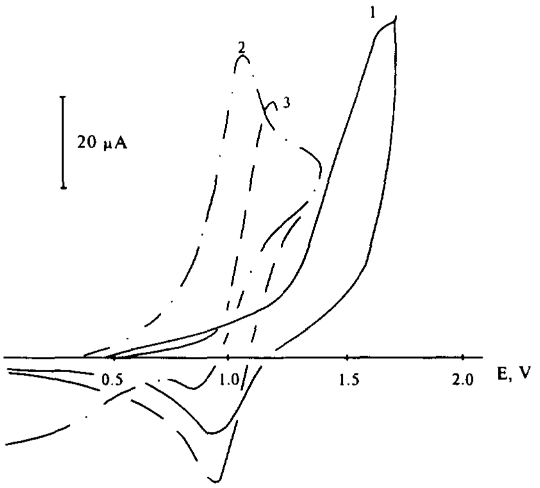


Fig. 1. Cyclic voltammogram for oxidation of $GeX_2 \cdot B$ complexes: (1) $GeCl_2 \cdot$dioxane; (2) $GeBr_2 \cdot$dioxane; (3) $GeCl_2 \cdot Py$ ($c = 2 \cdot 10^{-3}$ M, $v = 200$ mV s^{-1}).

positive ($AsPh_3$) or almost the same (PPh_3) oxidation potentials as $GeX_2 \cdot B$. This shows up in the absence of cathode peaks on the reverse scans of cyclic voltammograms for the oxidation.

Quasi-reversible reductions were found for the $GeCl_2 \cdot$ dioxane complex and GeI_2 (Fig. 2). Lifetimes of $[GeCl_2 \cdot \text{dioxane}]^{\cdot -}$ and $GeI_2^{\cdot -}$ ion radicals were estimated to be approx. 4 and 2.5 s at 20 °C, respectively.

The influence of the nature of ligand B on the oxidation and the reduction potentials of dihalogermylenes complexes was studied for the series of $GeCl_2 \cdot B$ complexes. The oxidation potentials increase in the order dip < $AsPh_3$ < Py ~ PPh_3 < dioxane. The reduction potentials tend to become more negative in the opposite sequence, dioxane < PPh_3 < Py < $AsPh_3$ < dip (Table 1). A good linear correlation ($r^2 = 0.96$) was found between the oxidation and reduction potentials of $GeCl_2 \cdot B$ (Fig. 3). The correlation suggests that the molecular orbitals involved in the electrochemical oxidation and reduction processes are located on the germaniun moiety. The results of the quantum chemical AM1 calculations confirm this view (see below).

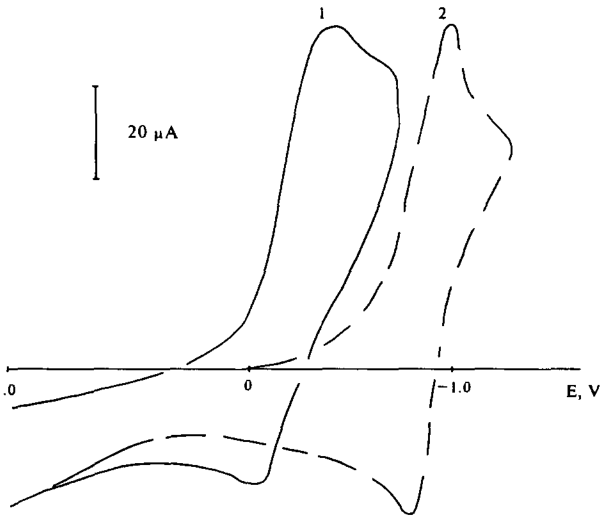


Fig. 2. Cyclic voltammogram for reduction of: (1) $GeCl_2 \cdot$dioxane; (2) GeI_2 ($c = 2 \cdot 10^{-3}$ M, $v = 200$ mV s^{-1}).

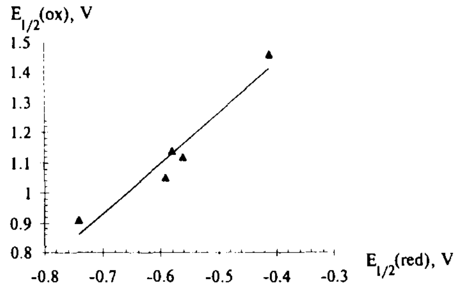


Fig. 3. Relationship between $E_{1/2}$(ox) and $E_{1/2}$(red) for $GeCl_2 \cdot B$ complexes.

The redox properties of $GeX_2 \cdot B$ complexes depend strongly on X. This can be illustrated by taking $GeX_2 \cdot PPh_3$ as an example. The oxidation potentials increase in the order I > Cl > Br, whereas the reduction potentials become more cathodic in the opposite direction (see Table 1). The electrochemical gap (*G*) increases in the order Br < Cl < I. The $GeBr_2 \cdot PPh_3$ complex has the smallest *G* value (1.10 V) among the dihalogermelynes (dihalostannylenes) and their complexes studied. Diiodostannylene has a *G* value (1.14 V) very close to that of the $GeBr_2 \cdot PPh_3$ complex. The largest electrochemical gaps are for GeI_2 and its complex $GeI_2 \cdot PPh_3$ ($G > 3.15$ V). Thus, one may expect that of the compounds studied, SnI_2 and the $GeBr_2 \cdot PPh_3$ complex, having both low oxidation and reduction potentials, will tend to undergo radical or SET ion radical reactions, while ionic processes should be more effective for $GeI_2 \cdot PPh_3$.

Other trends were observed for the series of dihalostannylenes SnX_2 (X = F, Cl, Br, I). The oxidation potentials decrease in the order F > Cl > Br > I. The reduction potentials become more negative in the series I < Cl < Br < F. The electrochemical gap falls considerably in the order F ≫ Br > Cl ≫ I. A good linear correlation ($r^2 = 0.996$) was found between ionization potentials (IP) [14] and $E_{1/2}$(ox) of SnX_2 in acetonitrile solution (Fig. 4). Its extrapolation to the IP of SnF_2 (11.5 eV) predicts an $E_{1/2}$(ox) value of 2.60 V for SnF_2.

For dichlorogermylene and dichlorostannylene complexes with the same Lewis base, the $ECl_2 \cdot$ dioxane (E = Ge, Sn) complexes can be compared. It turns out that $GeCl_2 \cdot$ dioxane both oxidizes and reduces more easily than $SnCl_2 \cdot$ dioxane. It also has a smaller *G* value (Table 1). Unfortunately we cannot compare the redox potentials of the corresponding "free" carbene

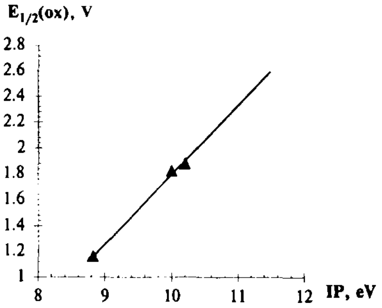


Fig. 4. Correlation between oxidation and ionization potentials of SnX_2 (X = F, Cl, Br, I).

analogues ECl_2 (E = Ge, Sn) because of the lack of a sample of $GeCl_2$ of good quality. However, we can compare them for EI_2 (E = Ge, Sn). It can be seen (Table 1) that diiodostannylene is oxidized and reduced considerably more easily than diiodogermylene.

Complexation with n-donors affects the redox properties of dihalogermylenes (stannylenes). It results in a decrease in the oxidation potentials. For example, GeI_2 does not oxidize up to 2.60 V, whereas its complex with PPh_3 is oxidized at 1.44 V. Likewise, $SnCl_2$ has an oxidation potential of 1.88 V, while its complex with dioxane oxidizes at 1.67 V. Complexation shifts the reduction potentials of EX_2 to a more cathodic value (for example, $E^{red}_{1/2}(GeI_2) = -0.99$ V vs. $E^{red}_{1/2}(GeI_2 \cdot PPh_3) = -1.71$ V and $E^{red}_{1/2}(SnCl_2) = -0.21$ V vs. $E^{red}_{1/2}(SnCl_2 \cdot \text{dioxane}) = -0.78$ V). The influence of complexation on the energies of the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO) of EX_2 have been studied theoretically (see below).

As expected, the values of the oxidation potentials of dihalogermylenes (stannylenes) and their complexes with the Lewis bases indicate that these compounds should act as good reducing agents. However, GeI_2 and SnF_2 are the exceptions; they do not oxidize at all up to + 2.6 V. But the most exciting and unexpected result we have obtained is that the most of the compounds studied are also quite strong oxidizing agents. For example, the reduction potentials of $GeX_2 \cdot B$ (X = Cl, Br; B = dioxane, PPh_3, $AsPh_3$, Py) lie in the region (from − 0.4 to − 0.60 V) typical of the convenient organic (e.g., *p*-benzoquinone; $E_{1/2}(\text{red}) = -0.52$ V; in MeCN; vs. Ag/AgCl) [15]) or inorganic (e.g., O_2, $E_{1/2}(\text{red}) = -0.82$ V; in MeCN; vs. s.c.e. [15]) oxidizing agents. The $GeCl_2 \cdot$ dip and $SnCl_2 \cdot$ dioxane complexes have more negative potentials (− 0.74 and − 0.78 V, respectively). Of the compounds studied, SnI_2 was found to be the most powerful oxidizing agent. Its reduction potential (− 0.02 V) is close to that of such a strong oxidant as TCNQ (+ 0.12 V vs. s.c.e. [15]).

The oxidizing properties of dihalogermylenes (dihalostannylenes) and their complexes with the Lewis bases can be illustrated by reference to several reactions. The oxidation of hexamethylditin and the derivative of 1,1,2,2-tetramethyl-1,2-digermacyclobutene-3 by $GeCl_2 \cdot$ dioxane ($E_{1/2}(\text{red}) = -0.41$ V) [6] has already been mentioned above. Similarly, $Me_3SnSnMe_3$ is readily oxidized by $GeCl_2 \cdot PPh_3$ ($E_{1/2}(\text{red}) = -0.58$ V) and SnI_2 ($E_{1/2}(\text{red}) = -0.02$ V) in benzene at 20 °C, quantitatively producing Me_3SnX and oligomers $(EX)_x$ (E = Ge, Sn; X = Cl, I).

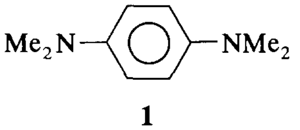
$$x\ Me_3SnSnMe_3 + 2x\ GeCl_2 \cdot PPh_3(SnI_2) \longrightarrow 2x\ Me_3SnX + 2\ (EX)_x$$

E = Ge, Sn; X = Cl, I

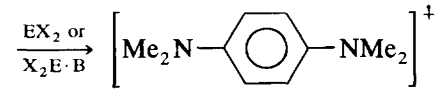
However, $SnCl_2 \cdot$ dioxane ($E_{1/2}(\text{red}) = -0.78$ V) and $GeCl_2 \cdot$ dip ($E_{1/2}(\text{red}) = -0.74$ V) complexes do not react with $Me_3SnSnMe_3$. Thus, the $E_{1/2}(\text{red})$ value of approx. − 0.6–(− 0.7) V is a threshold value: dihalogermylenes (dihalostannylenes) and their complexes with more negative $E_{1/2}(\text{red})$ values do not react with hexamethylditin.

Another example of a pure redox reaction of EX_2 and $EX_2 \cdot B$ was found when organic substrate *N,N N′,N′*-tetramethyl-*p*-phenylenediamine (**1**) was used as a reducing agent. This amine has two reversible oxidation waves. The first wave ($E_{1/2} = 0.14$ V) corresponds to the formation of the stable blue colored cation radical (Wurster's salt) which is further oxidized at $E_{1/2} = 0.55$ V (the second wave) to give diamagnetic diiminium salt (MeCN, 20 °C, vs. Ag/AgCl/KCl (sat.)).

It was found that most of the substrates react with **1** to give the blue Wurster's salt. The reaction of **1** with $GeCl_2 \cdot$ dioxane (complex:amine = 1:1), for example, is completed in 1 h (benzene or MeCN, 20 °C) and the conversion of **1** is 100% (according to the NMR spectra). Addition of the second equivalent of $GeCl_2 \cdot$ dioxane does not result in further oxidation of Wurster's salt. The same is true for the other dihalogermylenes (dihalostannylenes) and their complexes, except for diiodostannylene, SnI_2.

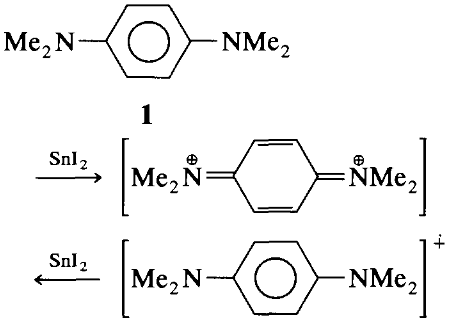


1



Diiodostannylene turns out to be so powerful an oxidizing agent ($E_{1/2}(\text{red}) = -0.02$ and − 0.51 V) that even in 1:1 stoichiometry it oxidizes **1** directly to the diiminium salt. We were not able to detect an intermediate formation of blue Wurster's salt during the reaction. Probably a two-electron oxidation takes place in this process. Wurster's salt prepared from **1** and $GeCl_2 \cdot$

dioxane was instantly decolorized upon addition of an equivalent of SnI_2.



Only three of the studied dihalogermylenes (dihalostannylenes) fails to oxidize **1**: GeI_2 ($E_{1/2}$(red) = -0.99 V), SnF_2 ($E_{1/2}$(red) = -0.94 V) and $GeI_2 \cdot PPh_3$ (which has no reduction wave up to -1.71 V). Thus, a threshold value of $E_{1/2}$(red) is approx. -0.9 V: dihalogermylenes (dihalostannylenes) with more negative reduction potentials do not oxidize **1**.

2.1. Quantum-chemical calculations

From the data of Table 1 one can see that the $GeCl_2 \cdot$ dioxane complex is unique in our series in that both its oxidation and reduction take place quasi-reversibly, indicating the formation of ion radicals. We have studied this complex and its ion radicals in detail by means of semi-empirical AM1 calculations. Calculations have also been carried out on the $GeCl_2 \cdot PH_3$ complex (a model for the experimentally studied $GeCl_2 \cdot PPh_3$ complex) and its ion radicals. No calculations have been carried out on the dihalogermylene complexes with Lewis bases.

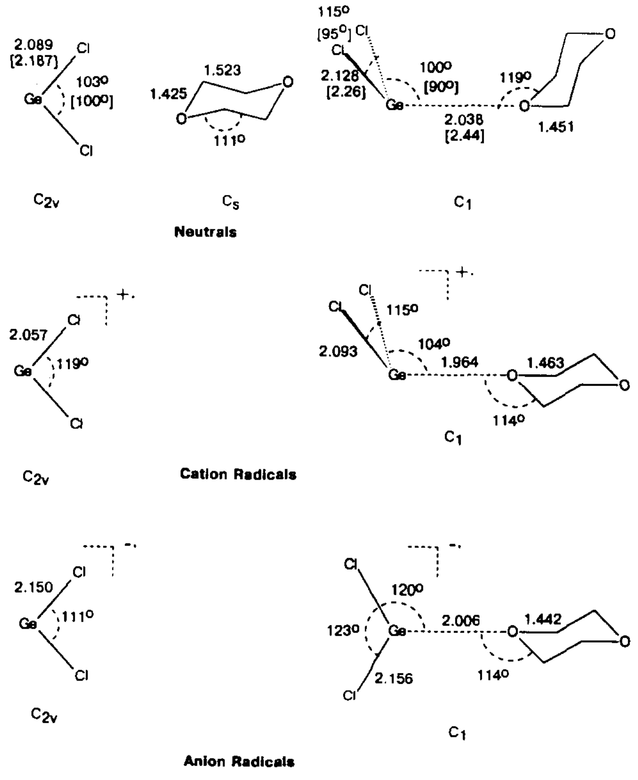


Fig. 5. AM1 calculated structures of $GeCl_2$, $GeCl_2 \cdot$dioxane and their ion radicals. Bond lengths are in angstroms, and bond angles are in degrees. Experimental values for $GeCl_2$ [5] and $GeCl_2 \cdot$dioxane [16] are given in brackets.

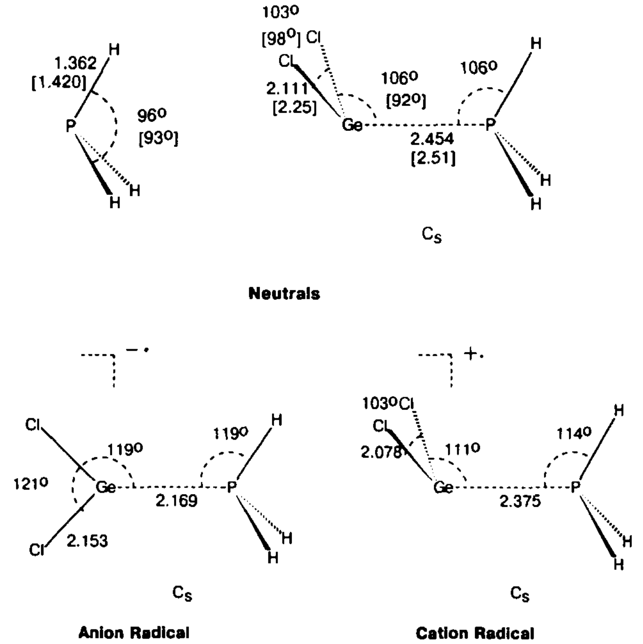


Fig. 6. AM1 calculated structures of PH_3, $GeCl_2 \cdot PH_3$ and their ion radicals. Bond lengths are in angstroms, and bond angles are in degrees. Experimental values for PH_3 [31] and $GeCl_2 \cdot PPh_3$ [17] are given in brackets.

The AM1 calculated geometries of $GeCl_2$, its ion radicals, and the corresponding neutral and charged complexes with dioxane and PH_3 are presented in Figs. 5 and 6, along with the available experimental structural data on $GeCl_2$ [5] and the neutral $GeCl_2 \cdot$ dioxane [16] and $GeCl_2 \cdot PPh_3$ [17] complexes. It can be seen that the AM1 calculated geometries of both the carbene analogue and its complexes are in a good agreement with the experimental ones (see Figs. 5 and 6). A slight lengthening of Ge–Cl bonds in the complex with dioxane is also predicted by the AM1 calculations. The calculated Ge $\cdots$ O distance is somewhat shorter than the experimental value. Because of this short Ge $\cdots$ O distance the calculated enthalpy of complexation (ΔH_c = 15.9 kcal mol^{-1}) is higher than the experimental value of 7.1 kcal mol^{-1} [18].

The $GeCl_2 \cdot$ dioxane complex is formed by interaction between the lowest unoccupied π-MO of $GeCl_2$ and a linear combination of the lone electron pairs of the dioxane oxygens. This interaction results in significant negative charge transfer to the $GeCl_2$ moiety (-0.21 e).

Analysis of charge distributions in the [GeCl$_2$ · dioxane]$^{+\cdot}$ and [GeCl$_2$ · dioxane]$^{-\cdot}$ ion radicals shows that the ionization of the complex occurs mainly by removal from or addition of an electron to the GeCl$_2$ moiety. In the anion radical the total negative charge on GeCl$_2$ is -1.02 e, whereas in the cation radical there is a significant delocalization of the positive charge (total positive charge on GeCl$_2$ is 0.64 e). Fig. 5 shows the changes in configuration of the complex due to ionization. Both oxidation and reduction result in shortening of Ge · · · O distance, but the effect is more pronounced in the former case. Changes in the geometry upon ionization are the same for free GeCl$_2$ and its complex.

The AM1 calculated geometry of the GeCl$_2$ · PH$_3$ complex (Fig. 2) is in a good agreement with the experimental one [17]. The AM1 calculated enthalpy of complexation ($\Delta H_c = 10.2$ kcal mol^{-1}) is close to the experimentally determined value (10.7 kcal mol^{-1} [12]). The geometry and the charge distributions in GeCl$_2$ · PH$_3$ complex indicate that it is stabilized by LUMO (GeCl$_2$)—HOMO (PH$_3$) interaction. The transfer of negative charge to the GeCl$_2$ moiety (-0.06 e) is significantly less than in the dioxane complex. Oxidation does not change the configuration of the complex but slightly tightens it, as noted above for the GeCl$_2$ · dioxane complex. As in the case of GeCl$_2$ · dioxane complex, an electron is removed from GeCl$_2$ moiety upon oxidation of GeCl$_2$ · PH$_3$: in the cation radical it has a positive charge of 0.78 e.

The complexation of GeCl$_2$ with PH$_3$ or dioxane increases the energy (destabilizes) of its HOMO, as can be clearly seen from the AM1 calculated orbital energies (e_{HOMO}) (Table 2). There is a good correlation between the HOMO energies (e_{HOMO}) and IP values. Calculations show (Table 2) that complexation results in a lowering of the IP of carbene analogues and thus should lower their oxidation potential. We have no experimental results to verify this prediction for "free" GeCl$_2$, but comparison of the oxidation potentials of GeI$_2$ and GeI$_2$ · PPh$_3$, as well as SnCl$_2$ and SnCl$_2$ · dioxane (Table 1), supports its validity.

The AM1 calculations of anion radicals show that the difference in the electron affinities (EA) of GeCl$_2$ and GeCl$_2$ · dioxane is small and does not correlate with the LUMO energies (e_{LUMO}).

Unfortunately, we cannot compare directly the calculated IPs and EAs with the experimentally observed oxidation and reduction potentials because such a comparison must take into account solvation effects. Calculations of this type are now in progress and will be reported soon.

The calculations on the ion radicals from the complexes show that oxidation significantly increases the stability of complexes towards dissociation into GeCl$_2^{+\cdot}$ and dioxane and PH$_3$ ($\Delta H_c^{\mathrm{cation}}$ values are 49.8 and 39.7 kcal mol^{-1} respectively), whereas reduction is slightly stabilizing ($\Delta H_c^{\mathrm{anion}} = 19.4$ kcal mol^{-1}) in the case of GeCl$_2$ · PH$_3$ and destabilizing ($H_c^{\mathrm{anion}} = 13.6$ kcal mol^{-1}) in the case of GeCl$_2$ · dioxane complexes, relative to $\Delta H_c^{\mathrm{neutral}}$ values of 15.9 kcal mol^{-1} (GeCl$_2$ · dioxane) and 10.2 kcal mol^{-1} (GeCl$_2$ · PH$_3$) (see Table 2).

The question what type of orbital (σ or π) is occupied by an unpaired electron in ion radicals of carbene analogues and their complexes with Lewis bases is of fundamental importance. Recently [10], we showed experimentally that the anion radicals of stable germylene and stannylene, [(Me$_3$Si)$_2$CH]$_2$E$^{-\cdot}$Na$^+$ (E = Ge, Sn), are π-radicals, i.e. an unpaired electron occupies the p-orbital of the carbene analogue. The results of our AM1 calculations predict that the GeCl$_2$ and GeCl$_2$ · B (B = dioxane, PH$_3$) anion radicals are also π-radicals. In contrast, the corresponding cation radicals are σ-radicals.

3. Experimental

Solvents were dried and distilled under argon; acetonitrile over CaH$_2$, and benzene and benzene-d$_6$ over sodium. The ^{1}H NMR spectra were recorded on a Bruker AC 200P (200 MHz) instrument, UV-visible spectra were recorded with a Specord M400 spectrophotometer, and GC/MS was carried out on a Finnigan MAT INCOS 50 instrument (RSL-200 column, 30 m × 0.25 mm).

Complexes of dihalogermylenes with Lewis bases were made by the known procedures: GeCl$_2$ · dioxane by the reaction between HGeCl$_3$ and dioxane [19] and GeCl$_2$ · B complexes by the reactions of the GeCl$_2$ · dioxane complex with the Lewis bases B: PPh$_3$ [20]; · AsPh$_3$ [20]; pyridine [21]; α,α,-dipyridyl [21].

Table 2
AM1 calculated energetic characteristics of GeCl$_2$, and its neutral and charged complexes with the Lewis bases

	ΔH_f (kcal mol^{-1})	IP (eV)	$-e_{\mathrm{HOMO}}$ (eV)	EA (eV)	$-e_{\mathrm{LUMO}}$ (eV)	$\Delta H_c^{\mathrm{neutr}}$ (kcal mol^{-1})	$\Delta H_c^{\mathrm{anion}}$ (kcal mol^{-1})	$\Delta H_c^{\mathrm{cation}}$ (kcal mol^{-1})
GeCl$_2$	-42.9	9.05 [a]	9.49	2.56	2.18	–	–	–
GeCl$_2$ · dioxane [b]	-153.8	7.58	8.21	2.46	1.49	15.9	13.6	49.8
GeCl$_2$ · PH$_3$ [b]	-42.9	7.77	8.37	2.96	1.67	10.2	19.4	39.7

[a] Experimental IP of GeCl$_2$ is 10.2 eV [5].

[b] AM1 calculated ΔH_f of dioxane is -95.0 kcal mol^{-1}, PH$_3$ is 10.2 kcal mol^{-1}.

The $GeBr_2 \cdot PPh_3$ complex was obtained in 82% yield by the reaction of $GeBr_2 \cdot$ dioxane with PPh_3 in THF as described for $GeCl_2 \cdot PPh_3$ [20]; ^{31}P NMR (δ, $CDCl_3$): -9.51 ppm. The $GeBr_2 \cdot$ dioxane complex was synthesized in 60% yield by the reaction of $HGeBr_3$ with dioxane by the method used for $GeCl_2 \cdot$ dioxane [19]. $GeI_2 \cdot PPh_3$ was synthesized by the reaction of GeI_2 with PPh_3 in *m*-xylole [22]. $SnCl_2 \cdot$ dioxane was obtained by the reaction of anhydrous $SnCl_2$ with dioxane [23].

The halides GeI_2 [24], $SnBr_2$ [25], and SnI_2 [26] were obtained by the known procedures. Commercially available $SnCl_2$, SnF_2 (both from Aldrich) and Bu_4NBF_4 (Chemapol) were used.

Electrochemical measurements were performed under argon with a PI-50-11 potentiostate using a platinum electrode (diameter 3.5 mm) and Bu_4NBF_4 as a supporting electrolyte. Potentials reported are vs. Ag/AgCl/KCl(sat.). The numbers of electrons in electrochemical processes were determined on a platinum rotating disk electrode ($v = 50\ s^{-1}$) by comparison of the wave height with the wave height for the oxidation of ferrocene at the same concentration.

Lifetimes of ion radicals were evaluated by the time necessary to sweep the voltage from the potential of the direct (cathode) peak to the potential of the reverse (anode) peak on the cyclic voltammogram at the slowest possible sweep rate.

Semi-empirical quantum chemical calculations were carried out by the AM1 method [27] implemented in the MOPAC (Version 6) package of programs [28]. The parameters for germanium, chlorine, and phosphorus are taken from Refs. [29–31], respectively. The geometries of all species studied were calculated with full optimization.

3.1. Reaction of $GeCl_2 \cdot PPh_3$ (SnI_2) with $Me_3SnSnMe_3$

A solution of 40 mg (0.1 mmol) of $GeCl_2 \cdot PPh_3$ and 16 mg (0.05 mmol) of $Me_3SnSnMe_3$ in 0.5 ml of C_6D_6 was stirred for 24 h at 20 °C. Yellow polymeric subchlorides $(GeCl)_x$ were precipitated. According to ^1H NMR and GC/MS spectral data Me_3SnCl was formed in a quantitative yield.

Under the same conditions Me_3SnI was obtained in a quantitative yield from the reaction of 37 mg (0.1 mmol) of SnI_2 and 16 mg (0.05 mmol) of $Me_3SnSnMe_3$ in 0.5 ml of C_6D_6.

3.2. Reactions of 1 with $EX_2 \cdot B$ (E = Ge, Sn) and SnX_2

A solution of 0.2 mmol of $EX_2 \cdot B$ (E = Ge, Sn) or SnX_2 and 0.2 mmol of **1** in 0.5 ml of MeCN was stirred for 1 h, during which the intense blue color of Wurster's salt appeared. Wurster's salt was identified by UV-visible spectral (λ_{max} 560 and 606 nm [32]) and cyclic voltammetry data.

Acknowledgments

This work received financial support from the International Science Foundation under Grant MHL000 and the Russian Foundation for Basic Research under the Grant No 95-03-09042.

References

[1] P.P. Gaspar, in M. Jones and R.A. Moss (eds.), *Reactive Intermediates*, Wiley, New York, Vol. 1, 1978, p. 229; Vol. 2, 1981, p. 335; Vol. 3, 1985, p. 333.

[2] W.P. Neumann, *Chem. Rev., 91* (1991) 311.

[3] O.M. Nefedov and M.P. Egorov, in A.R. Bassindale and P.P. Gaspar (eds.) *Frontiers of Organosilicon Chemistry*, The Royal Society of Chemistry, Cambrige, 1991, p. 145.

[4] J.K. Kochi, *Organometallic Mechanisms and Catalysis*, Academic Press, New York, 1978.

[5] O.M. Nefedov, M.P. Egorov, A.I. Ioffe, L.G. Menchikov, P.S. Zuev, V.I. Minkin, B.Ya. Simkin and M.N. Gluhovtsev, *Pure Appl. Chem., 64* (1992) 265.

[6] M.P. Egorov, A.M. Galminas, A.A. Basova and O.M. Nefedov, *Dokl. Akad. Nauk, 329* (1993) 594.

[7] M.J.S. Gynane, M.F. Lappert, S.J. Miles, A.J. Carty and N.J. Taylor, *J. Chem. Soc. Dalton Trans.*, (1977) 2009.

[8] M.F. Lappert, M.C. Misra, M. Onyszchuk, R.S. Rowe, P.P. Power and M.J. Slode, *J. Organomet. Chem., 330* (1987) 31.

[9] K. Mochida, A. Itani, M. Yokoyama, S. Worley and J. Kochi, *Bull. Soc. Chem. Jpn., 58* (1985) 2149.

[10] M.P. Egorov, O.M. Nefedov, T.-S. Lin and P.P. Gaspar, *Organometallics, 14* (1995) 1539.

[11] D. Bethell and V.D. Parker, *Acc. Chem. Res., 21* (1988) 400.

[12] S.P. Kolesnikov, I.S. Rogozhin, A.Ya. Shteinshneider and O.M. Nefedov, *Izv. Akad. Nauk Ser. Khim.* (1980) 799.

[13] D. DeFord and D.N. Hume, *J. Am. Chem. Soc., 73* (1951) 5321.

[14] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin and W.G. Mallard, *Gas-Phase Ion and Neutral Thermochemistry, J. Phys. Chem Ref. Data*, 1988, 17, Suppl. 1.

[15] C.K. Mann and K.K. Barnes, *Electrochemical Reactions in Nonaqueouse Systems*, Marcel Dekker, New York, 1970.

[16] V.I. Kuleshov, N.G. Bokii, Yu.T. Struchkov, O.M. Nefedov, S.P. Kolesnikov and B.L. Perlmutter, *Zh. Strulturn. Khim., 196* (1970) 71.

[17] N.G. Bokii, Yu.T. Struchkov, S.P. Kolesnikov, I.S. Rogozhin and O.M. Nefedov, *Izv. Akad. Nauk Ser. Khim.* (1975) 812.

[18] I.S. Rogozhin and S.P. Kolesnikov *Abstracts of II All-Union Conference on Carbene and Their Analogues Chemistry*, Moscow, 1977, p. 47.

[19] S.P. Kolesnikov, V.I. Shiryaev and O.M. Nefedov, *Izv. Akad. Nauk Ser. Khim.* (1966) 584.

[20] O.M. Nefedov, S.P. Kolesnikov and I.S. Rogozhin, *Izv. Akad. Nauk Ser. Khim.* (1973) 2824.

[21] O.M. Nefedov, S.P. Kolesnikov and I.S. Rogozhin, *Izv. Akad. Nauk Ser. Khim.* (1980) 170.

[22] R.B. King, *Inorg. Chem., 2* (1963) 199.

[23] E. Hough and O. Nicholson, *J. Chem.Soc. Dalton Trans.*, (1976) 1782.

[24] L.S. Foster, *Inorg. Synth. 3* (1950) 63.

[25] J. Kendall, E.D. Cristenden and H.K. Miller, *J. Am. Chem. Soc., 45* (1923) 963.

[26] R.A. Howie, W. Maser and I.C. Travena, *Acta Crystallogr., B28* (1972) 2965.

[27] M.J.S. Dewar, E.G. Zoebisch, E.F. Healey and J.J.P. Stewart, *J. Am. Chem. Soc., 107* (1985) 3902.

[28] J.J.P. Stewart, *MOPAC, A Semi-Empirical Molecular Orbital Program*, QCPE, 1983, p. 455.

[29] M.J.S. Dewar and C. Jie, *Organometallics, 8* (1989) 1544.

[30] M.J.S. Dewar and E.G. Zoebisch, *Theochem, 180* (1988) 1.

[31] M.J.S. Dewar and C. Jie, *Theochem, 187* (1989) 1.

[32] L. Michaelis, M.P. Schubert and S. Granick, *J. Am. Chem. Soc., 61* (1939) 1981.