ELECTRON TRANSFER IN THE REACTIONS OF GERMYLENES, STANNYLENES, AND THEIR COMPLEXES

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Abstract
The results of experimental and theoretical studies of electron transfer in the chemistry of germylenes, stannylenes and their complexes are discussed. Experimental evidences for the existence of relatively stable radical ions of germylenes, stannylenes and their complexes were obtained. Electronic structure and geometry of radical ions of $GeCl_2$, $GeCl_2$·dioxane, and $GeCl_2 \cdot PH_3$ were studied by computational methods. Electrochemistry of EX_2 (E= Ge, Sn; X=Hal), their complexes with Lewis bases $X_2E \cdot B$ (B = dioxane, PPh_3, $AsPh_3$, pyridine, α,α'-bipyridyl) and with transition metal carbonyls $(CO)_5M{=}GeCl_2 \cdot THF$ (M = Cr, Mo, W) was studied.

Introduction.

In recent years there has been a growing interest in studies of low coordinated derivatives of Group 14 elements, particularly carbene analogs R_2E (E=Si, Ge, Sn) [1-3]. These species are of great interest not only from the fundamental standpoint of their structure, reactivity and reaction mechanisms but also because of their involvement in chemical vapor deposition (CVD) of electronic materials and metallic coatings.

Typically, concerted and non-concerted radical mechanisms are considered in the chemistry of the carbene analogs [1-3]. Very little is known about the role of electron transfer in the reactions of E(II) species although redox processes in the chemistry of the derivatives of tetracoordinated Group 14 elements E(IV) (E = Si, Ge, Sn) have been studied [4]. At the same time, the relatively low values of ionization potentials (IP) and the significant values of electron affinities (EA) experimentally obtained or calculated for a number of carbene analogs suggest that these species can participate in electron transfer interactions with a variety of electron acceptors/donors. For example, the IP of the electrophilic $GeCl_2$ is 10.2 eV [5] (the AM1 calculated value is 9.49 eV [6]) and EA($GeCl_2$) is 2.6 eV [5] (the AM1 calculated value is 2.52 eV [6]). The values of IP and EA for the simple nucleophilic dialkylgermylene Me_2Ge have not been obtained experimentally. The AM1 calculated values are 7.94 eV (*cf.* experimentally known IP of $[(Me_3Si)_2CH]_2Ge$ is 7.75 eV [7]), and 1.97 eV, respectively [6]. The comparison of the IP and EA values of $GeCl_2$ and Me_2Ge with those for some typical reductants (e.g., IP(Mg) = 7.64 eV, IP($Me_3SnSnMe_3$) = 7.80 eV, IP(p-$(NH_2)_2C_6H_4$) = 6.87 eV; [5]) and oxidants (e.g., EA(TCE) = 3.17 eV, EA(TCNQ) = 2.80 eV, EA(p-benzoquinone) = 1.90 eV; [5]) indicates that in chemical reactions dimethylgermylene will have a tend to react as a reductant (as the donor of electron) while $GeCl_2$ can react not only as a reducing agent, but as an oxidizing agent too.

In this paper the results of our study of electron transfer in the reactions of germylenes, stannylenes and their complexes will be reviewed. Evidence for the existence of carbene analog radical ions will be given.

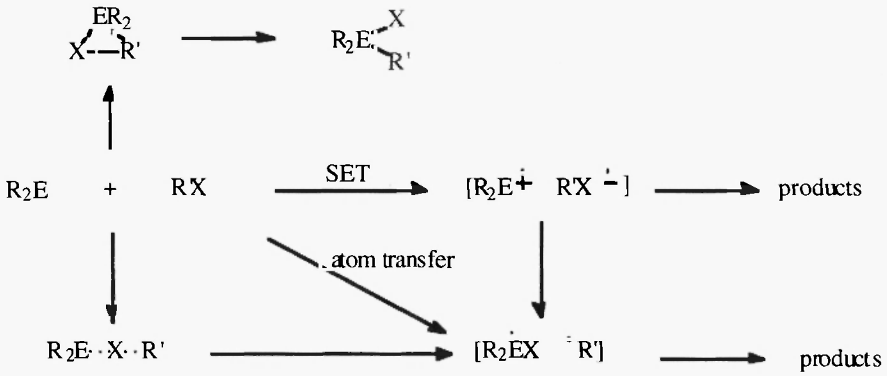
Results and Discussion.

One of carbene analog reaction which could include electron transfer is the insertion into σ-bonds or oxidative addition reaction. The reaction may occur either as a concerted or as a non-concerted process. Two mechanisms can be considered for non-concerted processes: an atom transfer and an electron transfer, or, using another terminology, inner-sphere or outer-sphere electron transfer [4]. For the particular case of the reaction of carbene analogs with organic halides these mechanisms are presented in scheme 1.

An atom transfer process is characterized by the formation of radicals via a complex (either as an intermediate or a transition state) in which the halogen atom is the bridging ligand, e.g., $R_2E \cdots X \cdots R'$. Indeed, we were able to detect in a low-temperature argon matrix at 12 K the formation of such a complex between difluorostannylene and methyl chloride [8]. Evidently, the possibility of atom transfer should depend on the carbon-halogen bond energy.

In an electron transfer process the breaking of carbon-halogen bond is not directly involved in the rate determining step (whereas it is an integral part of the atom transfer process) and the possibility of the reaction will not strongly depend on the energy of carbon-halogen bond. In contrast the reaction will depend on the values of electron attachment or reduction potentials of the organic halides.

Scheme 1

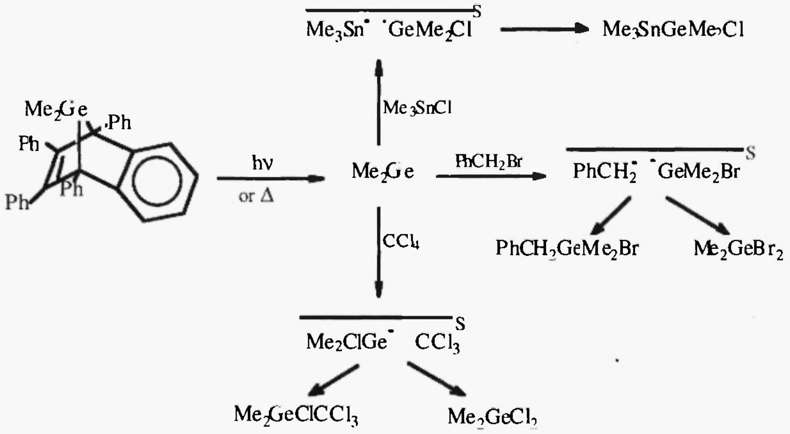


^1H CIDNP studies of the reaction between Me_2Ge (thermally or photochemically generated from 7-germanorbornadiene) and organic and metal halides have demonstrated that many of these processes occur via the formation of radical species and an atom transfer mechanism has been suggested for these reactions [9,10]. Examples of such reactions are given in Scheme 2

Table 1. **Dependence of reactivity of Me_2Ge towards RX (R_nMX_{4-n}) on the C-X (M-X) bond energy and reduction potentials of RX (R_nMX_{4-n}).**

	$GeCl_4$	$CHBr_3$	CCl_4	Me_3SnCl	BzBr	$CHCl_3$	AlkBr	BzCl
$E_{E\text{-}X}$, kcal/mol	81	57	73	101	55	78	66-70	69
$-E_{1/2}$,V	0.35	0.49	0.78	0.78	1.22	1.67	1.9-2.3	1.94
(vs. s.c.e.)	react with Me_2Ge					do not react with Me_2Ge		

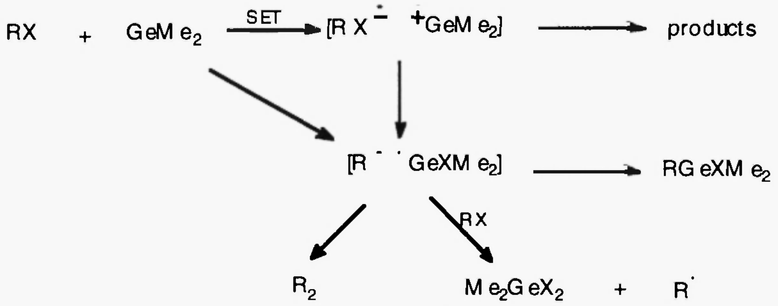
Scheme 2.



Further studies have demonstrated that the possibility of the reaction does not depend on the energy of the carbon-halogen or metal-halogen bonds [11]. For example, Me_2Ge reacts (abstracts a halogen atom) with CCl_4, $PhCH_2Br$, $GeCl_4$, Me_3SnCl ($E_{E\text{-}X}$=55 - 101 kcal/mol) but does not react (does not abstract a halogen atom) with $CHCl_3$, $C_nH_{2n+1}Cl$, $C_nH_{2n+1}Br$ ($E_{E\text{-}X}$=66 - 84 kcal/mol) (see Table 1). In contrast the dimethylgermylene reaction was found to depend on the reduction potential of a substrate (organic or metal halide) [11]. Indeed, Me_2Ge easily reacts with substrates having low reduction potentials, like CCl_4, CBr_4, $PhCH_2Br$, $Br(CH_2)_2Br$, $GeCl_4$, Me_3SnCl, but does not react with substrates having high reduction potentials e.g., $CHCl_3$, $PhCH_2Cl$, $C_nH_{2n+1}Br$, $Br(CH_2)_3Br$ (see Table 1). Apparently $-E_{1/2}$ (red) values of 1.2-1.4 V (vs. s.c.e.) are limiting values: organic and metal halides that have more negative $E_{1/2}$ values do not react with Me_2Ge.

Based on this fact the ion-radical mechanism of the reaction between Me_2Ge and organic and metal halides has been suggested [11] (Scheme 3):

Scheme 3



Lifetimes and the pathways of decomposition of radical ions in fact determine the final reaction products. It should be pointed out that electron transfer does not exclude the possibility of atom transfer under certain conditions. Apparently atom transfer will compete with electron transfer for substrates having weak E-X bond.

In fact a similar ion-radical mechanism was suggested by Lappert et al. in 1977 for the reaction of stable dialkyl and diaminostannylenes with alkyl and aryl halides [12,13]. The conclusion was based on spin trapping experiments, kinetics, the loss of optical activity of chiral 2-octyl chloride and ESR spectra. The evidences for a free radical chain process have also been reported. Electron transfer has also been considered as the rate determining step in other closely related oxidative addition reactions, e.g. in the Grignard reagent formation (insertion of Mg into a C-Hal bond) [14] and oxidative additions of transition metal complexes to C-Hal bonds [7].

Electron transfer from or to a carbene analog results in carbene analog radical ions. Very little is known about radical ions of heavier group 14 element carbene analogs. The silylene radical anion $SiH_2^{-\cdot}$ has been produced in a low-pressure discharge upon admission of SiH_4 and has been studied by laser photoelectron spectroscopy [15]. Photoionization mass spectrometry has been used to investigate silylene and germylene radical cations $EH_2^{+\cdot}$ (E = Si, Ge) [16,17]. The $^{28}SiH_2^{+\cdot}$ and $^{29}SiH_2^{+\cdot}$ radical cations have been detected by ESR upon ionization of SiH_4 in a neon matrix at 4K [18]. In the cases mentioned above the silylene and germylene radical ions were generated by discharge or photoionization under very severe conditions.

Recently we have obtained the first direct ESR evidence of the existence of germylene radical anions generated under very mild conditions[*] [19]. The corresponding stannylene radical anions have been also detected by ESR [19]. The germylene radical anion was obtained by reduction of the stable germylene $[(Me_3Si)_2CH]_2Ge$ by sodium in THF at room temperature:

$$[(Me_3Si)_2CH]_2Ge + Na \xrightarrow[\text{THF, 20 °C, 10-15 sec}]{Na} [(Me_3Si)_2CH]_2Ge^{\cdot-}\,Na^+$$

The characteristic yellow-orange color of $[(Me_3Si)_2CH]_2Ge$ (λ_{max} = 410 nm in THF) immediately turned to green (λ_{max} = 666 nm, THF), and a strong ESR signal appeared. The 1:2:1 triplet with a hyperfine splitting a = 2.6 G arises from two equivalent protons. The spectrum at higher gain shows four weak satellite lines appear on both sides of the central peak arising from the I = 9/2 nucleus of ^{73}Ge (7.8% abundance) (two other satellite peaks of the total of ten expected overlap with the strong central peak and are not observed) The a(^{73}Ge) value is 12.5 G. Under even higher gain, each of the satellite lines splits further into a triplet due to coupling with two equivalent protons. The g value of this radical species is 2.0125, which is typical for germanium-centered radicals (g ~ 2.0078 - 2.0100 [20]). Based on the hyperfine splitting patterns and the g-value, the ESR spectrum observed was unequivocally assigned to a $[(Me_3Si)_2CH]_2Ge^{-\cdot}$ radical anion [19].

The germylene radical anion is quite stable in solution at room temperature. It has a half-life time $t_{1/2}$ of ca. 1.5 h, which is however considerably shorter than the lifetime of the neutral species $[(Me_3Si)_2CH]_3Ge\cdot$ ($t_{1/2}$ is greater than four months [21]). The intensity of the ESR signal and of the electronic absorption maximum at 666 nm decrease at the same rate, consistent with the assignment of the λ_{max} = 666 nm absorption to germylene radical anion. The decay of the radical anion, simultaneously monitored by visible- and ESR-spectroscopy, obeys a second order rate law, suggesting its dimerization, a reaction typical for sterically non-overloaded germanium-centered $R_3Ge\cdot$ radicals [20]. Calculations have indicated that dimerization of the methylene radical anion $CH_2^{-\cdot}$ is feasible [22].

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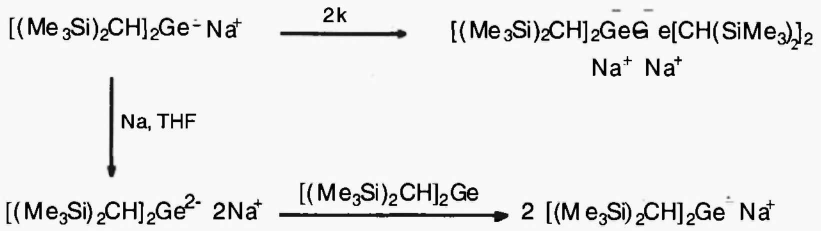
[*] This study has been carried out in cooperation with P. P.Gaspar and T.- S. Lin (Washington University, St. Louis, USA).



Further contact (1 - 2 min) of solutions of the germylene radical anion with sodium results in the complete disappearance of the ESR signal. Presumably the radical anion is reduced by sodium to the diamagnetic dianion. Germylene $[(Me_3Si)_2CH]_2Ge$ is reduced by this species to the radical anion $[(Me_3Si)_2CH]_2Ge^{-\cdot}$.

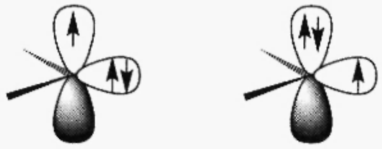
The dialkylstannylene radical anion $[(Me_3Si)_2CH]_2Sn^{-\cdot} Na^+$ was obtained by a brief contact (5 - 10 sec) with a sodium mirror of a solution of stable stannylene in THF at -80 °C [19]. The ESR spectrum was recorded at -80 °C. A broad singlet (line width 7G) was observed with a g value of 2.0177, close to that of the related neutral radical $[(Me_3Si)_2CH]_3Sn\cdot$ (g= 2.0094 [21]). Under increased gain two broad unresolved satellites from ^{117}Sn (I = 1/2, 7.7% abundance) and ^{119}Sn (I = 1/2, 8.7% abundance) were observed with a splitting of $a(^{117,119}Sn)$ = 116 G.

$$[(Me_3Si)_2CH]_2Sn \quad + \quad Na \xrightarrow[\text{THF, -80 °C, 5-10 sec}]{Na} [(Me_3Si)_2CH]_2Sn^{-\cdot} Na^+$$

The stannylene radical anion has a lifetime considerably shorter than that of the corresponding germylene anion radical: it decomposes in minutes at 20 °C.

The lack (probably caused by spectral broadening) of an observed hyperfine splitting due to the two adjacent CH-protons) makes the structural assignment for the tin radical species less certain. Nevertheless the ESR spectrum recorded was safely interpreted as belonging to the stannylene radical anion $[(Me_3Si)_2CH]_2Sn^{-\cdot}$ on the basis of the small value of the tin hyperfine coupling constant $a(^{117,119}Sn)$ = 116 G, clearly indicative of the π-character of this radical. The g and $a(^{117,119}Sn)$ values we have measured for the $[(Me_3Si)_2CH]_2Sn^{-\cdot}$ radical anion are close to those reported by Sita and Kinoshita [23] for the $Ar_2Sn^{-\cdot}$ (Ar= 2,6-diethylphenyl) radical anion (g = 2.024, $a(^{117,119}Sn)$ = 152 G) obtained by the reduction of *cyclo*-$(Ar_2Sn)_3$ with lithium in THF. Unlike the dialkylstannylene radical anion, the diarylstannylene radical anion turned out to be stable at room temperature [23].

In the radical anions of carbenes and their analogs, an unpaired electron can occupy either a σ- or a π-orbital:



π-radical σ-radical

Experimental data on radical cations of diphenylcarbene [24] and silylene [18] revealed that these species are σ-radicals and have a $^2A_1$ electronic ground state.

It is well-known that the a(M) splitting is proportional to the degree of s- character in the orbital on the M atom occupied by the unpaired electron. Therefore σ-radicals have considerably larger a(M) values than do π-radicals. For example, most of $a(^{13}C)$ coupling constants for carbon-centered σ-radicals are in the range 100 - 140 G vs. 24 - 26 G for π-radicals [24]. For the $Ph_2C^{+\cdot}$ radical cation, which is a σ-radical, $a(^{13}C)$ = 98.3 G [24].

Germanium- and tin-centered radicals are pyramidal, with a high degree of s- character in the orbital containing the odd electron. The range of hyperfine coupling constants $a(^{73}Ge)$ for $R_3Ge\cdot$ is 70-220 G [20], and $a(^{117,119}Sn)$ for $R_3Sn\cdot$ is 1400- 1800 G [25]. For example, the $a(^{73}Ge)$ value for $[(Me_3Si)_2CH]_3Ge\cdot$ is 92 G; for $[(Me_3Si)_2CH]_3Sn\cdot$ $a(^{117}Sn)$ = 1698 G, $a(^{119}Sn)$ = 1776 G [21]. Therefore the very small values of $a(^{73}Ge)$ = 12.5 G for $[(Me_3Si)_2CH]_2Ge^{-\cdot}$ and $a(^{117,119}Sn)$ = 116 G for $[(Me_3Si)_2CH]_2Sn^{-\cdot}$ clearly indicate the π-character of these germylene and stannylene radical anions and their $^2B_1$ ground electronic state [19].

Further evidences for the existence of carbene analog radical ions were obtained from the electrochemical studies. Electrochemistry has already proved its usefulness in the investigation of carbene radical ions [26]. However, the data concerning the electrochemistry and redox properties of carbene analogs are still lacking. Therefore we initiated a systematic study of the electrochemistry of stable germylenes, stannylenes and their complexes. Below the electrochemistry of dihalogermylenes, dihalostannylenes and their complexes with Lewis bases and transition metal compounds will be discussed*.

The electrochemistry of dihalogermylenes, dihalostannylenes and their complexes with Lewis bases is rather simple [27]. Cyclic voltammetry revealed one reduction and one oxidation peak (both are one-electron). The $E_{1/2}$ values are presented in the Table 2.

Table 2. Redox potentials and electrochemical gaps of dihalogermylenes (dihalostannylenes) 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(2e)	0.58	1.72
$GeCl_2$	$AsPh_3$	1.05	0.59	1.64
$GeCl_2$	Py	1.12[b]	0.56	1.68
$2GeCl_2$	bpy[e]	0.91(2e)	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. [e] bpy = α,α'-bipyridyl

Most of the reduction and oxidation waves of EX_2 and $EX_2 \cdot B$ were found to be irreversible, suggesting that the corresponding radical ions are very unstable. Quasi-reversible oxidation waves were observed for GeX_2•dioxane (X=Cl, Br) and $GeCl_2$•Py complexes [27].

Reversibility of tne processes increases in the order: $GeCl_2$•dioxane < $GeBr_2$•dioxane < $GeCl_2$•Py. The difference between oxidation potentials of a complex GeX_2•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 should have a considerably more positive oxidation potential compared to that of GeX_2•B in order to stabilize effectively the $GeX_2^{+\cdot}$ radical cations. Such a stabilization should be ineffective or impossible in the $GeCl_2$•B complexes with the nucleophilic ligands having a less positive ($AsPh_3$) or a nearly identical (PPh_3) oxidation potential as GeX_2•B.

Quasi-reversible reductions were found for the $GeCl_2$•dioxane complex and GeI_2. Lifetimes of $[GeCl_2\bullet dioxane]^{-\cdot}$ and $GeI_2^{-\cdot}$ radical anions were estimated to be ca. 4 and 2.5 sec at 20 °C, respectively [27].

Redox potentials of GeX_2•B complexes depend significantly on the nature of the Lewis base B. This can be due to the stability of the GeX_2•B complexes. We were able to determine the equilibrium formation constants K for $GeCl_2$•PPh_3 (K = 7•10^3 mol•L^{-1}, MeCN, 20 °C) and $GeCl_2$•$AsPh_3$ (K = 2•10^4 mol•L^{-1}, MeCN, 20 °C). The electrochemically determined K value for $GeCl_2$•PPh_3 is close to that obtained earlier by using UV spectroscopy (K = 2•10^3 mol•L^{-1}, 23 °C, n-Bu_2O) [28].

The following main tendencies in the redox potentials of dihalogermylenes, dihalostannylenes and their complexes should be mentioned.

The nature of the ligand B affects the redox properties of $GeCl_2$•B complexes. The oxidation potentials increase in the order: bpy < $AsPh_3$ < Py ~ PPh_3 < dioxane. The reduction potentials tend to become more negative in the opposite sequence: dioxane - PPh_3 - Py - $AsPh_3$ - bpy (Table 2).

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* This study has been carried out in cooperation with K. P. Butin and R. D. Rakhimov (M. V. Lomonosov Moscow State University, Moscow, Russia).

A good linear correlation ($r^2 = 0.96$) was found between oxidation and reduction potentials of $GeCl_2$•B (Fig. 1) [28]. The correlation suggests that the molecular orbitals involved in the electrochemical oxidation and reduction processes are located on the germanium moiety.

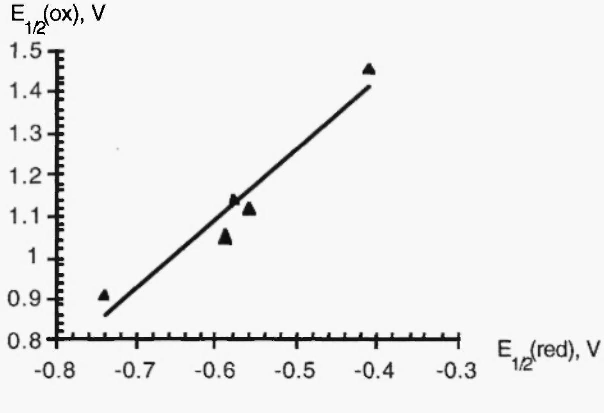


Figure 1. Relationship between $E_{1/2}$(ox) and $E_{1/2}$(red) for $GeCl_2$•B complexes.

Redox properties of GeX_2•PPh_3 depend on the nature of the halogen X. The oxidation potentials decrease in the order: I > Cl > Br, whereas the reduction potentials become more cathodic in the opposite direction (see Table 1). The electrochemical gap ($G = E_{ox} - E_{red}$) which characterizes the energy gap between HOMO and LUMO increases in the order: Br < Cl < I. The $GeBr_2$•PPh_3 complex has the smallest G value (1.10 V) of the dihalogermylenes (dihalostannylenes) and their complexes studied. Diiodostannylene has the G value (1.14 V) which is very close to that of the $GeBr_2$•PPh_3 complex. The largest electrochemical gaps are found for GeI_2 and its complex GeI_2•PPh_3 (G > 3.15 V). Thus, one may expect that of the compounds studied, SnI_2 and $GeBr_2$•PPh_3, having both low oxidation and reduction potentials, will have a tendency to react in radical or SET radical ion processes, while ionic processes would be more effective with GeI_2, GeI_2•PPh_3 and SnF_2.

The oxidation potentials of SnX_2 (X = F, Cl, Br, I) decrease in the order: F > Cl > Br > I. The reduction potentials become more negative in the series: I — Cl — Br — F. The electrochemical gap considerably decreases in the order: F >> Br > Cl >>I. A good linear correlation ($r^2 = 0.996$) was found between ionization potentials (IP) and $E_{1/2}$(ox) of SnX_2 in acetonitrile solution (Fig. 2) [28].

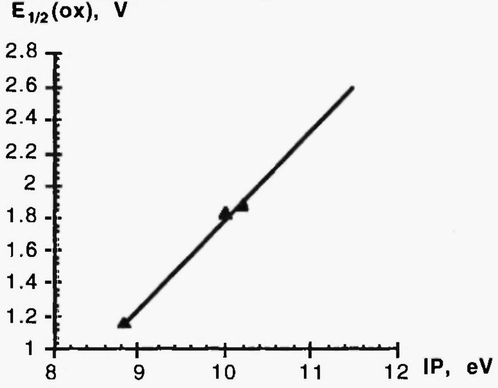


Figure 2. Correlation between oxidation and ionization potentials of SnX_2 (X=F, Cl, Br, I).

Complexation with n-donors results in a decrease of the oxidation potentials of EX_2. For example, GeI_2 does not oxidize up to 2.60 V while its complex with PPh_3 does at 1.44 V. Dichlorostannylene $SnCl_2$ 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 the cathodic region (for example, $E_{1/2}^{red}(GeI_2)=-0.99$ V vs. $E_{1/2}^{red}(GeI_2 \bullet PPh_3)=-1.71$ V and $E_{1/2}^{red}(SnCl_2)= -0.21$ V vs. $E_{1/2}^{red}(SnCl_2 \bullet dioxane) = -0.78$ V).

As expected, the values of the oxidation potentials of dihalogermylenes (stannylenes) and their complexes with Lewis bases indicate that these compounds should react as typical reducing agents. However, the most exciting and unexpected result we have discovered is that the most of the compounds studied are quite strong oxidizing agents too. For example, the reduction potentials of GeX_2•B (X = Cl, Br; B = dioxane, PPh_3, $AsPh_3$, Py) lie in the region –0.4 to –0.60 V, which is typical of the common organic (e.g., *p*-benzoquinone; $E_{1/2}$(red) = –0.52 V [29]) or inorganic (e.g., O_2, $E_{1/2}$(red) = –0.82 V [29]) oxidizing agents. Of the compounds studied SnI_2 was found to be the most powerful oxidizing agent. Its reduction potential (–0.02 V) is close to the reduction potential of such a strong oxidant as TCNQ (+0.12 V [29]).

The oxidizing properties of dihalogermylenes (dihalostannylenes) and their complexes with Lewis bases can be illustrated by several reactions.

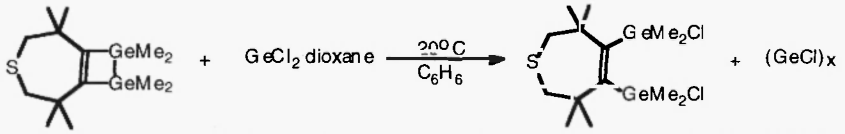
Hexamethylditin is easily oxidized by $GeCl_2$•PPh_3(dioxane) complexes and SnI_2 in benzene or MeCN at 20 °C quantitatively producing Me_3SnX and oligomers $(EX)_x$ (E = Ge, Sn; X = Cl, I).

$$x\,Me_3Sn{-}SnMe_3 \;+\; 2GeCl_2{\cdot}B\;(SnI_2) \xrightarrow[C_6H_6]{20^{o}C} 2x\,Me_3SnX \;+\; 2\,(EX)_x$$

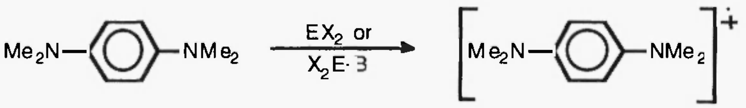
B= dioxane, PPh_3; E = Ge, Sn; X= Cl, I

However, $SnCl_2$•dioxane ($E_{1/2}$(red) = –0.78 V) and $GeCl_2$•bpy ($E_{1/2}$(red) = –0.74 V) complexes do not react with Me_3Sn-$SnMe_3$. Thus, the $E_{1/2}$(red) value of *ca.* –0.6 — (-0.7) V is a threshold value: dihalogermylenes (dihalostannylenes) and their complexes with more negative $E_{1/2}$(red) do not react with hexamethylditin.

The dioxane complex of dichlorogermylene oxidizes the Ge-Ge bond of the strained 1,1,2,2-tetramethyl-1,2-digermacyclobutene:



Most of the EX_2 and $EX_2{\cdot}B$ compounds were found to react with *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (**1**) forming Wurster's blue salt. The reaction of diamine **1** with e.g. $GeCl_2$•dioxane (complex:amine = 1:1) is complete in 1 h (benzene or MeCN, 20 °C) (the conversion of the diamine is 100% according to the NMR spectra). Addition of the second equivalent of $GeCl_2$•dioxane does not result in a further oxidation of Wurster's blue salt. The same is true for most of the other dihalogermylenes (dihalostannylenes) and their complexes.



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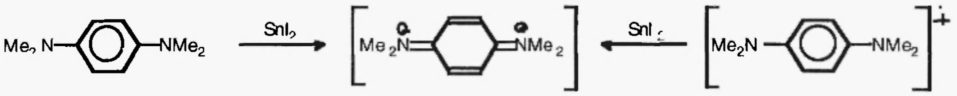
Diiodostannylene turns out to be such a powerful oxidizing agent ($E_{1/2}$(red) = –0.02 and –0.51 V) that even in 1:1 stoichiometry it oxidizes a diamine directly into a diiminium salt:



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Quantum-chemical calculations

We have studied the geometry, electron structure and energy parameters of $GeCl_2$. its ion radicals, and the corresponding neutral and charged complexes with dioxane and PH_3 by the semi-empirical AM1 method [27]. The AM1 calculated geometries of these molecules are presented in Fig. 3.

The analysis of charge distributions in the radical ions of $GeCl_2$•dioxane and $GeCl_2$•PH_3 complexes shows that the ionization of the complexes occurs mainly by removing an electron from or adding an electron to the $GeCl_2$ moiety. The same conclusion has already been deduced from the existence of the correlation between oxidation and reduction potentials of $GeCl_2{\cdot}B$ complexes (see above).

According to AM1 calculations complexation results in lowering the IP of the carbene analogs and thus should lower their oxidation potentials (Table 3). The comparison of the oxidation potentials of GeI_2 and GeI_2•PPh_3, as well as $SnCl_2$ and $SnCl_2$•dioxane confirms this conclusion (see above).

The calculations show that the oxidation significantly increases the stability of the complexes towards dissociation into the dichlorogermylene radical cation and the Lewis base and results in shortening of the Ge-O (Ge-P) bond. The reduction of the complexes is slightly stabilizing (in the case of $GeCl_2$•PH_3) or destabilizing (in the case of $GeCl_2$•dioxane) these species (Table 3).

Table 3. AM1 calculated energetic characteristics of $GeCl_2$, its neutral, and charged complexes with Lewis bases.

	$GeCl_2$	$GeCl_2$•dioxane	$GeCl_2$•PH_3
H_f, kcal/mol	–42.9	–153.8	–42.9
IP, eV	9.05*	7.58	7.77
e_{HOMO} eV	9.49	8.21	8.37
EA, eV	2.56*	2.46	2.96
e_{LUMO}, eV	2.18	1.49	1.67
H_c^{neutr}, kcal/mol	—	15.9	10.2
H_c^{anion}, kcal/mol	—	13.6	19.4
H_c^{cation}, kcal/mol	—	49.8	39.7

*Experimental values of IP and EA of $GeCl_2$ are 10.2 and 2.6 eV, respectively [5]

The results of our AM1 calculations predict that $GeCl_2$ and $GeCl_2$•B (B = dioxane, PH_3) radical anions are π-radicals, whereas the corresponding radical cations are σ-radicals.

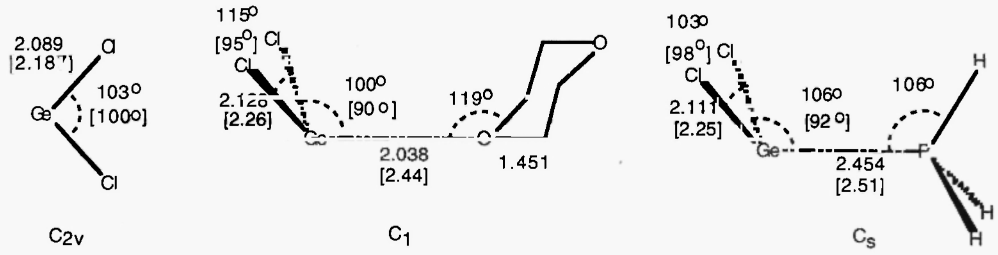
The electrochemistry of carbene analogs - transition metal complexes was studied using complexes of dichlorogermylene with pentacarbonyls of chromium, molybdenum, and tungsten $(CO)_5M{=}GeCl_2 \cdot THF$ (M = Cr, Mo, W).

Cyclic voltammetry of $(CO)_5M{=}GeCl_2 \cdot THF$ complexes (MeCN, platinum electrode, Bu_4NPF_6 as supporting electrolyte, 20 °C, $v = 50$ mV s^{-1}) shows two irreversible reduction peaks. The first reduction wave [-0.20(Cr), -0.17(Mo), -0.21(W) V; vs. Ag/AgCl/KCl(sat.)] is one-electron and the second one [-1.28(Cr), -1.11(Mo), -1.31(W) V] is two-electrons.

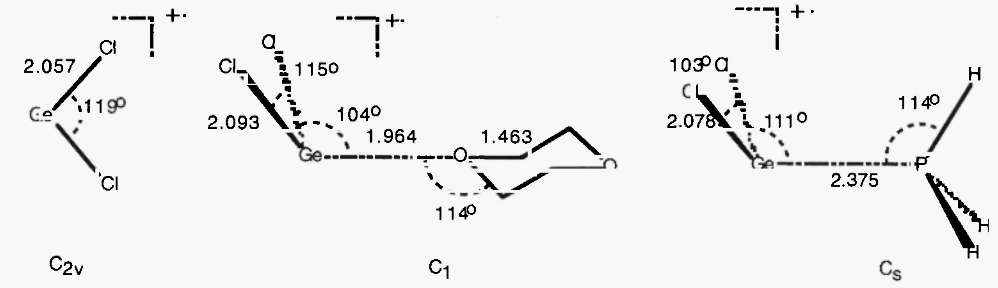
The first reduction waves of $(CO)_5M{=}GeCl_2 \cdot THF$ are rather close to the reduction potential of $GeCl_2 \cdot$dioxane (-0.41 V) and differ significantly from the reduction potentials of $M(CO)_6$ (from -2.07 to -2,37 V [30]) and $(CO)_5M \cdot MeCN$ (from -1.92 to -2.04 V [30]). It indicates that during the reduction of $(CO)_5M{=}GeCl_2 \cdot THF$ complexes an electron comes to the redox orbital which is mostly localized on the dichlorogermylene ligand (this orbital presumably is the LUMO orbital). This conclusion is in accordance with the results of MO calculations of Fischer carbene complexes showing that in these compounds the LUMO is situated on the carbene moiety [31]. The data of electrochemical [32] and ESR studies [33] of transition metal carbene complexes confirm that in the radical anions of Fischer carbene complexes an unpaired electron is localized on the carbene ligand.

Cyclic voltammograms for the oxidation of $(CO)_5M{=}GeCl_2 \cdot THF$ complexes show two irreversible oxidation peaks for M = Cr and W and one irreversible peak for M = Mo. The first oxidation potentials of $(CO)_5M{=}GeCl_2 \cdot THF$ complexes [1.10(Cr), 1.15(Mo), 1.19 (W) V] are rather close to those of $(CO)_5M \cdot L$ complexes with other ligands L (e.g., E_p(ox) of $(CO)_5W \cdot MeCN$ in MeCN is 1.12V [30]) but differ considerably from the oxidation potentials of the $GeCl_2 \cdot$dioxane complex ($E_{1/2}$(ox)=1.46 V). These facts indicate that the redox orbitals participating in the oxidation of $(CO)_5M{=}GeCl_2 \cdot B$ complexes are mostly localized on the transition metal moiety.

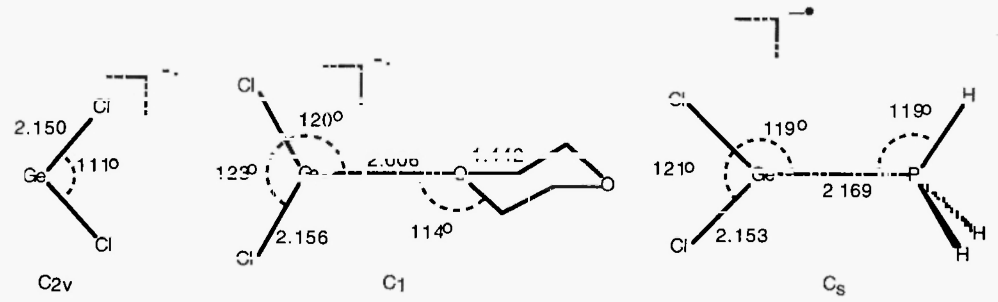
Thus the results of our electrochemical study confirm that the electronic structure of $(CO)_5M{=}GeCl_2 \cdot B$ complexes is similar to that of Fischer carbene complexes. The available structural [34] and computational [35] data concerning carbene analog transition metal complexes are in accordance with this conclusion.



Neutrals



Radical Cations



Radical Anions

Figure 3. AM1 calculated structures of $GeCl_2$, $GeCl_2$•dioxane, $GeCl_2$•PH_3 and their ion radicals. Experimental values are given in brackets.

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