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Electrochemistry of complexes of dichlorogermylene and dihalostannylenes with chromium, molybdenum, and tungsten pentacarbonyls

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Abstract

Electrochemical behaviour of the transition metal complexes of dichlorogermylene and dihalostannylenes, $(CO)_5M{=}EX_2 \cdot B$ (M = Cr, Mo, W; E = Ge, X = Cl; E = Sn, X = Cl, Br, I; B = THF, dioxane, DMF) has been studied in MeCN at 20°C. Both the reduction and the oxidation processes were found to be irreversible suggesting that the corresponding radical ions were unstable under these conditions; mechanisms of reduction and oxidation of $(CO)_5M{=}EX_2 \cdot B$ were proposed. Electrochemical data obtained show that the electronic structures of $(CO)_5M{=}EX_2 \cdot B$ complexes are similar to those of Fischer transition metal carbene complexes. Cyclic voltammetry data of $(CO)_5M{=}GeCl_2 \cdot B$ (M = Cr, W; B = THF, dioxane, DMF) in DMF solutions clearly testify to the fact that the solvolytic cleavage of M=Ge bond in these complexes takes place leading to $(CO)_5M \cdot DMF$ and $GeCl_2 \cdot DMF$ species formation. The reduction of $GeCl_2 \cdot$ dioxane complex in DMF is discussed. © 1999 Published by Elsevier Science S.A. All rights reserved.

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1. Introduction

The chemistry of transition metal carbene analogue complexes $L_nM{=}EX_2 \cdot B$ (E = Si, Ge, Sn) has been studied extensively in last decade [1–4]. These compounds are of great interest as regards their electronic structure, the nature of metal–metal bond, the mechanisms of their transformations, and the use in the organometallic synthesis; however, the reactivity of these species is still poorly investigated [1–5]. Moreover, the question of special interest is how the complexation with transition metal moieties affects the reactivity and properties (in particular, the redox properties) of carbene analogues—silylenes, germylenes, stannylenes.

Recently we have studied the effect of complexation of dihalogermylenes and dihalostannylenes with Lewis bases on their redox properties [6]. This work is focused on the electrochemical behaviour of transition metal complexes of dichlorogermylene and dihalostannylenes, $(CO)_5M{=}EX_2 \cdot THF$ (M = Cr, Mo, W; E = Ge, X = Cl; E = Sn, X = Cl, Br, I). One should note that the electrochemistry of transition metal carbene analogue complexes has not been studied so far.

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Table 1
Redox potentials of $(CO)_5M{=}EX_2 \cdot B$ in MeCN (platinum electrode, Bu_4NPF_6 as supporting electrolyte, versus Ag | AgCl/KCl (sat.), 20°C)

M	E	X	B	$E_{1/2}$ (ox), V	$-E_{1/2}$ (red), V[a]
Cr	Ge	Cl	THF	1.10 (1e); 1.82 (1.7e)	0.20 (1e); 1.28 (2e)
Mo	Ge	Cl	THF	1.15 (1e); 1.75 (0.65e)	0.17 (1e); 1.11 (2e)
W	Ge	Cl	THF	1.19 (2e)	0.13 (1e); 0.93 (2e)
W	Ge	Cl	DMF	1.22 (2e)	0.14 (1e); 0.98 (2e)
Cr	Ge	Cl	Dioxane	1.09 (1e); 1.82 (1e)	0.21 (1e); 1.31 (2e)
Cr	Sn	Cl	THF	1.25 (1e)	0.03 (1e); 1.97 (2e)
Cr	Sn	Br	THF	1.17 (1e)	−0.03 (1e); 1.75 (2e)
Cr	Sn	I	THF	[b]	−0.09[b]

[a] Positions of the second waves (or peaks in CVA experiments) depend strongly on thoroughness of the electrode surface cleaning; the data presented were obtained on the electrode surface thoroughly cleaned with a diamond paste. [b] Compound is unstable in solutions.

2. Results and discussion

2.1. Reduction in MeCN

Cyclic voltammetry (MeCN, platinum disk electrode, 0.05 M Bu_4NPF_6 as a supporting electrolyte, versus Ag | AgCl/KCl (sat.), 20°C) of $(CO)_5M{=}GeCl_2 \cdot THF$ and $(CO)_5Cr{=}SnX_2 \cdot THF$ complexes shows two irreversible reduction peaks: the first peak corresponds to one-electron, while the second one to the two-electron reduction. The corresponding $E_{1/2}$ (red) values are presented in Table 1.

The first reduction potentials of $(CO)_5M{=}EX_2 \cdot THF$ complexes are shifted by 100–400 mV to the less cathodic region in comparison with the parent carbene analogues $EX_2 \cdot THF$ (see Ref. [6]). This is in agreement with the electron-withdrawing character of $(CO)_5M$ moiety and indicates that in the reduction of $(CO)_5M = EX_2 \cdot B$ the additional electron occupies the redox orbital which is mostly localised at EX_2 ligand. Indeed, the first reduction potentials of $(CO)_5M{=}EX_2 \cdot B$ (B = THF, dioxane) complexes are rather close to the reduction potentials of EX_2 (−0.41 ($GeCl_2 \cdot$dioxane), −0.21 ($SnCl_2$), −0.40 ($SnBr_2$), −0.02 V (SnI_2) [6]) and differ significantly from the reduction potentials of solutions of $M(CO)_6$ (−2.07 to −2.37 V) and $(CO)_5M \cdot MeCN$ (−1.92 to −2.04 V) in acetonitrile [7]. According to the results of MO calculations [8], electrochemical [9], and ESR [10] studies of Fischer carbene complexes, the LUMO is also situated on the carbene ligand in these compounds.

The first oxidation potentials of $(CO)_5M{=}EX_2 \cdot B$ (Table 1) are 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 1.12 V, versus SCE [7]) but differ from the oxidation potentials of EX_2 (1.46 ($GeCl_2 \cdot$dioxane), 1.88 ($SnCl_2$), 1.82 V ($SnBr_2$), [6]). This indicates that the redox orbital involved in the oxidation of $(CO)_5M{=}EX_2 \cdot B$ (which is, evidently, the HOMO) is preferably localised at the transition metal moiety (for other details concerning the oxidation processes see below).

Thus, electrochemical data obtained show that the electronic structures of dichlorogermylene and dihalostannylene complexes of chromium, molybdenum, and tungsten pentacarbonyls are similar to those of Fischer transition metal carbene complexes [8–11].

Previously we have shown that the redox potentials of $GeCl_2 \cdot B$ (B = dioxane, PPh_3, $AsPh_3$, Py, bpy) complexes in MeCN depend on the nature of a Lewis base B [6] indicating that the equilibrium (1) in acetonitrile solutions of $GeCl_2 \cdot B$ is shifted towards the parent complex $GeCl_2 \cdot B$.

$$GeCl_2 \cdot B + MeCN \leftrightarrows GeCl_2 \cdot MeCN + B$$

The E···B bond in transition metal carbene analogue complexes $(CO)_5M{=}EX_2 \cdot B$ is considerably weaker than in $EX_2 \cdot B$ because the empty p-orbital of carbene analogue moiety, participating in E···B bond formation, is partially occupied with d-electrons from metal, M (back donation) [1–5]. Therefore, a base molecule B in $(CO)_5M{=}EX_2 \cdot B$ complexes can be substituted by a solvent molecule, and the equilibrium (1) might be shifted to the right side. Indeed, the data of Table 1 show that the redox potentials of complexes differing by Lewis bases only (e.g. $(CO)_5W{=}GeCl_2 \cdot B$, B = THF, DMF; $(CO)_5Cr{=}GeCl_2 \cdot B$, B = THF, dioxane) is independent of the nature of B in MeCN solutions. It means that a Lewis base (B) of $(CO)_5M{=}GeCl_2 \cdot B$ complexes, can be substituted in MeCN solutions with a solvent molecule:

$$(CO)_5M{=}GeCl_2 \cdot B + MeCN$$

$$\leftrightarrows (CO)_5M{=}GeCl_2 \cdot MeCN + B$$

Obviously, the same transformation of the other $(CO)_5M = EX_2 \cdot B$ complexes occurs in MeCN and, in fact, the redox potentials presented in Table 1 should correspond to acetonitrile complexes $(CO)_5M{=}EX_2 \cdot MeCN$. Similar exchange reactions of B in $(CO)_5M{=}GeCl_2 \cdot B$ complexes with various substrates containing atoms with a lone electron pair B′ (B′ = aldehydes, imines, oximes, nitrosobenzene, DMSO) were used to synthesize a series of new complexes $(CO)_5M{=}GeCl_2 \cdot B'$ [12]. We also applied this method to

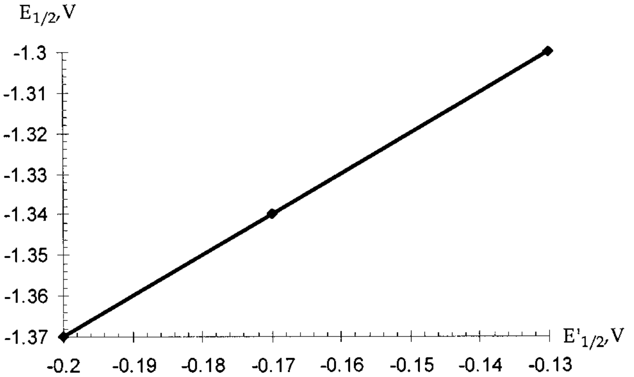


Fig. 1. Correlation between the reduction potentials of $(CO)_5M{=}GeCl_2 \cdot THF$ complexes ($E'_{\frac{1}{2}}$) and the reduction potentials of $(CO)_5M{=}C(OMe)(C_6H_4\text{-}p\text{-}CH_3)$ (M = Cr, Mo, W) carbene complexes ($E_{\frac{1}{2}}$) [9].

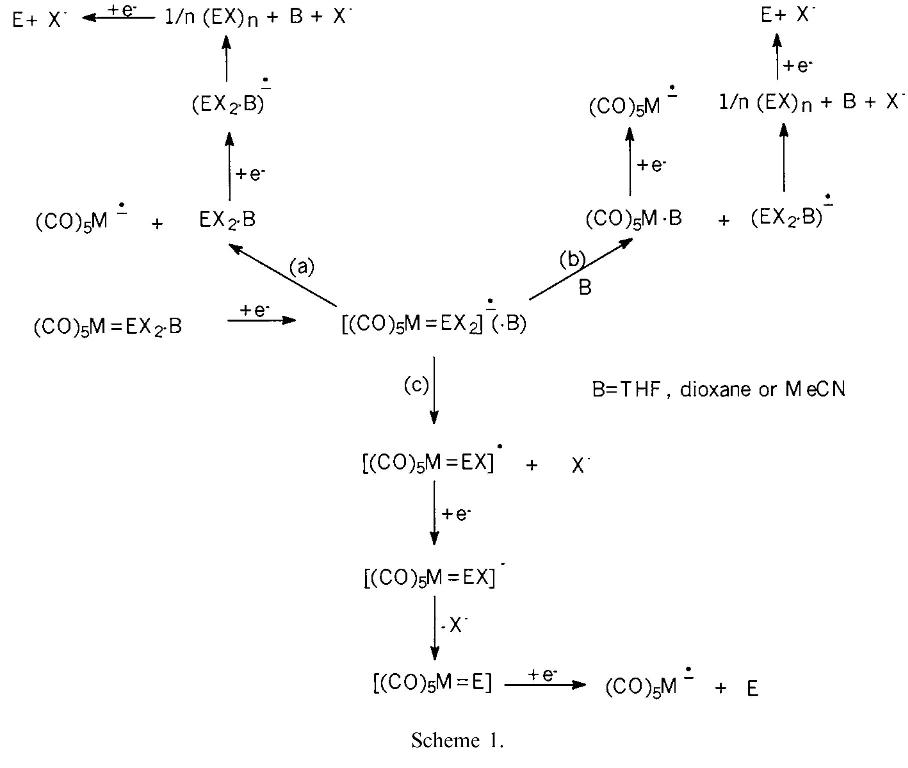
obtain the unknown $(CO)_5W{=}GeCl_2 \cdot DMF$ complex (see Section 3).

The reduction potentials of $(CO)_5M{=}GeCl_2 \cdot THF$ shift gradually to less cathodic region on going from M = Cr to W (see Table 1). The reduction potentials of $(CO)_5M{=}C(OMe)Ar$ [9], $M(CO)_6$ and $(CO)_5M \cdot MeCN$ [7] are changing in a similar order. There is a perfect correlation (the slope is equal to one, Fig. 1) between the reduction potentials of $(CO)_5M{=}GeCl_2 \cdot THF$ complexes and those of the corresponding $(CO)_5M{=}C(OMe)(p\text{-}CH_3C_6H_4)$ (M = Cr, Mo, W) carbene complexes in MeCN (the data for the carbene complexes are taken from Ref. [9]).

This fact shows the similarity of the electrochemical reduction behaviour of the transition metal complexes of carbenes and of their analogues. However, the electrochemical reversibility of these processes are different: the reductions of Fischer alkoxycarbene complexes are quasi-reversible processes in MeCN [9], while their dichlorogermylene analogues are reduced irreversibly in the same solvent suggesting that the corresponding radical anions are unstable in MeCN at 20°C. The lowering of temperature to −40°C does not result in the appearance of the reverse anodic peaks in the cyclic voltammograms. However, the second two-electron wave for E=Ge is bifurcated into two one-electron waves at this temperature. For instance, the second wave for $(CO)_5Cr{=}GeCl_2 \cdot THF$ at $E_{1/2} = -1.28$ V is transformed into two one-electron waves at $E_{1/2} = -1.11$ and -1.58 V, respectively.

Three mechanisms of $(CO)_5M{=}EX_2 \cdot B$ reduction in MeCN solutions can be considered depending on the pathway of fragmentation of radical anions generated at the first step of the reduction (Scheme 1). Each pathway corresponds to the overall transfer of three electrons. Pathways (a) and (b) include the M=E bond cleavage and lead to the formation of $(CO)_5M^{\bullet -}(\cdot B) + EX_2 \cdot B$ or $(CO)_5M \cdot B + EX_2^{\bullet -}(\cdot B)$ species, respectively (B is a Lewis base in the parent complexes or a solvent (MeCN) molecule). Pathway (c) includes an elimination of X^- to produce the radical $[(CO)_5M{=}EX]^{\bullet}$.

The pathway (c) is probably more important for E=Ge. Indeed, if the decomposition of the radical anion



Scheme 1.

$[(CO)_5M{=}EX_2]^{\bullet -}$ occurs according to path (a) one could expect the appearance of the reduction wave of $GeCl_2 \cdot B$ complex at ca. − 0.4 V [6] or a two-electron wave at − 0.2 to − 0.4 V corresponding to the simultaneous reduction of $(CO)_5M{=}GeCl_2 \cdot B$ and the product of its reductive fragmentation, the $GeCl_2 \cdot B$ complex. However, this is not the case (see Table 1). We failed to detect the reduction waves of $(CO)_5M \cdot MeCN$ complexes in the region − 1.92 to − 2.04 V [7] which should be observed if the decomposition takes place according to the pathway (b).

In the case when the decomposition of $[(CO)_5M{=}GeCl_2]^{\bullet -}$ radical anions occurs through the pathway (c) the second wave corresponding to the reduction of radical $[(CO)_5M{=}GeCl]^{\bullet}$ can appear. Indeed, we detected the second two-electron waves at − 0.92 to − 1.28) V in all cases (see Table 1).

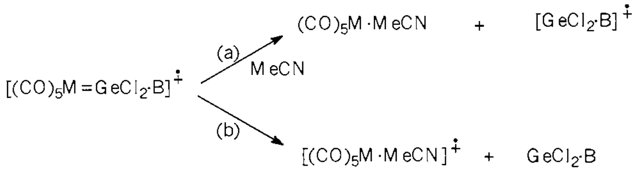
The reduction of $[(CO)_5M{=}GeCl]^{\bullet}$ radical can occur via the ECE mechanism. The first (electrochemical, E) step results in $[(CO)_5M{=}GeCl]^-$ anion formation. The anion eliminates Cl^- in the second (chemical, C) step producing a neutral species $[(CO)_5M{=}Ge]$ which can be reduced further to $[(CO)_5M]^{\bullet -}$ radical anion and Ge_{met}. In fact, we always observed the formation of a black film of Ge_{met}, on the surface of the working Pt-electrode at the end of the prolonged electrolysis at − 2.0 V.

When the chemical step is fast and the standard electrochemical potential of $[(CO)_5M{=}E]$ is less anodic than $[(CO)_5M{=}EX]$, the overall two-electron wave appears, as it takes place in the experiments at 20°C. At lower temperature (− 40°C) the rate of the chemical reaction decreases and the reduction occurs as a two-step process. Thus, the bifurcation of the second two-electron wave in the reduction of $(CO)_5M{=}GeCl_2 \cdot B$ can be related to the ECE mechanism.

The second waves of the reduction of dihalostannylene complexes $(CO)_5Cr{=}SnX_2 \cdot B$ unlike dichlorogermylene complexes (see Table 1) could correspond to the reduction of $(CO)_5Cr \cdot MeCN$ species because their potentials are rather close to those of $(CO)_5Cr \cdot MeCN$ (− 1.92 V [7]). Thus, the reduction of $(CO)_5Cr{=}SnX_2 \cdot THF$ complexes can occur through the path (b) (Scheme 1).

2.2. Oxidation in MeCN

The polarisation curve pattern for the oxidation of $(CO)_5M{=}EX_2 \cdot B$ depends on the nature of metal M as well as element E (Table 1). Two waves are observed for $(CO)_5Cr{=}GeCl_2 \cdot B$ with the first wave being one-electron. Only one wave was detected for both the $(CO)_5W{=}GeCl_2 \cdot THF$ and $(CO)_5Cr{=}SnX_2 \cdot THF$ complexes. In the case of $(CO)_5Mo{=}GeCl_2 \cdot THF$ complex one two-electron or two one-electron waves were detected depending on the experimental conditions. We believe that the reason why the second waves are not observed in each case is related to the electrode surface passivation by the reaction products. It should be noted that only one wave was found for the oxidation of carbene complexes $(CO)_5M{=}C(X)Y$ (M = Cr, W) [13].



Scheme 2.

Oxidation potentials corresponding to the first waves shift to the more anodic area on going from M = Cr to W. The first ionisation potentials of the corresponding metals M [14] increase in the same order; moreover, there is a correlation between these parameters.

The mechanism of electrochemical oxidation of $(CO)_5M{=}CXY$ (M = Cr, Mo, W) complexes has not been studied in details [13]. The following scheme was suggested for oxidation of $M(CO)_6$ [15]:

$$M(CO)_6 \xrightarrow{-e^-} M(CO)_6^+ \xrightarrow{\cdot Disp.} M(CO)_6^{2+} + M(CO)_6$$

The key step of this mechanism is the disproportionation of the initially formed radical cation.

The oxidation pattern of $(CO)_5Cr{=}GeCl_2 \cdot B$ differs from that of $(CO)_5W{=}GeCl_2 \cdot B$. The difference can not be explained in terms of the disproportionation of initially formed radical cation. As an alternative we suggest a scheme including different pathways for the radical cation fragmentation. Since in the compounds containing a metal–metal bond the latter is usually the weakest one we assume that it is the bond that will be cleaved during fragmentation of radical cations. Two pathways of fragmentation can be considered (Scheme 2).

We believe that the pathway (a) is realised when M = W. Indeed, in this case $(CO)_5W \cdot MeCN$ complex formed has the same oxidation potential (1.12 V [7]) as that of $(CO)_5W{=}GeCl_2 \cdot THF$ resulting in a two-electron wave which in fact was observed experimentally. The fragmentation pathway (b) probably takes place when M = Cr and E = Ge, Sn. The complex $(CO)_5$-$Mo{=}EX_2 \cdot THF$ has an intermediate position in fragmentation pathways between chromium and tungsten complexes. The fragmentation of this complex can occur according to pathway (a) or pathway (b) or both of them simultaneously depending on experimental conditions. Values of the first ionisation potentials of M metals (see Ref. [14]) confirm a tendency to form cations on going from Cr to Mo and, especially, W. The experimental data available does not allow us to interpret the second wave of $(CO)_5M{=}GeCl_2 \cdot B$ oxidation which is observed for Cr complex and sometimes for Mo one.

2.3. *Electrochemistry of $(CO)_5M{=}GeCl_2\cdot B$ (M = Cr, W; B = THF, dioxane, DMF) and $GeCl_2\cdot$ dioxane complexes in DMF*

The electrochemical behaviour of $(CO)_5M{=}GeCl_2\cdot B$ (M = Cr, W; B = THF, dioxane, DMF) and $GeCl_2\cdot$dioxane complexes in DMF differ significantly from that in MeCN. Indeed, the first and the second reduction potentials of the complexes are independent on the nature of transition metal M and Lewis base B and have the same values as those of $GeCl_2\cdot$dioxane complex in DMF (Table 2). The CVA recorded for the complex $(CO)_5M{=}GeCl_2\cdot DMF$ is in fact a superposition of CVAs for the reduction of $GeCl_2\cdot$dioxane and $(CO)_5W$ DMF complexes in DMF solutions (see Fig. 2).

Therefore the $(CO)_5W{=}GeCl_2\cdot DMF$ dissociates in a highly solvated solvent (DMF) at low concentrations to $(CO)_5W\cdot DMF$ and $GeCl_2\cdot DMF$ species with W=Ge bond cleavage (Eq. (4)). Evidently, the other $(CO)_5M{=}GeCl_2\cdot B$ complexes dissociate in a similar manner (e.g. $(CO)_5Cr{=}GeCl_2\cdot$dioxane; see Table 2):

$$(CO)_5M{=}GeCl_2\cdot DMF \overset{DMF}{\leftrightarrows} (CO)_5M\cdot DMF + GeCl_2\cdot DMF \qquad (4)$$

To our knowledge, this is the first experimental evidence of solvolitic M=E bond cleavage in carbene analogue transition metal complexes.

Since $(CO)_5M{=}GeCl_2\cdot B$ exists in DMF essentially as a mixture of $(CO)_5M\cdot DMF$ and $GeCl_2\cdot DMF$ complexes the peculiarities of electrochemical behaviour of the latter species in DMF was also studied. The reduction of $GeCl_2\cdot DMF$ shows two cathodic and one anodic peaks on CVA. The first cathodic peak (−0.53 V) has a diffusion-controlled nature as it follows from a linear dependence between its height and $v^{0.5}$ (v is a potential scan rate). The position of the peak is independent of the temperature or the scan rate. The CVA is completely reproducible during the repeat scans. For the first reduction step, the height of the forward cathodic and its back anodic peaks are the same ($i_{pa}/i_{pc} = 1$) at temperatures from 20 to −40°C, however, their potentials differ significantly: the $\Delta E_p = E_{pa} - E_{pc}$ value is ca. 260 mV. This fact means that (i) either the reduction is chemically reversible, but a thermodynamically irreversible process (because the charge transfer is slow in the CV time scale), or (ii) the return anodic peak does not correspond to the oxidation of the radical anion initially formed from $GeCl_2\cdot DMF$ but to

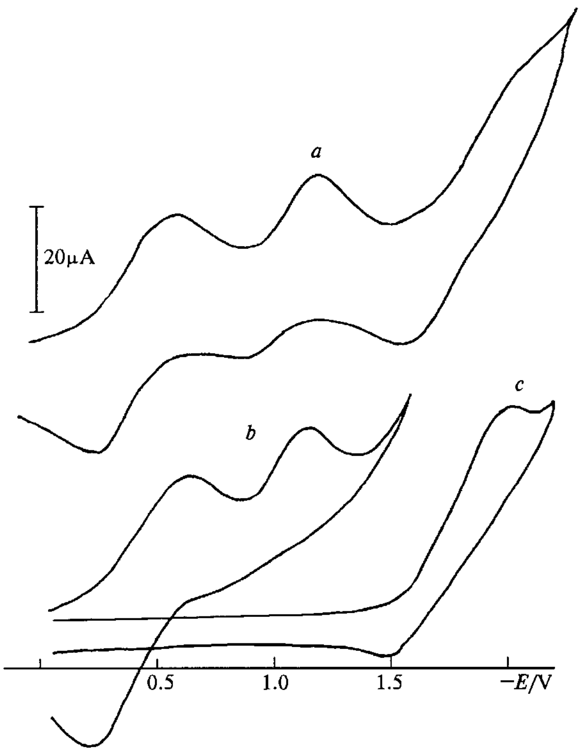


Fig. 2. Cyclic voltammogram for reduction of $(CO)_5W{=}GeCl_2\cdot DMF$ (a), $GeCl_2\cdot$dioxane (b), and $(CO)_5W\cdot DMF$ (c), in DMF at 20°C (Pt electrode, $c = 10^{-3}$ M, $v = 200$ mV s^{-1}).

Table 2

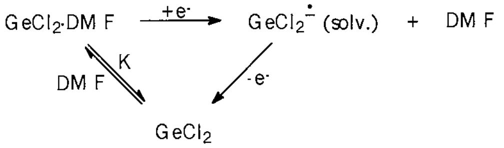
Reduction potentials of $(CO)_5M{=}GeCl_2\cdot B$ (M = Cr, W) and $GeCl_2\cdot$dioxane complexes in DMF (platinum electrode, Bu_4NPF_6 as supporting electrolyte, versus Ag | AgCl/KCl (sat.), 200 mV s^{-1}, 20°C)

Compound	$-E_{1/2}$ (red)/V	$-E_{pc}$/V	$-E_{pa}$/V	i_{pa}/i_{pc}
$GeCl_2\cdot$dioxane	0.44 (1e)	0.53	0.27	1
	1.24−1.54[a] (1e)	1.10	0.79	0.5
$(CO)_5W{=}GeCl_2\cdot DMF$	b	0.51, 1.10	0.28; 0.80	1; 0.5
		1.86	1.80[c]	0.1
$(CO)_5W\cdot DMF$	b	1.86	1.80[c]	0.1
$(CO)_5W{=}GeCl_2\cdot THF$	0.48 (1e)	0.51	0.29; 0.80	1
	1.23 (1e)	1.11		0.5
$(CO)_5Cr{=}GeCl_2\cdot$dioxane	0.51 (1e)	0.51, 1.19	0.26	0.8
	1.26 (1e)		0.80	0.4

[a] Depending on the electrode surface cleaning.

[b] The waves are not well-expressed.

[c] At −40°C.



Scheme 3.

some other species which can be reduced to the parent complex or to the compound which has the same reduction potential. We believe, that the second explanation is preferable. It can be illustrated by Scheme 3.

According to Scheme 3 the reduction of $\mathrm{GeCl_2 \cdot DMF}$ is accompanied by the loss of a coordinated DMF molecule. The solvated $\mathrm{GeCl_2}^{\bullet-}$ species is oxidised at the reverse scan to give a neutral dichlorogermylene which forms a complex with a DMF molecule again.

Fig. 3 explains the high ΔE_p value (ca. 260 mV) in terms of Scheme 3 which exceeds considerably the theoretical value for thermodynamically reversible redox pair (58 mV at 20 °C).

Curve a with the cathodic peak a_c and the anodic peak a_a corresponds to the reversible redox pair of dichlorogermylene which does not contain a Lewis base ($\mathrm{GeCl_2/GeCl_2^{\bullet-}}$). Curve b with the cathodic peak b_c and the anodic peak b_a corresponds to the reversible redox pair $\mathrm{GeCl_2 \cdot DMF/(GeCl_2 \cdot DMF)^{\bullet-}}$. Curve b is shifted to the cathodic area relative to curve a because the complexation of $\mathrm{EX_2}$ (E = Ge, Sn; X = Hal) with Lewis bases (DMF) is known to shift the reduction potential to a more cathodic value on one hand, and facilitate the oxidation of the radical anion formed on the other hand [6]. The distance between peaks a_a/a_c and b_a/b_c is 58 mV. If the equilibrium (5) occurs quickly, two peaks of the same heights (b_c and a_a) will be seen on the CVA curve.

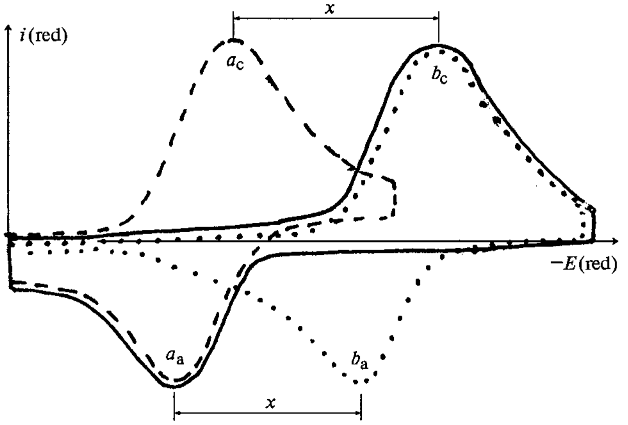


Fig. 3. Illustration of quasi-reversibility of the system described by Scheme 3 (solid line) based on schematic representation of voltammograms for redox pairs $\mathrm{GeCl_2/GeCl_2^{\bullet-}}$ (- - - -), $\mathrm{GeCl_2 \cdot B/(GeCl_2 \cdot B)^{\bullet-}}$ (….) (details are given in the text).

$$\mathrm{GeCl_2 \cdot DMF} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{GeCl_2} + \mathrm{DMF} \qquad (5)$$

$$K = k_1/k_{-1}$$

The distance between the peaks is ($x + 58$) mV. The x value depends on the equilibrium constant K. Experimentally observed x value is ca. 200 mV. Using the known [16] equation ($\Delta E = E°(\mathrm{GeCl_2}) - E°(\mathrm{GeCl_2 \cdot DMF}) = RT/nF \ln K$, where $n = 1$ and $\Delta E = 200$ mV) one can estimate the K value: $K = 2.1 \times 10^3$ mol $\mathrm{l^{-1}}$. The estimated value is in good agreement with equilibrium formation constants K of dichlorogermylene complexes with other Lewis bases ($\mathrm{GeCl_2 \cdot EPh_3^{\bullet}}$; E = P, As) determined earlier by electrochemically ($\mathrm{K(GeCl_2 \cdot PPh_3) = 7 \times 10^3}$, $\mathrm{K(GeCl_2 \cdot AsPh_3) = 2 \times 10^4}$) [6] and spectrophotometrically ($\mathrm{K(GeCl_2 \cdot PPh_3) = 2 \times 10^3}$ mol $\mathrm{l^{-1}}$, 23°C, n-$\mathrm{Bu_2O}$) [18].

3. Experimental

Solvents were dried and distilled under Ar. MeCN was distilled over $\mathrm{CaH_2}$ and DMF was purified by successive refluxing and distillation in vacuo over $\mathrm{CaH_2}$, $\mathrm{K_2CO_3}$, and anhydrous $\mathrm{CuSO_4}$. The ^{1}H-NMR spectra were recorded on a Bruker AC 200 spectrometer (200 MHz). The mass-spectra were recorded on a Finnigan MAT INCOS 50 instrument.

Electrochemical measurements were performed under Ar on a PI-50-1 potentiostat, using a platinum electrode (diameter 2.8 mm) and $\mathrm{Bu_4NPF_6}$ (Fluka) as a supporting electrolyte. Potentials reported were measured versus Ag | AgCl/KCl (sat.) with IR-compensation; the reference electrode had the potential − 0.43 V versus $\mathrm{Fc/Fc^+}$ pair in MeCN. The numbers of electrons in the electrochemical processes were determined on platinum rotating disk electrode by the comparison of a wave height with that for the oxidation of ferrocene of the same concentration. During the reduction of $\mathrm{(CO)_5M{=}GeCl_2 \cdot B}$ the electrode surface was found to be coated with a dark-grey film. On such coated surface the voltammograms have different pattern compared to non-coated ones and an anodic peak disappears for quasi-reversible processes. Therefore before a polarisation curve was taken, the surface of platinum electrode was thoroughly cleaned with diamond paste, washed with water, acetone and dried.

The $\mathrm{(CO)_5M{=}EX_2 \cdot B}$ complexes were obtained by the reaction of $\mathrm{GeCl_2 \cdot}$ dioxane or $\mathrm{SnX_2}$ (X = Cl, Br, I) with photochemically generated species $\mathrm{(CO)_5M \cdot THF}$ (THF, 20°C) according to the known procedure [17]; their melting points and IR spectral data were in accordance with the published ones (see Ref. [1]).

The $\mathrm{(CO)_5W{=}GeCl_2 \cdot DMF}$ complex was obtained by exchange reaction using the procedure described in Ref. [12]. DMF (0.08 ml, 1.03 mmol) was added to a suspension of 540 mg (1 mmol) of the $\mathrm{(CO)_5W{=}GeCl_2 \cdot THF}$

complex in hexane (10 ml) at 0°C. The reaction mixture was stirred at room temperature for 72 h. A dark green precipitate formed and was filtered off, washed with hot hexane and dried in vacuo. Crystals of $(CO)_5W{=}GeCl_2 \cdot DMF$ (480 mg, 0.89 mmol) were isolated in an 89% yield; m.p. 91–93°C. ^{1}H-NMR (CD_3CN, δ): 3.18 (s, 3H), 3.30 (s, 3H), 8.34 (s, 1H); MS (EI, 70 eV), *m/e* 540 $[M^+]$, 505 $[(M-Cl)^+]$, 467 $[(M-DMF)^+]$, 433 $[(M-DMF-2Cl)^+]$.

The $(CO)_5W \cdot DMF$ complex was generated by UV-irradiation (high pressure Hg lamp, 1000 W) of a DMF solution of $W(CO)_6$ in Ar atmosphere according to the procedure described in Ref. [19].

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