Russian Chemical Bulletin, International Edition, Vol. 50, No. 11, pp. 2071—2077, November, 2001 2071

Electrochemical study of redox properties of 2,3,4,5-tetraphenyl-1-heterocyclopenta-2,4-dienes $Ph_4C_4ER^1R^2$ (E = Si, Ge, Sn). A new method for generation of tetraphenylgermole dianion

A. A. Moiseeva,[a] R. D. Rakhimov,[a] E. K. Beloglazkina,[a] K. P. Butin,[a]
K. S. Nosov,[b] V. Ya. Lee,[b] and M. P. Egorov[b]*

[a]M. V. Lomonosov Moscow State University, Chemistry Department,
119899 Moscow, Leninskie gory, Russian Federation.
Fax: (095) 939 5546. E-mail: butin@org.chem.msu.su
[b]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: (095) 135 5328. E-mail: mpe@cacr.ioc.ac.ru

The electrochemical behavior of the sila-, germa-, and stannacyclopentadienes (metalloles) was studied by cyclic voltammetry. The oxidation and reduction mechanisms of these heterocyclic compounds were investigated. A new method for generation of tetraphenylgermole dianion involving the electrochemical reduction of the corresponding dichlorogermole is proposed. Electrochemical oxidation of the metallole dianions was first studied taking tetraphenylgermole dianion as an example.

Key words: silacyclopentadienes, germacyclopentadienes, stannacyclopentadienes, metalloles, metallole dianions, electrochemistry.

The structure and reactivity of heteroanalogs of cyclopentadiene, namely, 1-sila-, 1-germa-, and 1-stannacyclopentadienes (metalloles)[1,2] and the aromaticity of their mono- and dianions[3] have attracted increasing interest. A salient feature of the electronic structure of metalloles is low-lying LUMO. This is due to σ^*—π^* conjugation and allows these compounds to exhibit some useful properties. Recently,[4,5] it was found that metallole and, first of all, silole derivatives are promising materials for fabrication of conducting or semiconductor devices. For instance, homopolymeric poly-2,5-siloles that are structurally similar to *trans-s-cis*-polyacetylenes (organic conductors) have been the subject of intensive research (see, *e.g.*, Ref. 6 and references cited therein).

Up to now, studies of the redox processes with participation of metalloles are fragmentary. In particular, information on the electrochemical properties of metalloles is scarce and sometimes contradictory.[7—11] Therefore, the aim of this work was to carry out a systematic investigation of the redox properties of a large group of 2,3,4,5-tetraphenylsiloles (germoles, stannoles) in MeCN and THF solutions at a glassy-carbon (GC) electrode and to develop a novel, electrochemical approach to the generation of metallole dianions.

Results and Discussion

The electrochemical oxidation and reduction potentials of metalloles $Ph_4C_4ER^1R^2$ (E = Si, Ge, Sn) **1—3** and 1,2,3,4-tetraphenylcyclopentadiene, $Ph_4C_4CH_2$, obtained by cyclic voltammetry (CV) technique are listed in Table 1. Most of the compounds studied are irreversibly oxidized in three stages. The first two of them are one-

Table 1. Potentials of reduction (E_p^{red}) and oxidation (E_p^{ox}) peaks of 2,3,4,5-tetraphenylmetalloles $Ph_4C_4ER^1R^2$ in MeCN (with 0.05 *M* Bu_4NBF_4 as the supporting electrolyte, at a glassy-carbon electrode, 200 mV s^{-1}, *vs.* Ag/AgCl/KCl (sat.))

Compound	ER^1R^2	$-E_p^{red}$/V	E_p^{ox}/V
1a	SiH_2	1.98, 2.30	1.29, 1.47, 1.81
1b	$SiMe_2$	2.14, 2.47	1.35, 1.74, 2.33
1c	$SiCl_2$	2.00, 2.33	1.46, 1.81, 2.16
2a	GeH_2	1.73, 2.46	1.39, 1.54, 2.11
2b	$GeMe_2$	1.90, 2.39	1.29, 1.52, 1.96
2c	Ge(*cyclo*-C_3H_5)$_2$	2.07, 2.39	1.34, 1.75, 2.29
2d	$Ge(SiMe_3)_2$	2.40[a]	1.12, 1.51, 2.04
2e	$Ge(GeEt_3)_2$	2.22, 2.70	1.14, 1.38, 1.65, 1.86, 2.33
2f	$Ge(SnMe_3)_2$	1.97, 2.51	1.09, 1.28, 1.62, 1.82
2g	GeMeH	1.96, 2.74	1.36, 1.63, 2.15
2h	GeMeCl	1.70, 2.52	1.49, 1.79, 2.06
2i	$GeCl_2$	1.31, 2.65	1.65, 1.84, 2.23
3a	$SnMe_2$	2.01, 2.51, 2.72	1.23, 1.49, 1.72
3b	$SnPh_2$	1.93[a]	1.35, 1.74, 2.05
3c	$SnBr_2$	0.72, 1.56, 2.34	1.84[b]
4	CH_2	2.07	1.10, 1.37, 1.86
5	—	2.04, 2.63	1.40, 1.62, 2.26

[a] At a Pt electrode.
[b] 1.5-Electron peak.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 1980—1985, November, 2001.

1066-5285/01/5011-2071 $25.00 © 2001 Plenum Publishing Corporation

electron stages ($n_e = 1$), and the third stage corresponds to transfer of nearly two electrons (the experimentally found n_e values vary between 1.4 and 2). The exception is the oxidation of germoles **2e** and **2f** with the trialkylgermyl and trialkylstannyl substituents at the heteroatom, respectively, and compound **3c**. They are oxidized in five (**2e**), four (**2f**), and one stage (only one anodic peak corresponding to $n_e = 1.5$ was observed for **3c**).

Metalloles **1—3** are usually reduced in two one-electron stages; however, a third peak was observed at high cathodic potentials for stannoles **3a** and **3c**. The reduction of dihalometalloles **1c** and **2i** involves two two-electron stages. Stannole **3c** is oxidized in three stages, and the first two of them also correspond to transfer of two electrons. According to CV data in MeCN, all the redox transitions studied are electrochemically and chemically irreversible.

Since the tetraphenylbutadiene fragment is common to all the compounds studied in this work, we investigated the electrochemical behavior of (*E,E*)-1,2,3,4-tetraphenylbuta-1,3-diene (**5**). The shapes and potentials of three oxidation and two reduction peaks in the CV curves for this compound are close to those of the corresponding peaks in the CV curves recorded under the same conditions (MeCN, with 0.05 *M* Bu_4NBF_4 as the supporting electrolyte) for most of tetraphenylmetalloles and, in particular, tetraphenylgermoles (see Table 1). This suggests that the tetraphenylbutadiene fragment has strong effect on the electrochemical behavior of metalloles **1—3**. Nevertheless, the nature of the heteroatom (E) and substituents (R^1, R^2) at the E atom also affects the redox properties of metalloles.

From the data listed in Table 1 it can be seen that the reduction of compounds $Ph_4C_4EH_2$ occurs more easily in the order of E elements: C < Si < Ge. The electron affinity calculated in the B3LYP/6-31G(d)//AM1 approximation also increases on going from $Ph_4C_4CH_2$ to the silicon- and germanium-containing analogs.[12] The effect of substituents at the heteroatom on the reduction potentials can be followed taking substituted germoles as examples. Here, the reduction potentials increase in absolute value in the order of substituents: Cl, Cl < Cl, Me < H, H < Me, Me < $SnMe_3$, $SnMe_3$ < *cyclo*-C_3H_5, *cyclo*-C_3H_5 < Et_3Ge, Et_3Ge < Me_3Si, Me_3Si. The potentials of the first oxidation peaks of germoles also depend on the nature of substituents R^1, R^2 and increase in the order Me_3Sn, Me_3Sn < Me_3Si, Me_3Si < Et_3Ge, Et_3Ge< Me, Me < *cyclo*-C_3H_5, *cyclo*-C_3H_5 < H, Me < Cl, Me < H, H < Cl, Cl. A clearly seen correlation is observed between the reduction (oxidation) potentials of germoles **2** and the sum of the σ* Taft constants of substituents R^1 and R^2 (Fig. 1)

$$-E_p^{red} = -0.14 \cdot \Sigma\sigma^* + 2.07, \quad r^2 = 0.95;$$

$$E_p^{ox} = -0.08 \cdot \Sigma\sigma^* + 1.28, \quad r^2 = 0.98.$$

The results of 2D NMR studies of germoles **2** also point to the inductive nature of the effect of substituents R^1 and R^2 on the electron density distribution in germoles.[13]

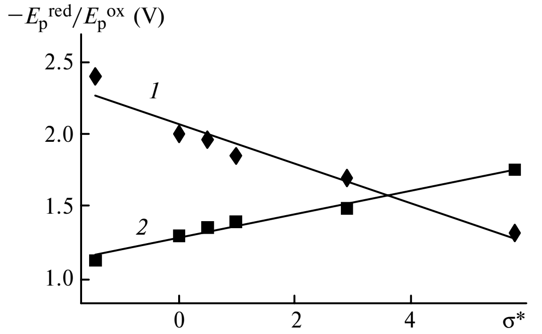


Fig. 1. Plots of $-E_p^{red}$ (*1*) and E_p^{ox} (*2*) for germoles $Ph_4C_4GeR^1R^2$ as functions of the sum of the σ* Taft constants of substituents R^1 and R^2.

The text below contains a more detailed consideration of the reduction and oxidation of metalloles.

1. Reduction

1.1. Reduction of compounds $Ph_4C_4EH_2$ (E = C, Si, Ge)

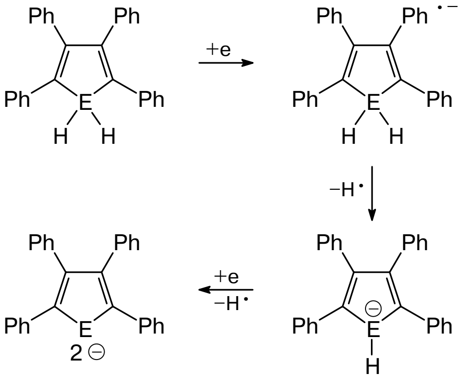
Up to now, the electrochemical studies of these compounds were reduced to 1,2,3,4-tetraphenylcyclopentadiene (**4**)[14] and cyclopentadiene.[15] At transition-metal (Fe, Pt, Ni, Co, V, Cu, Cr) electrodes, cyclopentadiene is reduced at high cathodic potentials (from −1.92 to −2.36 V in MeCN). Electrolysis of cyclopentadiene is accompanied by hydrogen gas evolution. According to coulometric studies, this reaction has a one-electron character.[15] Experiments on the reduction of cyclopentadiene at a rotating disk-ring electrode revealed an anodic oxidation wave of $C_5H_5^-$ anion at −0.32 V. Electrolysis of cyclopentadiene in a one-compartment cell with a soluble Fe anode results in ferrocene as the main product. The mechanism proposed[14] for the electrochemical reduction of cyclopentadiene **4** in DMF involves transfer of hydrogen atoms from the initial **4** to the radical anion $\mathbf{4}^{\bullet -}$. At temperatures below −30 °C, compound **4** is reduced in anhydrous solvents in two one-electron quasi-reversible (chemically reversible) stages to give (most likely) a dianion. However, at higher temperatures the CV patterns become more complicated due to the above-mentioned reaction:

$$Ph_4C_5H_2^{\bullet -} + Ph_4C_5H_2 \rightleftharpoons Ph_4C_5H_3^{\bullet} + Ph_4C_5H^-.$$

Only one reduction peak of **4** in MeCN was observed under conditions of our room-temperature experiments (see Table 1). Two one-electron irreversible peaks were observed for the reduction of corresponding silole **1a** and germole **2a**. The mechanism of electrochemical reduction of **1a** (**2a**) can be described by Scheme 1.

Irreversibility of the first stage of the reduction points to extremely short lifetimes of radical anions $\mathbf{1a}^{\bullet -}$ and

Scheme 1



E = Si, Ge.

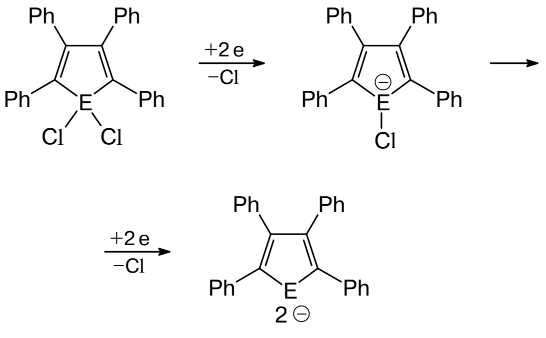
$2b^{\bullet-}$. Direct experimental proofs of the existence of these radical anions were recently obtained using optical detection of ESR spectra.[16] The lifetimes of $1a^{\bullet-}$ and $2b^{\bullet-}$ in decane were estimated to be of the order of several nanoseconds at 20 °C, which means that these radical anions cannot be detected in the CV time scale.

Scheme 1 is in good agreement with the known fact[17] that the action of alkali metals on compounds **1a** and **2b** in THF results in liberation of H_2 and formation of metallole dianions as the end products.

1.2. Reduction of dihalometalloles $Ph_4C_4EHal_2$ (E = Si, Ge, Sn; Hal = Cl, Br). Electrochemical generation of 2,3,4,5-tetraphenylgermole dianion

Dichlorosilole **1c** and dichlorogermole **2i** are reduced in two two-electron irreversible stages (Scheme 2). This corresponds to successive elimination of two Cl^- anions and the formation of mono- and dianions of the corresponding metalloles (the highly labile radical anion $2i^{\bullet-}$ was detected only by OD ESR spectroscopy.[16])

Scheme 2



6a,b

E = Si (**a**), Ge (**b**).

Intermediate formation of a monoanion is confirmed by the fact that an additional reduction peak of the monoalkylation product appears in the CV curve (at −1.72 V) when dichlorogermole **2i** is reduced in MeCN in the presence of Bu^nI. The potential of this peak virtually coincides with the reduction potential of chloroalkylgermole **2h** (see Table 1). We failed in detecting dianion **6b** using analogous procedure, since it is formed at such negative potentials at which the alkylating agent (Bu^nI) is reduced.

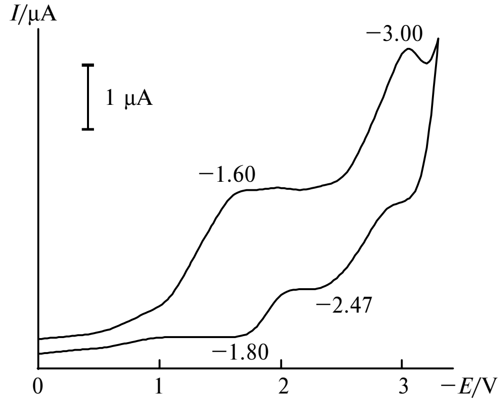


Fig. 2. A cyclic voltammogram of the solution of dichlorogermole **2i** ($1 \cdot 10^{-3}$ mol L^{-1}) in THF, with 0.1 *M* Bu_4NClO_4 as the supporting electrolyte. The potential scan rate was 200 mV s^{-1} (20 °C).

Since the dianion **6b** is less stable in MeCN than in THF, we studied the reduction of dichlorogermole **2i** in THF. The CV data for compound **2i** in THF (Fig. 2) show that two anodic peaks with different heights appear in the CV curve when the potential is back scanned. Taken together, the peaks correspond to a two-electron oxidation of the product that formed in the second reduction stage. Assuming the germole dianion **6b** to be this product, the anodic peaks at −2.47 and −1.80 V must correspond to successive oxidation of **6b**.

To confirm this assumption, we first studied the electrochemical oxidation of the metallole dianion taking **6b**, obtained by the action of four equivalents of metallic lithium in THF on dichlorogermole **2i**, as an example. The CV curve (Fig. 3) for the oxidation of **6b**

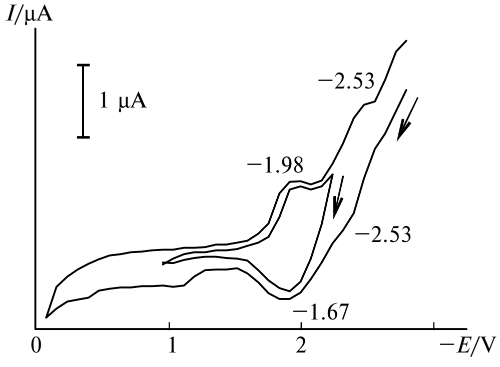
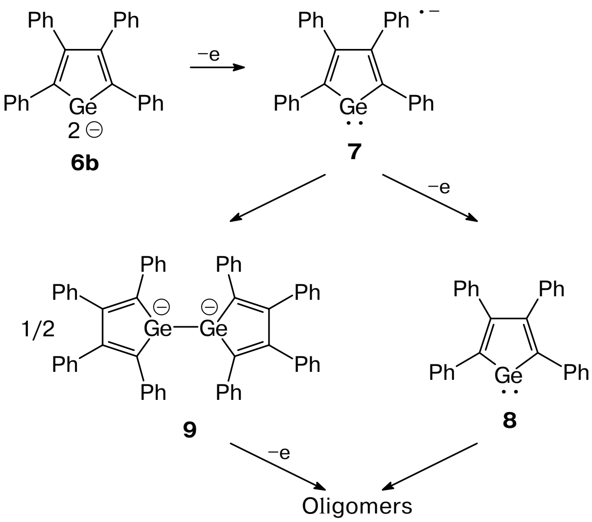


Fig. 3. Cyclic voltammograms of a 10^{-3} *M* $Ph_4C_4GeLi_2$ solution in THF, with 0.1 *M* Bu_4NClO_4 as the supporting electrolyte. The potential scan rate was 200 mV s^{-1} (20 °C).

also exhibits two oxidation peaks at −2.53 and −1.67 V, whose potentials are close to those of the anodic peaks in the CV curve of dichloride **2i** (−2.47 and −1.80 V, respectively). Slight differences between these curves seem to be due to the nature of the counterion (Li^+ or Bu_4N^+). The most plausible oxidation mechanism of dianion **6b** is presented in Scheme 3.

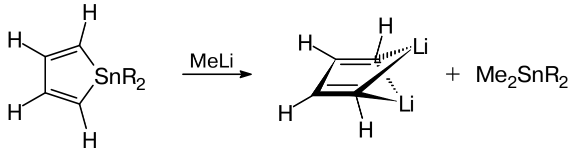
Scheme 3



The first stage of the oxidation results in the germylene radical anion **7**, which then either is oxidized to germylene **8** or, similarly to other germylene radical anions, undergoes a dimerization[18] into dianion **9**. The oxidation of **9** leads to oligomeric products. The existence of dianions of the type **9** was confirmed by their synthesis by the reduction of dihalogermoles and dihalosiloles with three equivalents of metallic potassium in THF.[19—22]

The formation of tetraphenylgermole dianion in the electrochemical reduction of its dihalo derivative is a new method for generation of metallole dianions.

In contrast to **1c** and **2i**, reduction of dibromostannole **3c** proceeds in three stages. The first two two-electron stages probably involve cleavage of the Sn—Br bonds. However, this can hardly result in the stannole dianion as the end product of the reduction of **3c**. Stannole dianions have not been reported as yet. In addition, the results of a study of the reduction of 1,1-dialkylstannoles with methyllithium showed that these compounds are prone to elimination of the organotin fragment to give a dilithium salt of butadiene[22]:



The third peak (at −2.34 V) in the CV curve of **3c** can originate from the reduction of the ring opening product and it is observed at more negative potentials than that of the cathodic peak of tetraphenylbutadiene **5** (−2.04 V). Indeed, the reduction potential of, *e.g.*, (1,2,3,4-tetraphenylbuta-1,3-dienyl)dimethyltin chloride is −2.25 V.[10] Cleavage of the carbon—tin bond can occur already at the early reaction stages. This is indicated by the results of our PM3 calculations of the geometry of tetraphenylstannole radical anion. For comparison, we performed analogous calculations for compounds $Ph_4C_4EH_2$ (E = C, Si Ge, Sn) and their radical anions (Table 2).

Table 2. Selected geometric parameters of molecules $Ph_4C_4EH_2$ (E = C, Si Ge, Sn) and their radical anions obtained from PM3 calculations and X-ray diffraction study

E	Method	Bond length/Å			Bond angle /deg		
		E—C(2)	C(2)—C(3)	C(3)—C(4)	C(2)—E—C(5)	E—C(2)—C(3)	C(2)—C(3)—C(4)
				$Ph_4C_4EH_2$			
C	PM3	1.506	1.363	1.472	104	109	109
	X-ray analysis	(1.496)	(1.366)	(1.478)	(104)	(109)	(109)
Si	PM3	1.849	1.352	1.484	92	108.1	115.8
	X-ray analysis[a]	(1.865)	(1.358)	(1.511)	(92.6)	(107.5)	(116)
Ge	PM3	1.922	1.346	1.477	90.9	106.5	118
	X-ray analysis[b]	(1.921)	(1.356)	(1.507)	(90.9)	(107.4)	(117.5)
Sn	PM3	2.143	1.344	1.483	83	108	120
	X-ray analysis[c]	(2.126)	(1.352)	(1.511)	(84.6)		
				Radical anions $Ph_4C_4EH_2^{\cdot -}$			
C	PM3	1.506	1.412	1.417	105	107	110
Si	PM3	1.843	1.399	1.421	95	105	117.5
Ge	PM3	1.919	1.392	1.418	93	104.5	119
Sn	PM3	2.279	1.363	1.457	78	109	121
	PM3	2.201	1.370			112	120

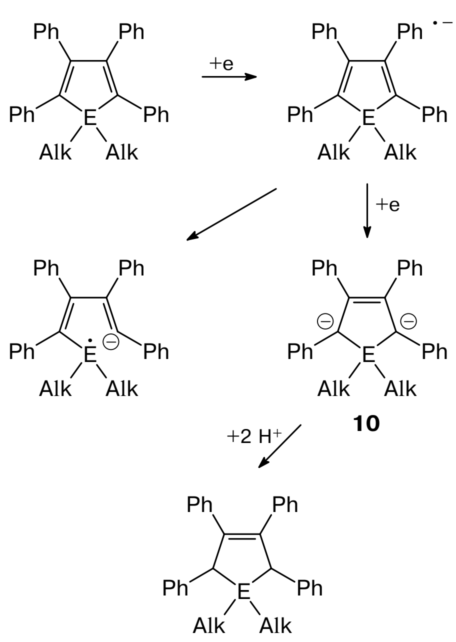
[a] For 1,1-dimethyl-2,3,4,5-tetraphenylsilole.[23]
[b] For 1,1-diethynyl-2,3,4,5-tetraphenylgermole.[24]
[c] For hexaphenylstannole.[25]

By and large, the calculated geometry of molecules $Ph_4C_4EH_2$ is in reasonable agreement with the experimental data. Since no structural data for the metallole radical anions are available, it was useful to compare the geometric parameters of radical anions $Ph_4C_4EH_2$ calculated in this work with the results of recent DFT calculations of the same radical anions $Ph_4C_4EH_2$ (E = C, Si, Ge).[12] Both computational approaches showed that the five-membered ring in radical anions $Ph_4C_4EH_2^{\bullet -}$ remains planar and that the endocyclic bonds C(2)—C(3) (C(4)—C(5)) are lengthened while the C(3)—C(4) bonds are shortened as compared to the corresponding bond lengths in the neutral molecules. The calculated structure of tetraphenylstannole radical anion also remains planar; however, the configuration of the tin atom changes from tetrahedral, as is the case of other metallole radical anions, to a distorted trigonal-pyramidal. The C(2)—Sn (C(5)—Sn) bonds were found to be longer than in the corresponding neutral molecule (see Table 2), one of them being appreciably longer (by 0.078 Å) than the other. This is not observed for other metalloles (E = Si, Ge) and cyclopentadiene, where the endocyclic E—C bond lengths are the same as or slightly smaller than in the corresponding neutral molecules. This suggests that the tetraphenylstannole radical anion exhibits a pronounced trend to cleavage of the C—Sn bonds.

1.3. Reduction of other metalloles

The mechanism of electrochemical reduction of 1,1-Alk_2- and 1,1-$(R_3E)_2$-substituted metalloles is still to be clarified. The most probable route involves further reduction of the metallole radical anion to dianion **10** followed by hydrolysis of the latter (Scheme 4).

Scheme 4

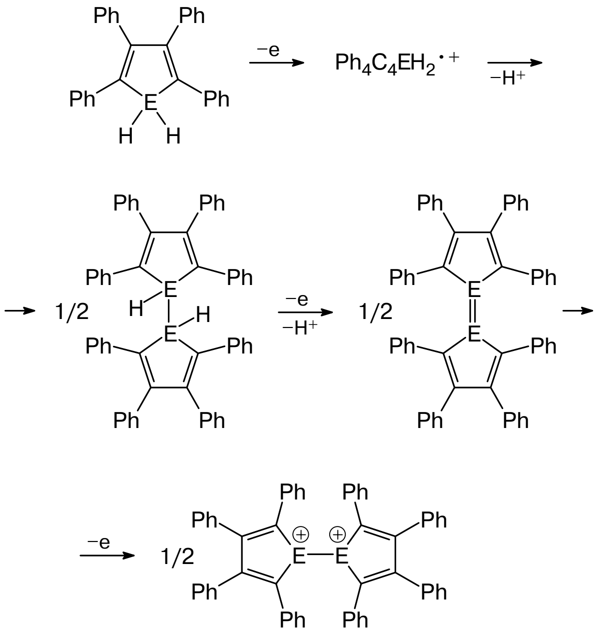


This assumption (*i.e.*, the formation of a dianion of the type **10**) is confirmed by the isolation of 1-phenyl-1,3,4-trimethyl-1-silacyclopent-3-ene after hydrolysis of the product of the reduction of 1-phenyl-1,3,4-trimethylsilole with alkali metal.[1]

However, we cannot also rule out the possibility for fragmentation of the metallole radical anion to occur, which can be followed by the opening of the heterocycle. This process seems to be most plausible for stannoles (see above).

2. Oxidation

Based on the results available at the moment, it is impossible to draw definite conclusions about the oxidation mechanism of metalloles. We can only say that substituents at the heteroatom E affect the oxidation potential by inductive mechanism (see Fig. 1). Most likely, the first electron is detached from the π-system of tetraphenylbutadiene. This is confirmed by close values of the first oxidation potentials of some metalloles containing no substituents with strong inductive effect at the E atom and the first oxidation potential of tetraphenylbutadiene **5** (see Table 1). Directions of further fragmentation of the radical cation obtained will apparently depend on the nature of substituents R^1 and R^2. For instance, the most probable oxidation scheme of the compounds $Ph_4C_4EH_2$ (E = C, Si, Ge) can look as follows:



The oxidation of metalloles **2d—f** (fragmentation of their radical cations is accompanied by elimination of Alk_3E^+, where E = Si, Ge, Sn) can also proceed by analogous scheme. Finally, the oxidative decomposition of metalloles can be accompanied by cleavage of the endocyclic C(sp^2)—E bond, as was found in studies of the reactions of metalloles with halogens, oxygen, or peracids (see review[1] and references cited therein).

Experimental

Electrochemical studies were carried out using a PI-50-1.1 potentiostat. The working electrode was a glassy-carbon rod (d = 1.8 mm) or a platinum wire (d = 3.5 mm), the supporting electrolyte was a 0.05 M Bu_4NBF_4 solution in MeCN or a 0.1 M Bu_4NClO_4 solution in THF, and the reference electrode was Ag/AgCl/KCl(sat.). All measurements were performed in argon atmosphere.

Quantum-chemical PM3 calculations with full optimization of the molecular and ion geometry were carried out using the "Hyperchem" program package (Hypercube Inc., Gainesville (FL), USA). A gradient magnitude of less than 10 cal mol^{-1} $Å^{-1}$ was chosen as convergence criterion.

Acetonitrile was purified by successive distillation over CaH_2 (10 g L^{-1}), H_2SO_4 (5 mL L^{-1}), KNO_3 (1 g L^{-1}), and P_2O_5 (5 g L^{-1}). Tetrahydrofuran was distilled over sodium benzophenone ketyl in argon atmosphere and then immediately transferred into the electrochemical cell.

Metalloles were synthesized following the known procedures.[26—37] A solution of lithium salt of dianion **6b** in THF was prepared using the reported procedure.[38] Tetraphenylbutadiene **4** (Aldrich) was purified by recrystallization from MeCN.

1-Methyl-1-chloro-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (2h). A filtered solution of a dilithium salt of 1,2,3,4-tetraphenylbuta-1,3-diene, which was obtained from diphenylacetylene (4.08 g, 0.023 mol) and small pieces of Li (0.176 g, 0.0245 mol) in 23 mL of anhydrous ether following the known procedure,[39] was added dropwise to a solution of $MeGeCl_3$ (2.23 g, 0.0115 mol) in 23 mL of anhydrous ether in an argon atmosphere. The reaction mixture was stirred for 1 h at room temperature. The solvent was removed *in vacuo* and the residue was dissolved in a minimum amount of CH_2Cl_2 and then filtered. The addition of hexane (30 mL) to the filtrate resulted in the precipitation of 1-methyl-1-chloro-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene as yellow crystals. The yield was 2.53 g (45%), m.p. 138 °C. ^1H NMR (C_6D_6, δ): 0.90 (s, 3 H, $C\underline{H}_3$); 6.80—7.40 (m, 20 H, Ph). Mass spectrum (m/z): 478 $[M]^+$, 356 $[M - GeMeCl]^+$.

1-Methyl-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (2g). To a suspension of $LiAlH_4$ (0.15 g, 4 mmol) in 20 mL of anhydrous ether, a suspension of 1-methyl-1-chloro-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (1.5 g, 3.13 mmol) in 200 mL of anhydrous ether was added portionwise (small portions). The reaction mixture was refluxed for 3 h with vigorous stirring, cooled, and then water (20 mL) and a 5% H_2SO_4 solution (20 mL) was added sequentially. The residue was filtered off, washed with water and then with ether, and dried *in vacuo*. The filtrate was dried over $CaCl_2$, ether was removed *in vacuo*, and the residue was recrystallized from hexane. The total yield of 1-methyl-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene was 1.3 g (93%), m.p. 205—207 °C. ^1H NMR ($CDCl_3$, δ): 0.80 (d, 3 H, $C\underline{H}_3$); 5.50 (m, 1 H, $Ge\underline{H}$); 6.80—7.20 (m, 20 H, Ph). Mass spectrum (m/z): 446 $[M]^+$, 356 $[M - GeHMe]^+$.

***(E,E)*-1,2,3,4-Tetraphenylbuta-1,3-diene (5).** To a solution of a dilithium salt 1,2,3,4-tetraphenylbutadiene in anhydrous diethyl ether, obtained from diphenylacetylene (3.0 g, 16.8 mmol) and metallic lithium (0.12 g, 17.1 mmol) following the known procedure,[39] water(20 mL) was added, the mixture was extracted with ether, and dried over $CaCl_2$. Ether was removed *in vacuo*, and the residue was recrystallized from hexane. The yield of 1,2,3,4-tetraphenylbuta-1,3-diene was 2.1 g (70%), m.p. 184 °C (*cf.* 185—186 °C for *cis,cis*-isomer[40]). ^1H NMR ($CDCl_3$, δ): 6.30 (s, 2 H, C—H); 6.70—7.50 (m, 20 H, Ph). Mass spectrum (m/z): 358 $[M]^+$.

This work was carried out with the financial support of the Russian Federation Ministry of Industry, Science, and Technologies in the framework of the State Subprogram "Fundamental Problems of Modern Chemistry" (Project No. 9.3.03) and of the INTAS (Grant No. 97-30344).

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Received May 7, 2001;
in revised form June 21, 2001