ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2018, Vol. 44, No. 4, pp. 258–271. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © M.G. Chegerev, A.V. Piskunov, 2018, published in Koordinatsionnaya Khimiya, 2018, Vol. 44, No. 2, pp. 109–122.

Chemistry of Complexes of Group 14 Elements Based on Redox-Active Ligands of the *o*-Iminoquinone Type

M. G. Chegerev and A. V. Piskunov*

Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
Nizhny Novgorod, 603600 Russia
**e-mail: pial@iomc.ras.ru*

Received September 15, 2017

Abstract—Specific features of the synthesis and structures of the complexes of Group 14 elements (Si, Ge, Sn, Pb) with *o*-iminoquinone ligands are discussed. The chemical reactions of the above indicated compounds accompanied by the transformation of the redox-active ligand in the coordination sphere of the complex-forming agent are considered.

Keywords: *o*-iminoquinone, redox-active ligands, silicon, germanium, tin, lead

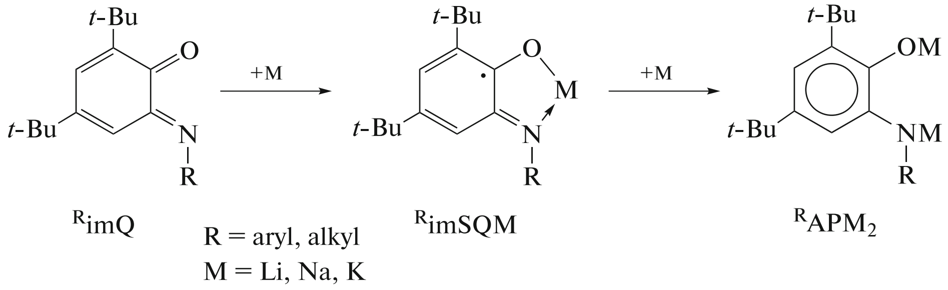
DOI: 10.1134/S1070328418040036

INTRODUCTION

Many works concerning the study of stable metal complexes based on redox-active *o*-iminoquinones in different redox states are known at the moment. This topic is considered in several reviews [1, 2]. However, all the studies are devoted to transition metal compounds, and the main attention of researchers is focused on the discussion of the molecular and electronic structures and magnetic properties of the compounds. The current state of research in the area of the complexes of Group 14 elements with the redox-active *o*-iminoquinone ligands of different denticity is considered in the present review.

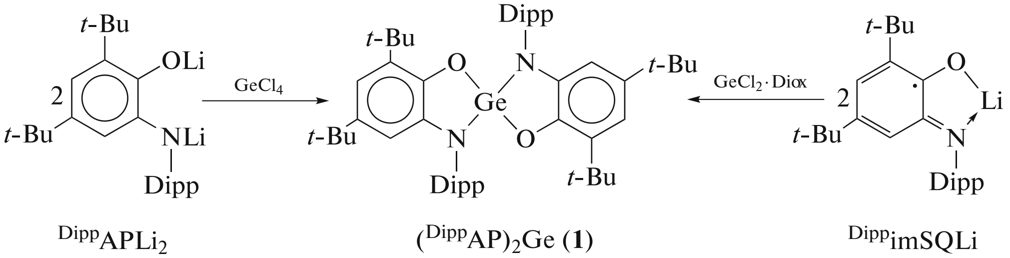
COMPLEXES OF GROUP 14 ELEMENTS WITH BIDENTATE *o*-IMINOQUINONE LIGANDS

The exchange reactions between quinone derivatives of alkaline metals and halides of other metals recommended themselves as a convenient tool for the synthesis of similar coordination compounds [3–7]. *o*-Iminoquinones are readily reduced with an alkaline metal (Li, Na, K) excess in media of both solvating and nonsolvating solvents [8, 9]. The neutral (^{R}imQ) and dianionic ($^{R}AP^{2-}$) species are diamagnetic, whereas the radical-anionic species ^{R}imSQ is paramagnetic (Scheme 1).



Scheme 1.

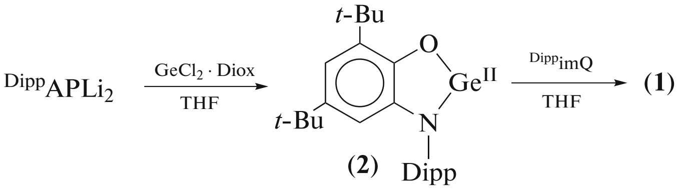
Germanium complexes. The chemistry of the germanium derivatives based on bidentate *o*-iminoquinones is studied rather poorly. There is only one published work [10] on the synthesis and study of the structures and reactivity of the germanium compounds based on sterically hindered 4,6-di-*tert*-butyl-*N*-(2,6-di-*iso*-propylphenyl)-*o*-iminoquinone (^{Dipp}imQ). The reaction of its dilithium salt ($^{Dipp}APLi_2$) (Dipp = 2,6-di-*iso*-propylphenyl) with $GeCl_4$ in a ratio of 2 : 1 in THF or hexane (Scheme 2) affords tetrahedral diamagnetic germanium(IV) bis(*o*-amidophenolate) ($^{Dipp}AP)_2Ge$ (**1**). It is shown that even the use of strongly coordinating THF as a solvent does not change the coordination number of the central atom in the final germanium bis(*o*-amidophenolate), which remains to be four, unlike the known penta- and hexacoordinated bis(catecholate) germanium derivatives containing coordinated solvent molecules [5, 11].



Scheme 2.

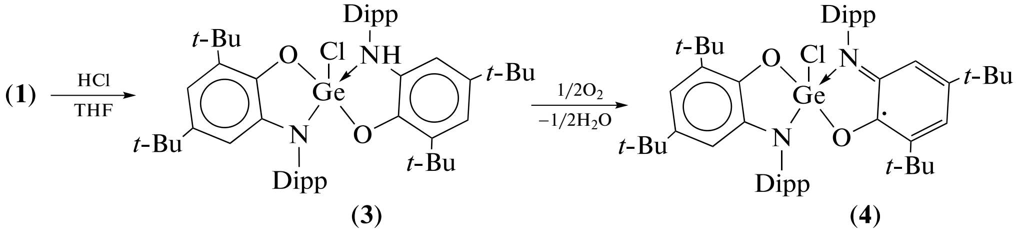
The reaction of paramagnetic $^{Dipp}imSQLi$ with germanium(II) dioxanate dichloride $GeCl_2{\cdot}Diox$ (Scheme 2) also gives compound **1**. It is remarkably that paramagnetic divalent germanium bis(*o*-iminosemiquinolate) $(^{Dipp}imSQ)_2Ge^{II}$ is not formed, which is caused by the intramolecular redox process followed by the formation of complex **1**.

The reaction of $GeCl_2{\cdot}Diox$ with $^{Dipp}APLi_2$ in THF is accompanied by the formation of amorphous O,N-heterocyclic chelate germylene $^{Dipp}APGe^{II}$ (**2**) [10]. The obtained germylane easily enters the oxidative addition reaction with ^{Dipp}imQ to form earlier described complex **1** as the product (Scheme 3).



Scheme 3.

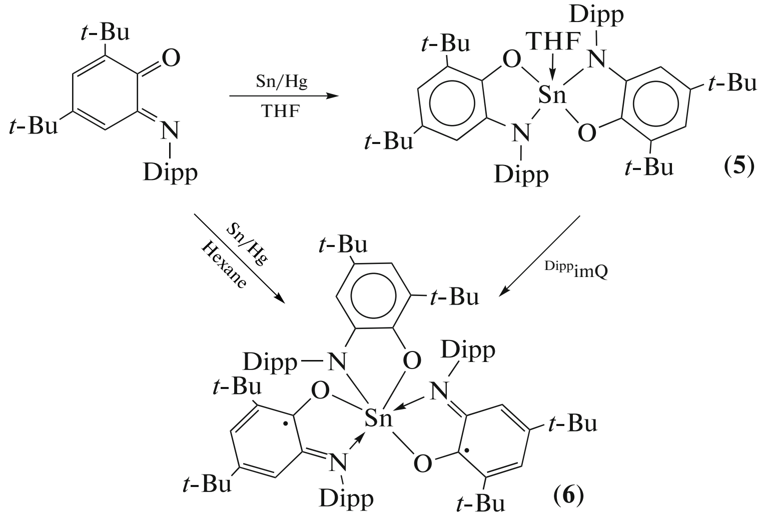
The product of acidic hydrolysis of complex **1** with anhydrous HCl is the pentacoordinated heteroligand aminoamidophenolate germanium(IV) complex $(^{Dipp}APH)Ge(^{Dipp}AP)Cl$ (**3**) easily oxidizable with air oxygen in an acetone solution to form paramagnetic *o*-iminosemiquinolate derivative **4** (Scheme 4). Both ligands in the complex are almost equivalent, and the bond lengths in them are intermediate between the corresponding distances in metal *o*-amidophenolates and *o*-iminosemiquinolates [12–15]. This is due to the delocalization of the charge and spin density over both redox-active ligands, which is confirmed by the data of EPR spectroscopy and quantum-chemical calculations.



Scheme 4.

Note that complex **4** is a rare example of the stable germanium compound isolated in the individual state and containing the redox-active ligand in the radical-anionic form. Only several examples of similar derivatives are known nowadays [16–21].

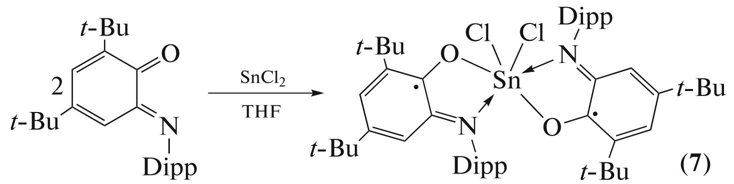
Tin complexes. Unlike the germanium derivatives, the chemistry of the tin compounds based on the bidentate *o*-iminoquinone ligands is studied much more widely. One of convenient methods for the synthesis of the metal complexes is the direct reduction of *o*-iminoquinone with tin amalgam [22, 23]. Interestingly, the reaction direction depends strongly on the solvent used (Scheme 5). When the reaction is carried out in strongly coordinating THF, the single product is diamagnetic pentacoordinated tin(IV) bis(*o*-amidophenolate) $(^{\mathrm{Dipp}}\mathrm{AP})_2\mathrm{Sn}\cdot\mathrm{THF}$ (**5**). However, the use of a nonpolar hydrocarbon, for example, *n*-hexane, as a solvent results in the formation of the paramagnetic tris(ligand) hexacoordinated tin(IV) complex (**6**). The *o*-iminoquinone ligands in complex **6** are equivalent. It was asserted on the basis of the X-ray diffraction results in combination with the data of EPR spectroscopy and quantum-chemical methods that the tris(ligand) complex contains two ligands in the radical-anionic form and one ligand in the dianionic form. The delocalization of the charge and spin density over all three *o*-iminoquinone ligands results in their equivalence.



Scheme 5.

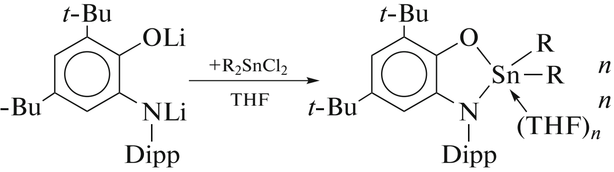
The mixing of complex **5** with an equimolar amount of $^{\mathrm{Dipp}}$imQ in both hexane and THF is accompanied by the substitution of the coordinated solvent molecule by the *o*-iminoquinone ligand and the subsequent formation of tris(ligand) complex **6** (Scheme 5).

The oxidative addition of free *o*-iminoquinone to tin dichloride affords (Scheme 6) the bis(ligand) biradical derivative of tetravalent tin $(^{\mathrm{Dipp}}\mathrm{imSQ})_2\mathrm{SnCl}_2$ (**7**) regardless of the initial ratio of reagents [24]. Remarkably, a similar reaction of SnCl_2 with 3,6-di-*tert*-butyl-*o*-benzoquinone (3,6-Q) (mole ratio 1 : 1 or 1 : 2) results only in monoligand diamagnetic dichlorotin catecholate (3,6-Cat)$\mathrm{SnCl}_2\cdot 2\mathrm{THF}$ [24].



Scheme 6.

The exchange reactions between the alkaline derivatives of *o*-iminoquinones and tin halides or organohalides also represent a convenient method for the introduction of redox-active ligands into the coordination sphere of the metal. The use of various alkyl- or aryltin halide derivatives in this reaction provides routes to the synthesis of new paramagnetic and diamagnetic complexes containing hydrocarbon substituents at the metallocenter differed in electronic properties and steric hindrances [25, 26]. The reactions of $^{\mathrm{Dipp}}\mathrm{APLi}_2$ with tin(IV) organodichlorides of the general formula $\mathrm{R}_2\mathrm{SnCl}_2$ in THF were shown to occur within several minutes at room temperature to form diamagnetic tin(IV) *o*-amidophenolate complexes (**8–10**) (Scheme 7).



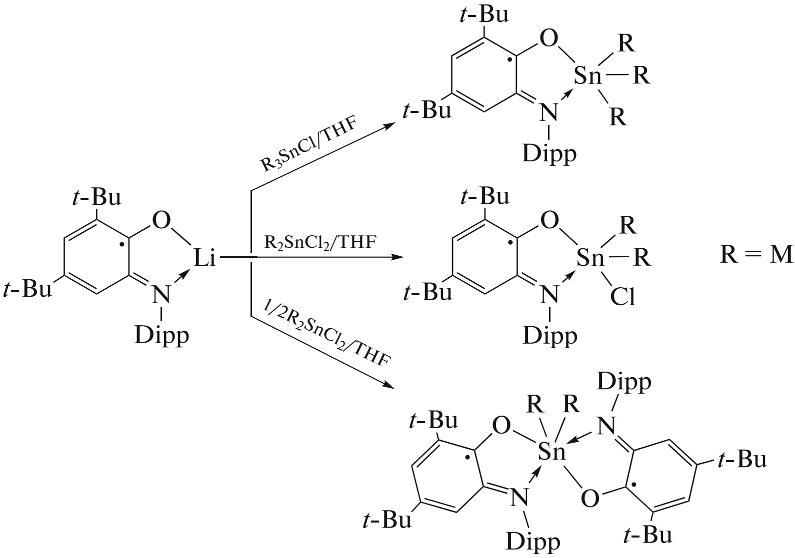
$n = 0$, R = t-Bu (**8**); Ph (**9**)
$n = 1$, R = Et (**10**)

Scheme 7.

As a rule, the organometallic *o*-semiquinone alkyl or phenyl tin derivatives are unstable and rapidly decompose in solutions via the bimolecular mechanism [27–29] except for the cases of less accepting phenanthrenequinone ligands [30, 31]. Similar derivatives for α-diimines are unknown. The use of *o*-iminoquinones made it possible to obtain stable radical-anionic alkyl and aryl tin(IV) derivatives [25, 26, 32].

The exchange reactions between ^{Dipp}imSQLi and tin trialkyl chlorides or dialkyl chlorides were used to obtain (^{Dipp}imSQ)SnR_3 or (^{Dipp}imSQ)SnR_2Cl derivatives, respectively (Scheme 8) [32]. The paramagnetic tris(alkyl) complexes with R = Me (**11**) and Ph (**12**) are stable in solutions and in the solid state, but the derivatives with R = Et (**13**) and *n*-Bu (**14**) rapidly decompose in solutions to form undetermined products. It is found that the replacement of one alkyl substituent at the tin atom by the halogen atom favors the enhancement of the stability of the obtained compounds. This made it possible to isolate and characterize a number of derivatives of the general type (^{Dipp}imSQ)SnR_2Cl (R = Me (**15**), Et (**16**), Ph (**17**), *n*-Bu (**18**), *tert*-Bu (**19**)).

The stable biradical organometallic tin(IV) derivatives were obtained by the reactions of R_2SnCl_2 with ^{Dipp}imSQLi in a mole ratio of 1 : 2 only in the cases of R = Me (**20**) and Ph (**21**). The ethyl (**22**) and *n*-butyl (**23**) complexes are unstable in solutions and decompose rapidly.



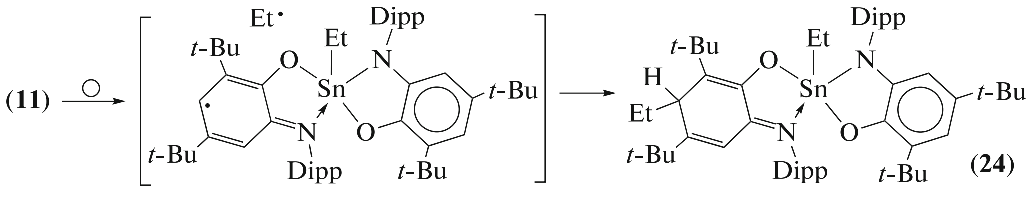
R = Me (**11**); Ph (**12**);
Et (**13**); *n*-Bu (**14**)

R = Me (**15**); Et (**16**); Ph (**17**);
n-Bu (**18**); *t*-Bu (**19**)

R = Me (**20**); Ph (**21**);
Et (**22**); *n*-Bu (**23**)

Scheme 8.

The conversion product of labile compound **22** is new complex **24** in which one of the ethyl groups at the tin atom migrates to position 5 of the *o*-iminoquinone ring to form the iminocyclohexa-1,4-dienolate ligand (^{Et}L) (Scheme 9) containing the sp^3-hybridized carbon atom [32, 33].

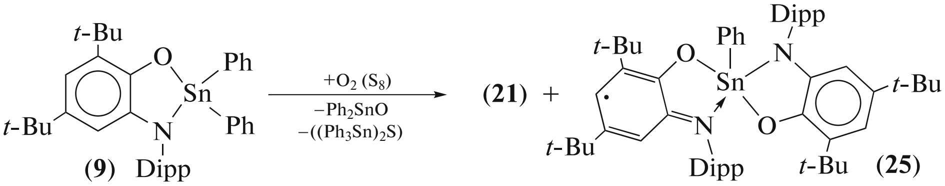


(24)

Scheme 9.

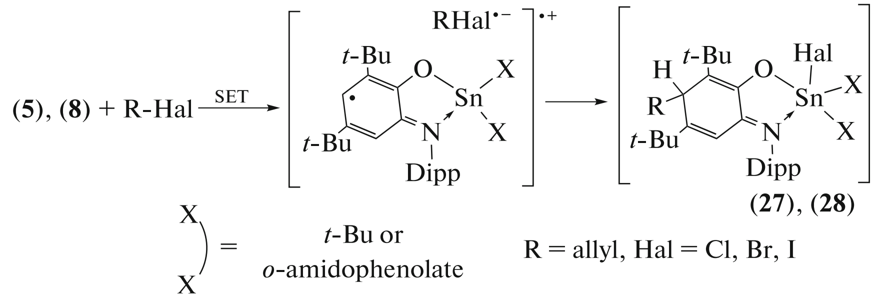
According to [32], the key criteria of stability of the obtained *o*-iminosemiquinolate tin(IV) derivatives are the following: (1) the degree of filling of the coordination sphere of the metal atom and (2) the difference in energies of the Sn–C bond depending on the hydrocarbon substituent. In particular, in the series of tin bis(*o*-iminosemiquinolates), complex **20** has the lowest degree of filling of the coordination sphere of the metal (91%), whereas labile hexacoordinated complex **22** (96%) is rearranged to the pentacoordinated complex characterized by a lower steric hindrance of the coordination center (92%).

The reactivities of the diphenyl (**9**) and diethyl (**10**) tin derivatives ($(^{Dipp}AP)SnR_2$) were studied [33]. The oxidation of the diphenyl derivatives with air oxygen results in the formation of stable diphenyltin(IV) bis(*o*-iminosemiquinolate) (**21**), and the reaction with elemental sulfur is accompanied by the formation of the bis(ligand) monoradical complex ($(^{Dipp}imSQ)Sn(^{Dipp}AP)Ph$) (**25**) (Scheme 10). Complex **10** also reacts with O_2 and S_8, but biradical derivative **22** was not observed among the products. Complex **24** containing the iminocyclohexa-1,4-dienolate ligand was isolated as the major product along with the minor monoradical product $(^{Dipp}imSQ)Sn(^{Dipp}AP)Et$ (**26**).



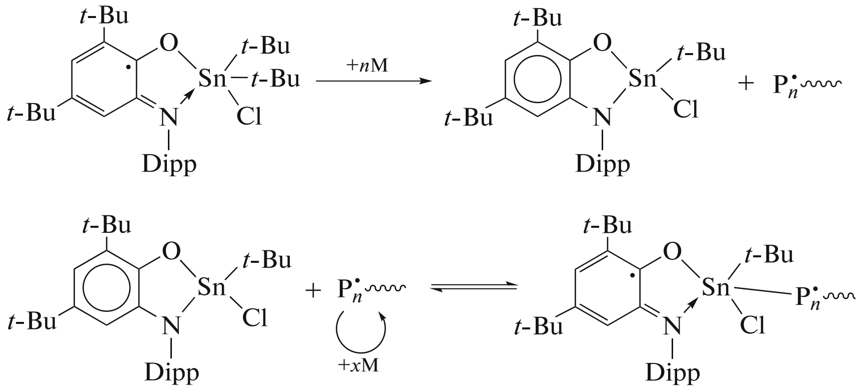
Scheme 10.

The bis- (**5**) and mono-*o*-amidophenolate (**8**) tin complexes were shown [34, 35] to add one equivalent of allyl halides to form diamagnetic compounds **27** and **28**, respectively (Scheme 11). This process has the ligand-centered character and is accompanied by the transformation of the *o*-amidophenolate ligand into the iminocyclohexa-1,4-dienolate species to form a new carbon–carbon bond. The central metal atom retains its oxidation state. The single-electron transfer (SET) from the redox-active ligand to the allyl halide molecule was proposed as a mechanism of the reaction and was confirmed by the data of EPR spectroscopy. Remarkably, in spite of two *o*-amidophenolate ligands, complex **5** adds only one equivalent of alkyl halide even with a threefold excess of the latter similarly to mono-*o*-amidophenolate **8** (Scheme 11).



Scheme 11.

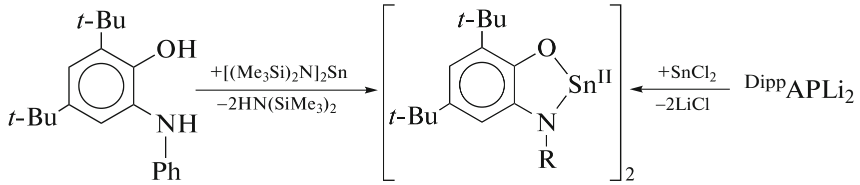
It was found for paramagnetic mono-*o*-iminosemiquinone complexes **15**–**19** that compounds of this type can act as organometallic iniferters (Scheme 12), i.e., can initiate and control the radical polymerization of vinyl monomers [36, 37]. The studies of the mechanism of the thermal decomposition of these compounds showed the elimination (in the first step) of the alkyl radical capable of initiating polymerization [26].



P_n is propagating macroradical, M is monomer molecule

Scheme 12.

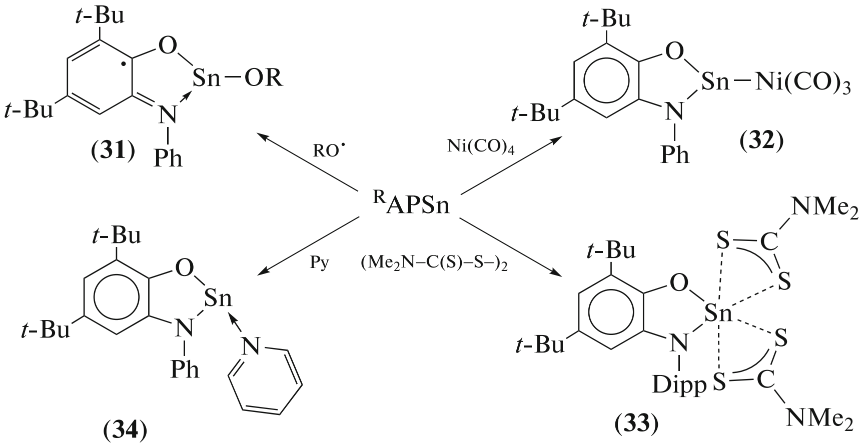
The chemistry of the low-valence tin *o*-iminoquinone derivatives was studied for two stannylenes: ^{Dipp}APSn (**29**) and ^{Ph}APSn (**30**) [22, 38]. Two approaches were proposed as convenient methods of synthesis: the elimination of amine (between *o*-aminophenol ^{R}APH$_2$ and tin silylamide $[(Me_3Si)_2N)]_2Sn$) and the salt metathesis reaction between ^{R}APLi$_2$ and $SnCl_2$ (Scheme 13). The vacant *p* orbital at the tin atom acts as a strong Lewis acid toward the lone electron pairs of the heteroatoms, which results in the dimeric structures of stannylenes **29** and **30**. A similar behavior is characteristic of both the catecholate complex [39] and a wide range of the tin(II) diamide derivatives [40–46].



R = Dipp (**29**), Ph (**30**)

Scheme 13.

Complexes **29** and **30** demonstrate rich reactivity (Scheme 14). Similar compounds can react with Lewis acids ($Ni(CO)_4$ after CO elimination) and bases (pyridine) and exhibit a dual nature in redox transformations: the redox-active ligand is responsible for the reactions with one-electron oxidants (phenoxyl radical RO$^•$), whereas the divalent metal ion is responsible for the reactions with two-electron oxidants (disulfide) [38].



Scheme 14.

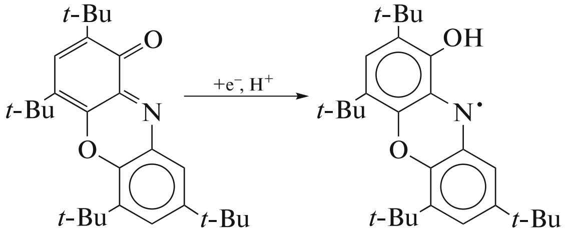
Stannylene **29** readily undergoes oxidative addition with one equivalent of ${}^{\mathrm{Dipp}}$imQ (Scheme 15). The composition of the final product depends on the solvent used: diamagnetic compound **5** is formed in a THF solution [22], whereas paramagnetic tris(ligand) complex **6** is formed in a hexane solution regardless of the initial reagent ratio [23].

$$({}^{\mathrm{Dipp}}\mathrm{AP})_2\mathrm{Sn}\cdot\mathrm{THF} \xleftarrow[\mathrm{THF}]{{}^{\mathrm{Dipp}}\mathrm{imQ}} {}^{\mathrm{Dipp}}\mathrm{APSn} \xrightarrow[\mathrm{Hexane}]{{}^{\mathrm{Dipp}}\mathrm{imQ}} ({}^{\mathrm{Dipp}}\mathrm{imSQ})_2\mathrm{Sn}({}^{\mathrm{Dipp}}\mathrm{AP})$$

(5) **(29)** **(6)**

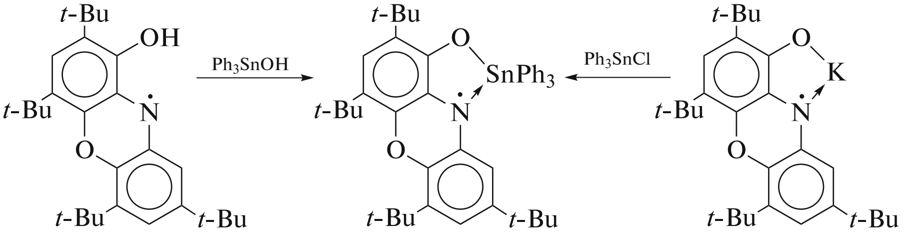
Scheme 15.

1*H*-1-Oxo-2,4,6,8-tetrakis(*tert*-butyl)phenoxazine (Phenox-imQ) is also stable bidentate *o*-iminoquinone (Scheme 16) capable of entering redox transformations to form metal complexes of various compositions [47, 48]. In addition, this compound forms stable 1-hydroxy-2,4,6,8-tetrakis(*tert*-butyl)phenoxazinyl radicals (Phenox-imSQ)H [47], which can also be used in the syntheses of the complexes (Scheme 16).



Scheme 16.

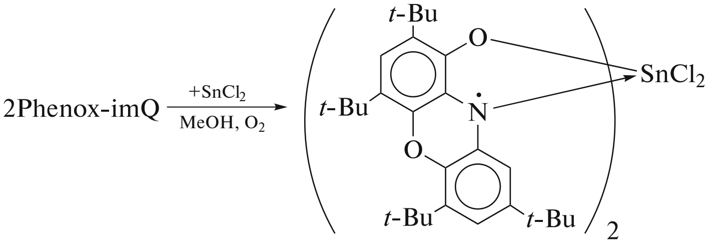
The paramagnetic complex (Phenox-imSQ)SnPh$_3$ (**35**) can be obtained by the reaction of Phenox-imSQH with Ph$_3$SnOH or by the reaction of (Phenox-imSQ)K potassium salt with Ph$_3$SnCl (Scheme 17) [47]. The obtained phenoxazinone tin complexes were not isolated in the individual state but were studied in solutions using EPR spectroscopy.



(35)

Scheme 17.

Later, the stable biradical bis(ligand) tin complex (Phenox-imQ)$_2$SnCl$_2$ (**36**) was synthesized by the oxidative addition of two equivalents of Phenox-imQ to SnCl$_2$ in methanol in the presence of air oxygen (Scheme 18) and was characterized [49].



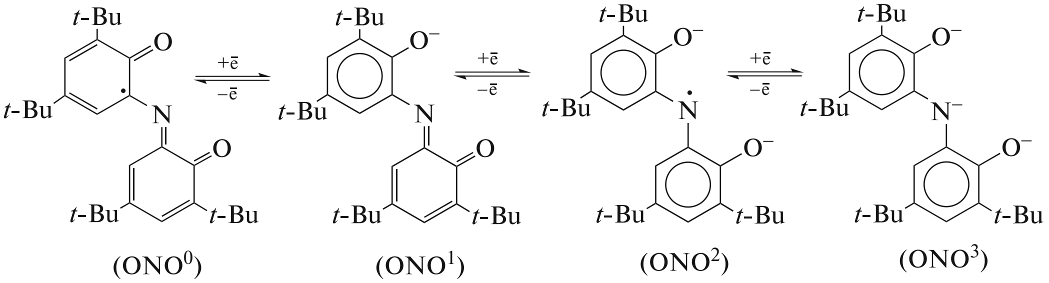
(36)

Scheme 18.

Unlike the germanium and tin derivatives, literature data on the silicon and lead *o*-iminoquinone derivatives are presently lacking.

COMPLEXES OF GROUP 14 ELEMENTS WITH TRIDENTATE *o*-IMINOQUINONES

In the 1970s [18, 50, 51], the metal derivatives based on tridentate redox-active 3,5-di-*tert*-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-*tert*-butylphenyl)imine (ONO) attracted attention of several research groups. Specific features of this ligand capable of chelating the metallocenter by two oxygen atoms and one nitrogen atom allow the ligand to exist in four different redox states [52] (Scheme 19).

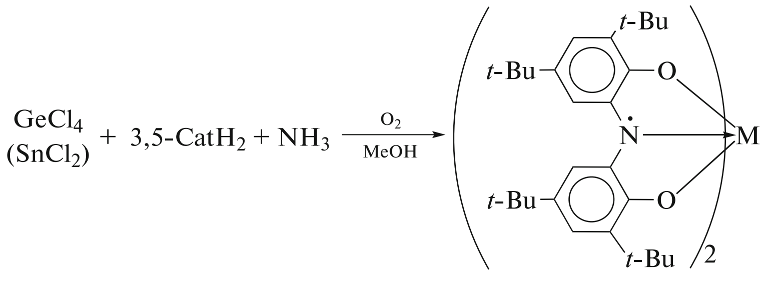


Scheme 19.

The neutral (ONO^0) and doubly reduced radical-dianionic (ONO^2) species of the ligand are paramagnetic, whereas its monoanionic (ONO^1) and trianionic (ONO^3) species are diamagnetic [52]. The ONO^1 and ONO^3 diamagnetic species of the ligand can also exist in the triplet state [53]. Various protonated forms of this ligand are also described: (ONO^1)H, $(ONO^3H)^{2-}$, and $(ONO^3H_4)^+$ [52, 54].

It is interesting that the considered tridentate *o*-iminoquinone does not exist in the individual state as ONO^0 and transforms rapidly into the earlier described bidentate phenoxazinone Phenox-imQ [55, 56]. Since the ONO^0 free ligand is unstable, there are two main approaches to the synthesis of the metal complexes based on this ligand: the template synthesis from 3,5-di-*tert*-butylpyrocatechol (3,5-$CatH_2$), ammonia, and the corresponding metal salts in an alcohol medium in the presence of air oxygen [16, 18, 51, 57–60] and the reactions of the protonated forms of the ligand with the corresponding halides or organohalides of Group 14 elements in acetonitrile in the presence of Et_3N and O_2 [61].

It is established [16] that the bis(ligand) derivatives of tetravalent metals of the $M(ONO^2)_2$ type (M = Ge (**37**), Sn (**38**)) can be obtained by the template synthesis from $GeCl_4$ or $SnCl_2$ with 3,5-$CatH_2$ in an ammonia–alcohol medium in the presence of air oxygen (Scheme 20). The use of PbF_2 in a similar reaction results in the formation of the bis(ligand) diamagnetic lead(II) derivative $Pb(ONO^1)_2$ (**39**) [58]. An analysis of the electronic structure of tin complex **38** shows the ground triplet state of the complex in which unpaired electrons are delocalized over two redox-active ligands [58].



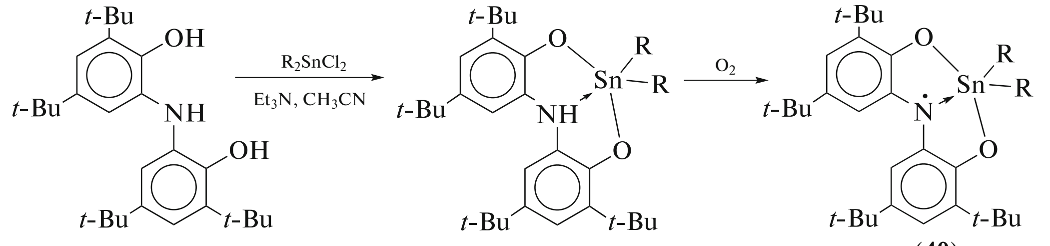
M = Ge (**37**), Sn (**38**)

Scheme 20.

The organometallic derivatives of Group 14 elements containing the organic substituents at the metallocenter are synthesized by the reactions of dialkyl and diaryl halides of the corresponding metals with 3,5-$CatH_2$ in an ammonia medium and in the presence of air oxygen. The reactions afford the monoligand derivatives of the $(ONO^2)MR_2$ type (M = Ge, Sn, Pb; R is alkyl, aryl) [18, 51, 57, 59, 60]. The use of tin triorganohalides R_3SnHal in this reaction also leads to the $(ONO^2)SnR_2$ derivatives [51, 60].

The tin complexes based on the ONO ligand can also be synthesized by the reactions of their protonated $(ONO^3)H_3$ forms with metal organohalides in the presence of air oxygen [61]. The tin derivatives of the $(ONO^2)SnR_2$ type (**40**) (R = Me, Et, *n*-Bu, *tert*-Bu, Ph) were obtained in high yields by the reactions of

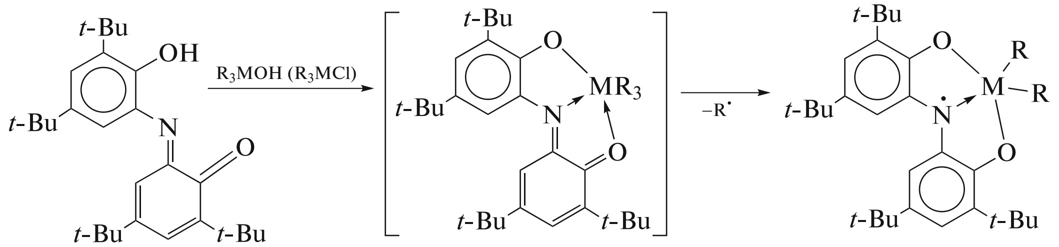
$(ONO^3)H_3$ and tin diorganohalides in the presence of Et_3N and O_2 [61]. In an acetonitrile medium this reaction ceases within several minutes (Scheme 20). This approach turned out to be much more efficient than the template synthesis characterized by lower yields and the formation of by-products. When this reaction is carried out in the absence of air oxygen, the diamagnetic *o*-aminophenolate metal complexes are formed (Scheme 21). However, the subsequent oxidation of a solution of the complex with air oxygen is accompanied by the instant coloration of the reaction mixture into violet and the appearance of the EPR signal [61].



R = Me, Et, *n*-Bu, *t*-Bu, Ph

Scheme 21.

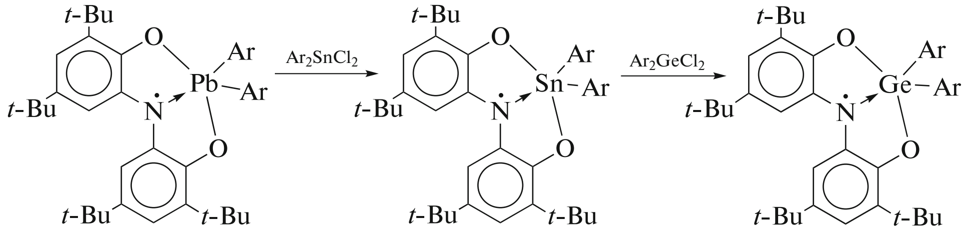
The use of the $(ONO^1)H$ monoprotonated species of the ligand as the starting reactant also turned out to be productive [61]. The addition of Ph_3SnOH to a solution of the ligand results in the formation of the previously considered paramagnetic diphenyltin derivative $(ONO^2)SnPh_2$. It is assumed that the unstable tris(aryl) complex $(ONO^1)SnPh_3$ is formed in the first step of the reaction, and one of the hydrocarbon radicals at the metal atom of this complex eliminates with the subsequent formation of paramagnetic complex **40**. In addition to tin, the organic derivatives of silicon (**41**) and lead (**42**) can be introduced into this reaction (Scheme 22). The use of Et_3N made it possible to carry out this reaction not only with metal hydroxides but also with the corresponding halides of the R_3MHal type. The formed intermediate complexes $(ONO^1)MR_3$ are also unstable and transform via the scheme presented below.



(**40**): M = Sn, R = Ph
(**41**): M = Si, R = Me
(**42**): M = Pb, R = Et, Ph

Scheme 22.

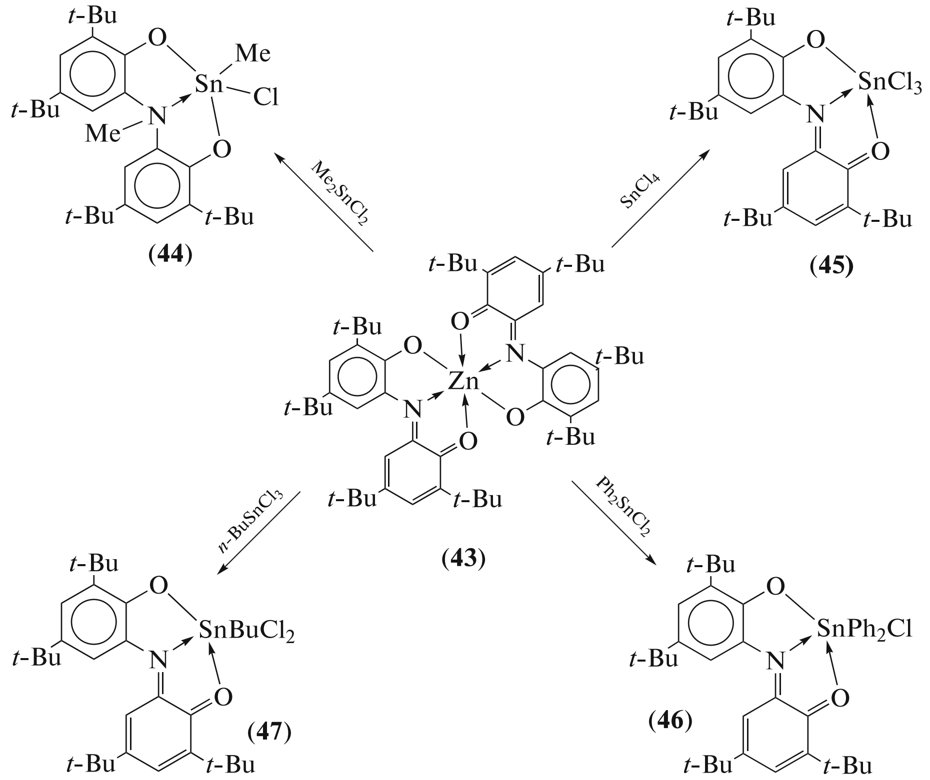
Note that diaryl dichlorides of Group 14 metals Ar_2MCl_2 (M = Ge, Sn) can displace elements located lower in the series of the periodic table from the $(ONO^2)MAr_2$ complexes (M = Sn, Pb) according to Scheme 23 [18].



Ar = Ph, *p*-$CH_3C_6H_4$

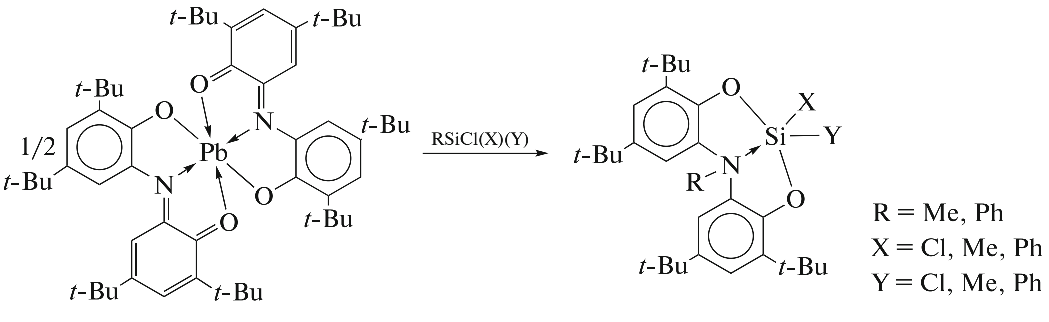
Scheme 23.

A cardinally new synthetic approach to the preparation of the tin complexes with the redox-active tridentate ligand was developed [62]. The novelty of the approach is the use of the octahedral zinc complex $Zn(ONO^1)_2$ **(43)** that readily enters the transmetallation reactions with tin organohalides of various compositions. The reactions lead to the formation of the penta- **(44)** and hexacoordinated **(45–47)** complexes with the ONO ligands in various redox states (Scheme 24). Interestingly, the transmetallation of tin dialkyl halides affords the pentacoordinated diamagnetic derivatives **(44)** in which one of the alkyl groups migrates from the metal to the nitrogen atom of the organic ligand. In the case of the aryl derivatives, this transformation is not observed [62].



Scheme 24.

Similar transformations are also characteristic for the silicon derivatives [63], which can be obtained by transmetallation from the lead complex $(ONO^1)_2Pb$ **(39)** [58] and silicon organochlorides. The migration of the hydrocarbon radical from the silicon atom to the nitrogen atom to form the pentacoordinated derivatives **(48)** was found for both the alkyl and aryl complexes of silicon (Scheme 25).

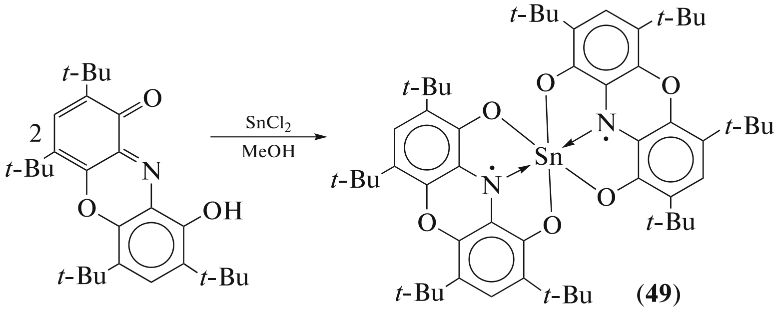


(39) (48)

Scheme 25.

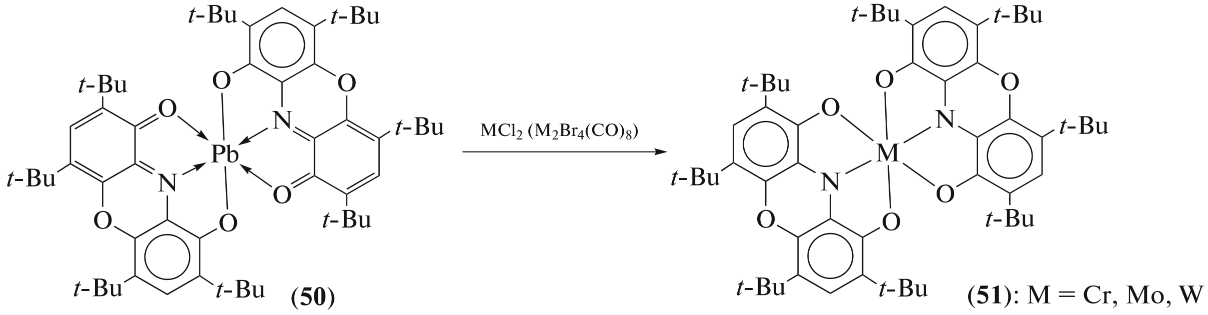
COMPLEXES BASED ON 2,4,6,8-TETRAKIS(*tert*-BUTYL)-9-HYDROXYPHENOXAZIN-1-ONE

The tridentate ligand based on substituted phenoxazine, 2,4,6,8-tetrakis(*tert*-butyl)-9-hydroxyphenoxazin-1-one (Phenox-ONO)H, is stable in the free state and can form chelates with metals [64, 65]. The paramagnetic biradical complex of tetravalent tin (**49**) was synthesized [49] by the reaction of (Phenox-ONO)H (2 equiv) and tin dichloride (1 equiv) in methanol. A weak ferromagnetic exchange between the radical centers is observed in this complex (Scheme 26).



Scheme 26.

The similar lead derivative $(\text{Phenox-ONO})_2\text{Pb}$ (**50**) was synthesized [66]. However, unlike paramagnetic tin complex **49**, the lead compound is diamagnetic. The metallocenter is in the oxidation state +2, and the both ligands exist in the monoanionic form. Complex **50** was also shown to be a convenient reagent for transmetallation and was used for the synthesis of the bis(ligand) derivatives (**51**) of Group VI elements (Cr, Mo, W) (Scheme 27) [66].



Scheme 27.

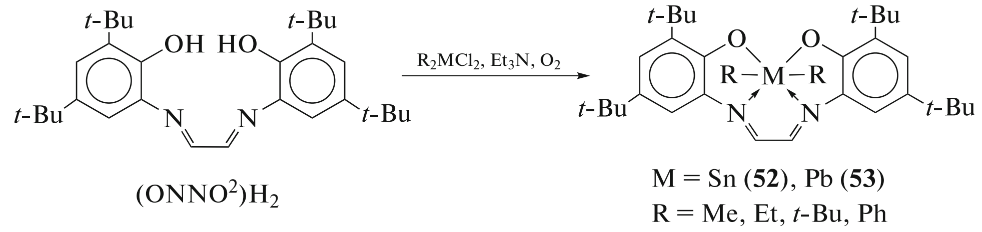
COMPLEXES OF 14 GROUP ELEMENTS WITH TETRADENTATE *o*-IMINOQUINONES

When two *o*-iminoquinone fragments are joined by the hydrocarbon bridge, a new family of tetradentate chelate ligands can be obtained. The variation of the structure and length of the bridge provides the preparation of a wide range of ligands and related metal complexes [67]. The ligands of this type can interact with the metallocenter by two oxygen atoms and two nitrogen atoms. The compounds based on glyoxal-bis(2-hydroxy-di-*tert*-butylanil) [68] and *N*,*N*'-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1,2-phenylenediamine are most studied [69]. The main method for the synthesis of complexes based on these compounds is the direct reaction of the ligand with metal salts under various conditions.

COMPLEXES WITH GLYOXAL-BIS(2-HYDROXY-3,5-DI-*tert*-BUTYLANIL)

The approach using the doubly protonated species $(\text{ONNO}^2)\text{H}_2$ of the standard glyoxal-bis(2-hydroxy-di-*tert*-butyl) ligand (Scheme 28) turned out to be convenient from the synthetic point of view [69, 70]. It is established that tin and lead diorganohalides readily react with $(\text{ONNO}^2)\text{H}_2$ in the presence of triethylamine (Scheme 28) to form diamagnetic alkyl- or aryl-containing metal complexes of the type

$(ONNO^2)MR_2$ (M = Sn (**52**), Pb (**53**)). In these compounds, the tetradentate ligand exists in the dianionic state. According to the X-ray diffraction data, the compounds are metal bis(phenolates) with two donor–acceptor metal–nitrogen bonds. Hexacoordinated derivatives **52** turned out to be capable of coordinating an additional solvent molecule to form heptacoordinated derivatives, which was proved by the data of electronic spectroscopy and ^1H and ^{19}Sn NMR spectroscopy [70].



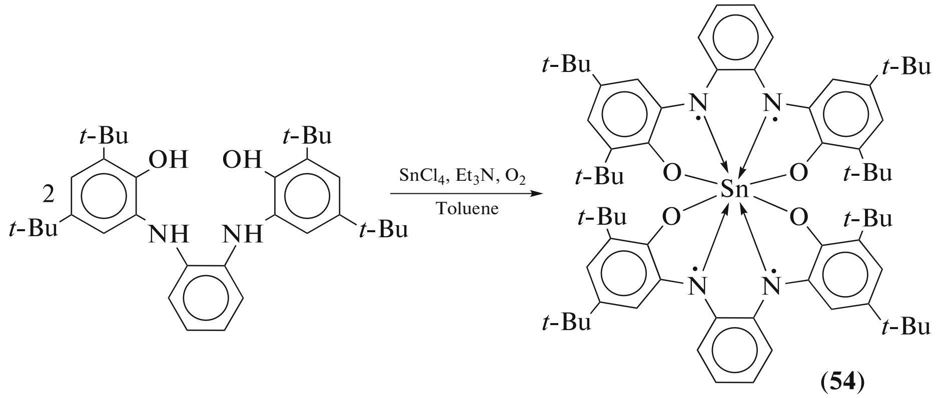
Scheme 28.

The redox-amphoteric character of complexes **52** and **53** was shown by cyclic voltammetry. The complexes are characterized by four reversible one-electron oxidation and reduction peaks. The occurring transformations correspond to a change in the redox state of the ligand in the complexes. The quantum-chemical calculations confirmed the obtained experimental data [70].

COMPLEXES BASED ON *N*,*N*'-BIS(3,5-DI-*tert*-BUTYL-2-HYDROXYPHENYL)-1,2-PHENYLENEDIAMINE

The tetradentate ligand based on *N*,*N*'-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1,2-phenylenediamine is stable in the free state only in the completely protonated $(ONNO^4)H_4$ form. It is interesting that the bis(ligand) tin complex $Sn(ONNO^2)_2$ (**54**) was synthesized by the reaction of $SnCl_4$ and $(ONNO^4)H_4$ in toluene in the presence of triethylamine (Scheme 29) [71].

The octacoordinated tin atom in complex **54** has a trigonal dodecahedral environment, and two redox-active ligands are nearly orthogonal to each other. An analysis of bond lengths in the organic ligands indicates that the tetradentate redox-active ligands contain two radical *o*-iminosemiquinone fragments linked by the *o*-phenylene bridge (Scheme 28). The paramagnetic centers interact antiferromagnetically resulting in the overall diamagnetic state of the compound.



(54)

Scheme 29.

To conclude, the section of coordination chemistry concerning the use in metal complexes of redox-active ligands capable of reversible changing the oxidation state has recently been newly incited to develop when using non-transition metals as complex-forming agents. The introduction of ligands of this type, in particular, *o*-iminoquinones, into the coordination sphere of the main group metals makes it possible to involve these compounds into the reactions of oxidative addition and reductive elimination, which are not characteristic themselves of compounds of non-transition elements. The bright examples of these reactions are processes of molecular oxygen fixation by the antimony(V) catecholate and *o*-amidophenolate complexes [72, 73] and the reversible/irreversible addition of alkynes to the gallium(III) [74] and aluminum(III) [75] complexes.

ACKNOWLEDGMENTS

This work was supported by the Russian Science Foundation, project no. 17-13-01428.

REFERENCES

1. Kaim, W., *Inorg. Chem.*, 2011, vol. 50, p. 9752.
2. Poddel'sky, A.I., Cherkasov, V.K., and Abakumov, G.A., *Coord. Chem. Rev.*, 2009, vol. 253, p. 291.
3. Lange, C.W., Conclin, B.J., and Pierpont, C.G., *Inorg. Chem.*, 1994, vol. 33, p. 1276.
4. Ozarowsky, A., McGarvey, B.R., El-Hadad, A.A., et al., *Inorg. Chem.*, 1993, vol. 32, p. 841.
5. Lado, A.V., Piskunov, A.V., Zhdanovich, I.V., et al., *Russ. J. Coord. Chem.*, 2008, vol. 34, no. 4, p. 251.
6. Blackmore, K.J., Ziller, J.W., and Heyduk, A.F., *Inorg. Chem.*, 2005, vol. 44, p. 5559.
7. Blackmore, K.J., Sly, M.B., Haneline, M.R., et al., *Inorg. Chem.*, 2008, vol. 47, p. 10522.
8. Patai, S. and Rappoport, Z., *The Chemistry of Quinonoid Compounds*, New York: Wiley, 1988.
9. Abakumov, G.A., Druzhkov, N.O., Kurskii, Yu.A., et al., *Russ. Chem. Bull.*, 2003, vol. 52, p. 712.
10. Piskunov, A.V., Aivaz'yan, I.A., Poddel'sky, A.I., et al., *Eur. J. Inorg. Chem.*, 2008, no. 9, p. 1435.
11. Riviere, P., Castel, A., Satge, J., et al., *J. Organomet. Chem.*, 1986, vol. 315, p. 157.
12. Abakumov, G.A., Poddel'sky, A.I., Bubnov, M.P., et al., *Inorg. Chim. Acta*, 2005, vol. 358, p. 3829.
13. Chun, H., Chaudhuri, P., Weyhermuller, T., et al., *Inorg. Chem.*, 2002, vol. 41, p. 790.
14. Chun, H., Verani, C.N., Chaudhuri, P., et al., *Inorg. Chem.*, 2001, vol. 40, p. 4157.
15. Abakumov, G.A., Cherkasov, V.K., Poddel'skii, A.I., et al., *Dokl. Chem.*, 2004, vol. 399, p. 207.
16. Bruni, S., Caneschi, A., Cariati, F., et al., *J. Am. Chem. Soc.*, 1994, vol. 116, p. 1388.
17. Fedushkin, I.L., Khvoinova, N.M., Baurin, A.Y., et al., *Inorg. Chem.*, 2004, vol. 43, p. 7807.
18. Stegman, H.B., Scheffler, K., and Stocker, F., *Angew. Chem., Int. Ed. Engl.*, 1971, vol. 10, p. 499.
19. Woodul, W.D., Carter, E., Muller, R., et al., *J. Am. Chem. Soc.*, 2011, vol. 133, p. 10074.
20. Chia, S.-P., Carter, E., Xi, H.-W., et al., *Angew. Chem., Int. Ed. Engl.*, 2014, vol. 53, p. 8455.
21. Lu, X., Cheng, H., Meng, Y., et al., *Organometallics*, 2017, vol. 36, p. 2706.
22. Piskunov, A.V., Aivaz'yan, I.A., Fukin, G.K., et al., *Inorg. Chem. Commun.*, 2006, vol. 9, p. 612.
23. Piskunov, A.V., Mescheryakova, I.N., Fukin, G.K., et al., *Heteroat. Chem.*, 2009, vol. 20, p. 332.
24. Lado, A.V., Poddelsky, A.I., Piskunov, A.V., et al., *Inorg. Chim. Acta*, 2005, vol. 358, p. 4443.
25. Piskunov, A.V., Aivaz'yan, I.A., Abakumov, G.A., et al., *Russ. Chem. Bull.*, 2007, vol. 56, p. 261.
26. Piskunov, A.V., Chegerev, M.G., Vaganova, L.B., et al., *Russ. Chem. Bull.*, 1981, vol. 30, p. 157.
27. Stegman, H.B., Schrade, R., Saur, H., et al., *J. Organomet. Chem.*, 1981, vol. 214, p. 197.
28. Abakumov, G.A., Tsaryapkin, V.A., Gorbunova, L.V., et al., *Russ. Chem. Bull.*, 1981, vol. 30, p. 157.
29. Razuvaev, G.A., Abakumov, G.A., Bayushkin, P.Ya., et al., *Russ. Chem. Bull.*, 1984, vol. 33, p. 1915.
30. Batsanov, A.S., Howard, J.A.K., Brown, M.A., et al., *Chem. Commun.*, 1997, vol. 7, p. 699.
31. Brown, M.A., McGarvey, B.R., Ozarowsky, A., et al., *J. Organomet. Chem.*, 1998, vol. 550, p. 165.
32. Piskunov, A.V., Meshcheryakova, I.N., Baranov, E.V., et al., *Russ. Chem. Bull.*, 2010, vol. 59, p. 361.
33. Piskunov, A.V., Mescheryakova, I.N., Fukin, G.K., et al., *Chem.-Eur. J.*, 2008, vol. 14, p. 10085.
34. Piskunov, A.V., Chegerev, M.G., and Fukin, G.K., *J. Organomet. Chem.*, 2016, vol. 803, p. 51.
35. Piskunov, A.V., Piskunova, M.S., and Chegerev, M.G., *Russ. Chem. Bull.*, 2014, vol. 63, p. 912.
36. Vaganova, L.B., Kaprinina, A.N., Meshcheryakova, I.N., et al., *Russ. Chem. Bull.*, 2014, vol. 63, p. 744.
37. Vaganova, L.B., Shchepalov, A.A., Meshcheryakova, I.N., et al., *Dokl. Chem.*, 2012, vol. 447, p. 286.
38. Chegerev, M.G., Piskunov, A.V., Maleeva, A.V., et al., *Eur. J. Inorg. Chem.*, 2016, no. 23, p. 3813.
39. Piskunov, A.V., Lado, A.V., Fukin, G.K., et al., *Heteroat. Chem.*, 2006, vol. 17, p. 481.
40. Veith, M. and Grosser, M., *Z. Naturforsch.*, 1982, vol. 37, p. 1375.
41. Veith, M., *Angew. Chem., Int. Ed. Engl.*, 1987, vol. 26, p. 1.
42. Braunschweig, H., Gehrhus, B., Hitchcock, P.B., et al., *Z. Anorg. Allg. Chem.*, 1995, vol. 621, p. 1922.
43. Hahn, F.E., Wittenbecher, L., Duc Le Van, and Zabula, A.V., *Inorg. Chem.*, 2007, vol. 46, p. 7662.
44. Mansell, S.M., Russell, C.A., and Wass, D.F., *Inorg. Chem.*, 2008, vol. 47, p. 11367.
45. Aysin, R.R., Leites, L.A., Bukalov, S.S., et al., *Inorg. Chem.*, 2016, vol. 55, p. 4698.
46. Zabula, A.V., Rogachev, A.Y., and West, R., *Chem.-Eur. J.*, 2014, vol. 20, p. 16652.
47. Karsanov, I.V., Ivakhnenko, E.P., Khandkarova, V.S., et al., *Russ. Chem. Bull.*, 1987, vol. 36, p. 56.
48. Karsanov, I.V., Ivakhnenko, E.P., Khandkarova, V.S,. et al., *Russ. Chem. Bull.*, 1987, vol. 36, p. 60.
49. Romanenko, G.V., Ivakhnenko, E.P., Minkin, V.I., et al., *Inorg. Chim. Acta*, 2014, vol. 418, p. 66.
50. Girgis, A.Y. and Balch, A.L., *Inorg. Chem.*, 1975, vol. 14, p. 2724.
51. Stegman, H.B. and Scheffler, K., *Chem. Ber.*, 1970, vol. 103, p. 1279.
52. Chaudhuri, P., Hess, M., Hildenbrand, K., et al., *Inorg. Chem.*, 1999, vol. 38, p. 2781.
53. Starikov, A.G., Minkin, V.I., Minyaev, R.M., et al., *J. Phys. Chem. A*, 2010, vol. 114, p. 7780.
54. Camacho-Camacho, C., Merino, G., Martinez-Martinez, F.J., et al., *Eur. J. Inorg. Chem.*, 1999, no. 6, p. 1021.

55. Stegman, H.B., Scheffler, K., Stoecker, F., et al., *Chem. Ber.*, 1968, vol. 101, p. 262.
56. Ivakhnenko, E.P., Karsanov, I.V., Khandkarova, V.S., et al., *Russ. Chem. Bull.*, 1986, vol. 35, p. 2526.
57. Camacho-Camacho, C., Tlahuext, H., North, H., et al., *Heteroat. Chem.*, 1998, vol. 9, p. 321.
58. McGarvey, B.R., Ozarowsky, A., Tian, Z., et al., *Can. J. Chem.*, 1995, vol. 73, p. 1213.
59. Stegman, H.B., Scheffler, K., and Stocker, F., *Angew. Chem., Int. Ed. Engl.*, 1970, vol. 9, p. 456.
60. Stegman, H.B., Uber, W., and Scheffler, K., *Z. Anal. Chem.*, 1977, vol. 286, p. 59.
61. Piskunov, A.V., Sukhoshkina, O.Yu., and Smolyaninov, I.V., *Russ. J. Gen. Chem.*, 2010, vol. 80, p. 790.
62. Camacho-Camacho, C., Mijangos, E., Castillo-Ramos, M.E., et al., *J. Organomet. Chem.*, 2010, vol. 695, p. 833.
63. Shekar, S. and Brown, S.N., *Organometallics*, 2013, vol. 32, p. 556.
64. Ivakhnenko, E.P., Starikov, A.G., Minkin, V.I., et al., *Inorg. Chem.*, 2011, vol. 50, p. 7022.
65. Simakov, V.I., Gorbanev, Yu.Yu., Ivakhnenko, T.E., et al., *Russ. Chem. Bull.*, 2009, vol. 58, p. 1361.
66. Ranis, L.G., Werellapatha, K., Pietrini, N.J., et al., *Inorg. Chem.*, 2014, vol. 53, p. 10203.
67. Min, K.S., Weyhermuller, T., Bothe, E., et al., *Inorg. Chem.*, 2004, vol. 43, p. 2922.
68. Haeussler, H. and Jadamus, H., *Chem. Ber.*, 1964, vol. 97, p. 3051.
69. Chaudhuri, P., Hess, M., Mueller, J., et al., *J. Am. Chem. Soc.*, 1999, vol. 121, p. 9599.
70. Piskunov, A.V., Trofimova, O.Y., Fukin, G.K., et al., *Dalton Trans.*, 2012, vol. 41, p. 10970.
71. Cherkasov, V.K., Trofimova, O.Yu., Smolyaninov, I.V., et al., *Dokl. Chem.*, 2013, vol. 448, p. 61.
72. Abakumov, G.A., Poddel'sky, A.I., Grunova, E.V., et al., *Angew. Chem., Int. Ed. Engl.*, 2005, vol. 44, p. 2767.
73. Cherkasov, V.K., Abakumov, G.A., Grunova, E.V., et al., *Chem.-Eur. J.*, 2006, vol. 12, p. 3916.
74. Fedushkin, I.L., Nikipelov, A.S., and Lyssenko, K.A., *J. Am. Chem. Soc.*, 2010, vol. 132, p. 7874.
75. Fedushkin, I.L., Moskalev, M.V., Baranov, E.V., et al., *J. Organomet. Chem.*, 2013, vol. 747, p. 235.

Translated by E. Yablonskaya