



Stannylenes

Multiple Reactivity of Sn^{II} Complexes Bearing Catecholate and o-Amidophenolate Ligands

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Dedicated to Professor Vladimir K. Cherkasov on the occasion on his 70th birthday

Abstract: The reactivity of tin(II) catecholate complex CatSn (1) (where Cat = 3,6-di-*tert*-butylcatecholate dianion) and two *o*-amidophenolate complexes ^{Dipp}APSn (2) and ^{Ph}APSn (3) [where ^{Dipp}AP = 4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)amidophenolate; ^{Ph}AP = 4,6-di-*tert*-butyl-*N*-(phenyl)amidophenolate dianions] towards different reagents is reported. Products of the insertion of 1 and 2 into the S–S bond of tetramethylthiuram disulfide were obtained and characterised by X-ray diffraction

analyses. The low temperature oxidation of complexes **1** and **2** with 2-ethoxy-3,6-di-*tert*-butylphenoxy radical enabled us to detect formation of paramagnetic tin(II) derivatives containing the radical-anion form of the redox-active ligand. The reaction of tin derivative **3** with Ni(CO)₄ leads to substitution of one of the CO groups in the latter with the formation of a new bimetal-lic product.

Introduction

Considerable interest in the chemistry of heavier carbene analogues^[1a-1c] developed following the isolation of the first stable *N*-heterocyclic carbene in 1991 by Arduengo III.^[1d] At present many stable silylenes,^[2] germylenes,^[3] stannylenes^[3f,4] and plumbylenes^[5] derived from different heterocycles have been prepared. Interest in these compounds arises from their electronic structures, chemical properties and their ability to act in catalytically active metal complexes as *N*-heterocyclic carbenes.^[6]

The variation of heteroatoms in the chelating fragment of various metallenes provides a useful means for tuning their reactivity. Replacement of nitrogen atoms in the metallocycle with O-atoms leads to the formation of chelate *O*,*N*-(*o*-amido-phenolate) and *O*,*O*-(catecholate) complexes (Scheme 1). Moreover, as mentioned above, N,N, O,N and O,O ligands are potentially redox-active, which significantly expands their scope of reactivity.

Redox ligands can be used as reservoirs of electrons for bond-making and bond-breaking reactions. They also can support multi-electron transformations required to promote atomand group-transfer reactions.^[7] The ability of *o*-quinones and *o*iminoquinones to exist in three different redox states provides the foundation for their rich coordination chemistries.^[7f,8] Such complexes are interesting as potential reagents in organic synthesis, especially for addition, activation or transfer reactions of

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R, R' = alkyl, aryl or hydrogen

Scheme 1. Stable heavier analogues of carbenes.

small molecules. In particular, these species have proven to be very convenient objects for EPR investigations.^[9]

The complexes under consideration possess four possible and useful aspects of reactivity (Scheme 2): a) low valence Sn^{II} atom, which can be involved in oxidative addition reactions with the following formation of Sn^{IV} species, b) the ability to donate a lone pair of electrons to Lewis acids, such as transition metals, giving bimetallic derivatives, c) a vacant *p*-orbital by which the compound can react with Lewis bases, and d) a redox-active ligand enabling participation in redox processes independent of metal oxidation state.



X = O, NR'; LA - Lewis acid; LB - Lewis base

Scheme 2. Possible reactivity centres of stannylenes.



The present work reports investigation of multiple reactivity modes of some stannylenes bearing catecholate and *o*-amidophenolate ligands.

Results and Discussion

We previously reported the synthesis of stannylene derivatives based on 3,6-di-*tert*-butyl-o-benzoquinone CatSn (**1**) and 4,6di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzoquinone ^{Dipp}APSn (**2**). White trimeric complex **1** was obtained earlier as a minor product (21 % yield) of the reduction of 3,6-di-*tert*butyl-o-benzoquinone by tin amalgam.^[10a] Herein we used the salt metathesis reaction between CatNa₂^[10b] and the dioxane complex of tin dichloride in THF solution. This pathway is more efficient and complex **1** was obtained with high yield (84 %) (Scheme 3). Dimeric *o*-amidophenolate supported stannylene complex **2** was obtained as a result of salt metathesis reaction between ^{Dipp}APLi₂ and SnCl₂·diox in THF solution as a yellow material soluble in most organic solvents.^[4c] The compounds obtained were found to be stable in both the solid state and in solutions under anaerobic conditions.



Scheme 3. Synthesis of complexes 1 and 2.

The (a) Pathway: Oxidative Addition

Bond homolysis is a very useful reaction for probing accessible ligand-based reactivity and disulfides were found to be versatile reagents for examining reduction reactivity of metal complexes with redox-active ligands.^[10b,11a-11c] On the other hand, it is known that stannylenes undergo oxidative addition with disulf-ides.^[4f,11d] We have found that complexes **1** and **2** react readily with equimolar amounts of tetramethylthiuram disulfide (**TMTD**) to give dark-red crystalline diamagnetic products **3** and **4** with high yields. The reaction is complete within a few hours at the room temperature. These conditions do not induce homolytic dissociation of **TMTD** which proceeds at T = 130-150 °C.^[12] The reaction involves the insertion of low valence tin



into the S–S bond and consequent formation of new hexacoordinate tin(IV) complexes $\bf 3$ and $\bf 4$ containing Sn–S bonds (Scheme 4).



Scheme 4. Oxidative addition of TMTD to stannylenes.

The molecular structures of **3** and **4** were determined by Xray diffraction analysis and are shown in Figure 1. Selected metrical parameters can be found in Table 1. Single crystals suitable for X-ray diffraction analysis were obtained from the chilled mixture of CH_2CI_2/n -hexane. Crystals of **3** contain one solvated dichloromethane molecule. The geometry of coordination polyhedra in **3** and **4** can be described as a distorted trigonal prism or octahedron. The univocal choice of the coordination polyhedron type is unclear. The authors^[13] propose the use of the torsion angle α between coordination centres of bidentate li-



Figure 1. Crystal structures of **3** (top) and **4** (bottom) with 30 % thermal probability ellipsoids. The H atoms are omitted for clarity.



gands for the definition of coordination geometry in hexacoordinate complexes. The α value is equal to zero for a perfect trigonal prism, whereas it becomes 60° for a pure octahedral geometry. In the case of **3** and **4** (α_{av} = 43.3° and 44.4°, respectively) the coordination geometry is intermediate between the two edge structures. The Sn(1)–O(1) [2.0479(9) Å] and Sn(1)–O(2) [2.0223(9) Å] distances for **3** and Sn(1)–O(1) [2.0439(13) Å] and Sn(1)–N(1) [2.0640(17) Å] bond lengths for **4** are less than the sum of the covalent radii of the corresponding elements (2.09 Å for Sn–O,^[14] 2.1 Å for Sn–N^[14]) and are quite close to those observed in tin(IV) catecholate complexes (1.995–2.080 Å)^[10] and known *o*-amidophenolate tin compounds.^[15]

Table 1. Selected bond lengths [Å] and angles [°] of 3-CH₂Cl₂, 4, 5 and 7.

Bond [Å]	3-CH ₂ Cl ₂	4	5	7
Sn(1)–O(1)	2.0479(9)	2.0439(13)	2.0438(11)	2.0411(7)
Sn(1)-O(2)	2.0223(9)	-	-	-
Sn(1)–N(1)	-	2.0640(17)	2.2583(12)	2.0892(8)
Sn(1)-N(2)	-	-	-	2.4090(9)
Sn(1)-S(1)	2.5269(4)	2.5598(9)	-	-
Sn(1)-S(2)	2.5417(4)	2.5400(9)	-	-
Sn(1)–S(3)	2.5339(4)	2.5407(9)	-	-
Sn(1)-S(4)	2.5211(4)	2.5714(11)	-	-
C(1)-O(1)	1.3667(17)	1.367(2)	1.3546(18)	1.3642(12)
C(2)-O(2)	1.3630(16)	-	-	-
C(2)-N(1)	-	1.397(2)	1.451(2)	1.4027(12)
C(1)-C(2)	1.4164(19)	1.420(3)	1.404(2)	1.4215(13)
C(2)-C(3)	1.401(2)	1.395(3)	1.397(2)	1.3951(13)
C(3)–C(4)	1.395(2)	1.391(3)	1.382(2)	1.4031(13)
C(4)–C(5)	1.388(2)	1.395(3)	1.405(2)	1.3933(14)
C(5)–C(6)	1.392(2)	1.403(3)	1.393(2)	1.4103(14)
C(6)–C(1)	1.403(2)	1.400(3)	1.410(2)	1.4001(14)
Angles [°]				
O(1)-Sn(1)-N(1)	-	80.78(6)	78.65(4)	79.84(3)
O(1)-Sn(1)-N(2)	-	-	-	84.84(3)
O(1)-Sn(1)-O(2)	80.88(4)	-	-	-
N(1)-Sn(1)-N(2)	-	-	-	99.74(3)
S(1)-Sn(1)-S(2)	71.650(12)	71.30(3)	-	-
S(3)-Sn(1)-S(4)	71.727(12)	70.764(19)	-	-

The geometric parameters of redox-active ligands [C(1)–O(1) 1.3667(17) Å, C(2)–O(2) 1.3630(16) Å and C(1)–O(1) 1.367(2) Å and C(2)–N(1) 1.397(2) Å distances for 3 and 4 respectively] are in the range typical for the dianion form of the o-quinonate or o-iminobenzoquinonate ligands.^[16] The C-C distances in the six-membered carbon rings {C(1)-C(6) ring [1.388(2)-1.4164(19)] for **3** and 1.391–1.420 Å for **4**} are close to the typical aromatic bonds. All these data support the dianionic nature of redoxactive ligands in 3 and 4. Each thiocarbamate ligand adopts a bidentate mode of chelatation to the tin centre thus forming four-membered {CS₂Sn} rings. The S-Sn-S angles are close to 72°. The Sn(1)–S(1,2,3,4) bonds are practically equivalent and have middle lengths equal to 2.531 ± 0.010 Å for **3** and lie in the range from 2.540 Å to 2.571 Å for 4. The carbon-sulfur bond lengths of the chelate rings lie in the range from 1.724 Å to 1.736 Å, which are intermediate between single and double bond lengths and suggest considerable delocalization of charge.^[17]

The methyl protons of two thiocarbamate ligands are equivalent in the $[D_6]$ benzene ¹H NMR spectra and appear as singlets at $\delta = 2.10$ and 2.25 ppm for **3** and **4** respectively. The tin



resonances are located at $\delta_{Sn} = -658$ ppm and $\delta_{Sn} = -661$ ppm in the ¹¹⁹Sn NMR spectra. This region of $\delta_{Sn} = -500$ to -750 ppm is characteristic for hexacoordinate bis(dithiocarb-amato)tin(IV) derivatives.^[17a,18]

The (b) Pathway: Reaction with Lewis Acid

Some adducts of stannylenes with Lewis-acids like boron compounds or $AlCl_3$ are known.^[19] Regarding the complexes of stannylenes with transition metals, it should be mentioned that stannylenes act in these cases as Lewis bases; they may be stabilized by coordination of one or two solvent molecules.^[20]

In an effort to obtain a new bimetallic product, catecholate complex **1** was treated with Ni(CO)₄ in a molar ratio of 1:1. Unfortunately, all attempts to yield a Ni⁰ compound coordinated with stannylene failed. Most likely this compound is unstable and decomposes in solution to afford unidentified products.

With the aim of obtaining the amidophenolate-supported bimetallic compound, we decided to prepare less sterically-hindered stannylene complex **5** containing a phenyl group at the nitrogen atom. Preparation of the *N*-phenyl-substituted stannylene **5** was achieved by an amine elimination reaction between bis[bis(trimethylsilyl)amido]tin(II)^[21] and ^{Ph}APH₂ [where ^{Ph}APH₂ = 4,6-di-*tert*-butyl-*N*-(phenyl)-*o*-aminophenol]^[22] in Et₂O solution (Scheme 5).



Scheme 5. Preparation of complex 5.

The molecular structure of **5** was determined by single crystal X-ray diffraction analysis and is shown in Figure 2. Selected bond lengths and angles are reported in Table 1. Single crystals suitable for X-ray diffraction analysis were obtained from a saturated toluene solution. It was found that stannylene **5** dimerizes in the solid state via two strong intermolecular Sn•••N (2.351 Å) donor-acceptor interactions (sum of covalent radii of Sn and N = 2.21 Å^[14]).

The empty *p*-orbital of this tin centre normally acts as a strong Lewis-acid towards the unshared pair of electrons on the N-atom of a neighbouring molecule. Notably, this property influences the aggregation behaviour of stannylenes.^[4]

Also, there is a short metal–metal contact Sn···Sn (3.548 Å) which is longer than double the tin covalent radii (2.94 Å) but significantly shorter than double van-der-Waals radii (4.4 Å).^[14] However, at present we are not able to confirm the existence of a bonding interaction between these two tin atoms. This pursuit requires additional research and will be the subject of further investigations. Furthermore it should be noted that **5** shows a weak Sn··· η^{6} -C₆ intermolecular $p-\pi$ contact (3.373 Å) between tin atoms and the aromatic six-membered rings lo-





Figure 2. Crystal structure of **5** (top) with 30 % thermal probability ellipsoids. One-dimensional motif in crystal packing of **5** (bottom). The H atoms are omitted for clarity.

cated at nearby dimers. These kinds of weak Sn•••aryl interactions are known in the literature.^[23a] However, the distances observed in **5** are much greater than those seen in the well-established examples of Sn••• η^6 -aryl interactions,^[23b–23d] where distances as small as 2.53 Å have been observed.^[23d]

The tin atom in **5** has a distorted trigonal pyramidal ligand environment. The O(1), N(1) and N(1A) atoms of ^{Ph}AP ligands form the base of the pyramid. The lone pair of electrons is located at the vertex of a pyramid. The C(1)–O(1) 1.354 Å and C(2)–N(1) 1.451 Å distances lie in the range typical of the dianion form of the *o*-iminobenzoquinone ligand.^[16] The C–C distances in the six-membered carbon ring (1.382–1.410 Å) of the *o*-amidophenolate ligand are close to the typical aromatic bond values. The Sn(1)–N(1) and Sn(1)–O(1) bond lengths are comparable with known amidophenolate tin complexes.^[4c] The skeletons of the amidophenolate ligands are planar and are practically parallel to each other.

The [D₆]benzene ¹H NMR spectrum of **5** shows two singlets at δ = 1.35 and 1.66 ppm representative of protons for two *tert*butyl groups. Aromatic protons of the amidophenolate fragment appear as singlets at δ = 7.20 and 7.27 ppm and the protons of the *N*-phenyl substituent are represented as multiplets in the range from 6.76–7.07 ppm. The tin resonance is located at δ_{sn} = –212 ppm in the ¹¹⁹Sn NMR spectrum.

The first homoleptic nickel(0) complex of an N-heterocyclic stannylene – a stannylene analogue of nickel tetracarbonyl – was prepared in 1990.^[24a] Homoleptic complexes with dialkyl stannylene ligands were first isolated in 1999.^[24b] The benzannulated bis-stannylenes react with Ni(cod)₂ to give intensely colored homoleptic Ni⁰ complexes.^[24c] It was found that yellow stannylene **5** reacts readily with equimolar amounts of Ni(CO)₄



at room temperature in toluene (Scheme 6). The interaction is accompanied by gas evolution without any colour change of the reaction mixture. In contrast to N-heterocyclic stannylenes^[24a,24c] the reaction of **5** with Ni(CO)₄ leads to the formation of new monosubstituted diamagnetic bimetallic product 6 [^{Ph}APSnNi(CO)₃], which was identified on the basis of multinuclear NMR and IR spectroscopy. Unfortunately, all attempts to obtain single crystals suitable for X-ray diffraction analysis failed. The constitution of 6 was therefore confirmed by analytical and spectroscopic data. In the case of the ¹H NMR spectrum of **6** in $[D_6]$ benzene, all resonances mentioned above (complex 5) are slightly shifted. The ¹³C NMR spectrum revealed new signals belonging to the carbonyl groups bonded to the nickel atom at $\delta_c = 191.4$ and 195.2 ppm. The tin resonance is downshifted (relative to that in compound **5**) and is located at δ_{sn} = -201 ppm in the ¹¹⁹Sn NMR spectrum of **6**. Additionally, the vibrations of the carbonyl CO bonds in 6 are present in the IR spectrum as strong absorption bands in the range 1970-2080 cm⁻¹.



Scheme 6. Reactivity of stannylene 5 towards Ni(CO)₄.

It is necessary to note that reactivity similar to that of the stannylene species towards tetracarbonylnickel(0) with the formation of monosubstituted derivatives of the type R₂Sn-Ni(CO)₃ was observed for dialkoxytin(II)^[25a] and dialkyltin(II)^[25b] derivatives and triamidostannate anion.^[25c]

The (c) Pathway: Reaction with Lewis Base

The presence of a vacant *p*-orbital at the tin atom endows stannylenes with Lewis-acid properties and makes it possible for these species to react with different reagents containing unshared electron pairs. Such reactivity towards Lewis-bases was partly addressed above. Notably, the tin(II) derivatives are known to dimerize in the solid state through intermolecular donor-acceptor Sn–O or Sn–N interactions.^[4]

We were interested in the synthesis of a monomeric stannylene complex with strong Lewis bases such as pyridine. Freshly prepared yellow microcrystalline amidophenolate complex **2** was dissolved in pyridine to give an orange solution. Single crystals of new complex **7** suitable for X-ray diffraction analysis were obtained from saturated toluene solution. The geometry of the coordination polyhedron in **7** is best described as a distorted trigonal pyramidal (Figure 3). The C(1)–O(1) (1.364 Å), C(2)–N(1) (1.403 Å) and Sn(1)–O(1) (2.041 Å) and Sn(1)–N(1) (2.089 Å) bond lengths are comparable with amidophenolate tin complexes **2**,^[4c] **4** and **5**. The value of the Sn(1)–N(2) distance (2.409 Å) is more than the sum of the covalent (2.21 Å)^[14]





but less than the sum of the van-der-Waals radii (3.8 Å)^[14] of the corresponding elements, indicating the donor–acceptor nature of this moiety.





Scheme 7. Oxidation of **1** and **2** by **RO**[•] (top). Coordination-decoordination equilibrium of complex **9** in solution (bottom).

Figure 3. Crystal structure of ${\bf 7}$ with 30 % thermal probability ellipsoids. The H atoms are omitted for clarity.

The chelating *o*-amidophenolate ligand has nearly a planar geometry. The coordinated molecule of pyridine is practically orthogonal to the dianion ligand plane (93.64°). The sum of angles around the tin atom in **7** is 264.4° with a narrow endocyclic O(1)–Sn(1)–N(1) angle of 79.8°. These data are indicative of p³ geometry with a noninteracting stereochemically active lone pair of electrons.

The (d) Pathway: Oxidation of the Redox-Active Ligand

Stannylenes **1** and **2** were found to react with **TMTD** through the (a)-pathway (Scheme 2) involving oxidation of a low-valence metal atom giving tin(IV) derivatives. During the reaction the redox-active ligand retained its oxidation state.

It has been previously shown that catecholate and diimine complexes of non-transition metals react with different radicals and subsequent oxidation of the redox-active ligand giving paramagnetic derivatives observable by EPR spectroscopy.^[9,10b,26]

In order to obtain paramagnetic stannylene derivatives, complexes **1** and **2** were treated with a THF solution of stable 2ethoxy-3,6-di-*tert*-butylphenoxy radical (**RO**').^[27] The latter was found to be a versatile radical source; it is a dimeric diamagnetic compound in the solid state which dissociates reversibly in solution to give two phenoxy radicals at 200–350 K.^[27] Stannylenes **1** and **2** were found to interact readily with **RO**[•] to produce radical derivatives **8** and **9**, respectively (Scheme 7). Reactions were realized in an EPR-cell with equimolar amounts of **RO**[•]. It is notable that paramagnetic adducts **8** and **9** were identified by EPR-spectroscopy only at low temperature (Figure 4 and Figure 5).

Metal complexes with paramagnetic organic ligands containing Sn^{II} or Sn^{IV} centres can be easily distinguished. Compounds containing low-valence tin are usually characterized by large



Figure 4. X-band EPR spectra of complex 8 in THF at 235 K.

hyperfine coupling constant (HFC) values $(a_i^{117,119}Sn \ge 90 \text{ G}).^{[26a,28]}$ In the case of Sn^{IV} derivatives, HFC values are usually decreased and located in the range from 20–50 G.^[29] This is known both for tin derivatives^[28] as well as for other non-transition metal compounds.^[30]

In the case of complex **8**, the hyperfine structure of the EPR spectrum arises from the HFC of an unpaired electron with two equivalent magnetic nuclei of ¹H (99.98 %, l = 1/2, $\mu_{\rm N} = 2.7928$) as well as satellite splitting on ¹¹⁷Sn (7.68 %, l = 1/2, $\mu_{\rm N} = 1.000$) and ¹¹⁹Sn (8.58 %, l = 1/2, $\mu_{\rm N} = 1.046$).^[31] The splitting parameters are as follows: $a_i(2^{1}\text{H}) = 3.73 \text{ G}$, $a_i(^{117}\text{Sn}) = 94.3 \text{ G}$, $a_i(^{119}\text{Sn}) = 98.6 \text{ G}$, $g_i = 2.0031$. The observation of HFCs with two equivalent hydrogens and large values of $a_i(^{117,119}\text{Sn})$ indicates the formation in the reaction system of a derivative containing a one-electron oxidized Cat ligand – *o*-semiquinone (SQ) with the Sn^{II} centre.





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Figure 5. X-band EPR spectra of the reaction mixture of complex **2** and (**RO**^{\cdot}) in THF at 235 K. (a – spectra of the complex **9**^{\prime}, b – **9** and exp – experimental spectra).

It should be noted that the EPR spectrum of compound 9 is a superposition of two signals (Figure 5, lines **a** and **b**) with different g-factors and ^{117,119}Sn satellite splitting. It can be explained by the existence of two forms of the radical complex in solution - three-coordinate 9' in which ethoxy group is not coordinated by metal centre and four-coordinate compound 9, where this bonding does, in fact, take place. The splitting parameters are as follows: for **9** $-a_i(^{1}H) = 4.69$ G, $a_i(^{14}N) = 6.69$ G, $a_i(^{117}Sn) = 167.3 \text{ G}, a_i(^{119}Sn) = 175 \text{ G}, g_i = 2.0018 \text{ and for } \mathbf{9'} - \mathbf{9'}$ $a_i({}^{1}\text{H}) = 4.69 \text{ G}, a_i({}^{14}\text{N}) = 6.69 \text{ G}, a_i({}^{117}\text{Sn}) = 100.9 \text{ G}, a_i({}^{119}\text{Sn}) =$ 105.6 G, $q_i = 2.0009$. The fact that we observe both isomers can be tentatively explained by the slow (on the EPR time scale) equilibrium between 9 and 9'. In the case of complex 8, we do not observe a three-coordinate derivative due to the reduced steric hindrance presented by the redox-active ligand, relative to 9. Analysis of the EPR data clearly indicates formation of compounds containing radical-anion redox-active ligands and the Sn^{II} centre.

Unfortunately, all attempts to isolate paramagnetic compounds **8** and **9** failed. It was established that increasing the temperature to 290 K led to disappearance of the EPR spectra for reaction mixtures and changed solution colours from blue (**8**) or green (**9**) to yellow. Complexes **8** and **9** were found to be labile in solution and to undergo transformations giving rise to diamagnetic products, which were identified on the basis of NMR as previously noted Sn^{IV} bis-catecholate Cat₂Sn(THF)₂^[10] and bis-amidophenolate AP₂Sn-THF^[4c] species, respectively. Bisphenoxy complex of divalent tin (**RO**)₂Sn was also formed as the result of these reactions. The presence of these compounds in the reaction mixture can be explained by symmetrisation of complexes **8** and **9** in solution with the subsequent formation of (**RO**)₂Sn and diradical species of low-valence tin – compounds **10** and **11**. Species **10** and **11** undergo intramolecular redox transformations^[10,32] (Scheme 8) to produce diamagnetic Cat₂Sn(THF)₂ and AP₂Sn-THF.



Scheme 8. Transformations of complexes 8 and 9. The benzene part of the ligands is omitted for clarity.

Conclusions

In summary, the multiple modes of reactivity for new stannylenes supported by redox-active ligands were investigated. Reaction with **TMTD** invokes oxidation of the tin(II) centre and leads to formation of new hexacoordinate tin(IV) derivatives. In the reaction with Ni(CO)₄ stannylene acts as a Lewis-base giving new bimetallic product **6**. Through a vacant *p*-orbital, metallene compound can react with Lewis-bases such as pyridine. Additionally, oxidation of the redox-active ligand at tin leads to formation of paramagnetic derivatives of divalent tin, which undergo intramolecular redox transformation giving derivatives of tin(IV).

Experimental Section

General Considerations: All reactants were purchased from Aldrich [Caution!!! Ni(CO)₄ is an exceedingly toxic material and requires careful handling]. Solvents were purified by standard methods.[33] o-Amidophenolate complex 2^[4c] and dimeric 2-ethoxy-3,6-di-tertbutylphenoxy radical^[27] were prepared according to known procedures. All manipulations on complexes were performed in vacuo under conditions in which oxygen and moisture were excluded. EPR spectra were recorded using a Bruker EMX spectrometer (working frequency \approx 9.75 GHz). The g_i values were determined using 2,2diphenyl-1-picrylhydrazyl (DPPH) as the reference ($g_i = 2.0037$). EPR spectra were simulated using Easyspin toolbox for Matlab.^[34] The infrared spectra of complexes in the 4000–400 $\rm cm^{-1}$ range were recorded with a FSM 1201 Fourier-IR spectrometer in nujol. NMR spectra were recorded in C₆D₆ solution using a Bruker Avance III 400 MHz instrument with TMS as an internal standard. The signals in the NMR spectra were assigned using 2D ge-COSY and ge-HSQC procedures. Elemental analyses were performed with an Elemental Analyzer Euro EA 3000 instrument. Metal atom percentages were estimated by pyrolysis of the investigated samples and subsequent weighing of the obtained metal oxide.





Synthesis of [CatSn]₃ (1): The straw-coloured solution of sodium catecholate^[10b] (1.57 g, 2.5 mmol) in THF (25 mL) was added to the THF (15 mL) solution of SnCl₂-diox (0.695 g, 2.5 mmol). The reaction mixture became cloudy and colourless in a few minutes. THF was removed under reduced pressure and the residue was dissolved in hexane (25 mL). The NaCl precipitate was removed by filtration. Trimeric complex **1** was obtained as a fine crystalline nearly colourless product. IR and NMR spectra of product obtained were identical to those previously reported^[10b] for **1**, yield 0.71 g (84 %).

The Interaction of Complex 1 with TMTD: The solution of TMTD (0.3 g, 1.25 mmol) in CH₂Cl₂ (20 mL) was added to the suspension of complex 1 (0.425 g, 1.25 mmol) in the same solvent (20 mL). The reaction mixture was kept for a few hours at room temperature. The colour of reaction mixture became intense orange-red. The residue was recrystallized from the mixture CH₂Cl₂/n-hexane (1:1). The obtained crystals lose solvated dichloromethane molecule under drying on vacuum conditions. Complex 3 was obtained as a red crystalline product, yield 0.57 g (78 %). C₂₀H₃₂N₂O₂S₄Sn (579.41): calcd. C 41.46, H 5.57, S 22.13, Sn 20.49; found C 41.50, H 5.60, S 22.09, Sn 20.43. ¹H NMR (C₆D₆, 20 °C): δ = 6.97 (s, 2 H, H_{Cat}); 2.10 (s, 12 H, Me); 1.84 [s, 18 H, (tBu)] ppm. ¹³C NMR (C₆D₆, 20 °C): δ = 197.3, 149.1, 132.9, 114.1, 64.4, 52.8, 45.0, 34.8, 30.0, 15.1 ppm. ¹¹⁹Sn NMR ($C_6 D_{61}$ 20 °C): $\delta = -657.5$ ppm. IR (Nujol): $\tilde{v} = 1550$ (s) , 1475 (s), 1400 (s), 1275 (s), 1250 (s), 1205 (m), 1170 (m), 1150 (m), 975 (s), 945 (w), 925 (m), 800 (w), 745 (w), 700 (m) cm⁻¹.

The Interaction of Complex 2 with TMTD: The solution of TMTD (0.24 g, 1.0 mmol) in CH₂Cl₂ (20 mL) was added to the solution of complex 2 (0.5 g, 1.0 mmol) in the same solvent (20 mL). The reaction mixture was kept for a few hours at room temperature. The colour of the reaction mixture became intense crimson-red. The residue was recrystallized from the mixture CH₂Cl₂/n-hexane (1:1). Complex 4 was obtained as a crystalline product, yield 0.61 g (82 %). C32H49N3OS4Sn (738.69): calcd. C 52.03, H 6.69, S 17.36, Sn 16.07; found C 52.1, H 6.63, S 17.40, Sn 16.10. ¹H NMR (C₆D₆, J/Hz, 20 °C): δ = 7.34–7.24 (m, 3 H, H_{aryl}); 7.05 [s, J_{H,H} = 2.6 Hz, 1 H, H_{AP}]; 6.33 (s, J_{H,H} = 2.6 Hz, 1 H, H_{AP}); 3.72 [sept, J_{H,H} = 6.8 Hz, 2 H, CH(*i*Pr)]; 2.25 (s, 12 H, Me); 1.91 [s, 9 H, (tBu)]; 1.40 [s, 9 H, (tBu)]; 1.33 [d, J_{H.H} = 6.8 Hz, 6 H, CH₃(*i*Pr)]; 1.20 [d, J_{H,H} = 6.8 Hz, 6 H, CH₃(*i*Pr)] ppm. ¹³C NMR (C₆D₆, 20 °C): δ = 198.8, 149.9, 147.1, 144.1, 140.8, 137.6, 132.8, 126.0, 123.9, 110.0, 107.8, 65.4, 52.8, 45.0, 35.3, 34.3, 31.9, 31.3, 30.2, 29.7, 28.0, 25.9, 24.7, 22.5, 15.1, 13.9 ppm. ¹¹⁹Sn NMR $(C_6D_6, 20 \text{ °C}): \delta = -660.6 \text{ ppm. IR (Nujol)}: \tilde{v} = 1582 \text{ (s)}, 1414 \text{ (s)}, 1359$ (m), 1329 (s), 1286 (m), 1266 (m), 1256 (m), 1232 (m), 1211 (s), 1111 (w), 1101 (w), 1051 (w), 1026 (m), 994 (s), 914 (w), 870 (s), 797 (s), 775 (w), 693 (w), 656 (m), 609 (m), 534 (w), 446 (w) cm⁻¹.

Synthesis of ^{Ph}**APSn (5):** The solution of Sn[N(SiMe₃)₂]₂^[21] (0.444 g, 1 mmol) in Et₂O (25 mL) was added to the solution of 4,6-di-*tert*-butyl-*N*-(phenyl)-*o*-aminophenol^[22] (0.3 g, 1 mmol) in the same solvent (15 mL). The reaction mixture became pale yellow in a few minutes. Et₂O was removed under reduced pressure and the residue was recrystallized from the hot toluene. Complex **5** was obtained as a fine crystalline yellow product, yield 0.33 g (80 %). C₂₀H₂₅NOSn (414.11): calcd. C 58.00, H 6.08, N 3.38, Sn 28.67; found C 58.06, H 6.04, N 3.40, Sn 28.62. ¹H NMR (C₆D₆, 20 °C): δ = 7.27 (s, 1 H, H_{AP}); 7.20 (s, 1 H, H_{AP}); 7.07–6.76 (m, 5 H, H_{aryl}); 1.66 [s, 9 H, (tBu)]; 1.35 [s, 9 H, (tBu)] ppm. ¹³C NMR (C₆D₆, 20 °C): δ = 156.8, 147.5, 140.8, 139.7, 138.3, 129.4, 121.9, 120.9, 118.3, 117.1, 35.4, 34.3, 31.7, 29.7 ppm. ¹¹⁹Sn NMR (C₆D₆, 20 °C): δ = -212.1 ppm.

The Interaction of Complex 5 with Ni(CO)₄: The Ni(CO)₄ (0.17 g, 1.0 mmol) was added to the frozen solution of complex **5** (0.42 g, 1.0 mmol) in toluene (25 mL). The reaction mixture was kept for a few days at room temperature. The colour of reaction mixture did

not change. During the reaction CO gas evolution was observed. The residue was recrystallized from the *n*-hexane. Complex **6** was obtained as a fine crystalline yellow product, yield 0.41 g (73 %). C₂₃H₂₅NNiO₄Sn (556.85): calcd. C 49.61, H 4.53; found C 49.66, H 4.50. ¹H NMR (C₆D₆, 20 °C): δ = 7.26 (s, 1 H, H_{AP}); 7.21 (s, 1 H, H_{AP}); 7.07–6.76 (m, 5 H, H_{aryl}); 1.67 [s, 9 H, (tBu]]; 1.34 [s, 9 H, (tBu]] ppm. ¹³C NMR (C₆D₆, 20 °C): δ = 195.2, 191.4, 156.9, 147.4, 140.7, 139.7, 138.3, 129.5, 122.0, 120.7, 118.1, 117.3, 35.5, 34.4, 31.6, 29.8 ppm. ¹¹⁹Sn NMR (C₆D₆, 20 °C): δ = –201. 6 ppm. IR (Nujol): \tilde{v} = 2073 (m), 2006 (m), 1988 (m), 1593 (m), 1482 (s), 1411 (s), 1296 (s), 1254 (s), 1236 (s), 1211 (s), 1180 (m), 1154 (m), 1120 (w), 1080 (w), 1030 (w), 963 (w), 915 (w), 873 (m), 840 (m), 820 (m), 766 (s), 756 (s), 694 (m) cm⁻¹.

Synthesis of Complex DippAPSnPy (7): Freshly prepared complex 2 (0.5 g, 1.0 mmol) was dissolved in excess pyridine (15 mL). The colour of reaction mixture became intense orange. Pyridine was removed under reduced pressure and the residue was recrystallized from hot toluene. Complex 7 was obtained as a crystalline orange product, yield 0.53 g (91 %). C₃₁H₄₂N₂OSn (577.38): calcd. C 64.49, H 7.33, Sn 20.56; found C 64.52, H 7.30, Sn 20.51. ¹H NMR (C₆D₆, J/ Hz, 20 °C): δ = 8.10 (m, 3 H, H_{Pv}), 7.29–7.20 (m, 3 H, H_{anyl}), 7.13– 7.08 [m, 2 H, H(C-H)]; 6.36 (m, 2 H, H_{Py}), 3.06 [sept, $J_{H,H}$ = 7.1 Hz, 2 H, CH(iPr)]; 1.91 [s, 9 H, CH₃(tBu)]; 1.35 [s, 9 H, CH₃(tBu)]; 1.10 [d, J_{H,H} = 7.1 Hz, 6 H, CH₃(*i*Pr)]; 0.83 [d, J_{H,H} = 7.1 Hz, 6 H, CH₃(*i*Pr)] ppm. ¹³C NMR (C_6D_6 , 20 °C): δ = 156.9, 153.1, 147.9, 147.1, 146.1, 141.6, 139.4, 139.1, 138.1, 137.3, 134.1, 123.9, 123.6, 121.5, 120.1, 110.1, 41.1, 35.3, 31.9, 31.4, 29.6, 28.8, 28.7, 27.7, 26.14, 25.8, 25.5, 25.3, 25.0, 24.5, 24.3, 23.5, 22.7, 22.6, 22.5 ppm. ¹¹⁹Sn NMR (C₆D₆, 20 °C): δ = -80.4 ppm.

The EPR-Experiment: Interactions of Complexes 1 and 2 with 3,6-di-tert-Butyl-2-ethoxyphenoxy Radical: The solution of 3,6-di-tert-butyl-2-ethoxyphenoxy radical (0.05 g, 0.1 mmol) in THF (2 mL) was placed in an EPR-cell. The solution was frozen at 77 K. The solution of complex 1 (0.03 g, 0.1 mmol) or complex 2 (0.05 g, 0.1 mmol) in toluene (2 mL) was added into this EPR-cell and the reaction mixture was frozen again. Generating radical complexes were registered by EPR-spectroscopy upon thawing without isolation. Paramagnetic compounds are unstable and undergo transformations giving diamagnetic products, which were identified by using NMR spectroscopy as previously obtained bis-catecholate Cat₂Sn(THF)₂^[10] and bis-amidophenolate AP₂Sn-THF^[4c] complexes.

X-ray Crystallographic Study of 3-CH₂Cl₂, 4, 5 and 7: The single crystals suitable for X-ray diffraction analysis were obtained from the mixture of CH_2Cl_2 /hexane (3· CH_2Cl_2 and 4) and toluene (5 and 7). Intensity data were collected at 100 K on a Smart Apex I (3) and Xcalibur Eos (4, 5 and 7) diffractometers with graphite monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å). The intensity data were integrated by the SAINT^[35] (for 3) and CrysAlisPro^[36] (for 4, 5 and 7) programs. SADABS^[37] and SCALE3 ABSPACK^[36] were used to perform area-detector scaling and absorption corrections. The structures 3-CH₂Cl₂, 4, 5 and 7 were solved by direct methods and were refined on F² using all reflections with SHELXTL package.^[38] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and refined in the "ridingmodel". Selected bond lengths and angles of complexes obtained are given in Table 1. Table 2 summarizes the crystal data and some details of the data collection and refinement.

CCDC 1470507 (for $\mathbf{3}$ - $\mathbf{CH}_2\mathbf{CI}_2$), 1470508 (for $\mathbf{4}$), 1470509 (for $\mathbf{5}$) and 1470510 (for $\mathbf{7}$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.





Table 2. Summary of crystal and refinement data for complexes 3-CH₂Cl₂, 4, 5 and 7.

	3-CH ₂ Cl ₂	4	5	7			
Empirical formula	$C_{21}H_{34}Cl_2N_2O_2S_4Sn$	$C_{32}H_{49}N_3OS_4Sn$	C ₄₀ H ₅₀ N ₂ O ₂ Sn ₂	$C_{31}H_{42}N_2OSn$			
Formula weight	664.33	738.67	828.20	577.36			
Temperature [K]	100(2)	150(2)	100(2)	100(2)			
Wavelength [Å]	0.71073	0.71069	0.71073	0.71073			
Crystal system	monoclinic	triclinic	monoclinic	monoclinic			
Space group	P21/n	PĪ	C2/c	P21/c			
Unit cell dimensions	a = 11.3701(6) Å	a = 11.674(5) Å	a = 30.2314(4) Å	a = 15.72609(14) Å			
	b = 16.4553(9) Å	<i>b</i> = 12.470(5) Å	<i>b</i> = 6.28481(8) Å	b = 9.99875(8) Å			
	c = 15.4319(8) Å	c = 13.199(5) Å	c = 20.0063(3) Å	c = 19.03126(17) Å			
	$\alpha = 90^{\circ}$	$\alpha = 98.756(5)^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$			
	$\beta = 96.8940(10)^{\circ}$	$\beta = 100.105(5)^{\circ}$	$\beta = 94.9298(11)^{\circ}$	$\beta = 105.5279(9)^{\circ}$			
	$\gamma = 90^{\circ}$	$\gamma = 102.285(5)^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$			
Volume [ų]	, 2866.4(3)	1812.1(13)	, 3787.12(8)	, 2883.27(4)			
Z	4	2	4	4			
Density (calculated) $[q \text{ cm}^{-3}]$	1.539	1.354	1.453	1.330			
Absorption coefficient [mm ⁻¹]	1.390	0.963	1.354	0.911			
Crystal size [mm ³]	0.21 × 0.16 × 0.09	$0.40 \times 0.24 \times 0.18$	$0.20 \times 0.10 \times 0.10$	$0.40 \times 0.40 \times 0.20$			
F(000)	1352	768	1680	1200			
Theta range for data collection,	1.82 to 24.00	3.20 to 28.88	3.25 to 27.00	3.05 to 30.00			
Reflections collected	14232	18740	29734	55278			
Independent reflections (R _{int})	4461 (0.0183)	8209 (0.0208)	4108 (0.0359)	8340 (0.0251)			
Absorption correction		semi-empirical from equivalents					
Max. and min. transmission	0.8851 and 0.7590	0.8457 and 0.6992	0.8765 and 0.7735	0.8388 and 0.7121			
Refinement method		full-matrix, least-squares on F^2					
Data/restraints/parameters	4461/0/423	8209/0/384	4108/0/214	8340/0/326			
Final R indices $[l > 2\sigma(l)]$	$R_1 = 0.0203,$	$R_1 = 0.0248,$	$R_1 = 0.0216,$	$R_1 = 0.0183,$			
	$wR_2 = 0.0498$	$wR_2 = 0.0596$	$wR_2 = 0.0449$	$wR_2 = 0.0440$			
R indices (all data)	$R_1 = 0.0233,$	$R_1 = 0.0337,$	$R_1 = 0.0314,$	$R_1 = 0.0214$			
	$wR_2 = 0.0507$	$wR_2 = 0.0621$	$wR_2 = 0.0473$	$wR_2 = 0.0453$			
Goodness-of-fit on F ²	1.056	1.050	1.050	1.039			

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Stannylenes

Multiple Reactivity of Sn^{II} Complexes Bearing Catecholate and *o*-Amidophenolate Ligands



Multiple modes of reactivity for selected stannylenes bearing redox-active catecholate and o-amidophenolate ligands towards different reagents are reported.

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