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The Reaction of 3,6-Di-*tert*-butyl-*o*-benzoquinone with Tin Amalgam: Synthesis and Structure of Tin Catecholato Complexes

Alexandr V. Piskunov, Aryna V. Lado, Georgy K. Fukin,
Evgeny V. Baranov, Ludmila G. Abakumova,
Vladimir K. Cherkasov, and Gleb A. Abakumov

G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 49 Tropinina Street, 603950 Nizhny Novgorod, Russia

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ABSTRACT: *The reduction of 3,6-di-tert-butyl-o-benzoquinone with tin amalgam gives the different tin catecholate complexes. The use of polar solvents for this reaction leads to the formation of* $Cat_2Sn \cdot L_2$ *species (where Cat—dianion of 3,6-di-tert-butylcatechol,* $L = Et_2O$*, THF, Py). The reaction carried out in toluene produces the mixture of dicatecholate tin(IV) and catecholate tin(II) derivatives. The complex* $Cat_2Sn \cdot (Et_2O)_2$ *was shown to be a good starting reagent for the preparation of different tin(IV) catecholate complexes of the type* $Cat_2Sn \cdot L'$ $(L' = $ *1,2-dimethoxyethane, 1,4-di-tert-butyldiazadiene-1,3, o-phenantrolyne,* α,α'*-dipyridyl) using ligand exchange reactions. Compounds* $Cat_2Sn \cdot (Et_2O)_2$*,* $Cat_2Sn \cdot (THF)_2$*,* $Cat_2Sn \cdot (Bu^tN{=}CHCH{=}NBu^t)$*, and* $(CatSn)_3$ *have been crystallographically characterized.* DOI 10.1002/hc.20271

INTRODUCTION

The direct element oxidation by *o*-quinones is a rich tool for the preparation of various *o*-quinone complexes of transition or nontransition metals and some nonmetals [1]. The heavier Group 14 elements have very different reactivity toward substituted *o*-quinones. Germanium reacts with 3,5-di-*tert*-butyl-*o*-benzoquinone slowly (boiling toluene, 12 days) to give GeQ_2, GeQ_3, or GeQ_4 (Q—one of the reduced or nonreduced form of 3,5-di-*tert*-butyl-*o*-benzoquinone) complexes depending on the initial ratio of reactants [2]. Lead reacts with *o*-quinones more rapidly to form lead(II) catecholate or bis(*o*-semiquinonate) derivatives [3,4]. The reaction between tin and *o*-chloranil in refluxing toluene produces bis(tetrachlorocatecholate)tin(IV) [5]. Different *o*-semiquinonate and catecholate tin species were postulated in reaction mixtures of tin and *tert*-butyl substituted *o*-quinones by use of various spectroscopic methods but no solid products were obtained [6,7].

In the present paper, we report the synthesis of various tin catecholate complexes $Cat_2Sn{\cdot}L_n$ (Cat—dianion of 3,6-di-*tert*-butylcatechol, L = different donor ligands, $n = 1, 2$) by the reaction between tin amalgam and 3,6-di-*tert*-butyl-*o*-benzoquinone (3,6-Q) in different solvents with subsequent ligand exchange procedures.

Correspondence to: Alexandr V. Piskunov; e-mail: pial@imoc.sinn.ru.

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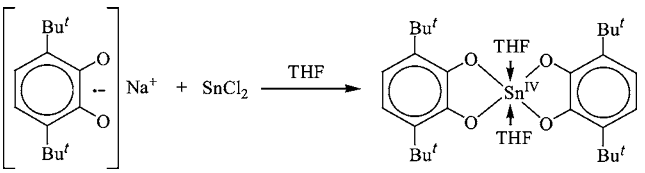
RESULTS AND DISCUSSION

The reaction between tin amalgam and 3,6-Q is accompanied by color change from green to light yellow. Tenfold excess of metal amalgam and polar solvent (diethyl ether, tetrahydrofuran or pyridine) allow this reaction to run to completion in 20 min at room temperature. The main products of this reaction are bis(3,6-di-*tert*-butylcatecholato)tin(IV) derivatives (Scheme 1). Compounds **1–3** were isolated with quantitative yields.

These compounds are white (**1, 2**) or light yellow (**3**) crystalline substances. They are sufficiently stable in solid state toward oxygen and moisture. The solutions of **1** and **2** are readily oxidized by being exposed to air.

In previous papers [6,7], a number of *o*-semiquinonate tin derivatives have been described using the reaction of tin metal or amalgam with 3,5- and 3,6-di-*tert*-butyl-*o*-benzoquinones. Authors [6] have proposed the formation of bis(*o*-semiquinonato)tin(II) derivative on the basis of EPR spectroscopy data. But no evidence for such compounds was provided. On the other hand, complexes **1–3** are potential "redox isomers" [8] of bis(*o*-semiquinonato)tin(II) (Scheme 2).

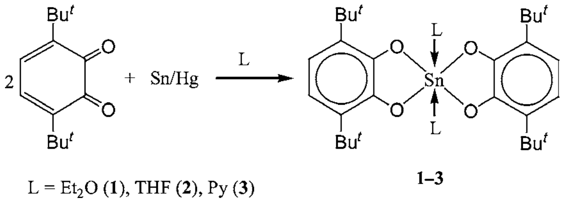
Compounds **1–3** are diamagnetic in solid state and in solution. Furthermore, they possess well-resolved NMR spectra. It proved that these complexes exist in form **B**. The X-ray analysis also confirms catecholate type of quinonoid ligands in **1, 2** and **5** (see below). All *o*-semiquinonate tin derivatives obtained in previous works [6,7] show EPR spectra with hyperfine coupling (*hfc*) constants with magnetic isotopes ^{117,119}Sn about 5–7 G. These values are typical for tin(IV) *o*-semiquinonate species [9]. Paramagnetic tin(II) complexes have *hfc* constants with tin magnetic isotopes about 150 G [10,11]. Thus, the existence of bis(*o*-semiquinonato)tin(II) derivatives containing 3,5- or 3,6-di-*tert*-butyl-*o*-benzosemiquinone ligands is unlikely. Moreover, we have obtained additional evidence for this assertion. The reaction between $SnCl_2$ and two equivalents of sodium 3,6-di-*tert*-butyl-*o*-benzosemiquinonate in THF solution is accompanied by the immediate disappearance of EPR-signal and mixture discoloration. Complex **2** was isolated with good yield after recrystallization from CCl_4 (Scheme 3).



SCHEME 3

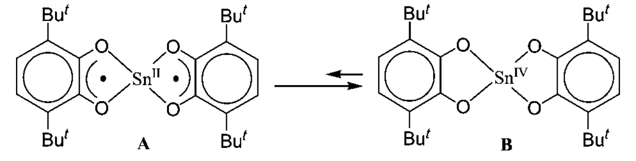
The crystal structures of **1** and **2** have been determined by single-crystal X-ray diffraction. Molecular structures of **1** and **2** are shown in Figs. 1 and 2, respectively. There are two crystallographically unique molecules in the asymmetric unit of **2**, but their geometries around the metal center are similar and only Sn(1) molecule is discussed.

Tin atoms have octahedral geometry with *trans*-disposition of ligands in both **1** and **2** complexes. The Sn(1) atom lies on the twofold axis in **1** and on the inversion center in **2**. All angles in SnO_6 fragment of **1** and **2** are close to 90°. There is no deviation of Sn(1) from the O(1)O(2)O(1A)O(2A) plane. Oxygen atoms of catecholate ligands O(1), O(2), O(1A), and O(2A) occupy equatorial positions, and ether molecules are at the apical sites. Sn(1)–O(1,2) distances in **1** and **2** are in the range of 1.986(2)–1.997(2) Å. These values



1–3

SCHEME 1



SCHEME 2

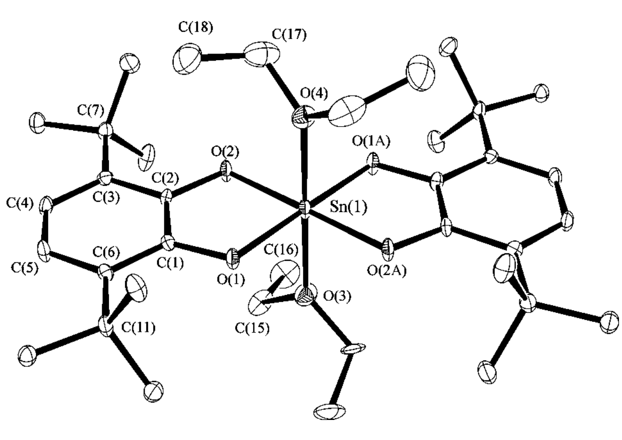


FIGURE 1 An ORTEP view of **1** with 30% probability ellipsoids (H atoms are omitted for clarity).

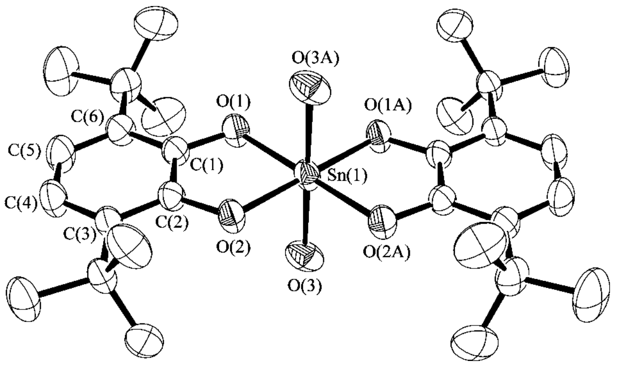
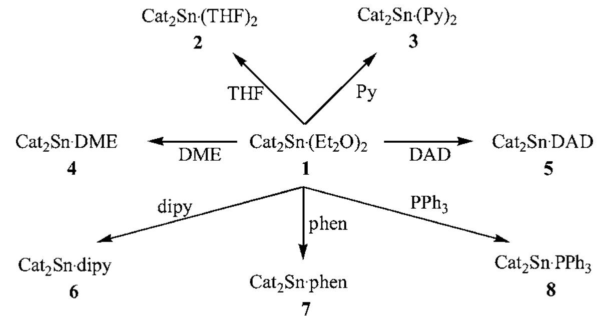


FIGURE 2 An ORTEP view of **2** with 30% probability ellipsoids (H atoms and THF carbons are omitted for clarity).



SCHEME 4

are in good agreement with the sum of covalent atom radii [12]. Lengths of Sn(1)–O(3) and Sn(1)–O(4) bonds (2.232(3) and 2.243(3) Å, respectively for **1** and Sn(1)–O(3) bond (2.229(3) Å) for **2** are longer than in known tin(IV) derivatives containing Et_2O or THF coordinated molecules—$SnCl_4{\cdot}(Et_2O)_2$ (Sn–O, 2.190(3)) [13] and $SnCl_4{\cdot}(THF)_2$ (Sn–O, 2.166(2)) [14]. Most likely, this is caused by steric hindrances of bulky *tert*-butyl substituents of catecholate ligands. Distances between THF molecules and tin atom are slightly shorter than in the case of Et_2O. It points to stronger interaction between cyclic ether and metal. The average C–O bond lengths (1.370(4) Å for **1**, 1.366(5) Å for **2**) are close to those observed for known catecholate tin(IV) derivatives (1.34–1.38 Å) [15].

Complex **1** is a good starting reagent for the preparation of various bis(3,6-di-*tert*-butylcatecholato)tin(IV) compounds. The ether molecules in **1** can be readily replaced in the coordination sphere of tin by mono- or bi-dentate ligands. The treatment of **1** with toluene solutions of various O-, N-, and P-donor ligands (THF), pyridine (Py), 1,2-dimethoxyethane (DME), α,α'-dipyridyl (dipy), 1,4-di-*tert*-butyldiazabutadiene-1,3 (DAD), 1,10-phenanthroline (phen), and PPh_3) gives new five- (in the case of PPh_3) or six-coordinated tin complexes with quantitative yields (Scheme 4).

It is necessary to note that complexes **2, 4, 5**, and **8** can be transformed to **3, 6**, and **7** by the interaction with corresponding N-donor ligands.

Complexes **3, 4–8** are less soluble in most organic solvents and more stable toward oxygen and moisture than **1** and **2**.

The molecular structure of complex **5** was determined by X-ray diffraction analysis. There are two crystallographically unique molecules in the asymmetric unit of **5**, but their geometries around metal center are similar and only Sn(1) molecule is discussed. Crystal of **5** contains one molecule of toluene per molecule of **5**. Complex **5** has a distorted octahedral geometry with *cis*-located equal catecholate ligands (Fig. 3). In contrast to Sn—O distances obtained for **1** and **2**, there are significant discrepancies between Sn(1)–O(1) and Sn(1)–O(2) distances in **5** (2.006(2) and 2.035(2) Å, respectively. This difference can result from the steric interaction between Bu^t groups of catecholate and diimine ligands. The intramolecular C(12)···C(18) distance is 3.601(4) Å (from the direction of Sn(1)–O(2) bond), whereas the C(9)···C(17A) distance is 3.840(4) Å (from the direction of Sn(1)–O(1) bond). Also the nonbonding interaction between Bu^t groups leads to decrease of the O(1)Sn(1)O(2) (82.33(8)°) angle in comparison with analogous values in **1** (84.32(8)°) and **2** (83.97(9)°). Consequently, the Sn(1)–N(1, 1A) bond lengths (2.312(2) Å) are also longer than the analogous distances in $(Cat)_2Sn{\cdot}dipy$ (2.252 Å) complex [15a]. Bond distances N(1)–C(19) and C(19)–C(19A) in DAD are equal to values in free ligand (1.268, 1.469, respectively, [16]).

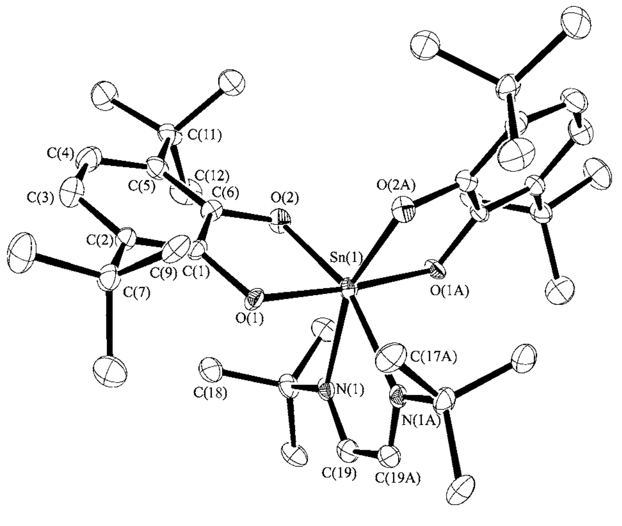


FIGURE 3 An ORTEP view of **5** with 50% probability ellipsoids (H atoms are omitted for clarity).

The reaction between tin amalgam and 3,6-Q in toluene is not as fast as in polar solvents. The reaction needs about 3 h for completion under effective stirring at 80°C. The evaporation of the solvent gives a light yellow solid product. The elemental analysis of the crude product (C 56.01, H 6.68, Sn 26.56%) is very close to calculated one for 3,6-di-*tert*-butylcatechol–tin ratio about 3:2 (Calc. for $C_{42}H_{60}O_6Sn_2$: C 55.80, H 6.67, Sn 26.45%). The NMR spectra of the latter show three singlets (δ (ppm): 1.36, 54H, *t*-Bu; 6.40, 4H, H_{arom}; and 6.73, 2H, H_{arom}) related to two different 3,6-di-*tert*-butylcatecholate ligands (ratio 2:1), which are different by H_{arom} proton signals. The treatment of the reaction mixture after the reaction of 3,6-Q and Sn/Hg in toluene with diethyl ether is completed, produces the complex **1** with 45% yield counting upon initial *o*-quinone. On the other hand, white crystals of the 3,6-di-*tert*-butylcatecholate tin(II) trimer (**9**) (21% yield counting upon initial *o*-quinone) were separated after prolonged crystallization of this reaction mixture from toluene.

The loss of the tin amalgam mass after completion of the reaction is close to 0.66 mol per 1 mol of *o*-quinone. These results demonstrate the existence of equimolar mixture of bis(3,6-di-*tert*-butylcatecholato)tin(IV) and 3,6-di-*tert*-butylcatecholate tin(II) in the crude product (Scheme 5).

A complementary experiment was made to prove this assertion. Tin(II) derivatives are known to be readily oxidized by *o*-quinone to give corresponding tin(IV) catecholates [15a,e,f]. The resulting filtered reaction mixture (Scheme 5) was treated with additional 1 mol of *o*-quinone in the toluene. The color of *o*-quinone immediately disappeared.

We were unable to isolate pure unsolvated bis(3,6-di-*tert*-butylcatecholato)tin(IV), but the injection of the diethyl ether produced complex **1** with quantitative yield (Scheme 6).

$$3\ 3{,}6\text{-Q} + 2\text{Sn/Hg} \xrightarrow{\text{toluene}} \text{Cat}_2\text{Sn}^{\text{IV}} + \text{CatSn}^{\text{II}}$$

SCHEME 5

$$\text{Cat}_2\text{Sn}^{\text{IV}} + \text{CatSn}^{\text{II}} + 3{,}6\text{-Q} \xrightarrow{\text{toluene}} 2\text{Cat}_2\text{Sn}^{\text{IV}} \xrightarrow{\text{Et}_2\text{O}} 2\text{Cat}_2\text{Sn}\cdot(\text{Et}_2\text{O})_2$$

SCHEME 6

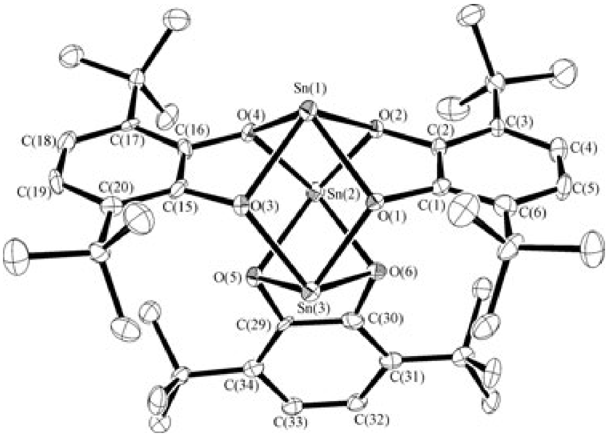


FIGURE 4 An ORTEP view of **9** with 30% probability ellipsoids (H atoms are omitted for clarity).

The crystal structure of **9** has been determined by single-crystal X-ray analysis. It is the first structurally characterized tin(II) catecholate derivative. Complex **9** has a trimeric structure (Fig. 4). The oxygen atoms of catecholate groups are located in the apexes of a distorted prism (Fig. 5).

The O(1)O(2)O(6) and O(3)O(4)O(5) fragments lie in the base of prism. The dihedral angle between bases is 1.5°, and the distance between geometrical centers of the O(1)O(2)O(6) and O(3)O(4)O(5) planes is 2.534 Å. Tin atoms are located approximately above the centers of each face. They form a triangle close to isosceles (Sn(1)···Sn(2) 3.513(1) Å, Sn(2)···Sn(3) 3.468(1) Å, Sn(1)···Sn(2) 3.512(1) Å; Sn(1)Sn(2)Sn(3) 60.41(5)°, Sn(2)Sn(3)Sn(1) 60.44(5)°, Sn(3)Sn(1)Sn(2) 59.15(5)°) without any bonding between metal atoms. For known covalent Sn_3 species, the metal–metal bond is

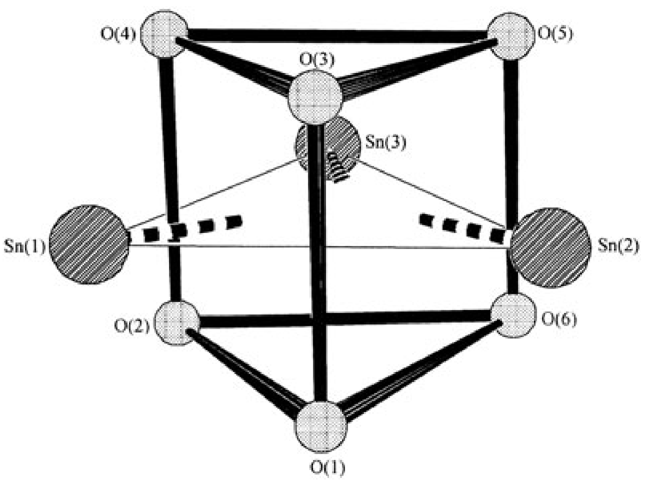


FIGURE 5 An ORTEP view core of **9**.

about 2.854(7) Å [17]. The O(1)C(1)C(6)O(2) and O(3)C(15)C(16)O(4) catecholate fragments lie at the same plane and are orthogonal to the O(5)C(29)C(34)O(6) fragment. The Sn—O distances vary in the range of 2.201(4)–2.334(4) Å (average 2.247(4) Å), which is significantly longer than covalent bonds in complexes **1, 2** and **5**. This difference is similar to the difference of the ionic radii for Sn(II) and Sn(IV) [12]. It is necessary to note that the Sn(1) atom has a bonding with two catecholate ligands (O(1, 2) and O(3, 4) atoms) whereas Sn(2) and Sn(3) with three ligands (O(5, 6), O(3), O(1) atoms for Sn(2) and O(5, 6), O(4), O(2) for Sn(3)). The OSnO angles (about 70–80°) are typical for tetragonal tin(II) complexes [18]. The average C–O distance (1.391(7) Å) is slightly longer than those obtained for **1, 2** and **5** or another known tin(IV) catecholato derivatives (1.34–1.38 Å) [15]. In the crystal of **9**, there are shortening interatomic Sn(1)· · ·Sn(1) (4.202(2) Å) contacts in comparison with sum of van der Waals radii (4.4 Å [19]). This contact leads to the formation of dimer pairs. Note that the structure of **9** is sufficiently unexpected. It was thought that the 3,6-di-*tert*-butylcatecholate ligand is not prone to form bridging bonds in contrast to the 3,5-substituted analog [20]. The structure of **9** is a first example of μ_2- and μ_3-type of 3,6-di-*tert*-butylcatecholate ligand.

CONCLUSION

The reaction between tin amalgam and 3,6-di-*tert*-butyl-*o*-benzoquinone in polar solvents gives octahedral bis(3,6-di-*tert*-butylcatecholate)tin(IV) complexes containing two molecules of the corresponding coordinated solvent. A row of neutral ligands capable of replacing each other in the coordination sphere of tin(IV) catecholate complexes is established. The reduction of 3,6-di-*tert*-butyl-*o*-benzoquinone with tin amalgam in toluene produces equimolar mixture of bis(3,6-di-*tert*-butylcatecholato)tin(IV) and 3,6-di-*tert*-butylcatecholate tin(II). The X-ray structure determination was carried out for $Cat_2Sn{\cdot}(Et_2O)_2$, $Cat_2Sn{\cdot}(THF)_2$, $Cat_2Sn{\cdot}DAD$, and $(CatSn)_3$. The unexpected trimeric structure was found for complex $(CatSn^{II})_3$.

EXPERIMENTAL

General

Reagents were obtained from Aldrich, Fluka, and Strem, and were used as purchased. Solvents were purified by standard methods [21]. 3,6-Q [22] and 1,4-di-*tert*-butyldiazadiene-1,3 [23] were synthesized according to literature procedures. Tin amalgam was prepared by dissolution of tin metal in liquid mercury [24]. All reactions were carried out under vacuum.

IR spectra were recorded on Specord M-80. NMR spectra were obtained by use of "Bruker Avance DPX 200" NMR spectrometer.

*Synthesis of Bis(3,6-di-tert-butylcatecholato)tin(IV) Complexes $Cat_2Sn{\cdot}L_2$ (**1–3**) ($L = Et_2O$ (**1**), THF (**2**), Pyridine (**3**))*

The general procedure followed for the synthesis of tin(IV) catecholate complexes is described here. The solution of 3,6-Q (1.1 g, 5 mmol) in the appropriate solvent (20 mL) was stirred with tenfold excess of tin amalgam at room temperature until *o*-quinone color disappeared. The reaction mixture was filtered and the solvent was removed under reduced pressure. The residue was recrystallized from the suitable solvent. Yields (per initial 3,6-Q), solvents used, and analytical results for all complexes are given in Table 1.

Reaction of $SnCl_2$ with Sodium 3,6-Di-tert-butyl-o-benzosemiquinonate

The solution of 3,6-Q (0.55 g, 2.5 mmol) in THF (20 mL) was treated with an excess of sodium dispersion until *o*-quinone color disappeared. This solution was filtered and added to 3,6-Q (0.55 g, 2.5 mmol) to give a deep blue solution of sodium 3,6-di-*tert*-butyl-*o*-benzosemiquinonate. $SnCl_2$ (0.474 g, 2.5 mmol) in 10 mL THF was added dropwise to sodium 3,6-di-*tert*-butyl-*o*-benzosemiquinonate solution. The reaction mixture became light yellow. The solvent was evaporated, and the residue was dissolved in toluene and filtered. The recrystallization from CCl_4 gives 1.306 g (1.85 mmol, 73.6 % yield) of the complex **2**.

Ligand Exchange Reactions

The toluene solution of complex **1** (0.353 g, 0.5 mmol) was treated with 1 mmol of a solid ligand in the same solvent (or with 1 mL of the liquid ligand). The mixture was stirred at room temperature during 1 h. The solvent was evaporated to dryness and the residue was recrystallized from the appropriate solvent. Yields of complexes **4–8** (counting upon initial complex **1**), solvents, and analytical results for all complexes are given in Table 1.

TABLE 1 Yields, Solvents Used, and Analytical Results of Spectroscopic Data for Complexes **1–9**

Complex Number	*Color*	*Yield (%)*	*Solvent 1. Reaction 2. Recrystallization*	*Microanalysis*		*IR (Nujol)(cm^{-1}), ν(CO), ν(CN)*	*^{1}H NMR (CDCl$_3$)^a, δ, J (Hz)*
				Found (%)	*Calc. (%)*		
$Cat_2Sn{\cdot}(Et_2O)_2$ (**1**)	White	94	1. Et_2O 2. CH_2Cl_2	C 60.80; H 8.47; Sn 16.69	For $C_{36}H_{60}O_6Sn$: C 61.13; H 8.49; Sn 16.79	1260, 1240, 1205, 1150	0.88, s, 12H, OCH_2CH_3; 1.41, s, 36H, Bu^t; 3.45, s, 8H, OCH_2CH_3; 6.77, s, 4H, H$_{arom}$, $J(^{117/119}Sn—H)$ 6.0
$Cat_2Sn{\cdot}(THF)_2$ (**2**)	White	87	1. THF 2. CCl_4	C 61.25; H 7.91; Sn 17.09	For $C_{36}H_{56}O_6Sn$: C 61.48; H 7.97; Sn 16.89	1285, 1235, 1205, 1050	1.47, s, 36H, Bu^t; 1.71, m, 8H, β-CH_2; 3.88, m, 8H, α - CH_2; 6.65, s, 4H, H$_{arom}$, $J(^{117/119}Sn—H)$ 6.2
$Cat_2Sn{\cdot}(Py)_2$ (**3**)	Light yellow	95	1. Py 2. Toluene	C 63.40; H 7.13; Sn 16.25	For $C_{38}H_{50}O_4N_2Sn$: C 63.63; H 6.98; Sn 16.56	1595, 1325, 1285, 1245, 1210, 1180, 1150	1.42, s, 36H, Bu^t; 6.53, s, 4H, H$_{arom}$, $J(^{117/119}Sn—H)$ 5.8; 7.33–7.40, m, 4H, β-H$_{arom}$ (Py); 7.76–7.83, m, 2H, α-H$_{arom}$ (Py); 8.64–8.67, m, 4H, γ-H$_{arom}$ (Py)
$Cat_2Sn{\cdot}DME$ (**4**)	White	85	1. DME 2. Toluene	C 59.18; H 7.77; Sn 18.50	For $C_{32}H_{50}O_6Sn$: C 59.20; H 7.70; Sn 18.30	1270, 1240, 1205, 1150, 1080, 1035	1.39, s, 36H, Bu^t; 3.31, s, 6H, OCH_3; 3.47, s, 4H, OCH_2; 6.47, s, 4H, H$_{arom}$, $J(^{117/119}Sn—H)$ 5.6
$Cat_2Sn{\cdot}DAD$ (**5**)	Brown	91	1. Toluene 2. Toluene	C 62.86; H 8.37; Sn 16.18	For $C_{38}H_{60}O_4N_2Sn$: C 62.75; H 8.26; Sn 16.33	1675, 1240, 1200, 1150, 1100	1.35, s, 36H, Bu^t; 1.55, s, 18H, Bu^t; 6.45, s, 4H, H$_{arom}$, $J(^{117/119}Sn—H)$ 5.5; 8.96, s, 2H, CH, $J(^{117}Sn—H)$ 73.5, $J(^{119}Sn—H)$ 76.8
$Cat_2Sn{\cdot}dipy$ (**6**)	Orange	89	1. Toluene 2. THF	C 63.82; H 6.65; Sn 16.69	For $C_{38}H_{48}O_4N_2Sn$: C 63.80; H 6.72; Sn 16.61	1615, 1325, 1290, 1245, 1150	1.27, s, 36H, Bu^t; 6.39, s, 4H, H$_{arom}$, $J(^{117/119}Sn—H)$ 5.8; 8.05–8.12, m, 2H, H$_{arom}$ (dipy); 8.59, m, 2H, H$_{arom}$ (dipy); 8.93–9.03, m, 4H, H$_{arom}$ (dipy)
$Cat_2Sn{\cdot}phen$ (**7**)	Red-orange	94	1. Toluene 2. Toluene	C 64.95; H 6.55; Sn 16.00	For $C_{40}H_{48}O_4N_2Sn$: C 64.98; H 6.50; Sn 16.09	1650, 1290, 1245, 1150	1.22, s, 36H, Bu^t; 6.39, s, 4H, H$_{arom}$, $J(^{117/119}Sn—H)$ 5.8; 7.17–7.19, m, 2H, H$_{arom}$ (phen); 8.33–8.39, m, 2H, H$_{arom}$ (phen); 9.13–9.25, m, 4H, H$_{arom}$ (phen)
$Cat_2Sn{\cdot}PPh_3$ (**8**)	Orange	83	1. Toluene 2. Toluene	C 67.20; H 7.00; Sn 14.46; P 3.78	For $C_{46}H_{55}O_4PSn$: C 67.18; H 6.79; Sn 14.44; P 3.89	1265, 1245, 1150, 1105	1.41, s, 36H, Bu^t; 6.77, s, 4H, H$_{arom}$, $J(^{117/119}Sn—H)$ 5.6, 7.84, m, 15H, H$_{arom}$ (PPh_3)
$(CatSn)_3$ (**9**)	White	21	1. Toluene 2. Toluene	C 49.80; H 5.77; Sn 34.89	For $C_{42}H_{60}O_6Sn$: C 49.60; H 5.91; Sn 35.04	1290, 1255, 1220, 1165	1.36, s, 18H, Bu^t; 6.73, s, 2H, H$_{arom}$ $J(^{117/119}Sn—H)$ 5.8

[a] For 4–8 $(CD_3)_2CO$.

TABLE 2 The Details of Crystallographic, Collection, and Refinement Data for Complexes **1, 2, 5** and **9**

	1	**2**	**5**	**9**
Empirical formula	$C_{36}H_{60}O_6Sn$	$C_{36}H_{56}O_6Sn$	$C_{38}H_{60}O_4N_2Sn(C_7H_8)$	$C_{42}H_{60}O_6Sn_3$
Formula weight	707.53	703.50	727.48	1016.97
Temperature (K)	100(2)	293(2)	100(2)	100(2)
Crystal system	Tetragonal	Monoclinic	Monoclinic	Triclinic
Space group	*P*4 (3) 2 (1) 2	*P*2(1)/*c*	*C*2/*c*	*P*-1
Unit cell dimensions	$a = 9.9198(11)$ Å, $\alpha = 90°$ $b = 9.9198(11)$ Å, $\beta = 90°$ $c = 36.813(6)$ Å, $\gamma = 90°$	$a = 11.6921(5)$ Å, $\alpha = 90°$ $b = 15.8849(7)$ Å, $\beta = 99.7630(10)°$ $c = 20.2147(9)$ Å, $\gamma = 90°$	$a = 26.237(3)$ Å, $\alpha = 90°$ $b = 16.0803(16)$ Å, $\beta = 105.240(3)°$ $c = 21.515(2)$ Å, $\gamma = 90°$	$a = 11.1402(12)$ Å, $\alpha = 67.192(2)°$ $b = 14.2239(7)$ Å, $\beta = 86.266(2)°$ $c = 14.9670(16)$ Å, $\gamma = 75.438°$
Volume (Å^3)	3622.5(8)	3700.1(3)	8758.0(15)	2114.6(4)
Z	4	4	8	2
Density (calculated) (Mg/m^3)	1.297	1.263	1.243	1.597
Absorption coefficient (mm^{-1})	0.746	0.730	0.625	1.801
F(0 0 0)	1496	1480	3472	1020
Crystal size (mm^3)	0.16 × 0.80 × 0.04	0.50 × 0.30× 0.20	0.18 × 0.07 × 0.07	0.10 × 0.10 × 0.10
Reflections collected/unique	20280/3199 [*R*(int) = 0.0629]	24252/5156 [*R*(int) = 0.0289]	23997/7699 [*R*(int) = 0.0742]	9938/6046[*R*(int) = 0.0400]
Absorption correction	SADABS	SADABS	SADABS	SADABS
Max. and min. transmission	0.9708; 0.8900	0.8677; 0.7166	0.9576; 0.8959	0.9982; 0.8404
Data/restraints/ parameters	3199/10/308	5156/52/419	7699/0/738	6046/0/460
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0353$, $wR2 = 0.0699$	$R1 = 0.0377$, $wR2 = 0.1041$	$R1 = 0.0443$, $wR2 = 0.0701$	$R1 = 0.0383$, $wR2 = 0.0758$
R indices (all data)	$R1 = 0.0404$, $wR2 = 0.0714$	$R1 = 0.0589$, $wR2 = 0.1125$	$R1 = 0.0888$, $wR2 = 0.0787$	$R1 = 0.0657$, $wR2 = 0.0840$
Goodness-of-fit on F^2	1.113	1.067	0.976	0.973
Largest differential peak and hole (e Å^{-3})	0.676; −0.427	0.417; −0.295	0.979; −0.499	1.069; −0.531

[a] $R = \sum ||F_0| - |F_c|| \sum |F_0|$.

[b] $\omega R = R(\omega F^2) = \{\sum[\omega(F_0^2 - F_c^2)^2]/\sum[\omega(F_0^2)^2]\}^{1/2}$; $\omega = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_0,0)]/3$.

[c] $S = \text{Goof} = \{\sum [\omega(F_0^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where *n* is the number of reflections and *p* is the number of refined parameters.

TABLE 3 Selected Bond Distances (Å) and Angles (°) for **1** and **2**

	Complex			*Complex*	
Bond Distance	**1**	**2**	*Bond Angle*	**1**	**2**
Sn(1)—O(1)	1.987(2)	1.992(2)	O(1)Sn(1)O(1A)	178.68(12)	180.0
Sn(1)—O(2)	1.997(2)	1.995(2)	O(1)Sn(1)O(2A)	95.68(8)	96.03(9)
Sn(1)—O(3)	2.243(3)	2.229(3)	O(1)Sn(1)O(2)	84.32(8)	83.97(9)
Sn(1)—O(4)	2.232(3)	–	O(2A)Sn(1)O(2)	179.38(13)	180.00(11)
C(1)—O(1)	1.365(3)	1.367(4)	O(1)Sn(1)O(3A)	–	91.25(11)
C(1)—C(2)	1.375(3)	1.366(4)	O(1)Sn(1)O(4)	90.66(6)	–
C(2)—O(2)	1.397(4)	1.409(5)	O(1)Sn(1)O(3)	89.34(6)	88.75(11)
C(2)—C(3)	1.419(4)	1.400(5)	O(2)Sn(1)O(3)	89.69(6)	88.86(10)
C(3)—C(4)	1.393(4)	1.383(5)	O(2)Sn(1)O(3A)	–	91.14(10)
C(4)—C(5)	1.361(5)	1.378(5)	O(2)Sn(1)O(4)	90.31(6)	–
C(5)—C(6)	1.399(4)	1.390(5)	O(3)Sn(1)O(3A)	–	180.0(13)
C(1)—C(6)	1.408(4)	1.392(5)	O(3)Sn(1)O(4)	180.0	–
C(5)—C(7)	1.524(4)	1.534(5)	C(1)O(1)Sn(1)	110.37(18)	110.55(19)
C(6)—C(11)	1.517(4)	1.538(5)	C(2)O(2)Sn(1)	109.70(18)	110.43(19)
			O(1)C(1)C(2)	117.8(3)	117.4(3)
			O(2)C(2)C(1)	117.7(3)	117.5(3)

Reaction of 3,6-Q with Tin Amalgam in Toluene

The solution of 3,6-Q (1.1 g, 5 mmol) in toluene (20 mL) was stirred with tenfold excess of tin amalgam at 80°C until the o-quinone color disappeared. The loss of the tin amalgam mass was 0.38 g (3.2 mmol of tin). The reaction mixture was filtered. There are four different experiments for examination of this reaction mixture:

a. Reaction mixture was evaporated to dryness and a light yellow solid was obtained. The elemental analysis of this crude product (C 56.01, H 6.68, Sn 26.56%) corresponds to the compound(s) containing three 3,6-di-*tert*-butylcatechol ligands per two tin atoms (Calc. for $C_{42}H_{60}O_6Sn_2$: C 55.80, H 6.67, Sn 26.45%). The NMR spectra of the latter show three singlets (δ (ppm): 1.36, 54H, *t*-Bu; 6.40, 4H, H_{arom}; and 6.73, 2H, H_{arom}).
b. The filtrate was evaporated up to half volume. The solution was kept at room temperature for 3 months. A white crystalline precipitate of bis(μ_3-3,6-di-*tert*-butylcatecholato-O,O,O′,O′)–(μ_2-3,6-di-*tert*-butylcatecholato-O,O,O′,O′)-tri-tin(II **9** (0.189 g, 1.06 mmol, yield: 21% per initial 3,6-Q) was collected by filtration. Solvents and analytical results for complex **9** are given in Table 1.
c. The reaction mixture was evaporated until it was dry and the residue was treated with Et_2O. After recrystallization from CH_2Cl_2, compound **1** (0.798 g, 1.13 mmol) was obtained.
d. The reaction mixture was added to the solution of 3,6-Q (0.352 g, 1.6 mmol) in toluene (10 mL). The color of *o*-quinone immediately disappeared. The reaction mixture was evaporated until it was dry and the residue was treated with Et_2O. After recrystallization from CH_2Cl_2, compound **1** (1.97 g, 2.8 mmol; yield: 85% per total quantity of 3,6-Q) was obtained.

X-ray Diffraction Studies

The suitable crystals for X-ray diffraction were prepared by the prolonged crystallization from CH_2Cl_2 solution for **1**, CCl_4 solution for **2**, and toluene solution for **5** and **9**.

X-ray diffraction experiments were carried out on a Smart Apex diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) in the φ–ω scan mode ($\omega = 0.3°$, 10 s on each frame). The intensity data were integrated by SAINT program [25]. SADABS [26] was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined on F^2 using all reflections with SHELXTL package [27]. All non-hydrogen atoms were refined anisotropically. One part of hydrogen atoms was placed in calculated positions and refined in the "riding-model," and the other part found from Fourier synthesis was refined isotropically in **1, 5** complexes. All H atoms were placed in calculated positions and refined in the "riding-model" in **2, 9** complexes. A solvate molecule of toluene was found in **6**. The details of crystallographic collection and refinement data are shown in Table 2. The selected bond distances and angles are shown in Table 3 for **1** and **2**, Table 4 for **5**, and Table 5 for **9**.

TABLE 4 Selected Bond Distances (Å) and Angles (°) for **5**

Bond Distance		*Bond Angle*	
Sn(1)—O(1)	2.0063(18)	O(1)Sn(1)O(1A)	175.32(11)
Sn(1)—O(2)	2.035(2)	O(1)Sn(1)O(2A)	94.68(8)
Sn(1)—N(1)	2.312(2)	O(1)Sn(1)O(2)	82.33(8)
O(1)—C(1)	1.363(3)	O(2A)Sn(1)O(2)	101.04(11)
O(2)—C(6)	1.366(3)	O(1)Sn(1)N(1A)	86.56(8)
N(1)—C(19)	1.264(4)	O(2A)Sn(1)N(1A)	94.31(9)
N(1)—C(15)	1.514(4)	O(2)Sn(1)N(1A)	161.69(8)
C(1)—C(2)	1.406(4)	O(1)Sn(1)N(1)	97.22(8)
C(1)—C(6)	1.425(4)	N(1A)Sn(1)N(1)	72.64(13)
C(2)—C(3)	1.383(4)	C(1)O(1)Sn(1)	111.83(16)
C(2)—C(7)	1.525(4)	C(6)O(2)Sn(1)	111.51(17)
C(3)—C(4)	1.383(4)	C(19)N(1)C(15)	119.8(3)
C(4)—C(5)	1.387(4)	C(19)N(1)Sn(1)	113.5(2)
C(5)—C(6)	1.399(4)	O(1)C(1)C(2)	121.7(3)
C(5)—C(11)	1.543(4)	O(1)C(1)C(6)	117.4(2)
C(19)—C(19A)	1.469(7)	O(2)C(6)C(5)	122.3(3)
		O(2)C(6)C(1)	116.3(3)
		N(1)C(19)C(19A)	120.15(19)

TABLE 5 Selected Bond Distances (Å) and Angles (°) for **9**

Bond Distance		*Bond Angle*	
Sn(1)—O(3)	2.201(4)	O(3)Sn(1)O(2)	108.85(14)
Sn(1)—O(2)	2.209(4)	O(3)Sn(1)O(1)	70.23(14)
Sn(1)—O(1)	2.238(4)	O(2)Sn(1)O(1)	70.47(15)
Sn(1)—O(4)	2.241(4)	O(3)Sn(1)O(4)	71.12(14)
O(1)—C(1)	1.384(7)	O(2)Sn(1)O(4)	70.24(15)
O(1)—Sn(2)	2.214(4)	O(1)Sn(1)O(4)	110.03(14)
Sn(2)—O(3)	2.233(4)	Sn(2)O(1)Sn(1)	104.21(17)
Sn(2)—O(6)	2.253(4)	O(1)Sn(2)O(3)	70.08(14)
Sn(2)—O(5)	2.289(4)	O(1)Sn(2)O(6)	80.77(14)
O(2)—C(2)	1.377(7)	O(3)Sn(2)O(6)	117.05(14)
O(2)—Sn(3)	2.229(4)	O(1)Sn(2)O(5)	116.17(14)
Sn(3)—O(4)	2.244(4)	O(3)Sn(2)O(5)	78.41(14)
Sn(3)—O(5)	2.283(4)	O(6)Sn(2)O(5)	66.42(14)
Sn(3)—O(6)	2.334(4)	Sn(1)O(2)Sn(3)	104.64(15)
O(3)—C(15)	1.389(7)	O(2)Sn(3)O(4)	69.82(14)
O(4)—C(16)	1.392(7)	O(2)Sn(3)O(5)	115.83(15)
O(5)—C(29)	1.410(7)	O(4)Sn(3)O(5)	79.89(14)
O(6)—C(30)	1.394(7)	O(2)Sn(3)O(6)	80.68(14)
Sn(1)···Sn(2)	3.513(1)	O(4)Sn(3)O(6)	117.37(14)
Sn(2)···Sn(3)	3.468(1)	O(5)Sn(3)O(6)	65.19(14)
Sn(1)···Sn(3)	3.512(1)	Sn(1)O(3)Sn(2)	104.82(16)
		Sn(1)O(4)Sn(3)	103.09(16)
		Sn(3)O(5)Sn(2)	98.65(15)
		Sn(2)O(6)Sn(3)	98.20(15)

SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre (CCDC) no. 263014 for compound **1**, CCDC no. 263015 for compound **2**, CCDC no. 263017 for compound **5**, and CCDC no. 263016 for compound **9**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033); e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

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