



Synthesis of aromatic tetracyclic tin compounds by template and transmetallation reactions: Alkyl vs aryl migration from tin to nitrogen

Carlos Camacho-Camacho^a, Edgar Mijangos^b, Maria E. Castillo-Ramos^b, Adriana Esparza-Ruiz^b, Aurora Vásquez-Badillo^b, Heinrich Nöth^c, Angelina Flores-Parra^{b,*}, Rosalinda Contreras^{b,*}

^a Departamento de Sistemas Biológicos, Universidad A. Metropolitana, Xochimilco, Calzada del Hueso 1100, Col. Villa Quietud, CP 04960, México DF, Mexico

^b Departamento de Química, Cinvestav México, AP 14-740, CP 07000, México DF, Mexico

^c Department Chemie, Ludwig-Maximilians, Universität, Butenandt-Strasse 5-13 (Haus D), D-81377 Munich, Germany

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ABSTRACT

The syntheses of [bis(3,5-di-*tert*-butyl-2-hydroxy-2-phenyl)amine]diphenyltin (**1**) and [bis(3,5-di-*tert*-butyl-2-hydroxy-2-phenyl)amine]dichloro-phenyl-stannate (**2**) by template reactions using 3,5-di-*tert*-butylcatechol, aqueous ammonia and SnPh₂Cl₂ are reported. We also report the syntheses of compounds **2**, [bis(3,5-di-*tert*-butyl-2-hydroxy-2-phenyl)amine]trichloro-stannate (**4**), [bis(3,5-di-*tert*-butyl-2-hydroxy-2-phenyl)methylamine]chloro-methyltin (**5**), and [bis(3,5-di-*tert*-butyl-2-hydroxy-2-phenyl)-*n*-butylamine]*n*-butyl-chlorotin (**6**) and [bis(3,5-di-*tert*-butyl-2-hydroxy-2-phenyl)amine]*n*-butyl-dichloro-stannate (**7**), performed by transmetallation reactions of the octahedral zinc coordination compound Zn[3,5-di-*tert*-butyl-1,2-quinone-(3,5-di-*tert*-butyl-2-hydroxy-1-phenyl)imine]₂ (**3**) with SnPhCl₃ or SnPh₂Cl₂, SnCl₄, SnMe₂Cl₂, Sn(*n*Bu)₂Cl₂ and Sn(*n*Bu)Cl₃, respectively. The X-ray diffraction structures of compounds **1**, **2**, **4** and **6** are reported. The transmetallation reactions with Sn(alkyl)₂Cl₂ afforded pentacoordinated tin compounds, where an alkyl group migrated from tin to nitrogen, while similar reactions with Sn-Ph compounds did not present any phenyl group migration.

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1. Introduction

We are currently working on the chemistry of tin heterocycles derived from planar and aromatic ligands such as diphenoloxamides [1–3] and diphenolamines [4,5]. The combination of planar aromatic polycyclic ligands and tin atoms produces suitable models for biological studies as biocides, due to the potential anticancer activity of tin compounds [6–11] and to the biocidal activity of diphenolamine [12]. Interest in these molecules is based on their polyfunctional nature, high reactivity and unusual electronic and structural properties. The phenolate ligands increase the Lewis acidic character of the metallic centers allowing stabilization of uncommon species, due to their electronegativity, planar framework and rigidity [13–18].

The diphenolamines can be prepared as reported by Frye from reaction of iodoanisole and copper powder followed by 2-aminoanisole and cleavage of the resulting dimethyl ether with BBr₃ [19]. This apparently simple method can be problematic as the ligand is easily oxidised during purification. Therefore, the template methods for the synthesis of diphenolamine derivatives are better as was shown by template reactions of 3,5-di-*tert*-butylcatechol,

aqueous ammonia, oxygen and metallic salts which afforded a series of main group coordination compounds derived from bis[4,6-di-*tert*-butylphenol]amine [18].

2. Results and discussion

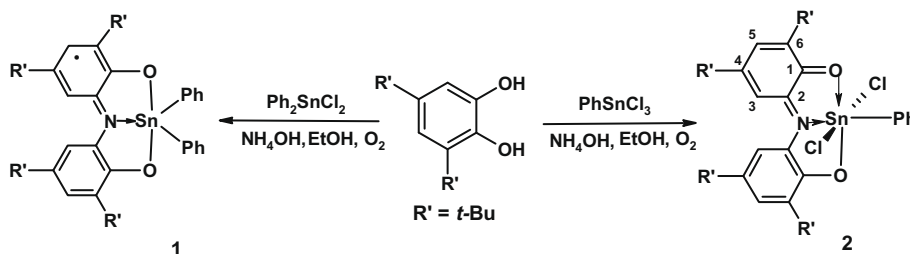
2.1. General comments

Herein, we report the synthesis of two tetracyclic compounds (**1** and **2**) by template reactions using 3,5-di-*tert*-butylcatechol, aqueous ammonia and SnPh₂Cl₂ or SnPhCl₃ (Scheme 1). Similar reactions for alkyl substituents gave the pentacoordinated dimethyltin when the reaction was performed with SnMe₂Cl₂ and the hexacoordinated *n*-butyldichloro tin compound when the reagent is Sn(*n*Bu)Cl₃ [18].

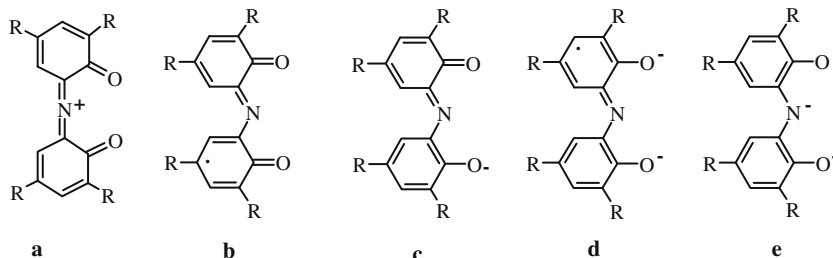
An interesting characteristic of diphenolamine ligands is that they can be found in different oxidation states depending on the coordination number and the oxidation state of associated metal ions. (Scheme 2) [20,21]. As a consequence, their pentacoordinated tin compounds are paramagnetic where the ligand oxidation state corresponds to structure **d**, whereas the hexacoordinated compounds are diamagnetic with the ligand in oxidation state **e**.

Stegmann and Scheffler reported in 1970 [22] that the reaction of 2-amino-4,6-di-*tert*-butyl-phenol with SnPh₂Cl₂ afforded a para-

* Corresponding authors. Tel.: +55 5061 3720; fax: +55 5061 3389 (A. Flores-Parra).
E-mail address: aflores@cinvestav.mx (A. Flores-Parra).



Scheme 1. Template reactions for the synthesis of compounds **1** and **2**.



Scheme 2. Oxidation states of the bis(3,5-di-*tert*-butyl-2-hydroxy-2-phenyl)amine [21].

magnetic tetracoordinated tin compound forming an eight membered heterocycle. In our hands, the template reaction of 3,5-di-*tert*-butylcatechol and SnPh_2Cl_2 in the presence of NH_4OH , ethanol and O_2 afforded the paramagnetic compound **1**. The X-ray diffraction analyses of **1** showed a pentacoordinated tin atom in a tetracyclic framework, which could be the actual structure of the Stegmann and Scheffler compound. A similar reaction with SnPhCl_3 gave the hexacoordinated stannane bearing a SnPhCl_2 group (**2**). The ^{119}Sn NMR spectrum [$^{119}\text{Sn} \delta = -426$ ppm] gave a characteristic signal for a hexacoordinated compound. The structure was confirmed by X-ray diffraction analysis.

We also report the preparation of compounds **2**, **4–7** by transmetallation reactions using the octahedral zinc coordination compound **3** and SnCl_4 , SnPhCl_3 , SnPh_2Cl_2 , SnBu_2Cl_2 , SnMe_2Cl_2 , SnBuCl_3 (Scheme 3). The zinc compound **3** was synthesized from a template reaction using 3,5-di-*tert*-butylcatechol, ammonium hydroxide and $\text{Zn}(\text{OAc})_2$ in ethanol [23], Scheme 4.

The reaction of compound **3** with SnCl_4 in toluene gave in good yield (65% after purification) the diamagnetic compound **4**. The ^{119}Sn NMR resonance ($\delta = -514$ ppm) was attributed to a hexacoordinated tin heterocycle bearing a SnCl_3 group. The X-ray diffraction analysis confirmed the structure. Each molecule of zinc compound reacted with two SnCl_4 molecules giving two tin heterocycles and one molecule of ZnCl_2 .

The reaction of the zinc compound **3** with SnPhCl_3 gave compound **2** by elimination of a chlorine atom from tin and formation of ZnCl_2 ($^{119}\text{Sn} \delta = -427$ ppm). The reaction of **3** with SnPh_2Cl_2 could give different compounds: the SnPh_2 pentacoordinated compound **1** or the hexacoordinated derivatives bearing groups SnPhCl_2 or SnPh_2Cl . The ^{119}Sn NMR resonance ($\delta = -427$ ppm) showed that the product was again compound **2** and that a phenyl group instead of the chlorine atom was substituted, with ZnPh_2 being a probable product. This behavior is explained by the fact that chlorine atoms better stabilize the hexacoordinated stannate by withdrawing electron density from it.

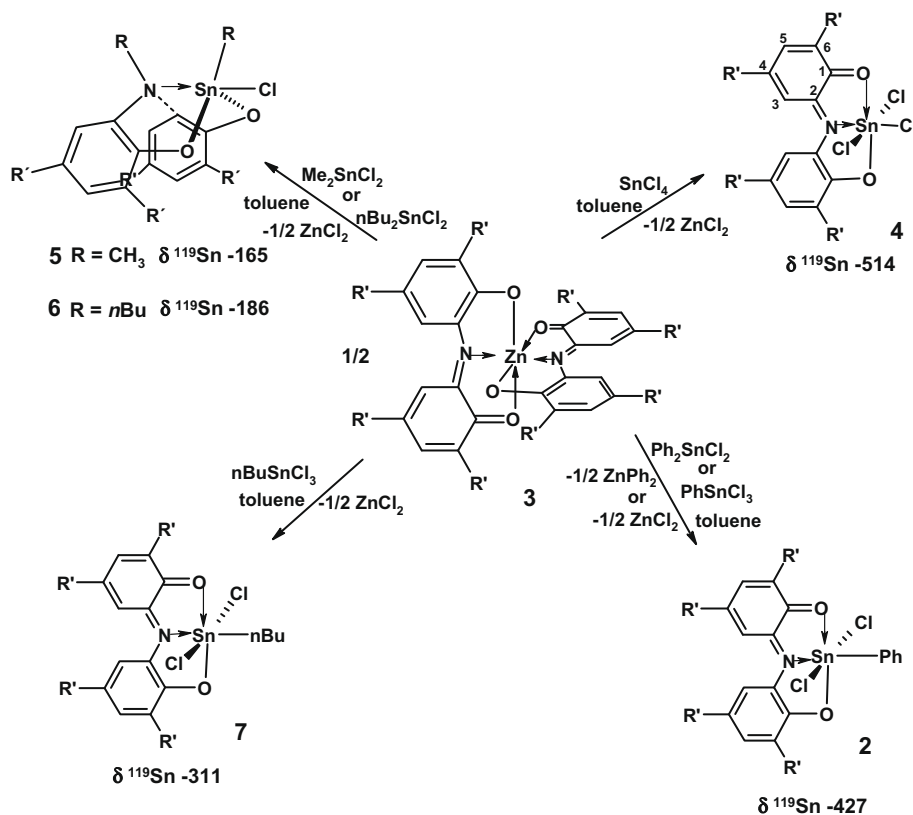
The reaction of the zinc compound **3** with SnMe_2Cl_2 or $\text{Sn}(n\text{-Bu})_2\text{Cl}_2$ in refluxing toluene, gave unexpectedly diamagnetic compounds (**5** and **6**, respectively), Scheme 3. The ^{119}Sn resonances (**5** $\delta = -65$ ppm and **6** $\delta = -186$ ppm) indicated pentacoordinated

compounds. The NMR spectral data showed two different *n*-butyl or methyl groups, which is not consistent with a symmetric structure where the tin is bound to two alkyl groups. The explanation for this spectral behavior was found in the solid state structure of compound **6** which showed a folded tetracyclic structure. The new structure is derived from the *n*-butyl group migration from tin to nitrogen. The product has a tetrahedral coordinated nitrogen atom instead of the planar sp^2 tricoordinated nitrogen found in compounds **1**, **2** and **4**. The $\text{N} \rightarrow \text{Sn}$ coordination afforded a pentacoordinated tin atom bearing in addition to the ligand one alkyl group and one chlorine atom. The ^{13}C NMR data, characteristic for a phenalamine and not for a quinone, are explained by the loss of the planar arrangement of the ligand which inhibits the electronic delocalization through the nitrogen but not through the phenolic groups. Based on the analogy of the NMR spectral data for compounds **5** and **6**, we have concluded that compound **5**, obtained from SnMe_2Cl_2 , is structurally similar to **6**.

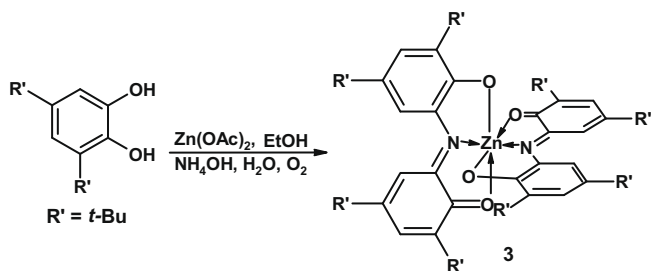
The reaction of one equivalent of compound **3** with two of $\text{Sn}(n\text{-Bu})\text{Cl}_3$ after 3 h in refluxing toluene gave compound **7**. The ^{119}Sn spectrum ($\delta \text{ }^{119}\text{Sn} = -311$ ppm) shows that **7** is the main product (90%) together with a signal for compound **4** (5%). The X-ray diffraction structure of compound **7** is known, however its NMR data were not previously reported [18].

Some comments are pertinent. As we have previously reported, the direct template reactions with catechol and alkyltin reagents: SnMe_2Cl_2 or $\text{Sn}(n\text{-Bu})\text{Cl}_3$ afford the respective planar compounds analogous to **1** and **2**, without migration of the alkyl group [18]. However the transmetallation reactions using the zinc compound favored the migration of alkyl groups from tin to nitrogen in dialkyltin halides. The migration was selective for alkyl groups and does not occur with phenyl groups.

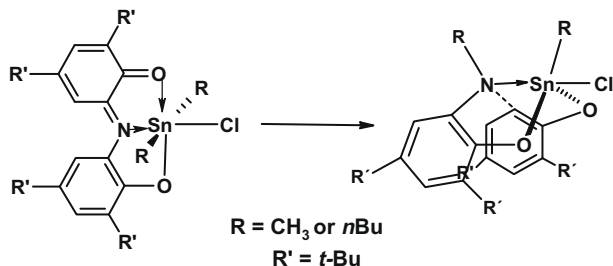
The intermolecular alkyl transference from tin to carbon in the presence of palladium reagents is known [24] as well as the preference for the methyl groups transference over phenyl groups [25–27]. In compounds **5** and **6** the transformation from the hexacoordinated to pentacoordinated compounds could be catalyzed by the zinc compounds present in the reaction medium, Scheme 5. Zinc mediated intramolecular acyl and imine transfer reactions of aryl iodides are known [28]. The synthesis of compound **2** by the



Scheme 3. Synthesis of compounds **2**, **4**–**7** by transmetalation reactions of the zinc compound **3**.



Scheme 4. Synthesis of compound **3** by template reactions [23].



Scheme 5. Possible hexacoordinated tin compound intermediate in the synthesis of compounds **5** and **6**.

zinc transmetalation reaction with SnPh₃Cl, indicates also that elimination of a phenyl group is preferred over that of a chlorine atom giving ZnPh₂.

The syntheses of compounds **2** and **7** indicate also that electron withdrawing groups such as chlorine and phenyl groups are necessary for stabilization of hexacoordinated tin atoms.

2.2. X-ray diffraction analyses

The X-ray diffraction analyses of compounds **1**, **2**, **4** and **6** were performed. Crystallographic data is in Table 1, and selected bond angles and lengths are in Tables 2–5.

Compound **1** crystallized from CH₂Cl₂/methanol and its structure was obtained by X-ray diffraction analysis. There are two molecules in the asymmetric unit (**1a** and **1b**). The tin atoms have distorted tbp geometries, Fig. 1. The oxygen atoms are at the apical positions. The symmetry in the bond lengths of the heterobicycle shows that it is a delocalized system. The O–Sn bond lengths are shorter 2.084(3) and 2.098(3) Å than that of N–Sn 2.145(4) and 2.161(4) Å, which is the coordination bond. For the two molecules **1a** and **1b** the phenyl groups are oriented, in such a way, that four intramolecular hydrogen bonds are formed between the *ortho* C–H protons and the oxygen atoms (within distances of 2.57–2.88 Å), (Fig. 2).

The solid state structure of compound **2** showed that the tin atom is hexacoordinated with a distorted octahedral geometry due to the tension of the planar ligand. The O–Sn–O angle is 149.57(9)°, Fig. 3. The phenyl group is *anti* to the nitrogen atom (N–Sn–C angle is 179.7(2)°) and is lying in the same plane as the tin and the two chlorine atoms. The halides are in *anti* position [Cl–Sn–Cl angle is 164.09(7)°], and slightly oriented towards the nitrogen atom indicating a slight interaction Cl···N. It is also noteworthy that the two C–H in *ortho* position to the nitrogen have a shorter distance (1.8 Å) than the sum of the van der Waals radii (2.4 Å). These interactions have been reported for peptide structures [29].

The *ortho* C–H groups of the phenyl group form hydrogen bonds with the chlorine (2.71 and 2.74 Å). The bond lengths around the tin atom [Sn–O 2.112(2), Sn–C 2.117(7); Sn–N 2.268(5) and Sn–Cl 2.450(2) and 2.453(2) Å] indicate the coordination bond character of the Sn–N bond.

Table 1
Crystal data for compounds **1**, **2**, **4** and **6**.

	1	2	4	6
Empirical formula	C ₄₀ H ₅₀ N ₁ O ₂ Sn ₁	C ₃₄ H ₄₅ Cl ₂ N ₁ O ₂ Sn ₁	C ₂₈ H ₄₀ Cl ₃ N ₁ O ₂ Sn ₁	C ₃₆ H ₅₈ Cl ₁ N ₁ O ₂ Sn ₁
Formula weight	695.53	689.33	647.68	691
Temperature (K)	193	193	193	193
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> m	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	24.3068(3)	11.333(2)	10.833(3)	12.6895(9)
<i>b</i> (Å)	14.6458(2)	15.879(3)	28.016(8)	20.5584(15)
<i>c</i> (Å)	20.9481(3)	9.4530(19)	11.235(3)	15.1216(10)
α (°)	90	90	90	90
β (°)	100.5067(3)	96.67(3)	117.596(4)	102.2720(10)
γ (°)	90	90	90	90
<i>V</i> (Å ³)	7332.33 (17)	1689.5(6)	3021.9(14)	3854.7(5)
<i>Z</i>	8	2	4	4
<i>D</i> _{calc} (Mg/m ³)	1.26	1.355	1.423	1.191
μ (mm ⁻¹)	0.73	0.943	1.14	0.76
Absorption correction		None		None
<i>T</i> _{maximum} , <i>T</i> _{minimum}	0.75, 0.88	0.75, 0.83	0.67, 0.92	0.71, 0.85
<i>F</i> (0 0 0)	2904	712	1328	1456
Crystal size (mm)	0.25 × 0.22 × 0.2	0.3 × 0.3 × 0.2	0.35 × 0.35 × 0.07	0.49 × 0.45 × 0.22
Crystal color	Black	Violet	Dark violet	Violet
2 θ Range (°)	3.3 to 50.5	4.4 to 54.8	2.9 to 59.0	3.2 to 57.7
Index ranges	-32 ≤ <i>h</i> ≤ 24, -18 ≤ <i>k</i> ≤ 18, -26 ≤ <i>l</i> ≤ 26,	-14 ≤ <i>h</i> ≤ 14, -20 ≤ <i>k</i> ≤ 20, -11 ≤ <i>l</i> ≤ 11,	-15 ≤ <i>h</i> ≤ 15, -38 ≤ <i>k</i> ≤ 38, -15 ≤ <i>l</i> ≤ 15,	-15 ≤ <i>h</i> ≤ 16, -26 ≤ <i>k</i> ≤ 26, -20 ≤ <i>l</i> ≤ 13,
Reflection collected	43 025	12 008	5489	22 560
Independent reflections	13 643	3629	5489	7074
Reflections for <i>F</i> ₀	>2.0 $\sigma(I)$ 8558	> 3.0 $\sigma(I)$ 1882	> 2.0 $\sigma(I)$ 3849	> 3.0 $\sigma(I)$ 3595
<i>R</i> _{int}	0.054	0.034	0.0	0.035
Completeness to θ (°)	25.24, 86.5%	26.62, 99.5%	25.07, 84.9%	25.10, 86.4%
Goodness-of-Fit (GOF) on <i>F</i> ²	1.07	1.08	1.01	1.02
Final <i>R</i> ₁	0.046 (<i>I</i> > 2.0 σ)	0.021 (<i>I</i> > 3.0 σ)	0.039 (<i>I</i> > 2.0 σ)	0.058 (<i>I</i> > 3.0 σ)
Final <i>wR</i> ₂	0.039	0.026	0.045	0.076

Table 2
Selected bond lengths (Å) for compounds **1** and **6**.

	1a	1b	6
<i>Bond lengths</i>			
Sn–O1	2.098(3)	2.084(3)	1.990(6)
Sn–N	2.145(4)	2.161(4)	2.323(6)
Sn–O2	2.096(3)	2.086(3)	1.998(5)
Sn–Cl(C3)	2.132(6)	2.130(6)	2.381(2)
Sn–C4	2.122(5)	2.127(5)	2.13(1)

Table 3
Selected bond angles (°) for compounds **1** and **6**.

	1a	1b	6
<i>Bond angles</i>			
O1–Sn–N	76.6(1)	76.6(1)	78.0(2)
O1–Sn–O2	152.3(1)	151.4(1)	116.7(2)
O1–Sn–Cl(C3)	99.4(2)	98.7(2)	91.1(2)
O1–Sn–C4	94.4(2)	93.4(2)	114.1(4)
N–Sn–O2	76.7(1)	76.5(1)	77.9(2)
N–Sn–Cl(C3)	110.6(2)	106.5(2)	156.6(2)
N2–Sn–C4	127.5(2)	129.5(2)	102.6(3)
O3–Sn–Cl(C3)	96.7(2)	98.1(2)	89.0(2)
O3–Sn–C4	96.0(2)	96.1(2)	127.9(4)
C4–Sn–Cl(C3)	121.9(2)	124.0(2)	100.7(3)

Table 4
Selected bond lengths (Å) for compounds **2** and **4**.

	2	4
<i>Bond lengths</i>		
Sn–O1	2.112(2)	2.096(3)
Sn–N	2.268(5)	2.198(5)
Sn–O3	2.112(2)	2.110(3)
Sn–Cl4	2.450(2)	2.375(2)
Sn–Cl5	2.453(2)	2.369(2)
Sn–Y	2.117(7)	2.331(2)

The structure of compound **4** is similar to that of **2**, Fig. 4. The tin atom is hexacoordinated, the ligand is not completely planar. The O–Sn–O angle is 149.9(2)°. The three chlorine atoms and the nitrogen atom are in the same plane. The chlorine atom *anti* to the nitrogen has the shortest bond length [2.331(2) Å], the others are 2.375(2) and 2.369(2) Å. The molecule has intermolecular interactions produced by C–H...Cl hydrogen bonds, (Fig. 5).

The X-ray diffraction analysis of compound **6** showed that the diphenolamine is folded, with one *n*-butyl group at the nitrogen, and the other at the tin atom, (Fig. 6). The N–Bu and the Sn–Bu bonds are in *gauche* conformation, in order to minimise their repulsion. The dihedral angle C18–Sn–N–C30 is 26.3°. The tin atom

Table 5
Selected bond angles (°) for compounds **2** and **4**.

Bond angles	2	4
O1–Sn–N	74.84(6)	75.2(1)
O1–Sn–O3	149.57(9)	149.9(2)
O1–Sn–Cl4	89.19(7)	87.75(9)
O1–Sn–Cl5	86.67(7)	90.09(9)
O1–Sn–Y	105.1(1)	104.9(1)
N–Sn–O3	74.84(6)	75.0(1)
N–Sn–Cl4	81.9(1)	88.0(1)
N–Sn–Cl5	82.2(1)	87.7(1)
N–Sn–Y	179.7(2)	179.3(1)
O3–Sn–Cl4	89.2(7)	87.0(1)
O3–Sn–Cl5	86.67(7)	92.87(9)
O3–Sn–Y	105.15(6)	105.0(1)
Cl4–Sn–Cl5	164.09(7)	175.50(7)
Cl4–Sn–Y	98.4(2)	92.77(6)
Cl5–Sn–Y	97.5(2)	91.60(6)

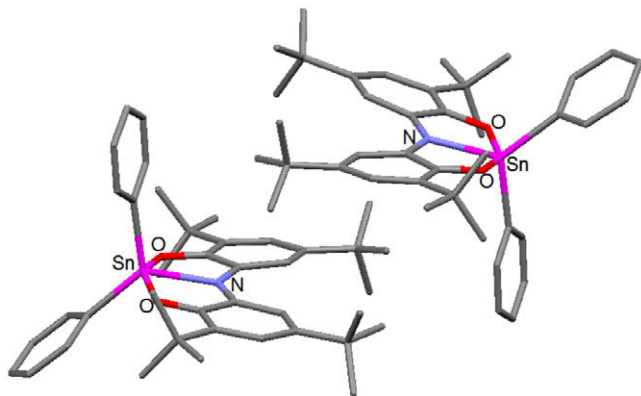


Fig. 1. X-ray diffraction structures of compound **1**. Two molecules (**1a**, **1b**) were found in the asymmetric unit. The hydrogen atoms are not shown for clarity.

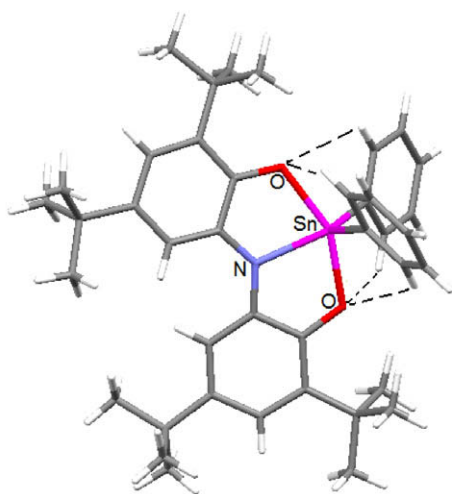


Fig. 2. Hydrogen bonds between *ortho* C–H of the Sn–Ph groups and the oxygen atoms for compound **1** are shown. The distances vary from 2.57 to 2.88 Å.

is pentacoordinated and has a distorted *tbp* geometry. The chlorine and nitrogen atoms are in apical positions as is deduced from the N–Sn–Cl angle 156.6(2)° whereas, two oxygen atoms and the *n*-butyl group are equatorial. The O–Sn–O angle is 116.7(2)°. The bond

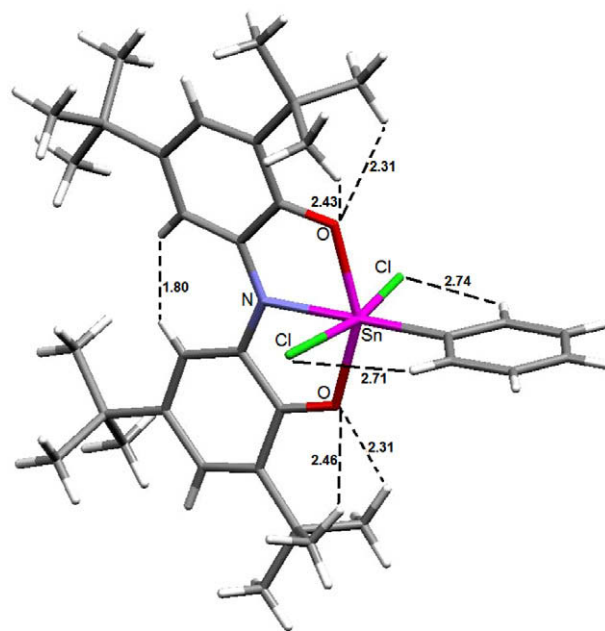


Fig. 3. X-ray diffraction analysis of compound **2**, the distance between the two C–H *ortho* to the nitrogen is shown together with intramolecular C–H...Cl and C–H...O bonds.

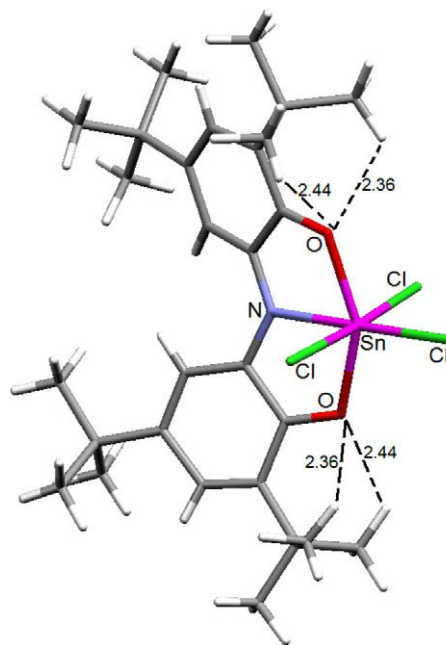


Fig. 4. X-ray diffraction analysis of compound **4**. The C–H...O distances are 2.36 and 2.44 Å.

lengths of Sn–O [1.998(5) and 1.990(6) Å], Sn–C [2.13(1) Å] and Sn–Cl [2.381(2) Å] are characteristic of strong covalent bonds. The N–Sn [2.323(6) Å] bond length indicates a coordination bond. The phenylene rings are completely aromatic.

Some features are general for compounds **1–2**, **4–7**. Two C–H from the *tert*-butyl groups form two intramolecular hydrogen bonds with each oxygen atom (within distances 2.27–2.45 Å) as is shown for compounds **2** (Fig. 3) and **4** (Fig. 4).

In all compounds, the two phenylene rings are not exactly coplanar. The dihedral angles between the phenylene rings and

the C–H...H–C distance for compounds **1**, **2**, **4** and **6** are in Table 6. In all cases, the C–H...H–C distances are shorter than the van der Waals radii (2.4 Å).

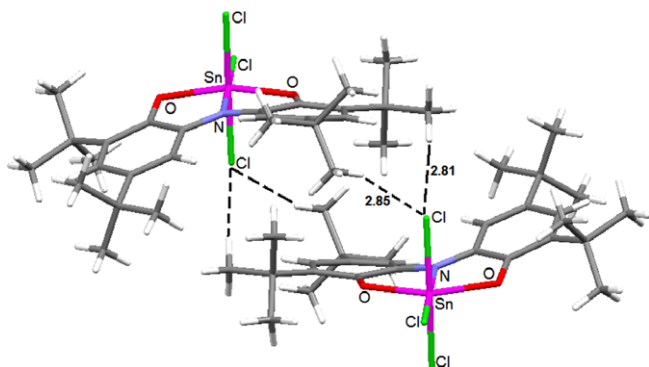


Fig. 5. Intermolecular interactions in compound **4**.

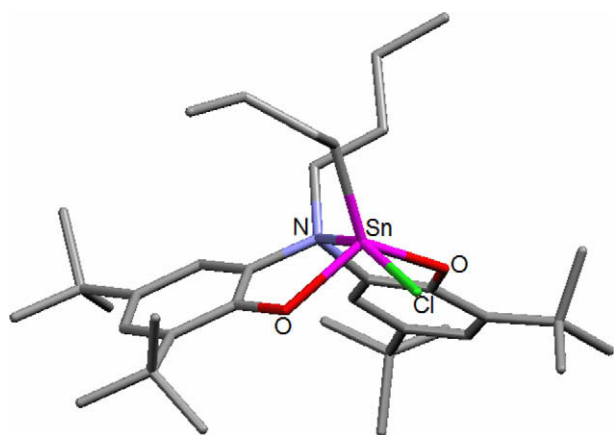
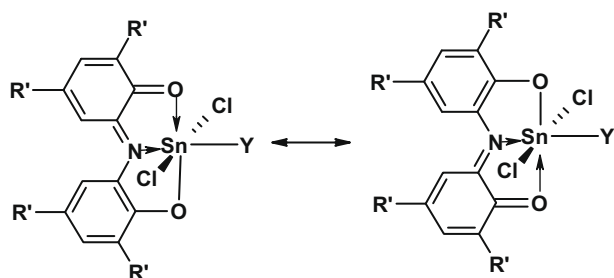


Fig. 6. Solid state of compound **6**, the tin geometry is a distorted tp.

Table 6
Phenylene rings dihedral angles and *ortho* C–H...H–C distances.

Compounds	Phenylene rings dihedral angle (°)	<i>ortho</i> C–H...H–C distances (Å)
1a	14.8	1.96
1b	9.5	1.89
2	13.0	1.80
4	27.8	1.98
6	56.3	2.30



Scheme 6. Resonance contributors in compounds **2** (Y=Ph) and **4** (Y=Cl).

The analysis of bond lengths in the hexacoordinated compounds **2** and **4** shows a symmetric pattern which indicates a resonance system (coordination bond ↔ covalent bond) for the ligand acting as a phenolate iminoquinone, structure **c** in Scheme 2. The two resonance contributors of compounds **2** and **4** are shown in Scheme 6 [30].

3. Summary

The syntheses of pentacoordinated and hexacoordinated tin compounds derived from bis[4,6-di-*tert*-butylphenol]amine are reported. Transmetalation reactions using a zinc coordination compound are compared with synthesis using template reactions. Migrations of alkyl groups from tin to nitrogen were observed. ^{119}Sn NMR data and the solid state structures of some of the compounds are reported.

4. Experimental

4.1. General comments

All solvents were freshly distilled before use according to established procedures. The tin reagents are commercial. Melting points were measured on a Mel-Temp II apparatus and are uncorrected. The ^1H , ^{13}C , and ^{119}Sn NMR spectra were recorded with JEOL GX-270 (^1H 270 MHz) or JEOL Eclipse (^1H 400 MHz) and Bruker (^1H 300 MHz) instruments. ^1H and ^{13}C (ppm) are referenced to TMS and ^{119}Sn to SnMe_4 . Assignments were performed by 2D NMR experiments. High resolution mass spectra were obtained by LC/MSD TOF on an Agilent Technologies instrument with APCI as ionization source. Elemental analyses were performed in an Eager 300 analyzer.

X-ray diffraction studies of single crystals were determined on a Bruker SMART instrument with an area detector using graphite-monochromated $\text{Mo K}\alpha$ radiation at 193 K. Intensities were measured using hemisphere scans. All structures were solved using direct methods, using Shelxl-97 [31] and the refinement (based on F^2 of all data) was performed by full-matrix least-squares techniques with Crystals 12.84 [32]. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were located in the difference map and allowed to ride on their respective atoms.

4.2. Syntheses

4.2.1. Zn[3,5-di-*tert*-butyl-1,2-quinone-(3,5-di-*tert*-butyl-2-hydroxy-1-phenyl)imine] $_2$ (**3**)

Compound **3** was prepared according to reported method [23]. 3,5-Di-*tert*-butylcatechol (5.34 g, 24 mmol) was dissolved in 150 mL of ethanol and added to a solution of $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ (1.15 g, 6.1 mmol) in 25 mL of water and 20 mL of NH_4OH . The reaction mixture was air bubbled and stirred for 24 h. Compound **3** is a dark green powder (4.1 g, 75%).

4.2.2. [Bis(3,5-di-*tert*-butyl-2-hydroxy-2-phenyl)amine]diphenyltin (**1**)

To a solution of 3,5-di-*tert*-butylcatechol (1.11 g, 5 mmol) in 15 mL of ethanol at 0 °C, conc. aqueous ammonia (3 mL) was added followed by SnPh_3Cl (964 mg, 2.5 mmol) in 10 mL of ethanol. After 2 h at 0 °C, the reaction was set aside for 48 h at room temperature. The reaction mixture was filtered and washed with water and ethanol and vacuum dried. The solid was extracted with CH_2Cl_2 . The solvent was evaporated under vacuum and the violet crystalline product was recrystallized from CH_2Cl_2 : ethanol (820 mg, 47%). Mp 161–163 °C. Anal. Calc. for $\text{C}_{40}\text{H}_{50}\text{NO}_2\text{Sn}$: C, 69.08; H, 7.25; N, 2.01. Found: C, 68.74; H, 7.14; N, 2.13.

4.2.3. [Bis(3,5-di-tert-butyl-2-hydroxy-2-phenyl)amine]dichlorophenylstannate (**2**)

4.2.3.1. Method A. To a solution of 3,5-di-tert-butylcatechol (1.11 g, 5 mmol) in 15 mL of ethanol at 0 °C of conc. aqueous ammonia (3 mL) was added followed by SnPhCl₃ (755 mg, 2.5 mmol) in 10 mL of ethanol. After 2 h at 0 °C, the reaction was continued at room temperature for 48 h. The reaction mixture was filtered and the solid washed with water and ethanol and dried. The solid was dissolved in CH₂Cl₂ and filtered. The solution was evaporated under vacuum. Dark green crystals were obtained that were recrystallized from CH₂Cl₂ : ethanol (360 mg, 21%).

4.2.3.2. Method B. A solution of compound **3** (300 mg, 0.33 mmol) and SnPh₂Cl₂ (227 mg, 0.66 mmol) or SnPhCl₃ (254 mg, 0.66 mmol) in 10 mL of toluene was heated at 100 °C. After 3 h, the solvent was evaporated under vacuum. The solid was washed with water and the main product extracted with CH₂Cl₂. The solvent was evaporated and the crystalline product was recrystallized from [1:1] CH₂Cl₂:hexane (340 mg, 75%).

Mp 216–218 °C. NMR (CDCl₃, ppm), ¹¹⁹Sn δ = –427, ¹H δ = H3 7.56, H5 7.50, tBu: 1.39, 1.33, Ph: Ho and Hp 8.20, Hm 7.67. ¹³C δ = C1 174.3, C2 135.0 [83 Hz], C3 116.2 [49.5 Hz], C4 145.2 [26 Hz], C5 138.9, C6 149.8, tBu quater 35.8, 35.5, tBu CH₃ 30.0, 29.2, Ph: Ci 144.5, Co 133.8 [86 Hz], Cm 128.8 [138 Hz], Cp 130.4 [28 Hz]. Mass – TOF found 689.1858 calculated for C₃₄H₄₅NO₂SnCl₂ 689.1849. Anal. calc. for C₃₄H₄₅Cl₂NO₂Sn: C, 59.24; H, 6.58; N, 2.03. Found: C, 59.43; H, 6.82; N, 1.96.

4.2.4. [Bis(3,5-di-tert-butyl-2-hydroxy-2-phenyl)amine]trichlorostannate (**4**)

Compound **3** (0.3 g, 0.33 mmol) and SnCl₄ (0.1 mL, 0.45 mmol) in 10 mL of toluene were heated at 90 °C. After 3 h, the solvent was evaporated under vacuum. The solid product was washed with water and the main product extracted with CH₂Cl₂. The solvent was evaporated in vacuum and the product recrystallized from [1:1] CH₂Cl₂:hexane (200 mg, 65%). Mp 222–224 °C. NMR (CDCl₃, ppm), ¹¹⁹Sn δ = –514, ¹H δ = H3 7.65, H5 7.44, H9 1.45, H10 1.34. ¹³C δ = C1 174.1, C2 133.1, C3 115.4, C4 145.4, C5 140.4, C6 151.1, tBu quater 35.9, 35.6, tBu CH₃ 29.6, 29.2. Mass – TOF found 647.1138, calc for C₂₈H₄₀NO₂SnCl₃ 647.1147. Anal. Calc. for C₂₈H₄₀NO₂SnCl₃: C, 51.93; H, 6.23; N, 2.16. Found: C, 51.62; H, 5.92; N, 2.44.

4.2.5. [Bis(3,5-di-tert-butyl-2-hydroxy-2-phenyl)methylamine]chloromethyltin (**5**)

A solution of compound **3** (300 mg, 0.33 mmol) and SnMe₂Cl₂ (145 mg, 0.66 mmol) in 10 ml of toluene was refluxed for 3 h. The solvent was then evaporated under vacuum. The solid was extracted with hexane, filtered and the solvent evaporated. Compound **5** was crystallized from [1:1] CH₂Cl₂:hexane (140 mg, 49%). Mp 250–252 °C. NMR (CDCl₃, ppm), ¹¹⁹Sn δ = –165. ¹H δ = H3 7.35, H5 7.23, tBu: 1.46, 1.34, CH₃ 1.93. ¹³C δ = C1 150.8, C2 135.2 [35.1 Hz], C3 116.6 [10.9 Hz], C4 140.8, C5 122.9, C6 138.6 [39.5 Hz], C7 31.8.6, C8 29.7, C9 35.7, C10 34.7, Sn-CH₃ 30.0. N-CH₃ 56.5. Anal. calc. for C₃₀H₄₇ClO₂NSn: C, 59.28; H, 7.79; N, 2.30. Found: C, 59.38; H, 7.64; N, 2.31.

4.2.6. [Bis(3,5-di-tert-butyl-2-hydroxy-2-phenyl)butylamine]n-butylchlorotin (**6**)

The same procedure as for compound **5**, was followed using compound **3** (300 mg, 0.33 mmol) and SnBu₂Cl₂ (200 mg, 0.66 mmol) in 10 mL of toluene. Dark violet crystals were obtained (200 mg, 44%). Mp 129–131 °C. NMR (CDCl₃), ¹¹⁹Sn δ = –186; ¹H δ = H3 7.37, H5 7.24, tBu: 1.46, 1.34, Sn-nBu CH₃ 0.84 [14.64]; N-nBu CH₂ 3.36, 1.47, 1.45, CH₃ 0.93. ¹³C δ = C1 151.6 [32] C2 137.4 [34.5], C3 116.9 [8.5] C4 140.0 C5 122.5 C6 138.6 [38.5],

tBu quartet: 34.6 and 29.6, tBu CH₃: 35.5 and 31.7, Sn-nBu: 29.8, 28.0, 20.4, 13.9 N-nBu 60.0, 31.7, 24.7, 13.6. Mass – TOF found 726.2856 calc. for C₃₆H₅₈NO₂SnCl₂ 726.2867. Anal. calc. for C₃₆H₅₉ClO₂NSn: C, 62.48; H, 8.59; N, 2.02. Found: C, 62.50; H, 8.39; N, 1.96.

4.2.7. [Bis(3,5-di-tert-butyl-2-hydroxy-2-phenyl)amine]n-butyl-dichlorostannate (**7**)

A solution of compound **3** (300 mg, 0.33 mmol) and SnCl₃nBu (0.11 mL, 0.66 mmol) in 15 ml of toluene was refluxed for 3 h and the solvent was evaporated under vacuum. A violet solid was obtained (260 mg, 59%). The ¹¹⁹Sn spectrum of the reaction product showed a main signal for compound **7** (δ = –311 90%), and 5% of compound **4**. The -TOF mass spectrum showed a main peak at 704.1866, calc 704.1851 for C₃₂H₄₉NO₂SnCl₃ which corresponds to compound **7** plus a chlorine atom. Mp 130–137 °C. NMR (CDCl₃, ppm), ¹H δ = H3 7.37, H5 7.27, tBu: 1.44, 1.32, nBu 3.55, 2.37, 1.26 0.87. ¹³C δ = C1 174.1, C2 132.5, C3 116.9, C4 141.7, C5 138.6, C6 149.7, tBu quater 35.6, 34.8, tBu CH₃ 31.7, 29.7, nBu 29.4, 28.2, 20.3 13.9.

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Appendix A. Supplementary material

CCDC 711032, 711033, 711034 and 711035 contain the supplementary crystallographic data for compounds **1**, **2**, **5** and **3** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.12.025](https://doi.org/10.1016/j.jorganchem.2009.12.025).

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