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Transmetallation reaction of Schiff-base-type arylmercury compounds with metallic tin

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Abstract

The transmetallation reaction of 14 Schiff-base-type arylmercury compounds with metallic tin has been carried out in refluxing xylene. It was found that the reaction proceeds in the same manner as that of chloro[2-(phenylazo)phenyl]mercury(II) to give dichlorobisaryltin(IV). The ^1H nuclear magnetic resonance spectra of the products and an X-ray diffraction study of dichlorobis[2-(benzylideneamino)-5-tolyl]tin(IV) have provided evidence for the presence of N → Sn intramolecular coordination in their molecules. The formation of dichlorobisaryltin(IV) as a unique product probably arises from the N → Sn intramolecular coordination, which results in an increase in the stability of the molecule.

1. Introduction

The main advantage of organomercury compounds as transmetallating reagents over the classical organolithium and Grignard reagents is the wider range of organic groups, including the functionalized groups that can be transferred. Therefore they have been widely used in the synthesis of other organometallic compounds [1]. In particular, chloro[2-(phenylazo) phenyl]mercury(II), in which there exists an intramolecular N → Hg coordination via a five-membered ring [2], has been used in the synthesis of some palladium(II), platinum(II), nickel(II), manganese(I), tellurium(IV), gold(III), thallium(IV) and tin (IV) 2-(phenylazo)phenyl complexes [3]. It has been found in our previous work that in the Schiff-base-type arylmercury compounds there exists an intramolecular coordination between imino nitrogen and mercury atom via a four-membered ring [4]. It has been known that the reaction of chloro[2-(phenylazo)phenyl]mercury(II) with metallic tin in refluxing xylene leads to dichlorobisaryltin(IV) [3l], which is different from that of other arylmercury compounds with metallic tin [5]. The main difference between these two reactions is that, of the following reactions, only process (1) is observed in the first case:

$$6ArHgCl + 3Sn \longrightarrow 3Ar_2SnCl_2 + 6Hg \quad (1)$$

$$3Ar_2SnCl_2 \longrightarrow 2Ar_3SnCl + SnCl_4 \quad (2)$$

$$SnCl_4 + Sn \longrightarrow 2SnCl_2 \quad (3)$$

We speculate that the cause of the formation of dichlorobisaryltin(IV) in the reaction of chloro[2-(phenylazo)phenyl]mercury(II) may be the existence of N → Sn intramolecular coordination in the molecule of products. In order to investigate the effect of the ortho-coordinating group on the transmetallation reaction of arylmercury compounds with metallic tin and the application of Schiff-base-type arylmercury compounds to the synthesis of organotin compounds, the transmetallation reaction of 14 Schiff-base-type arylmercury compounds with metallic tin has been carried out. The structure of one of the transmetallation products, dichlorobis[2-(benzylideneamino)-5-tolyl]

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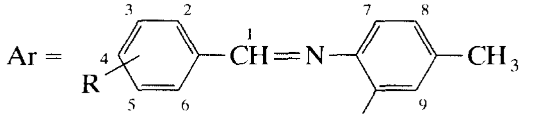
tin(IV), has also been determined by X-ray diffraction and is reported in the present paper.

2. Results and discussion

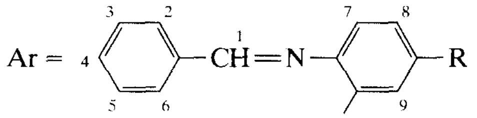
2.1. Transmetallation reaction

It was found that the transmetallation reaction of chloro[2-(substituted benzylideneamino)aryl]mercury (II) (**1a**–**1n**) with metallic tin proceeds in the same manner as that of chloro[2-(phenylazo)phenyl]mercury(II) to give dichlorobisaryltin(IV) (**2a**–**2n**).

$$\underset{\mathbf{1a-1n}}{2ArHgCl} + Sn \longrightarrow \underset{\mathbf{2a-2n}}{Ar_2SnCl_2} + 2Hg$$



R = H(**a**), *o*-Cl(**b**), *m*-Cl(**c**), *p*-Cl(**d**), *m*-Br(**e**), *p*-Br(**f**), *o*-CH_3O(**g**), *m*-CH_3O(**h**), *p*-CH_3(**i**), *p*-NMe_2(**j**);



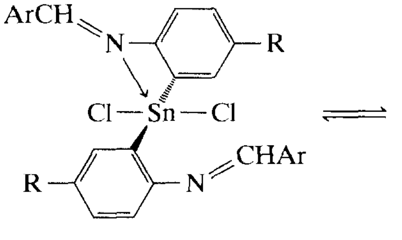
R = Cl(**k**), Br(**l**), I(**m**), CH_3O(**n**).

When **1a**–**1n** were heated to reflux in xylene with metallic tin (2 : 1.1) for 2–10 h, white or pale-yellow solutions and a precipitate of metallic mercury were obtained. After filtration the solutions were concentrated by vacuum distillation and then cooled to room temperature. The resulting solids were filtered and washed with methanol, and they were subsequently recrystallized from xylene or other solvents to give the corresponding transmetallation products **2a**–**2n**. Their analytical data, non-conductivities in acetone solutions and spectral data (IR and ^1H nuclear magnetic resonance (NMR)) indicate the composition of the products to be dichlorobisaryltin(IV) (Ar_2SnCl_2) rather than chlorotriaryltin(IV) (Ar_3SnCl). The influence of different substituents of aromatic rings on the yields of the reaction does not show obvious regularity. However, when the chloro[2-(4-nitrobenzylideneamino)-5-tolyl]-mercury(II) compounds were treated with metallic tin in refluxing xylene for 24 h, no product was formed.

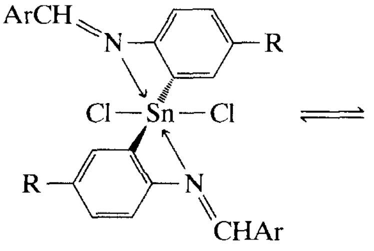
2.2. Spectral properties of transmetallation products

The IR spectra of **2a**–**2n** show absorption bands at about 3060 cm^{-1}, 1600–1450 cm^{-1} and 1624–1612 cm^{-1} which can be attributed to the ν_{Ar-H}, ν_{C-C} and ν_{C-N} respectively. Moreover, when the aromatic rings are substituted in different patterns, in the range of 900–650 cm^{-1} the corresponding δ_{Ar-H} bands appear.

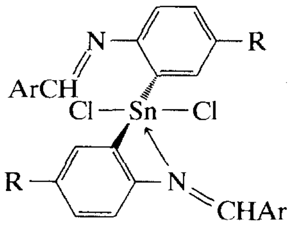
The ^1H NMR spectra of **2a**–**2n** show that the δ values of methine proton range from 8.38 to 8.85 ppm. In the majority the signal of a methine proton is a broad singlet, and simultaneously the peaks of aromatic protons become complicated. This phenomenon is thought to be associated with the presence of the N → Sn intramolecular coordination in the molecules of **2a**–**2n** and an equilibration between conformation **I** and **III** via **II** in dimethylsulphoxide-d_6 (DMSO-d_6):



I



II



III

The substituent effect on this equilibrium can be observed from the changes in peak shape of the methine proton with different substituents (as shown in Fig. 1). It was found that, when the phenyl ring bears an electron-donating group, the peak of methine proton exhibits a broader singlet and, on the contrary, when the phenyl ring bears an electron-withdrawing group, the peak of the methine proton appears as a relatively sharp singlet. Moreover, the influence of substituent at the *N*-phenyl ring is much greater than that of the substituent at the *C*-phenyl ring. These results can be explained in terms of the substituent effect on the strength of N → Sn intramolecular coordination. The electron-donating group increases the electron population of the imino nitrogen atom, leading to a relatively strong N → Sn intramolecular coordination, and as a result causes a comparatively slow equilibration **I** ⇌ **III**

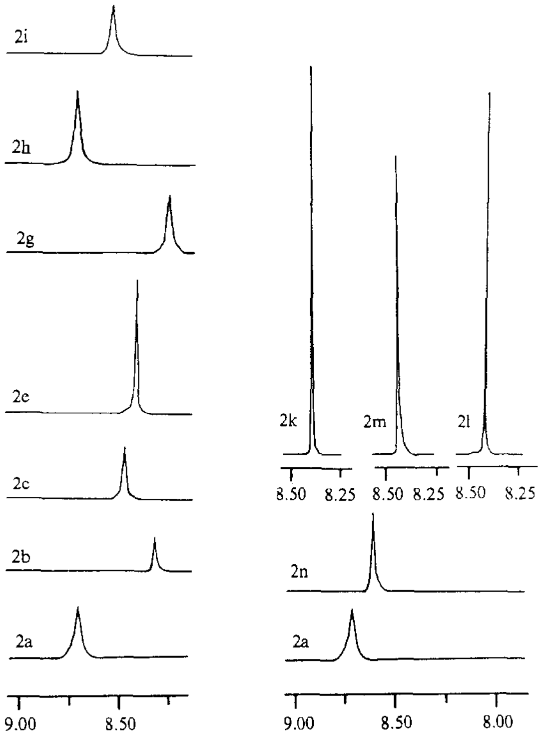


Fig. 1. Comparison of the peak shapes of the methine proton in the different compounds **2a**–**2n**.

and a broader singlet of methine proton. On the contrary, the electron-withdrawing group weakens the N → Sn intramolecular coordination and therefore causes a comparatively fast equilibration **I** ⇌ **III** and a relatively sharp singlet of the methine proton.

2.3. Crystal structure of 2a

In order to provide further structural evidence for the presence of N → Sn intramolecular coordination in the molecule of the transmetallation products, an X-ray crystal structure determination of dichlorobis[2-(benzylideneamino)-5-tolyl]tin(IV) (**2a**) has been carried out. Figure 2 shows the molecular structure of dichlorobis[2-(benzylideneamino)-5-tolyl]tin(IV). Selected bond lengths and bond angles are listed in Table 1, and the atomic coordinates in Table 2. The crystal structure consists of discrete molecules separated by the van der Waals distances. The tin atom, as shown in Fig. 2 and Table 1, is bonded covalently to two chlorine atoms and two carbon atoms of *N*-phenyl rings. The C–Sn and Cl–Sn bond distances (average values of 2.11 and 2.38 Å respectively) are similar to those found in the complex of dichlorobis[2-(phenylazo)phenyl]tin(IV), in the molecule of which two azo nitrogen atoms coordinate with tin atom via a five-membered ring [31]. In the molecular structure of **2a**, the n electrons of two imino nitrogen atoms face the central tin atom, and the atoms Sn, C(1), C(6), N(1) and Sn, C(15), C(20), and N(2) are coplanar respectively. The Sn...N distances of 2.750(5) Å (Sn...N(1)) and 2.859(5) Å (Sn...N(2)) are much shorter than the sum of the van der Waals radii for Sn and N (about 3.6 Å) [6], suggesting the presence of significant N → Sn secondary interaction via a four-membered ring. The C=N bond lengths of 1.279(6) Å (N(1)–C(7)) and 1.283(6) Å (N(2)–C(21)) are longer than those found in substituted benzylideneanilines (1.24–1.27 Å) [7], and are similar to the C=N bond length (1.283(12) Å) determined for chloro[2-(4-nitrobenzylideneamino)-1-naphthyl]mercury(II), in which the presence of N → Hg intramolecular coordination via a four-membered ring has been suggested [5a]. The bond angles of N(1)–C(6)–C(1) (113.2(4)°), Sn–C(1)–C(6) (110.4(4)°), Sn–C(15)–C(20) (112.9(4)°) and N(2)–C(20)–C(15) (114.4(4)°) are less than 120°. All these phenomena are considered to be associated with the N → Sn interaction. The small values of the angles N(1)–Sn–C(1) (55.6(1)°) and N(2)–Sn–C(15) (53.6(1)°) are due to the constraint of the four-membered chelate ring. It is of interest to note that the twist angles of both the *N*-phenyl and the *C*-phenyl rings out of the plane C–C=N–C in the Schiff-base moieties are very small. The atoms in the Schiff-base

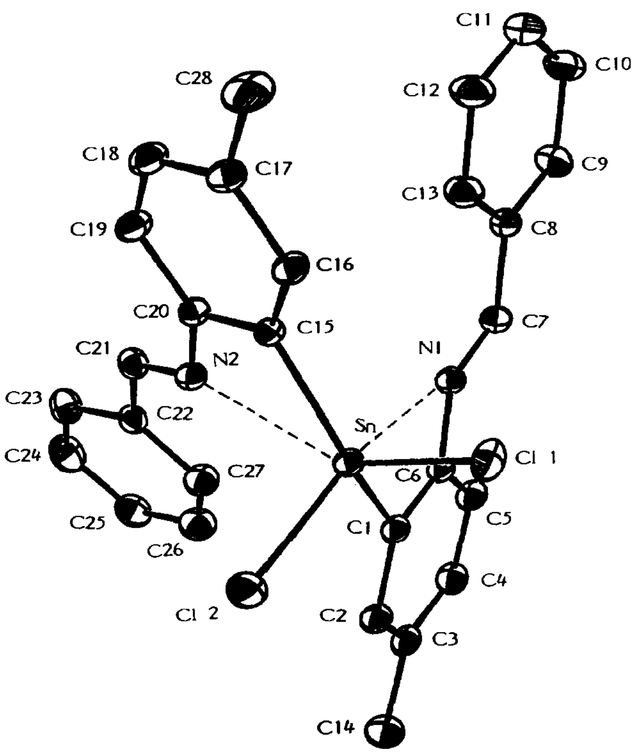


Fig. 2. Molecular structure of **2a**.

moieties are almost coplanar, the maxium deviations from the mean planes being 0.166 Å. Table 3 lists the deviations of atoms from the mean plane. This structure forms a striking contrast with those of substituted benzylideneanilines, in which the twist angles of *N*-phenyl ring out of the plane C–C=N–C range from 41.1° to 55.2° [7]. The greater changes in the structures of the Schiff-base moieties upon the *ortho* position of *N*-phenyl displaced by a tin atom may be caused by the N → Sn intramolecular coordination, which holds the Schiff-base moieties in near-planar geometry. On the contrary, the N → Sn intramolecular coordination will increase the stability of the molecule of dichlorobisaryltin(IV) and, as a result, the transmetallation reaction is stopped at the formation of dichlorobisaryltin(IV) (process (1)) without the conversion of dichlorobisaryltin(IV) to chlorotriaryltin(IV) (process (2)). On account of the N → Sn intramolecular coordination, the Sn atom is six-coordinated in a very distorted octahedral fashion with two *cis* chlorine and *cis* imino nitrogen atoms in the equatorial plane and two carbon atoms of the *ortho*-metallated *N*-phenyl groups considerably displaced from the *trans* axial position (C(1)–Sn–C(15) = 139.3(2)°).

3. Conclusion

From the existence of N → Sn intramolecular coordination and the composition of the products, it can be concluded that in the transmetallation reaction of Schiff-base-type arylmercury compounds with metallic tin, the formation of dichlorobisaryltin(IV) as a unique product may be caused by the presence of N → Sn intramolecular coordination, which enhances the stability of the molecule. The substituent effect on the ^{1}H NMR spectra of the transmetallation products can also be reasonably explained in terms of N → Sn intramolecular coordination.

4. Experimental details

4.1. Materials and instruments

All reactions were performed in reagent-grade solvents. Compounds **1a–1n** were prepared by the procedure described in the literature [4a] and were characterized by melting-point (m.p.) and IR data. The m.p.s. were measured on a WC-1 apparatus and were uncorrected. Elemental analysis was determined with a

TABLE 1. Selected bond distances and angles for **2a** (estimated standard deviations in parentheses)

	Bond distance (Å)		Bond distance (Å)		Bond angle (°)		Bond angle (°)
Sn–Cl(1)	2.378(1)	C(8)–C(13)	1.391(7)	Cl(1)–Sn–Cl(2)	99.70(5)	C(7)–C(8)–C(9)	119.3(4)
Sn–Cl(2)	2.387(1)	C(9)–C(10)	1.392(8)	Cl(1)–Sn–C(1)	107.5(1)	C(7)–C(8)–C(13)	121.2(4)
Sn–C(1)	2.104(4)	C(10)–C(11)	1.381(8)	Cl(1)–Sn–C(15)	100.6(1)	C(9)–C(8)–C(13)	119.5(4)
Sn–C(15)	2.119(4)	C(11)–C(12)	1.360(8)	Cl(2)–Sn–C(1)	101.0(1)	C(8)–C(9)–C(10)	120.6(6)
Sn...N(1)	2.750(5)	C(12)–C(13)	1.385(7)	Cl(2)–Sn–C(15)	102.7(1)	C(9)–C(10)–C(11)	119.3(5)
Sn...N(2)	2.859(5)	C(15)–C(16)	1.386(6)	C(1)–Sn–C(15)	139.3(2)	C(10)–C(11)–C(12)	120.3(5)
N(1)–C(6)	1.424(5)	C(15)–C(20)	1.371(6)	Cl(1)–Sn–N(1)	92.2(1)	C(11)–C(12)–C(13)	121.1(5)
N(1)–C(7)	1.279(6)	C(16)–C(17)	1.393(7)	Cl(1)–Sn–N(2)	152.7(1)	C(8)–C(13)–C(12)	119.3(5)
N(2)–C(20)	1.414(5)	C(17)–C(18)	1.374(7)	Cl(2)–Sn–N(1)	156.3(1)	C(16)–C(15)–C(20)	122.0(4)
N(2)–C(21)	1.283(6)	C(18)–C(19)	1.384(7)	Cl(2)–Sn–N(2)	95.5(1)	C(15)–C(16)–C(17)	119.7(4)
C(1)–C(2)	1.400(6)	C(19)–C(20)	1.407(6)	N(1)–Sn–N(2)	82.5(1)	C(16)–C(17)–C(18)	118.4(4)
C(1)–C(6)	1.373(7)	C(21)–C(22)	1.462(6)	N(1)–Sn–C(1)	55.6(1)	C(16)–C(17)–C(28)	120.5(5)
C(2)–C(3)	1.395(6)	C(22)–C(23)	1.373(7)	N(1)–Sn–C(15)	95.1(1)	C(18)–C(17)–C(28)	121.1(4)
C(3)–C(4)	1.390(7)	C(22)–C(27)	1.401(7)	N(2)–Sn–C(1)	91.6(1)	C(17)–C(18)–C(19)	122.3(4)
C(3)–C(14)	1.519(6)	C(23)–C(24)	1.408(8)	N(2)–Sn–C(15)	53.6(1)	Sn–C(15)–C(20)	112.9(4)
C(4)–C(5)	1.387(6)	C(24)–C(25)	1.388(8)	C(6)–N(1)–C(7)	121.9(4)	C(18)–C(19)–C(20)	119.1(4)
C(5)–C(6)	1.400(6)	C(25)–C(26)	1.366(8)	C(20)–N(2)–C(21)	121.1(4)	N(2)–C(20)–C(15)	114.4(4)
C(7)–C(8)	1.472(6)	C(26)–C(27)	1.402(7)	C(2)–C(1)–C(6)	121.5(4)	N(2)–C(20)–C(19)	127.1(5)
C(8)–C(9)	1.381(7)	C(17)–C(28)	1.518(7)	C(1)–C(2)–C(3)	118.8(4)	C(15)–C(20)–C(19)	118.5(5)
				C(2)–C(3)–C(4)	118.9(5)	N(2)–C(21)–C(22)	123.9(4)
				C(2)–C(3)–C(14)	120.1(5)	C(21)–C(22)–C(23)	118.6(4)
				C(4)–C(3)–C(14)	121.1(5)	C(21)–C(22)–C(27)	120.9(4)
				C(3)–C(4)–C(5)	122.7(4)	C(23)–C(22)–C(27)	120.5(4)
				C(4)–C(5)–C(6)	117.7(4)	C(22)–C(23)–C(24)	119.7(6)
				Sn–C(1)–C(6)	110.4(4)	C(23)–C(24)–C(25)	120.4(5)
				N(1)–C(6)–C(1)	113.2(4)	C(24)–C(25)–C(26)	119.5(6)
				N(1)–C(6)–C(5)	126.4(5)	C(25)–C(26)–C(27)	121.4(5)
				C(1)–C(6)–C(5)	120.4(4)	C(22)–C(27)–C(26)	118.8(5)
				N(1)–C(7)–C(8)	121.4(4)		

Carlo-Erba 1106 instrument. IR spectra were recorded on a Shimadzu IR-435 spectrometer using KBr pellets. ^{1}H NMR spectra were obtained on a Brucker AM-400 at 20°C in DMSO-d_6 with tetramethysilane as an internal reference standard ($\delta = 0$ ppm). Conductivities were measured in approximately 5×10^{-4} M acetone solutions with a DDS-11A conductimeter.

4.2. General procedure for the transmetallation reactions

Suspensions of **1a–1n** (2 mmol) and powdered metallic tin (0.13 g, 1.1 mmol) were refluxed in dry xylene (25 ml) for 2–10 h. After filtration, the solutions were concentrated by vacuum distillation and cooled to room temperature. The crude products were obtained by filtration and then washed with 5 ml of methanol. Afterwards, they were recrystallized from xylene or other solvents to give **2a–2n** as white or pale-yellow crystals. The compounds prepared by this procedure are as follows.

TABLE 2. Atomic coordinates and equivalent isotropic thermal parameters (estimated standard deviations in parentheses)

Atom	x	y	z	B (Å^2)
Sn	0.40333(4)	0.03592(3)	0.21663(3)	2.996(7)
Cl(1)	0.4924(2)	0.1247(1)	0.0945(1)	4.53(3)
Cl(2)	0.6091(2)	−0.0797(1)	0.2392(1)	4.86(4)
N(1)	0.0915(5)	0.0884(3)	0.1674(3)	3.11(9)
N(2)	0.3174(6)	0.0327(3)	0.4063(3)	3.4(1)
C(1)	0.1979(7)	−0.0732(4)	0.1434(4)	3.1(1)
C(2)	0.1903(8)	−0.1833(4)	0.1155(4)	3.7(1)
C(3)	0.0383(8)	−0.2426(4)	0.0743(4)	4.0(1)
C(4)	−0.0997(8)	−0.1901(5)	0.0604(5)	4.2(1)
C(5)	−0.0929(7)	−0.0809(7)	0.0871(4)	3.8(1)
C(6)	0.0598(7)	−0.0229(4)	0.1310(4)	3.0(1)
C(7)	−0.0210(7)	0.1489(4)	0.1567(4)	3.7(1)
C(8)	0.0127(7)	0.2636(4)	0.1959(4)	3.7(1)
C(9)	−0.1127(8)	0.3258(5)	0.1830(5)	4.8(2)
C(10)	−0.0843(9)	0.4346(5)	0.2195(6)	5.5(2)
C(11)	0.071(1)	0.4795(5)	0.2701(6)	5.5(2)
C(12)	0.194(1)	0.4183(5)	0.2831(6)	5.8(2)
C(13)	0.1683(8)	0.3102(5)	0.2462(5)	4.8(2)
C(14)	0.025(1)	−0.3626(5)	0.0467(6)	5.8(2)
C(15)	0.4765(6)	0.1561(4)	0.3453(4)	3.0(1)
C(16)	0.5731(7)	0.2509(5)	0.3505(4)	3.7(1)
C(17)	0.6151(8)	0.3231(5)	0.4401(5)	4.1(1)
C(18)	0.5618(9)	0.2964(5)	0.5218(5)	4.4(1)
C(19)	0.4649(8)	0.2021(5)	0.5173(4)	4.2(1)
C(20)	0.4199(7)	0.1304(4)	0.4262(4)	3.2(1)
C(21)	0.2534(7)	−0.0004(5)	0.4747(4)	3.7(1)
C(22)	0.1386(7)	−0.0971(4)	0.4578(4)	3.5(1)
C(23)	0.0940(8)	−0.1317(5)	0.5388(5)	4.7(1)
C(24)	−0.0210(9)	−0.2225(6)	0.5241(5)	5.6(2)
C(25)	−0.0883(9)	−0.2773(5)	0.4284(6)	5.4(2)
C(26)	−0.0427(9)	−0.2422(5)	0.3484(6)	5.4(2)
C(27)	0.0706(9)	−0.1517(5)	0.3608(5)	4.6(1)
C(28)	0.719(1)	0.4280(6)	0.4470(6)	6.1(2)

*4.2.1. Dichlorobis[2-(benzylideneamino)-5-tolyl]tin(IV)(**2a**)*

Following the general procedure, the crude product was recrystallized from xylene to yield 0.37 g (64%) of **2a** as white crystals (m.p., 270–271°C; $\Lambda = 0\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$). Anal. Found: C, 58.16; H, 4.16; N, 4.70. $C_{28}H_{24}Cl_2N_2Sn$ calc.: C, 58.16; H, 4.15; N, 4.85%. IR (KBr): 3065w, 3050w, 2898w, 1620s, 1598m, 1570s, 1492m, 1472s, 1448s, 888m, 813vs, 750vs, 680vs cm^{-1}. ^{1}H NMR (DMSO-d_6): 8.74 (s, 1H, H-1), 7.80 (s, 1H, H-9), 7.59 (d, 1H, $J = 8.2$ Hz, H-8), 7.45–7.38 (m, 4H, H-2, H-4, H-6, H-7), 7.21 (t, 2H, $J = 7.2$ Hz, H-3, H-5), 2.47 (s, 3H, Ar–CH_3) ppm.

*4.2.2. Dichlorobis[2-(2-chlorobenzylideneamino)-5-tolyl]tin(IV) (**2b**)*

Following the general procedure, the crude product was recrystallized from xylene to give 0.45 g (70%) of **2b** as white crystals (m.p., 254–256°C; $\Lambda = 0\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$). Anal. Found: C, 51.97; H, 3.53; N, 4.13. $C_{28}H_{22}Cl_4N_2Sn$ calc.: C, 51.96; H, 3.40; N, 4.33%. IR (KBr): 3065w, 2910w, 1612s, 1589s, 1577w, 1560w, 1478s, 1461w, 882m, 815vs, 759vs cm^{-1}. ^{1}H NMR (DMSO-d_6): 8.54 (s, 1H, H-1), 7.72 (s, 1H, H-9), 7.46–6.80 (m, 6H, H-3–H-8), 2.45 (s, 3H, Ar–CH_3) ppm.

*4.2.3. Dichlorobis[2-(3-chlorobenzylideneamino)-5-tolyl]tin(IV) (**2c**)*

Following the general procedure, the crude product was recrystallized from xylene to give 0.28 g (44%) of **2c** as white crystals (m.p., 239.5–241°C; $\Lambda = 0\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$). Anal. Found: C, 51.70; H, 3.47; N, 4.40. $C_{28}H_{22}Cl_4N_2Sn$ calc.: C, 51.96; H, 3.40; N, 4.33%. IR (KBr): 3070w, 2910w, 1620vs. 1560vs, 1476s, 882m, 815s, 862w, 800s, 675s cm^{-1}. ^{1}H NMR (DMSO-d_6): 8.65 (s, 1H, H-1), 7.76 (s, 1H, H-9), 7.54 (d, 1H, $J = 8.3$ Hz, H-8), 7.47–7.41 (m, 3H, H-2, H-6, H-7), 7.34 (d, 1H, $J = 7.7$ Hz, H-4), 7.27 (t, 1H, $J = 8.2$, 8.0 Hz, H-5), 2.45 (s, 3H, Ar–CH_3) ppm.

*4.2.4. Dichlorobis[2-(4-chlorobenzylideneamino)-5-tolyl]tin(IV) (**2d**)*

Following the general procedure, the crude product was recrystallized from xylene to give 0.23 g (35%) of **2d** as pale-yellow crystals (m.p., above 350°C; $\Lambda = 0\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$). Anal. Found: C, 51.85; H, 3.49; N, 4.07. $C_{28}H_{22}Cl_4N_2Sn$ calc.: C, 51.96; H, 3.40; N, 4.33%. IR (KBr): 3080w, 2915w, 1619vs, 1590s, 1560m, 1485s, 1470m, 1450w, 882m, 821vs, 828sh cm^{-1}. This compound cannot be dissolved in DMSO-d_6, and the proper ^{1}H NMR spectrum was not obtained.

*4.2.5. Dichlorobis[2-(3-bromobenzylideneamino)-5-tolyl]tin(IV) (**2e**)*

Following the general procedure, the crude product was recrystallized from xylene to give 0.37 g (50%) of

2e as white crystals (m.p., 246–248°C; $\Lambda = 0\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$). Anal. Found: C, 45.58; H, 3.07; N, 3.71. $C_{28}H_{22}Br_2Cl_2N_2Sn$ calc.: C, 45.67; H, 2.99; N, 3.81%. IR (KBr): 3060w, 2940w, 2910w, 1620vs, 1558s, 1478s, 883m, 815s, 861w, 780s, 678vs cm^{-1}. ^{1}H NMR (DMSO-d_6): 8.61 (s, 1H, H-1), 7.75 (d, 1H, $J = 1.5$ Hz, H-9), 7.64 (s, 1H, H-2), 7.59 (dd, 1H, $J = 7.8$, 2.2 Hz, H-8), 7.53 (d, 1H, $J = 8.2$ Hz, H-7), 7.41 (dd, 1H, $J = 8.2$ Hz, 1.8 Hz, H-6), 7.40 (d, 1H, $J = 7.8$ Hz, H-4), 7.19 (t, 1H, $J = 7.8$ Hz, H-5), 2.45 (s, 3H, Ar–CH_3) ppm.

4.2.6. *Dichlorobis[2-(4-bromobenzylideneamino)-5-tolyl]tin(IV) (2f)*

Following the general procedure, the crude product was recrystallized from xylene to give 0.30 g (41%) of **2f** as pale-yellow crystals (m.p., above 350°C; $\Lambda = 0\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$). Anal. Found: C, 45.26; H, 3.21; N, 3.84. $C_{28}H_{22}Br_2Cl_2N_2Sn$ calc.: C, 45.67; H, 2.99; N, 3.81%. IR (KBr) 3080w, 2910w, 1619s, 1590m, 1579m, 1559m, 1484s, 1470m, 887m, 821vs, 828sh cm^{-1}. This compound cannot be dissolved in DMSO-d_6, and the proper ^{1}H NMR spectrum was not obtained.

4.2.7. *Dichlorobis[2-(2-methoxybenzylideneamino)-5-tolyl]tin(IV) (2g)*

Following the general procedure, the crude product was recrystallized from xylene to give 0.25 g (39%) of **2g** as pale-yellow crystals (m.p., 267–269°C; $\Lambda = 0\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$). Anal. Found: C, 56.28; H, 4.51; N, 4.41. $C_{30}H_{28}Cl_2N_2O_2Sn$ calc.: C, 56.46; H, 4.39; N, 4.39%. IR (KBr): 3065w, 2920w, 2830w, 1614s 1599s, 1581m, 1487m, 1470s, 1461s, 1253vs, 1028s, 884m, 814s, 750s cm^{-1}. ^{1}H NMR(DMSO-d_6): 8.39 (s, 1H, H-1), 7.71 (s, 1H, H-9), 7.44 (d, 1H, $J = 8.2$ Hz, H-7), 7.37 (d, 1H, $J = 7.4$ Hz, H-8), 7.18–6.88 (m, 4H, H-3, H-4, H-5, H-6), 3.41 (s, 3H, OCH_3), 2.43 (s, 3H, Ar–CH_3) ppm.

4.2.8. *Dichlorobis[2-(3-methoxybenzylideneamino)-5-tolyl]tin(IV) (2h)*

Following the general procedure, the crude product was recrystallized from xylene to give 0.45 g (71%) of **2h** as pale-yellow crystals (m.p., 252–254°C; $\Lambda = 0\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$). Anal. Found: C, 56.88; H, 4.63; N, 4.07. $C_{30}H_{28}Cl_2N_2O_2Sn$ calc.: C, 56.46; H, 4.39; N, 4.39%. IR (KBr). 3065w, 2950w, 2930w, 2905w, 2830w, 1621s, 1598s, 1572s, 1490m, 1485m, 1465s, 1452s, 1271s, 1040s, 873m, 814s, 858m, 780s, 680s cm^{-1}. ^{1}H NMR (DMSO-d_6): 8.85 (s, 1H, H-1), 7.72 (s, 1H, H-9), 7.49 (d, 1H, $J = 8.2$ Hz, H-8), 7.42–7.38 (m, 2H, H-2, H-6), 7.18 (d, 1H, $J = 7.7$ Hz, H-7), 7.02 (d, 1H, $J = 8.4$ Hz, H-4), 6.55 (s, 1H, H-5), 3.77 (s, 3H, OCH_3), 2.45 (s, 3H, Ar–CH_3) ppm.

4.2.9. *Dichlorobis[2-(4-methoxybenzylideneamino)-5-tolyl]tin(IV) (2i)*

Following the general procedure, the crude product was recrystallized from xylene to give 0.61 g (96%) of **2i** as pale-yellow crystals (m.p., 302–304°C; $\Lambda = 0\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$). Anal. Found: C, 56.21; H, 4.42; N, 4.49. $C_{30}H_{28}Cl_2N_2O_2Sn$ calc.: C, 56.46; H, 4.39; N, 4.39%. IR (KBr): 3065w, 2950w, 2920w, 2910w, 2835w, 1615sh, 1600s, 1582s, 1570s, 1510s, 1470m, 1460m, 1252s, 1028s, 890m, 818sh, 824s cm^{-1}. ^{1}H NMR (DMSO-d_6): 8.71 (s, 1H, H-1), 7.88–7.35 (m, 4H, H-2, H-6, H-8, H-9), 7.12

TABLE 3. Deviations of the atoms from their mean planes

Atom	d (Å) from plane 1 [a]	Atom	d (Å) from plane 2 [b]	Atom	d (Å) from plane 3 [c]	Atom	d (Å) from plane 4 [d]
C(1)	0.077	C(15)	−0.150	Sn	−0.004	Sn	−0.007
C(2)	0.042	C(16)	−0.049	C(1)	0.009	C(15)	0.016
C(3)	−0.054	C(17)	0.127	C(6)	−0.001	C(20)	−0.020
C(4)	−0.080	C(18)	0.166	N(1)	0.006	N(2)	0.011
C(5)	−0.032	C(19)	0.070				
C(6)	0.023	C(20)	−0.080				
C(7)	0.051	C(21)	−0.068				
C(8)	0.026	C(22)	−0.044				
C(9)	0.057	C(23)	−0.129				
C(10)	0.032	C(24)	−0.059				
C(11)	−0.043	C(25)	0.086				
C(12)	−0.077	C(26)	0.166				
C(13)	−0.038	C(27)	0.109				
N(1)	0.017	N(2)	−0.145				

[a] Equation for plane 1: $0.3458x + 0.3085y - 0.8662z + 1.7011 = 0$.

[b] Equation for plane 2: $-0.8140x + 0.5589y - 0.1582z + 2.3056 = 0$.

[c] Equation for plane 3: $0.3265x + 0.3264y - 0.8870z - 1.6837 = 0$.

[d] Equation for plane 4: $-0.8144x + 0.5072y - 0.2819z - 3.1053 = 0$.

(d, 1H, $J = 8.7$ Hz, H-7), 6.76 (d, 2H, $J = 8.3$ Hz, H-3, H-5), 3.78 (s, 3H, OCH_3), 2.48 (s, 3H, Ar-CH_3) ppm.

*4.2.10. Dichlorobis[2-(4-dimethylaminobenzylideneamino)-5-tolyl]tin(IV) (**2j**)*

Following the general procedure, the crude product was recrystallized from xylene to give 0.35 g (53%) of **2j** as yellow crystals (m.p., 315–317°C; $\Lambda = 0\ \Omega^{-1}\ cm^2\ mol^{-1}$). Anal. Found: C, 57.67; H, 5.13; N, 8.30. $C_{32}H_{34}Cl_2N_4Sn$ calc.: C, 57.86; H, 5.12; N, 8.44%. IR (KBr): 3065w, 2970w, 2900m, 2890w, 2850w, 2800w, 1615sh, 1599s, 1570s, 1542s, 1525s, 1468m, 1362s, 1164s, 888w, 816vs cm^{-1}. ^1H NMR (DMSO-d_6): 8.57 (s, 1H, H-1), 7.79 (s, 1H, H-9), 7.64–7.41 (m, 2H, H-7, H-8), 7.28 (d, 2H, $J = 8.9$ Hz, H-2, H-6), 6.48 (d, 2H, $J = 8.9$ Hz, H-3, H-5), 2.99 (s, 6H, NMe_2), 2.48 (s, 3H, Ar-CH_3) ppm.

*4.2.11. Dichlorobis[2-(benzylideneamino)-5-chlorophenyl]tin(IV) (**2k**)*

Following the general procedure, the crude product was recrystallized from xylene to give 0.40 g (65%) of **2k** as pale-yellow crystals (m.p., 288–289°C; $\Lambda = 0\ \Omega^{-1}$ $cm^2\ mol^{-1}$). Anal. Found: C, 50.06; H, 3.02; N, 4.69. $C_{26}H_{18}Cl_4N_2Sn$ calc.: C, 50.44; H, 2.91; N, 4.53%. IR (KBr): 3065w, 1614vs, 1594s, 1576s, 1559s, 1492m, 1452s, 882s, 820s, 754s, 680s cm^{-1}. ^1H NMR (DMSO-d_6): 8.38 (s, 1H, H-1), 7.81 (d, 1H, $J = 2.1$ Hz, H-9), 7.64 (dd, 1H, $J = 8.4$, 2.2 Hz, H-8), 7.57 (d, 1H, $J = 8.6$ Hz, H-7), 7.42 (t, 1H, $J = 7.4$ Hz, H-4), 7.37 (d, 2H, $J = 7.8$ Hz, H-2, H-6), 7.21 (t, 2H, $J = 7.6$ Hz, H-3, H-5) ppm.

*4.2.12. Dichlorobis[2-(benzylideneamino)-5-bromophenyl]tin(IV)(**2l**)*

Following the general procedure, the crude product was recrystallized from xylene to give 0.39 g (55%) of **2l** as pale-yellow crystals (m.p., 291–292°C; $\Lambda = 0\ \Omega^{-1}$ $cm^2\ mol^{-1}$). Anal. Found: C, 44.01; H, 2.65; N, 3.97. $C_{26}H_{18}Br_2Cl_2N_2Sn$ calc.: C, 44.09; H, 2.54; N, 3.96%. IR (KBr): 3065w, 1612vs, 1598m, 1577s, 1550w, 1490w, 1450s, 880m, 818s, 752s, 680s cm^{-1}. ^1H NMR (DMSO-d_6): 8.40 (s, 1H, H-1), 7.95 (d, 1H, $J = 2.2$ Hz, H-9), 7.77 (dd, 1H, $J = 8.6$, 2.2 Hz, H-8), 7.51 (d, 1H, $J = 8.6$ Hz, H-7), 7.44 (t, 1H, $J = 8.0$ Hz, H-4), 7.37 (d, 2H, $J = 7.2$ Hz, H-2, H-6), 7.21 (t, 2H, $J = 7.6$ Hz, H-3, H-5) ppm.

*4.2.13. Dichlorobis[2-(benzylideneamino)-5-iodophenyl]tin(IV) (**2m**)*

Following the general procedure, the crude product was recrystallized from xylene to give 0.74 g (92%) of **2m** as white crystals (m.p., 295–297°C; $\Lambda = 0\ \Omega^{-1}\ cm^2$ mol^{-1}). Anal. Found: C, 38.90; H, 2.33; N, 3.51. $C_{26}H_{18}Cl_2I_2N_2Sn$ calc.: C, 38.92; H, 2.25; N, 3.49%. IR (KBr): 3060w, 1614vs, 1598m, 1576s, 1547m, 1540w, 1450vs, 880m, 815s, 753s, 681s cm^{-1}. ^1H NMR (DMSO-d_6): 8.47 (s, 1H, H-1), 8.13 (d, 1H, $J = 1.8$ Hz, H-9), 7.92 (m, 2H, H-7, H-8), 7.47–7.37 (m, 3H, H-2, H-4, H-6), 7.23 (t, 2H, $J = 7.6$ Hz, H-3, H-5) ppm.

*4.2.14. Dichlorobis[2-(benzylideneamino)-5-methoxyphenyl]tin(IV) (**2n**)*

Following the general procedure, the crude product was recrystallized from 1,4-dioxane–chloroform (1/1) to give 0.35 g (57%) of **2n** as white crystals (m.p., 257–259°C: $\Lambda = 0\ \Omega^{-1}\ cm^2\ mol^{-1}$). Anal. Found: C, 55.24; H, 4.00; N, 4.51. $C_{28}H_{24}Cl_2N_2O_2Sn$ calc.: C, 55.12; H, 3.94; N, 4.59%. IR (KBr): 3060w, 2950w, 2835w, 1615vs, 1599m, 1580s, 1566m, 1474vs, 1222s, 1038s, 884m, 820s, 753s, 682s cm^{-1}. ^1H NMR (DMSO-d_6): 8.65 (s, 1H, H-1), 7.68 (d, 1H, $J = 8.9$ Hz, H-7), 7.47 (d, 1H, $J = 2.7$ Hz, H-9), 7.42–7.35 (m, 3H, H-2, H-4, H-6), 7.22–7.16 (m, 3H, H-3, H-5, H-8), 3.92 (s, 3H, OCH_3) ppm.

*4.3. X-ray crystal structure determination for **2a***

Single crystals of **2a** suitable for an X-ray diffraction study were obtained by slow evaporation of the dilute solution of **2a** in xylene at room temperature.

4.3.1. Crystal data

$C_{28}H_{24}Cl_2N_2Sn \cdot C_8H_{10}$; $M = 684.277$; triclinic; $a = 8.393(1)$ Å, $b = 12.857(1)$ Å and $c = 13.856(1)$ Å; $\alpha = 99.07(1)°$, $\beta = 100.89(1)°$ and $\gamma = 95.17(1)°$; $V = 1438.7$ Å^3; $P\bar{1}$; $D_{calc} = 1.455\ g\ cm^{-3}$; $Z = 2$; $F(000) = 636$; λ (Cu Kα) = 1.5418 Å; μ(Cu Kα) = 91.52 cm^{-1}.

4.3.2. Data collection and reduction

A single crystal of approximate dimensions 0.28 mm × 0.26 mm × 0.19 mm was mounted on the end of a glass fibre. The X-ray diffraction intensity data of 5109 independent reflections, of which 4854 with $I > 3\sigma(I)$ were observable, were collected with an Enraf–Nonius CAD-4 four-circle diffractometer at 298 K using graphite-monochromated Cu Kα radiation in the ω–2θ scan mode within the range of $2° \leqslant 2\theta \leqslant 130°$. Throughout data collection the intensities of three standard reflections were monitored at regular intervals and this indicated no significant crystal decomposition: The intensities were corrected for Lorentz and polarization effects and an absorption correction based on ψ scans was applied with transmissions of 99.59–87.74%.

4.3.3. Structure solution and refinement

The structure was solved by Patterson methods using an Enraf–Nonius SDP program package [8] on a

PDP 11/44 computer. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included in the calculated positions with isotropic thermal parameters equal to the isotropic of their carrier atoms. The final $R = \Sigma \| F_o | - | F_c \| / | F_o | = 0.039$, $R_w = \Sigma \| F_o | - | F_c \| w^{1/2} / \Sigma | F_o w^{1/2} | = 0.053$ with $w = 1$ for observed reflections. The final positional parameters are given in Table 2.

Full tables of bond lengths and angles, torsional angles, hydrogen coordinates, anisotropic thermal parameters and the figure of unit cell are available from the authors.

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