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ORIGINAL PAPER

Reactivity of diorganotin(IV) dichlorides towards N, P, and O donor ligands: crystal structure of [$SnMe_2Cl_2$(phendione)]

B. Z. Momeni · R. Kia · S. Ghanbarzadeh

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Abstract The reactions of diorganotin(IV) dichlorides SnR_2Cl_2 (R = Me, *n*-Bu) with a series of ligands having N, P, or O donor atoms have been investigated. The reaction of SnR_2Cl_2 (R = Me, *n*-Bu) with the bidentate chelating pyridyl ligands of phendione (1,10-phenanthroline-5,6-dione) and ndppz (11-nitrodipyrido[3,2-*a*:2′,3′-*c*]phenazine) affords new hexa-coordinated 1:1 adducts with general formula SnR_2Cl_2L (R = Me, *n*-Bu; L = phendione, ndppz). On the other hand, $SnMe_2Cl_2$ reacted with xantphos [9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene] to yield the hexa-coordinated 1:2 adduct [$SnMe_2Cl_2$(xantphos)$_2$] in the solid state. However, it dissociates in solution to give the penta-coordinated 1:1 complex [$SnMe_2Cl_2$(xantphos)]. Notably, the analogous *n*-Bu derivative does not react, even under forcing conditions. Finally, the tin(IV) compounds SnR_2Cl_2 (R = Me, *n*-Bu) react with dppap [2-(diphenylphosphinoamino)pyridine] to give the penta-coordinated 1:1 adducts [SnR_2Cl_2(dppap)] (R = Me, *n*-Bu). The resulting complexes have been characterized by nuclear magnetic resonance (NMR) spectroscopy and elemental analysis. The X-ray crystal structure determination of [$SnMe_2Cl_2$(phendione)] reveals that the compound crystallized with two independent molecules in the asymmetric unit with a *trans*-[$SnMe_2$] configuration.

Keywords Organotin · Coordination · Pyridyl · NMR · Crystal structure

B. Z. Momeni (✉) · S. Ghanbarzadeh
Department of Chemistry, K.N. Toosi University of Technology, P.O. Box 16315-1618, 15418 Tehran, Iran
e-mail: momeni@kntu.ac.ir

R. Kia
X-ray Crystallography Lab, Plasma Physics Research Center, Science and Research Branch, Islamic Azad University, Tehran, Iran

R. Kia
Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran

Introduction

Pyridyl derivatives of tin(IV) compounds play an important role in developing the coordination and organometallic chemistry of tin [1–4]. It is well known that there is a relation between the antitumor activity of organotin(IV) adducts containing N donor ligands and Sn–N bond length [5, 6]. These versatile ligands adopt various modes of coordination to form 1:1 or 1:2 adducts, affording penta- or hexa-coordinated complexes of tin(IV) [7]. The common geometries for organotin(IV) compounds are a trigonal bipyramidal or an octahedral geometry [8]. Notably, the unusual seven-coordinated dimethyltin(IV) dichloride adduct in a pentagonal bipyramidal geometry has been isolated with a tridentate pyridyl heterocycle [2,4,6-tris(2-pyridyl)-1,3,5-triazine] [9]. The geometries of organotin(IV) adducts are affected by the nature of the organic group (R), halide or pseudohalide, and donor ligand [10]. Many organotin(IV) adducts dissociate in solution, and the behavior in solution is dependent upon the nature of the organotin(IV) compound and solvent [2, 11]. As part of our interest in the investigation of the coordination chemistry of tin, particularly that of organotin compounds, we prepared some diorganotin(IV) adducts including two bidentate pyridyl ligands: 1,10-phenanthroline-5,6-dione (phendione) and 11-nitrodipyrido-[2,3-*a*:2′,3′-*c*]phenazine (ndppz). It has been shown that phendione can interact with the metal centers through quinonoid or diiminic functionality [12]. On the other hand, the

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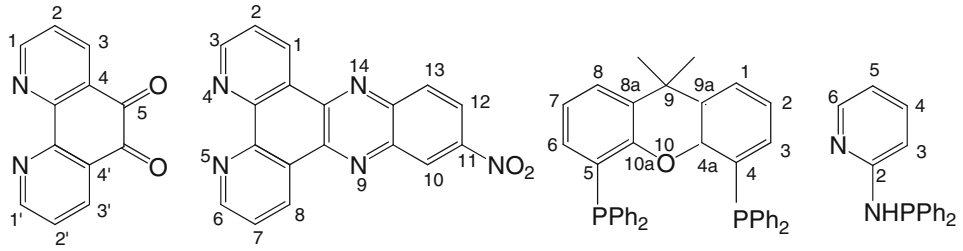
Scheme 1



presence of two types of basic centers P and O atoms in 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos) or P and N atoms in 2-(diphenylphosphinoamino)pyridine (dppap) makes them the ideal ligands to study the different coordinating abilities of two sets of donor atoms (Scheme 1). Interestingly, both of these phosphinoheteroarenes can act as monodentate or bidentate ligands. We used these types of ligands to obtain more information about the relative reactivities of organotin(IV) complexes towards N, P, or O donor ligands.

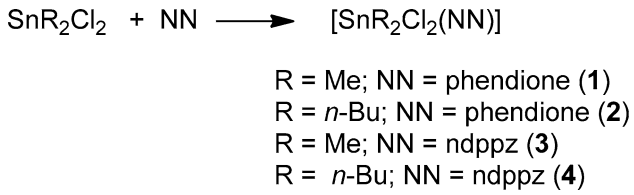
Results and discussion

NMR studies

Reactions of diorganotin(IV) dichlorides (SnR_2Cl_2, R = Me, *n*-Bu) with the bidentate pyridyl ligand phendione resulted in formation of hexa-coordinated 1:1 complexes [SnR_2Cl_2(phendione)] [R = Me (**1**), *n*-Bu (**2**)] as shown in Scheme 2. The products were characterized unambiguously by ^{1}H and ^{119}Sn NMR spectroscopy and elemental analysis.

The ^{1}H NMR of the complex [$SnMe_2Cl_2$(phendione)] (**1**) in $CDCl_3$ shows a signal at $\delta = 1.2$ ppm with $^2J(^{119}Sn–H) = 77.6$ Hz and $^2J(^{117}Sn–H) = 74.4$ Hz (Fig. 1), different from that of the starting complex $SnMe_2Cl_2$, which shows $^2J(^{119}Sn–H) = 68.6$ Hz and $^2J(^{117}Sn–H) = 65.7$ Hz in $CDCl_3$ [13]. The magnitude of the coupling constant of the methyl protons with ^{119}Sn is a useful guide for determination of the geometry of the tin atom. This coupling constant is in the range of the penta-coordinated dimethyltin(IV) complexes [14, 15]. These data suggest that the interaction between $SnMe_2Cl_2$ and phendione is not maintained in solution and the complex undergoes partial dissociation to afford the penta-coordinated tin(IV) complex.

The complex **1** was insoluble in most of the common organic solvents such as acetone, dichloromethane, dichloroethane, and tetrachloroethane to provide a satisfactory ^{119}Sn NMR spectrum. Therefore, the ^{119}Sn NMR spectrum of complex **1** was recorded in acetone-d_6 in the presence of small amounts of dimethyl sulfoxide (DMSO)-d_6. The ^{119}Sn



Scheme 2

NMR spectrum of complex **1** displayed a signal at $\delta = -184$ ppm. It has been reported that δ values range from +200 to −60 ppm for four-coordinated, from −90 to −190 ppm for five-coordinated, and from −210 to −400 ppm for six-coordinated tin complexes in solution [16]. Thus, the signal at −184 ppm is in the range of those reported for the penta-coordinated diorganotin(IV) complexes. The signal at $\delta = -184$ ppm confirms that the complex **1** is not stable in solution and dissociates to some extent to afford the penta-coordinated tin(IV) complex. The chemical shift of **1** is significantly more upfield to the starting complex $SnMe_2Cl_2$ ($\delta = 137.2$ ppm in $CDCl_3$) [17], resulting from the coordination of an N atom to the tin center.

On the other hand, the reaction of dibutyltin(IV) dichloride with phendione resulted in the formation of the complex [$SnBu_2Cl_2$(phendione)] (**2**) (Scheme 2). The ^{1}H NMR spectrum of complex **2** in $CDCl_3$ contains a triplet at $\delta = 0.87$ ppm with $^3J(HH) = 7.4$ Hz due to the methyl groups of the butyl ligands as shown in Fig. 1. The CH_2CH_3 resonance appears as a multiplet at $\delta = 1.32$ ppm with $^3J(HH) = 7.2$ Hz, while the protons of $SnCH_2$ and $SnCH_2CH_2$ groups of the butyl ligands appear as a broad multiplet at $\delta = 1.58$–1.80 ppm. Therefore, the tin satellites could not be resolved. The ^{119}Sn NMR spectrum of complex **2** in acetone-d_6 shows a signal at $\delta = -194$ ppm which clearly indicates the presence of a hexa-coordinated adduct of dibutyltin(IV) in solution.

The complex [$SnMe_2Cl_2$(ndppz)] (**3**) was prepared by reaction of $SnMe_2Cl_2$ with ndppz, as shown in Scheme 2. It was readily characterized by its ^{1}H NMR spectrum, which contained a signal at $\delta = 1.19$ ppm with $^2J(^{119}Sn–H) = 105.2$ Hz and $^2J(^{117}Sn–H) = 101.2$ Hz in $CDCl_3$. These coupling constants are in the range of the other hexa-coordinate dimethyltin(IV) complexes [2, 18]. Moreover,

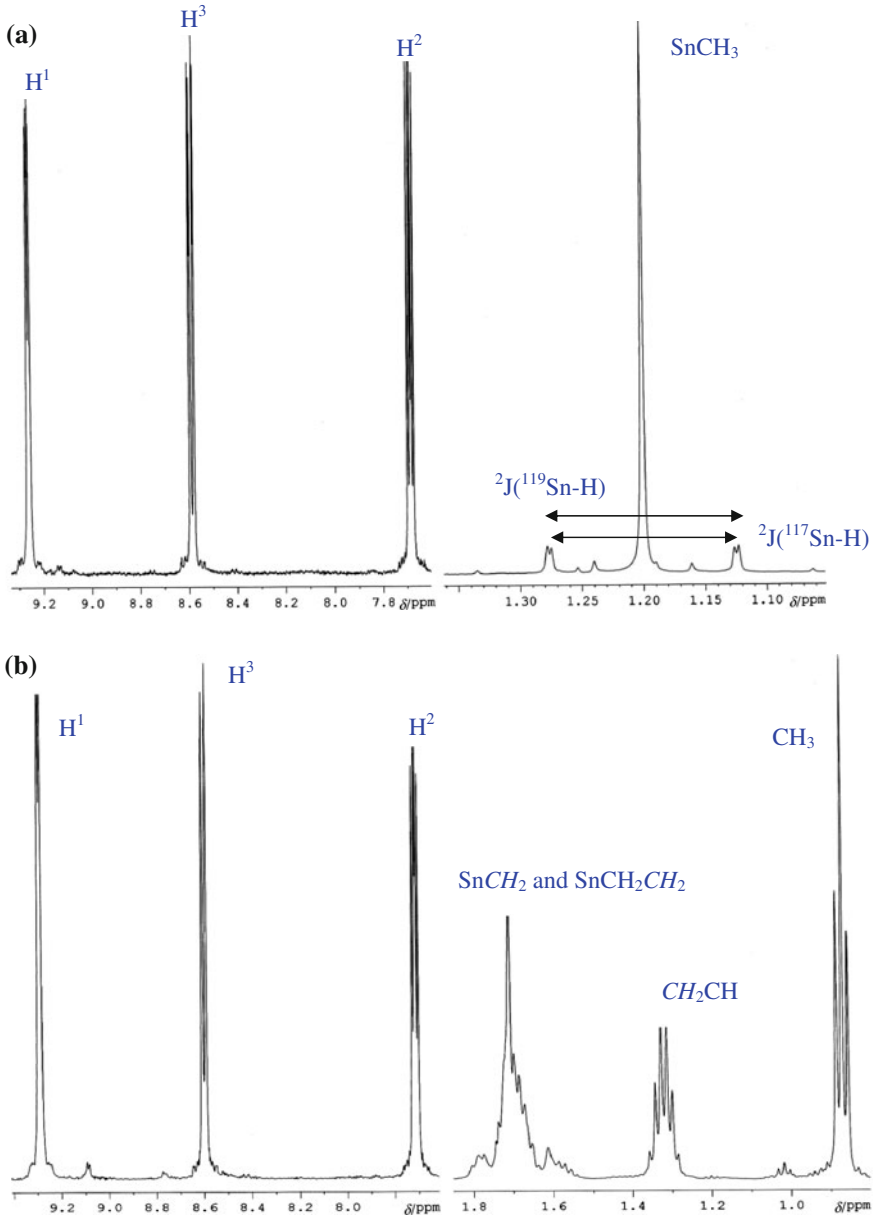


Fig. 1 ^{1}H NMR spectra of **a** [$SnMe_2Cl_2$(phendione)] (**1**) and **b** [$SnBu_2Cl_2$(phendione)] (**2**) in $CDCl_3$

reaction of $SnBu_2Cl_2$ with ndppz affords the hexa-coordinated complex [$SnBu_2Cl_2$(ndppz)] (**4**). The formation of a 1:1 adduct has been supported by elemental analysis.

Of particular note, the reaction of $SnMe_2Cl_2$ with xantphos resulted in formation of complex [$SnMe_2Cl_2$(xantphos)$_2$] (**5**) in the solid state; however, it dissociates in solution to give the complex [$SnMe_2Cl_2$(xantphos)] (**6**) (Scheme 3).

The ^{1}H NMR of complex [$SnMe_2Cl_2$(xantphos)] (**6**) in $CDCl_3$ shows a signal at $\delta = 1.2$ ppm with $^{2}J(^{119/117}\text{Sn–H}) =$ 70.7 Hz. This coupling constant is in the range of the other penta-coordinated dimethyltin(IV) complexes [14, 15]. On the other hand, the ^{31}P NMR of complex **6** in $CDCl_3$ shows a signal at $\delta = -16.8$ ppm which is very close to that observed for xantphos [19]. The elemental analysis results show that there is a 1:2 Sn:xantphos molar ratio which indicates the formation of a hexa-coordinated organotin(IV) adduct in the solid state, i.e., [$SnMe_2Cl_2$(xantphos-κ O)$_2$] (**5**). On the basis of these data, we suggest that $SnMe_2Cl_2$ is ligated by xantphos with two coordinated oxygen atoms, giving the

Scheme 3

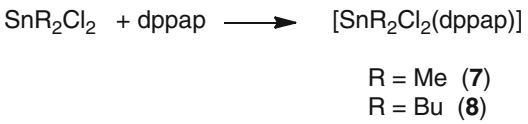
$SnMe_2Cl_2$ —xantphos→ [$SnMe_2Cl_2$(xantphos-κO)$_2$] → [$SnMe_2Cl_2$(xantphos-κO)]

5 (solid state) **6** (solution)

complex (**5**) in the solid state. However, it dissociates in solution, resulting in the formation of the penta-coordinated complex [$SnMe_2Cl_2$(xantphos-κ *O*)] (**6**). This indicates that the same structure is not retained in the two phases. In contrast, in the case of reaction of Sn(*n*-Bu)$_2Cl_2$ with xantphos, isolation of 1:1 or 1:2 dibutyltin dichloride adducts was not successful. Moreover, growth of single crystals from reaction of [$SnBu_2Cl_2$] with xantphos in CH_2Cl_2/hexane indicated the presence of the starting materials, consistent with the literature [19]. It can be seen that the simple substitution of the Me to *n*-Bu groups prevents the formation of a dibutyltin(IV)-xantphos adduct. The most significant conclusion of the reaction of diorganotin(IV) dichloride with xantphos is the formation of 1:1 or 1:2 adduct (acid to base), due to the less bulky methyl groups on the diorganotin(IV) dichloride. It may be possible that excessive steric repulsion between the bulky phenyl substituents on the phosphorus atoms and butyl units inhibits the formation of 1:1 or 1:2 adducts in the reaction of $SnBu_2Cl_2$ with xantphos.

In addition, we have investigated the reaction of diorganotin dichlorides with dppap. This ligand exhibits a number of coordination modes which have been extensively studied [20–22]. Dimethyltin(IV) dichloride and dibutyltin(IV) dichloride reacted with dppap to give the complexes [SnR_2Cl_2(dppap)] [R = Me (**7**), Bu (**8**)] in solution (Scheme 4).

The nature of 1:1 adducts for **7** and **8** in the solid state was verified by elemental analysis results. The ^{1}H NMR of complex **7** in $CDCl_3$ shows a signal at $\delta = 1.2$ ppm with $^2J(^{119/117}Sn–H) = 72.3$ Hz, indicating the presence of the penta-coordinated adduct [$SnMe_2Cl_2$(dppap)] (**7**) in solution. Moreover, the coupling between methyl hydrogens and ^{31}P nuclei could not be observed, largely due to the N ligating atom of pyridyl. It was known that the phosphine oxides are much more reactive towards tin(IV) compounds relative to phosphine ligands. There are relatively few examples of tin(IV)-phosphine adducts having P donor atoms. In most of the cases, the resulting coordination compounds were isolated by using oxidized P donors [23, 24]. In view of the fact that the interaction between tin(IV) compounds and P donor ligands is not well recognized and the absence of the coupling between hydrogen and phosphorus nuclei, we propose that interaction between SnR_2Cl_2 takes place via the *N*-pyridyl atom. Unfortunately, the complexes **3**–**8** were too insoluble, even in DMSO, to provide ^{13}C or ^{119}Sn NMR spectra.



Scheme 4

It can be seen that the formation of penta- or hexa-coordinate species is influenced by both the nature of the ligand and the nature of diorganotin compound. In summary, the basicities towards diorganotin dichlorides vary as expected: *N*-pyridyl > O > P donor ligands.

*Description and discussion of the crystal structure of **1***

The molecular structure of [$SnMe_2Cl_2$(phendione)] (**1**) is shown in Fig. 2. Selected bond distances and angles are also given in Table 1. Two independent molecules of compound **1** form the asymmetric unit, labeled (1) and (2).

The crystal structure of **1** shows that the tin atom exists in an octahedral geometry as revealed by the C(1)–Sn–C(2) angles which deviate insignificantly from linearity [171.6(3)° to 175.2(4)°]. The chlorine atoms are *cis* to each other, while the methyl groups are *trans*. This is consistent with the other diorganotin dihalide adducts containing bidentate ligands which have *cis* halogens [25, 26]. Phendione acts in a bidentate manner, as expected through both of the nitrogen atoms adopting *cis* conformation. Interestingly, there is one structure with planar phendione with O(4)–C(22)–C(23)–O(3) torsion angle of −0.8(10)° and another one with a slightly distorted phendione ligand resulting from the nonaromaticity of the central quinoid ring with O(2)–C(8)–C(9)–O(1) torsion angle of 10.6(15)°. The Sn–C bond distances are not equal [for example, Sn(1)–C(14) = 2.097(7) Å and Sn(1)–C(13) = 2.123(7) Å]. The Sn–Cl bonds are also inequivalent [for example, Sn(1)–Cl(1) = 2.4739(19) and Sn(1)–Cl(2) = 2.506(2) Å]. The bond lengths of the two Sn–N bonds are different with Sn(1)–N(2) [2.469(5) Å] and Sn(2)–N(3) [2.453(5) Å] being longer than Sn(1)–N(1) [2.436(5) Å] and Sn(2)–N(4) [2.401(6) Å], respectively, which is due to the packing of the crystal. The N1–Sn(1)–N2 and N3–Sn(2)–N4 bite angles are 67.34(17)° and 68.11(18)°, respectively, which are consistent with those observed for other chelating diimine ligands [2]. The crystal structure of [$SnMe_2Cl_2$(phendione)] reported here may be compared to that of [$SnPh_2Cl_2$(phendione)] [27]. The inequivalent Sn–N and Sn–Cl bond distances have also been observed in the crystal structure of [$SnPh_2Cl_2$(phendione)]·2Me_2CO; however, the phenyl groups are in *cis* sites.

The interesting features of the crystal structure are short intermolecular C–H···Cl contacts (Table 2) which link neighboring molecules together into chains along the *a*-axis, which seems to be effective in the stabilization of the crystal packing (Fig. 3).

Experimental

Dichloromethane was distilled from P_2O_5, and diethyl ether was distilled from sodium/benzophenone ketyl. Acetone

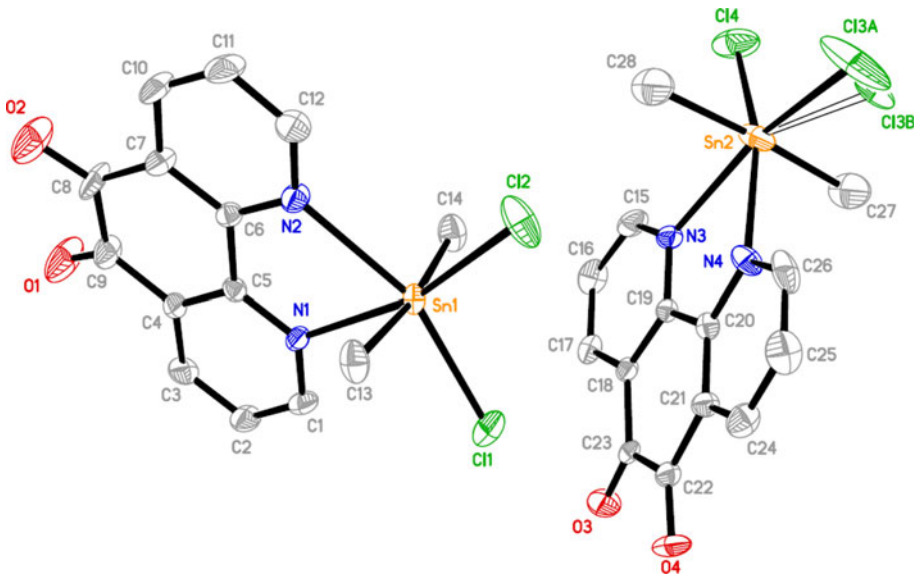


Fig. 2 The molecular structure of complex **1**, showing 30% probability displacement ellipsoids and the atomic numberings. H atoms are omitted for clarity. The open bond shows the minor component of the disordered Cl atom

Table 1 Selected bond distances (Å) and bond angles (°) for complex **1**

Sn(1)–C(14)	2.097(7)	C(13)–Sn(1)–Cl(2)	90.1(2)
Sn(1)–C(13)	2.123(7)	N(1)–Sn(1)–Cl(2)	165.49(13)
Sn(1)–N(1)	2.436(5)	N(2)–Sn(1)–Cl(2)	98.19(14)
Sn(1)–N(2)	2.469(5)	Cl(1)–Sn(1)–Cl(2)	102.61(8)
Sn(1)–Cl(1)	2.4739(19)	C(28)–Sn(2)–C(27)	175.2(4)
Sn(1)–Cl(2)	2.506(2)	C(28)–Sn(2)–N(4)	89.9(3)
O(1)–C(9)	1.196(9)	C(27)–Sn(2)–N(4)	89.8(3)
O(2)–C(8)	1.211(8)	C(28)–Sn(2)–N(3)	89.2(3)
Sn(2)–C(28)	2.111(9)	C(27)–Sn(2)–N(3)	86.3(3)
Sn(2)–C(27)	2.123(8)	N(4)–Sn(2)–N(3)	68.11(18)
Sn(2)–N(4)	2.401(6)	C(28)–Sn(2)–Cl(3A)	89.4(7)
Sn(2)–N(3)	2.453(5)	C(27)–Sn(2)–Cl(3A)	95.4(7)
Sn(2)–Cl(3A)	2.5094(10)	N(4)–Sn(2)–Cl(3A)	92.2(5)
Sn(2)–Cl(3B)	2.5100(10)	N(3)–Sn(2)–Cl(3A)	160.2(5)
Sn(2)–Cl(4)	2.557(2)	C(28)–Sn(2)–Cl(3B)	99.4(6)
C(14)–Sn(1)–C(13)	171.6(3)	C(27)–Sn(2)–Cl(3B)	85.3(6)
C(14)–Sn(1)–N(1)	86.4(2)	N(4)–Sn(2)–Cl(3B)	84.7(5)
C(13)–Sn(1)–N(1)	89.4(2)	N(3)–Sn(2)–Cl(3B)	151.6(5)
C(14)–Sn(1)–N(2)	87.2(3)	Cl(3A)–Sn(2)–Cl(3B)	12.5(6)
C(13)–Sn(1)–N(2)	84.5(3)	C(28)–Sn(2)–Cl(4)	89.5(3)
N(1)–Sn(1)–N(2)	67.34(17)	C(27)–Sn(2)–Cl(4)	89.3(3)
C(14)–Sn(1)–Cl(1)	96.6(2)	N(4)–Sn(2)–Cl(4)	161.40(15)
C(13)–Sn(1)–Cl(1)	90.8(2)	N(3)–Sn(2)–Cl(4)	93.28(14)
N(1)–Sn(1)–Cl(1)	91.89(12)	Cl(3A)–Sn(2)–Cl(4)	106.4(5)
N(2)–Sn(1)–Cl(1)	158.68(14)	Cl(3B)–Sn(2)–Cl(4)	113.7(5)
C(14)–Sn(1)–Cl(2)	92.2(2)		

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1/2, y, z$

Table 2 Hydrogen bond data

D–H···A	H···A/Å	D···A/Å	D–H···A/°
C(1)–H(1A)···Cl(1)	2.80	3.475(8)	130
C(2)–H(2A)···O(4)[a]	2.44	3.351(8)	168
C(17)–H(17A)···O(1)[b]	2.48	3.39(1)	168
C(25)–H(25A)···O(1)[c]	2.52	3.31(1)	142
C(28)–H(28C)···Cl(2)	2.83	3.744(9)	160

Symmetry codes: [a] $1 - x, 1 - y, 1 - z$; [b] $x, 3/2 - y, 1/2 + z$; [c] $x, -1 + y, z$

and the other reagents were used without further purification. Dimethyltin dichloride and dibutyltin dichloride were purchased from Merck, and xantphos was purchased from Aldrich. Phendione, ndppz, and dppap were prepared according to the literature [12, 20, 28]. All solvents and reagents were used without further purification. NMR spectra were recorded using a Bruker Avance DRX 500 spectrometer. Data are reported relative to the residual protonated solvent signal (^{1}H), $SnMe_4$ (^{119}Sn), or 85% H_3PO_4 (^{31}P). All chemical shifts and coupling constants are reported in ppm and Hz, respectively. Elemental analyses were performed on a PerkinElmer 2400 II elemental analyzer.

X-ray diffraction measurements were made on a STOE IPDS 2T diffractometer with graphite monochromated Mo K_α radiation. The yellow block crystal was mounted on a glass fiber and used for data collection. Data collection and reduction were performed by X-AREA 1.52 [29] program. The multiscan absorption correction was performed by MULABS routine [30]. The structure was solved by direct methods using SHELXS97 and subsequent difference Fourier map and then refined by a full-matrix least-squares on F^2 by SHELXL97 in SHELXTL package [31]. Non-hydrogen atoms were refined anisotropically. All of the H atoms were positioned geometrically and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2$ or 1.5 $U_{eq}(C)$. One of the chlorine atoms (Cl3) was disordered in

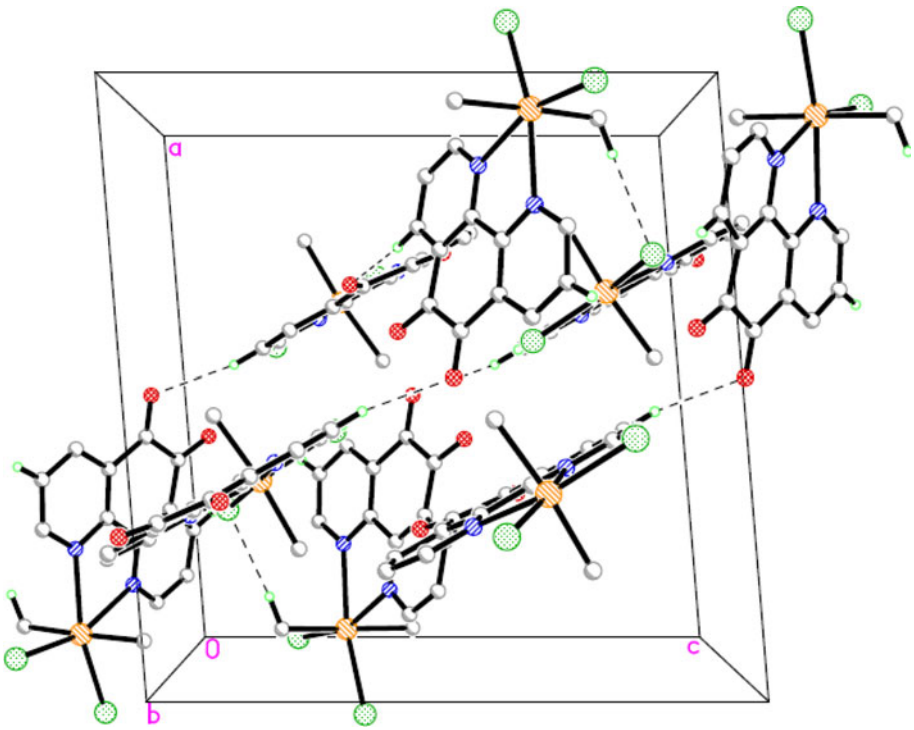


Fig. 3 The crystal packing of complex **1**, viewed down the *c*-axis, showing linking of the neighboring molecules through intermolecular C–H···O interactions along the *a*-axis. H atoms except those involving the interactions are omitted for clarity. Intermolecular interactions are shown as *dashed lines*

two positions as Cl3A and Cl3B with refined site occupancy ratio of 0.71(5)/0.29(5). All refinements were performed using the SHELXTL crystallographic software package. All calculations were done using PLATON [32]. A summary of the crystal data, experimental details, and refinement parameters is given in Table 3. CCDC 787513 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or e-mail: deposit@ccdc.cam.ac.uk.

Dichlorodimethyl(1,10-phenanthroline-5,6-dione-κ^2-N,N′)tin(IV) (**1**, $C_{14}H_{12}Cl_2N_2O_2Sn$)

A solution of 100 mg phendione (0.48 mmol) in 10 cm^3 dichloromethane was added to a solution of 105 mg $SnMe_2Cl_2$ (0.48 mmol) in 6 cm^3 dichloromethane to afford a yellow solid. The product was then filtered off, washed with diethyl ether, and air dried. Crystals suitable for X-ray structure determination were grown from an acetone/hexane solution. Yield: 89%; m.p.: 190 °C (dec); ^{1}H NMR ($CDCl_3$): $\delta = 1.20$ (s, 6H, $^2J(^{119}Sn–H) = 77.6$ Hz, $^2J(^{117}Sn–H) = 74.4$ Hz, Sn–Me), 7.68 (dd, 2H, $^3J(HH) = 7.8$ Hz, $^4J(HH) = 4.8$ Hz, H^2), 8.59 (dd, 2H, $^3J(HH) = 7.8$ Hz, $^4J(HH) = 1.8$ Hz, H^3), 9.26 (dd, 2H, $^3J(HH) = 4.7$ Hz, $^4J(HH) = 1.6$ Hz, H^1) ppm; ^{119}Sn NMR (acetone-d_6/DMSO-d_6): $\delta = -184$ ppm.

Dibutyldichloro(1,10-phenanthroline-5,6-dione-κ^2-N,N′)tin(IV) (**2**, $C_{20}H_{24}Cl_2N_2O_2Sn$)

Following the same procedure as for the preparation of **1**, a solution of 100 mg phendione (0.48 mmol) in 10 cm^3 dichloromethane was added to a solution of 146 mg Sn(*n*-Bu)$_2$Cl$_2$ (0.48 mmol) in 10 cm^3 dichloromethane. The solution was stirred for 24 h. The resultant yellow solution was evaporated to yield a yellow solid which was filtered off. The solid was washed with diethyl ether and air dried. Yield: 85%; m.p.: 101–102 °C; ^{1}H NMR ($CDCl_3$): $\delta = 0.87$ (t, 6H, $^3J(HH) = 7.4$ Hz, CH_3), 1.32 (m, 4H, $^3J(HH) = 7.2$ Hz, CH_2CH_3), 1.58–1.80 (m, 8H, $SnCH_2$ and $SnCH_2CH_2$), 7.71 (dd, 2H, $^3J(HH) = 7.8$ Hz, $^4J(HH) = 4.8$ Hz, H^2), 8.60 (d, 2H, $^3J(HH) = 7.8$ Hz, H^3), 9.28 (d, 2H, $^3J(HH) = 4.4$ Hz, H^1) ppm; ^{119}Sn NMR (acetone-d_6): $\delta = -194$ ppm.

Dichlorodimethyl(11-nitrodipyrido[3,2-a:2′,3′-c]phenazine-κ^2-N,N′)tin(IV) (**3**, $C_{20}H_{15}Cl_2N_5O_2Sn$)

A solution of 100 mg ndppz (0.31 mmol) in 20 cm^3 dichloromethane was added to a solution of 67 mg $SnMe_2Cl_2$ (0.31 mmol) in 6 cm^3 dichloromethane. The resultant solution was stirred for 24 h. The solvent was evaporated to give a brown solid. The solid was filtered off, washed with diethyl ether, and air dried. Yield: 82%; m.p.: 266 °C; ^{1}H NMR ($CDCl_3$): $\delta = 1.20$ (s, 6H, $^2J(^{119}Sn–H) = 105.2$ Hz, $^2J(^{117}Sn–H) = 101.2$ Hz, Sn–Me), 8.19 (m, 2H, $^3J(HH) = 5.3$ Hz, $H^{2,7}$), 8.63 (d, 1H, $^3J(HH) = 9.2$ Hz,

Table 3 Experimental details, crystal data, and refinement parameters for complex **1**

Empirical formula	$C_{14}H_{12}Cl_2N_2O_2Sn$
Formula weight/g mol^{-1}	429.85
Temperature/K	293 (2)
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Z	8
a/Å	14.7050 (10)
b/Å	15.3702 (14)
c/Å	14.4135 (9)
β/°	94.652 (5)
Volume/Å^3	3,247.0 (4)
D_{calc}/g cm^{-3}	1.759
Absorption coefficient/mm^{-1}	1.907
F (000)	1,680
θ range/°	1.92–25.50
Index ranges	$-17 \le h \le 17$, $-18 \le k \le 17$, $-16 \le l \le 17$
Reflections collected	12,181
Independent reflections [R_{int}]	5,462/0.056
Observed reflections	3,552 [$I > 2\sigma(I)$]
Max./min. transmission	0.772/1.000
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5,462/8/381
Goodness of fit (GOF)	0.916
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0477$, $wR_2 = 0.0933$
R indices (all data)	$R_1 = 0.0872$, $wR_2 = 0.1033$
Largest differences in peak, hole/e Å^{-3}	1.157, −1.512

H^{13}), 8.79 (dd, 1H, ^3J(HH) = 9.2 Hz, ^4J(HH) = 2.3 Hz, H^{12}), 9.38 (d, 1H, ^4J(HH) = 2.4 Hz, H^{10}), 9.88 (m, 2H, ^3J(HH) = 3.6 Hz, H^{1,8}), 9.95 (dd, 2H, ^3J(HH) = 8.0 Hz, ^4J(HH) = 1.8 Hz, H^{3,6}) ppm.

Dibutyldichloro(11-nitrodipyrido[3,2-a:2′,3′-c]phenazine-κ^2-N,N′)tin(IV) (**4**, $C_{26}H_{27}Cl_2N_5O_2Sn$)

Following the same procedure for the preparation of **2**, a solution of 100 mg ndppz (0.31 mmol) was reacted with 93 mg Sn(*n*-Bu)$_2$Cl$_2$ (0.31 mmol) to afford a brown solid. The solid was recrystallized from CH_2Cl_2/diethyl ether. Yield: 73%; m.p.: 188 °C; ^{1}H NMR ($CDCl_3$): δ = 0.69 (t, 6H, ^3J(HH) = 7.3 Hz, CH_3), 1.12 (m, 4H, ^3J(HH) = 7.4 Hz, CH_2CH_3), 1.48 (m, 4H, ^3J(HH) = 8.0 Hz, $SnCH_2CH_2$), 1.64 (m, 4H, ^3J(HH) = 7.2 Hz, $SnCH_2$), 8.16 (m, 2H, ^3J(HH) = 4.8 Hz, H^{2,7}), 8.62 (d, 1H, ^3J(HH) = 9.2 Hz, H^{13}), 8.77 (dd, 1H, ^3J(HH) = 9.2 Hz, ^4J(HH) = 2.2 Hz, H^{12}), 9.36 (d, 1H, ^4J(HH) = 2.0 Hz, H^{10}), 9.81 (br, 2H, H^{1,8}), 9.93 (m, 2H, ^3J(HH) = 6.3 Hz, H^{3,6}) ppm.

Dichlorodimethylbis[9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene-κ-O]tin(IV) (**5**, $C_{79}H_{70}Cl_2O_2P_4Sn$)

A solution of 100 mg xantphos (0.17 mmol) in 30 cm^3 dichloromethane was added to a solution of 38 mg $SnMe_2Cl_2$ (0.17 mmol) in 6 cm^3 dichloromethane. The solution was stirred for 10 h. The resultant colorless solution was evaporated to dryness to afford a white solid. The product was then filtered off, washed with *n*-hexane, and air dried. Yield: 72%; m.p.: 206–208 °C (dec).

NMR data for [$SnMe_2Cl_2$(xantphos-κ *O*)] (**6**): ^{1}H NMR ($CDCl_3$): δ = 1.21 (s, 6H, $^2J(^{119/117}Sn–H)$ = 70.7 Hz, Sn–Me), 1.66 (m, 6H, CH_3), 6.56 (d, 2H, ^3J(HH) = 6.2 Hz, H^{1,8}), 6.96 (t, 2H, ^3J(HH) = 7.6 Hz, H^{2,7}), 7.19–7.27 (m, phenyl groups), 7.40 (d, 2H, ^3J(HH) = 7.2 Hz, H^{3,6}) ppm; ^{31}P NMR ($CDCl_3$): δ = −16.8 ppm.

Dichlorodimethyl[2-(diphenylphosphinoamino) pyridine-κ-N]tin(IV) dichoromethane hemisolvate (**7**, $C_{19}H_{21}Cl_2N_2PSn{\cdot}0.5CH_2Cl_2$)

A solution of 100 mg dppap (0.36 mmol) in 20 cm^3 dichloromethane was added to a solution of 79 mg $SnMe_2Cl_2$ (0.36 mmol) in 6 cm^3 dichloromethane to give a white solid. The product was then filtered off, washed with *n*-hexane, and air dried. Yield: 86%; m.p.: 350–352 °C (dec); ^{1}H NMR ($CDCl_3$): δ = 1.26 (s, 6H, $^2J(^{119/117}Sn–H)$ = 72.3 Hz, Sn–Me), 6.81 (t, 1H, ^3J(HH) = 6.6 Hz, H^5), 7.06 (d, 1H, ^3J(HH) = 8.8 Hz, H^3), 7.41 (m, 1H, H^4), 7.52 (m, 1H, H^6), 7.74 (d, 1H, $^2J(^{31}P–H)$ = 5.8 Hz, NH), 7.75–7.81 (m, phenyl groups) ppm.

Dibutyldichloro[2-(diphenylphosphinoamino)pyridine-κ-N]tin(IV) (**8**, $C_{25}H_{33}Cl_2N_2PSn$)

Following the same procedure as for the preparation of **7**, a solution of 100 mg dppap (0.36 mmol) in 20 cm^3 dichloromethane was added to a solution of 109 mg Sn(*n*-Bu)$_2$Cl$_2$ (0.36 mmol) in 10 cm^3 dichloromethane to afford a white solid. The solid was then filtered off, washed with *n*-hexane, and air dried. Yield: 80%; m.p.: 328 °C (dec); ^{1}H NMR ($CDCl_3$): δ = 0.87 (t, 6H, ^3J(HH) = 7.0 Hz, CH_3), 1.32 (m, 4H, ^3J(HH) = 5.3 Hz, CH_2CH_3), 1.75 (br, 8H, $SnCH_2$, $SnCH_2CH_2$), 6.74 (t, 2H, ^3J(HH) = 6.5 Hz, H^5), 7.19 (d, 1H, ^3J(HH) = 8.7 Hz, H^3), 7.38 (m, 1H, H^4), 7.44 (d, 1H, ^3J(HH) = 6.4 Hz, H^6), 7.67 (d, 1H, $^2J(^{31}P–H)$ = 6.0 Hz, NH), 7.71–7.79 (br m, phenyl groups) ppm.

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