EurJIC European Journal of Inorganic Chemistry
ChemPubSoc Europe

FULL PAPER

DOI:10.1002/ejic.201400089

# Attachment of Chelating Ligand Pockets to Tinorganyl Moieties

**Beatrix E. K. Barth,[a] Klaus Harms,[a] and Stefanie Dehnen*[a]**

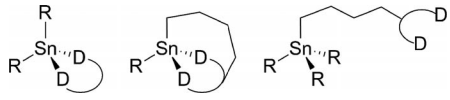
**Keywords:** Tin / N ligands / Halogenation

Several approaches have been undertaken to realize the synthesis of a new tinorganyl compound with a 2,2′,6′,2′′-terpyridine moiety. A synthesis pathway consisting of five steps with an overall yield of 51 % was successful in producing $Ph_3Sn(CH_2)_3OPhttpy$ [HOttpy = 2,6-bis(2′-pyridyl)-4′-(*p*-hydroxyphenyl)pyridine], and insight has been gained into (partial) halogenation reactions with this unprecedented tinorganyl compound. Halogenation with hydroiodic acid produced a new dinuclear complex cation that resulted from head-to-tail coordination of two monocations. Furthermore, synthesis and yields of already known intermediates have been optimized. The products were analyzed and identified by $^{119}Sn$ NMR, $^{1}H$ NMR, and $^{13}C$ NMR spectroscopy and ESI mass spectrometry, as well as by means of single-crystal X-ray diffraction.

## Introduction

Organotin(IV) compounds do not only play a prominent role in current organoelement chemistry research because of their numerous applications,[1] but they are also well known for their multifaceted coordination chemistry that comes with various coordination modes and coordination numbers for the Sn atom, which range from 4 to 6 in most cases. With the introduction of appropriate chelating ligands these values can be exceeded (up to a coordination number of 8).[2]

There are two common modes for installing chelating ligands at tinorganyl moieties: A reaction of free ligands with the tin moiety,[1e,1f,3] or the pre-connection of the ligand with the tin atoms by a Sn–C bond away from the chelating unit. In this case, the chelating ligand may then coordinate to the tin atom,[1e,4] or, keep away from the tin atom to produce a vacant chelating pocket to the tin atom, which bears the additional opportunity to trap further metal atoms (Scheme 1).[4a,5]




Scheme 1. Schematic representation of known attachment modes of chelating ligands at $Sn^{IV}$ organyl compounds. D denotes electronegative donor atom (N, P, O, S).

[a] Fachbereich Chemie and Wissenschaftliches Zentrum für Materialwissenschaften der Universität Marburg,
Hans-Meerwein-Straße, 35043 Marburg, Germany
E-mail: dehnen@chemie.uni-marburg.de
http://www.uni-marburg.de/fb15/ag-dehnen

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201400089.

Until now, the latter has been quite rare; it has only been known for chelating ligands comprising acetate or amine groups, whereas there have not been any examples known for further chelating groups, such as polypyridine ligands. The intramolecular attack of the tin atom by the donor atoms of the chelating ligand is directed by the steric and electronic situation at the tin atom, which in turn is influenced by the nature of the additional ligands R. Electron-withdrawing substituents, such as halide ligands, for instance, enhance the acidity of the tin atom and therefore facilitate intramolecular coordination.[6]

## Results and Discussion

One of our current aims regarding the formation and properties of functionalized tin chalcogenide clusters[7] is the installation of chelating ligands on the Sn/S cluster surfaces for further metal atom/ion trapping. For this, we are currently extending organotin chemistry towards polypyridyl ligands.[8] The syntheses of organotin trihalides for conversion with chalcogenide sources is usually preferred over organotin compounds of the general type $R_3SnR^f$; $R^f$ denotes the functional ligand $R_f$ that is next to three organic groups that are usually replaced by halide ligands by Kocheshkov redistribution reactions with $SnX_4$ (X = Cl, Br).[5d,9]

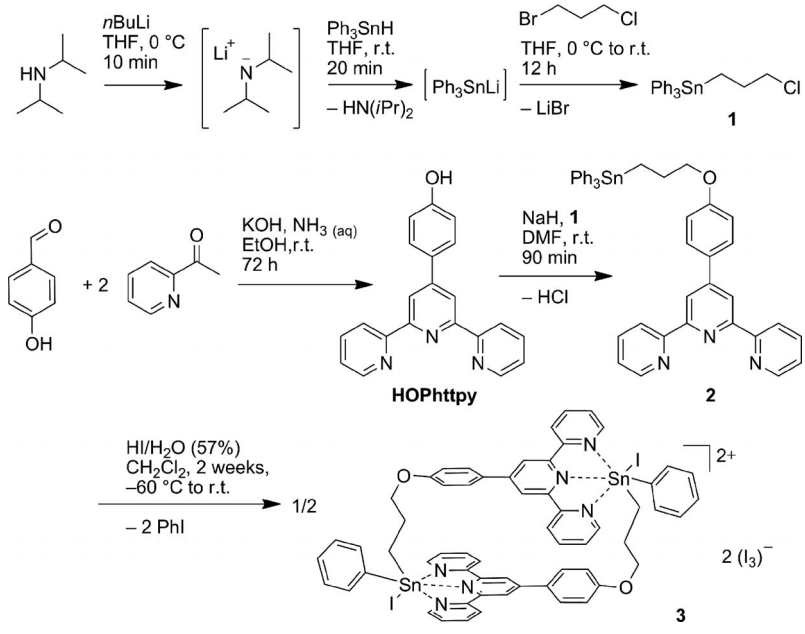
In the following we describe a synthesis pathway used to obtain the novel organotin precursor $[Ph_3Sn(CH_2)_3OPhttpy]$ [**2**; 2,6-bis(2′-pyridyl)-4′-(*p*-hydroxyphenyl)pyridine = HOPhttpy], bearing a 2,2′,6′,2′′-terpyridine moiety. It is known that for $R_f$, comprising an unoccupied terpyridyl group, the application of a Kocheshkov redistribution reaction is ruled out, since $SnX_4$ does not only halogenate

the tin atom, but may at the same be captured by the ligand pocket.[9a] This also affects other halogenation reactions like those that are performed by using boron, titanium, bismuth, or mercury halide compounds.[10] To avoid this, a halogenation reaction can be achieved by means of simple electrophilic substitution reactions, if the tinorganyl accords have the general formula DL–$CH_2$–$SnR_3$ (DL = chelating/donor ligand, R = Ph, Cy, AcO).[11] As we report herein, reaction of **2** with aqueous HI solution indeed leads to (partial) iodination; however, the high affinity of the terpyridyl unit to $Sn^{IV}$ was further enhanced by the attachment of the halide substituent. Hence, we isolated the dinuclear complex {[PhISn$(CH_2)_3$OPhttpy]$_2$}$(I_3)_2$ (**3**). It represents a coordination dimer with the terpyridyl ligand of one of the organotin monoiodides coordinating to the tin atom of the other.

First attempts to produce compound **2** by reacting allyl bromide with HOPhttpy, followed by hydrostannylation of this allyl compound,[12] succeeded in the synthesis of the allyl terpyridine derivative, but led to undesirable redistribution processes for the final hydrostannylation step, as already reported for similar reactions.[11a] Hence, a new synthesis method was chosen and is described below (Scheme 2). As a final step, we planned the coupling of HOPhttpy with (3-chloropropyl)triphenylstannane (**1**) by a Williamson ether synthesis.

HOPhttpy was synthesized in a one-pot reaction based on reaction conditions published by Wang and Hanan et al.[13] For the synthesis of **1**, hydrostannylation of allyl chloride/allyl bromide was attempted with triphenyltin hydride in the presence of AIBN at 50 °C. However, this method was a failure, as larger amounts of byproducts were obtained. Hence, an optimized synthesis route based on the method reported by Pinoie et al. was chosen instead;[11b] a mild lithiation of triphenyltin hydride by in situ-generated lithium diisopropylamide (Scheme 2). Indeed, fewer byproducts formed and much better yields (71%) were realized than under the reaction conditions reported by Weichmann et al. (38%)[14] or by Christoffers et al. (3%).[15] Compound **1** was then reacted in the planned manner to produce compound **2** in 72% yield (Scheme 2) as a colorless solid. NMR investigations of **2** (Figures S6–S8) indicate that the observed $J(^{119}Sn–^{13}C)$ coupling constants for Sn$CH_2$ ($\delta$ = 7.1 ppm, $J$ = 391 Hz), $CH_2$ ($\delta$ = 26.4 ppm, $J$ = 19.6 Hz) and $CH_2O$ ($\delta$ = 70.7 ppm, $J$ = 66.0 Hz), and the $^{119}$Sn NMR signal at $\delta$ = –99.3 ppm (Figure S8) are in good agreement with those reported for the known compound $Ph_3Sn(CH_2)_3NMe_2$, with a four-coordinate tin atom.[16] The $^{119}$Sn NMR chemical shift reported for $Ph_3Sn$*n*Bu ($\delta$ = –101.5 ppm) is also very similar.[17] The calculations of the C–Sn–C bond angle $\theta$ of **2** in solution depending on the $^1J(^{119}Sn^{13}C)$ coupling constants were realized by following two different methods.[18] A simple linear correlation as given by Lockhart et al.[18a] leads to an estimate of $\theta$ = 111 ± 5°. According to the method by Holeček et al.[18b] the angle is $\theta$ = 114 ± 17°. Both results correlate with the experimentally found values for the C–Sn–C angles in **2** that range from 108.5(2)° (C21–Sn1–C14) to 109.26(19)° (C15–Sn1–C14).

Compound **2** is soluble in chlorinated solvents, and crystallizes in the monoclinic space group $P2_1$. The molecular structure of **2** is shown in Figure 1, the arrangement of the molecules in the unit cell is shown in Figure 2. Compound **2** comprises a 2,2′,6′,2′′-terpyridine unit, in which the terminal pyridine rings are rotated such that the nitrogen atoms point towards opposite directions. The three pyridine rings are not exactly coplanar. Their planes deviate from each other by 12.7(3)° (pyridine ring including N2 in rela-




Scheme 2. Synthesis pathway for the terpyridine functionalized tinorganyl **2** with an overall yield of 51%, and subsequent reaction to form the dinuclear complex cation within compound **3**.

tion to central pyridine ring) or by 4.5(3)° (pyridine ring including N3 in relation to the central pyridine ring).

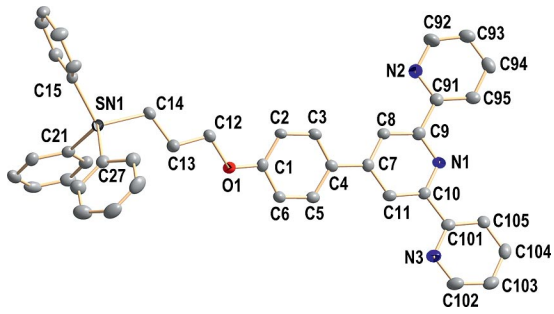



Figure 1. Molecular structure of the 2,2′,6′,2′′-terpyridine-functionalized tinorganyl in **2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

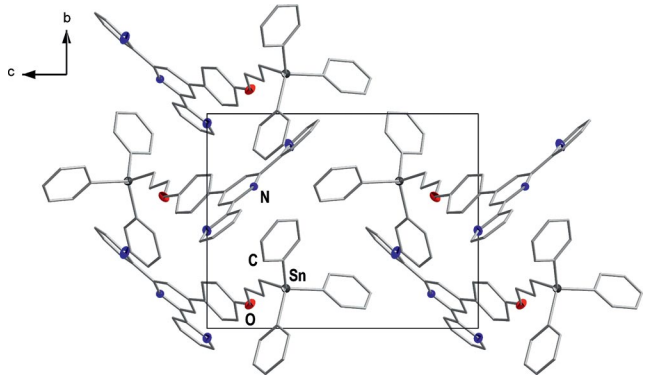



Figure 2. Arrangement of the molecules in the crystal structure of **2**. H atoms and disordered solvent molecules are omitted for clarity. C atoms are denoted as sticks. Thermal ellipsoids are drawn at 50% probability.

This unit is attached to a phenyl group and linked by O1 to a propylene spacer that connects the chelating ligand with the tin atom. The planes defined by the phenyl ring and the central pyridine ring of the terpyridine unit also deviate by 15.5(2)° from each other. Apart from this bulky ligand, the tin atom is bound to three distorted phenyl groups (for selected angles see Table S1). In contrast to many *O*-functionalized tinorganyl compounds[5c,6,7c,19] O1 does not undergo an intermolecular O→Sn coordination, which is, however, common for triphenyltin propyl ether derivatives.[20]

Eventually it turned out that only treatment of **2** with a $HI/H_2O$ solution (57%) led to a reaction towards a tin halide product. Compound **3** formed after stirring the reaction mixture for 2 weeks. Nevertheless, similar to further attempts of halogenation[5c,11b,11c,21,22] an insoluble, yellow solid was produced, which was filtered and washed with EtOH; from the filtrate, yellow crystals of **3** were obtained by layering with *n*-hexane. The concentration of **3** in the reaction mixture is too low for the detection of $^{119}$Sn NMR signals. Upon treatment of the product with coordinating, non-protic solvents like pyridine or THF, further reaction took place such that the mixture turned into a pink color, again with the lack of any $^{119}$Sn NMR signals.

During the reaction of **2** with $HI/H_2O$, the cleavage of two Sn–C(phenyl) bonds per molecule obviously took place to yield $PhRSnI_2$ as an intermediate species. We assume that after this step, traces of $I_2$ removed one of the iodide ligands from this intermediate, to produce $(I_3)^-$ anions with the $[RSnPhI]^+$ cationic complexes. An intermolecular reaction of the latter finally formed the complex dicationic dimer in **3** by a head-to-tail coordination. This replenishes the already known organotin dications in the literature.[23] Since the reaction of **2** with $HI/H_2O$ was carried out under strict exclusion of air and light, we assume that the commercially available HI solution that was used as received, already contained $I_2$ (in agreement with its brown color). Compound **3** crystallizes as yellow needles in the triclinic space group $P\bar{1}$ and has a crystallographic inversion symmetry. The molecular structure is provided in Figure 3, the packing of cations and anions is shown in Figure 4.

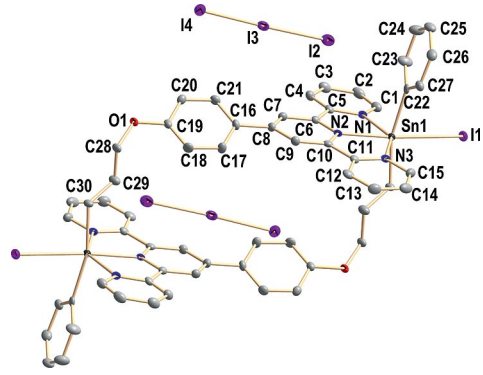



Figure 3. Molecular structure of the complex dication in **3** with $(I_3)^-$ counterions. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

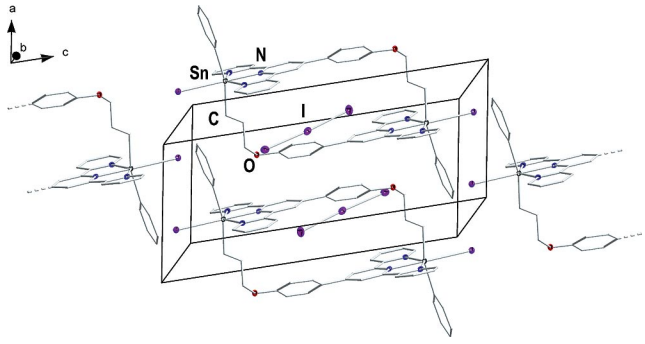



Figure 4. Arrangement of the molecules in the crystal structure of **3**. H atoms are omitted for clarity. C atoms are denoted as sticks. Thermal ellipsoids are drawn at 50% probability.

The terpyridine–Sn–I units contribute to a distorted octahedral coordination environment around the tin atoms and each unit further binds to one phenyl group and one aliphatic propylene unit. The latter exhibits a slight C–Sn–C bending towards the iodide ligand in support of a better bite of the chelating Phttpy unit [C30$^{i}$–Sn1–C22 165.06(17)°, i = –*x*, 1 – *y*, 1 – *z*]. The propylene group is stretched in a way that excludes any π–π stacking between the phenyl or pyridine rings of the Phttpy building blocks.

Mean planes including atoms C7, C8, C9 and C7$^{i}$, C8$^{i}$, C9$^{i}$ (i = –*x*, 1 – *y*, 1 – *z*) of the chelating ligands are 5.618(3) Å from each other. The void does not include any electron density, which might be assigned as solvent molecule atoms. Sn–N distances range from 2.277(4) Å (Sn1–N1) to 2.320(4) Å (Sn1–N3) [Sn1–N2 2.238(4) Å] and are slightly smaller than the Sn–N bonds published for halogenated tinorganyl compounds with N-donor ligands.[24]

An unexpectedly long Sn–I distance of 3.1038(5) Å occurs, which is much larger than distances of already published tinorganyl compounds. However, to the best of our knowledge, a $C_2N_3I$ coordination environment for tin has been found only once by Gustavson et al. for the tin analogue of the tetraphenyl cyclopentadienyl anion that was not further analyzed by X-ray diffraction.[25] This might be the reason for the observed difference from that of the reported Sn–I distances. The three pyridine rings are nearly coplanar. The mean planes of the pyridine rings, including N3 or N2, deviate from the mean plane of the central pyridine by only 5.7(2)° (py-N3) and 2.0(2)° (py-N1). The phenyl group is even more distinctly displaced from the mean terpyridine plane, of which it deviates by 29.4(2)°. This comes along with H bonding interactions of the nearby triiodide anions [3.11 Å for H18···I3 and 3.16 Å for H20···I3i (i = *x*, 1 + *y*, *z*)] that are shorter than the sum of the van der Waals radii.[26]

## Conclusions

Herein we report on recent success in the extension of organostannane chemistry by the attachment of a multipyridyl ligand. This served to enrich the common pool of chelating alcohol or ester ligands at organotin moieties. A synthesis route has been developed that allows good yields for (3-chloropropyl)triphenylstannane (**1**) as the intermediate for the preparation of the 2,2′,6′,2′′-terpyridine-decorated tinorganyl (**2**) in five steps with an overall yield of 51%. Attempts of a halogenation of the tin atoms in compound **2** have been undertaken for chloride, bromide, as well as iodide ligands. This was, however, only possible in the case of (partial) iodination, which yielded compound **3**. The latter comprises a head-to-tail dimer of two tin complexes in a rare coordination environment. The products have been characterized by means of $^{1}$H NMR, $^{13}$C NMR, and $^{119}$Sn NMR spectrometry, mass spectrometry and/or single-crystal X-ray diffraction analysis, and EDX spectroscopy.

## Experimental Section

**General Methods:** All manipulation steps were performed under an Argon atmosphere, unless otherwise noted. All solvents were dried and freshly distilled prior to use: dimethylformamide (DMF), tetrahydrofuran (THF). All synthesis steps were performed with strict exclusion of air and external moisture (Ar atmosphere at a high-vacuum, double-manifold Schlenk line). Diisopropylamine (DIA) was dried with calcium hydride ($CaH_2$), distilled, and immediately used in reaction. All solvents were dried and freshly distilled prior to use. Water was degassed by applying a dynamic vacuum (10–3 mbar) for several hours. Silica gel used for chromatography (particle size 0.063–0.2 mm) was obtained from Macherey–Nagel. Chemicals (Aldrich, Fluka, Lancaster, and Merck) were used without further purification. HI solution (57% in $H_2O$, purity 99.99%) was obtained from Sigma–Aldrich (no. 210013). EDX spectroscopic analyses were performed using the EDX device Voyager 4.0 of Noran Instruments coupled with the electron microscope CamScan CS 4DV. Data acquisition was performed with an acceleration voltage of 20 kV and 100 s accumulation time. For the analyses multiple single crystals of **3** and the light yellow precipitate were used. Sn–L and radiation emitted by the atoms was analyzed.

**(3-Chloropropyl)triphenylstannane (1):** According to a method reported by Pinoie et al.[11b] a solution of *n*-butyllithium (1.6 M, 9.36 mmol) was added to a solution of diisopropylamine (0.95 g, 9.36 mmol) in THF (16 mL) at 0 °C. After 10 min, $Ph_3SnH$ (4.01 g, 11.41 mmol) was added and the mixture was stirred for 20 min at room temperature. The clear yellow solution was added dropwise to a chilled solution of 1-bromo-3-chloropropane (1.47 g, 9.36 mmol) in THF (16 mL). The colorless solution was stirred for 12 h at room temperature. Dichloromethane (20 mL) was added under air, and the mixture was washed with saturated aqueous solutions of $NH_4Cl$ (15 mL), $NaHCO_3$ (15 mL), and brine (15 mL). It was dried with $MgSO_4$, filtered, and concentrated in vacuo. Pure compound **1** was isolated as a white solid after purification by chromatography with dichloromethane/*n*-hexane (90:10), yield 2.83 g, 71%. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.63–7.45 (m, 6 H, *ortho-Ph*), 7.42–7.34 (m, 9 H, *meta*/*para-Ph*), 3.53 (t, 2 H, C$H_2$-Cl), 2.25–2.01 (m, 2 H, C$H_2$-$CH_2$Cl), 1.69–1.44 (m, 2 H, Sn-C$H_2$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 138.4 ($^{1}J_{C,Sn}$ = 497.4 Hz, 3 C, Sn-Ar*C*), 137.2 (6 C, Ar *ortho-C*), 129.3 (3 C, Ar *para-C*), 128.8 (6 C, Ar *meta-C*), 48.3 ($^{3}J_{C,Sn}$ = 84.8 Hz, 1 C, *C*$H_2$Cl), 30.1 ($^{2}J_{C,Sn}$ = 16.2 Hz, 1 C, *C*$H_2$-$CH_2$C), 8.2 ($^{1}J_{C,Sn}$ = 381.7 Hz, 1 C, Sn*C*$H_2$) ppm. $^{119}$Sn NMR (149 MHz, $CDCl_3$): $\delta$ = 99.7 ppm. MS (ESI): *m*/*z* (%) = 429.0 (24) [M + H]$^{+}$, 351.0 (53) [M – Ph]$^{+}$. $C_{21}H_{21}ClSn$ (427,56): calcd. C 58.99, H 4.95, Cl 8.29, Sn 27.76; found C 59.21, H 4.89, Cl 8.31, Sn 27.69.

**(tppy-3-Oxopropyl)triphenylstannane (2):** NaH (7.561 mmol, 0.302 g) was washed with *n*-pentane (3 mL) several times under an inert atmosphere. DMF (20 mL) was added and a suspension of 2,6-bis(2′-pyridyl)-4′-(*p*-hydroxyphenyl)pyridine (HOPhttpy; 0.47 mmol, 0.17 g) in DMF (3 mL) was added slowly at room temperature. It was stirred for 90 min, in that time the evolution of gas was observed. Afterwards, **1** (6.258 mmol, 2.954 g) in DMF (25 mL) was added to the orange solution. The mixture was heated to 70 °C for 1.5 h and cooled to room temperature. After quenching with aqueous KOH (10%, 30 mL), the mixture was extracted with dichloromethane (80 mL) several times. It was dried with $MgSO_4$ and the volatiles were removed in vacuo. The product was purified by recrystallization from ethyl acetate. Colorless needles of **2** were obtained within 1 d by slow evaporation of a dichloromethane solution, yield 3.22 g (4.505 mmol), 72%. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.75–8.71 (m, 2 H, NC*H*), 8.70 (s, 2 H, NCC*H*), 8.69–8.64 (m, 2 H, NCCH), 7.87 (dd, $^{3}J$ = 1.8, 7.7 Hz, 2 H, NCCH*C*H), 7.84–7.78 (m, 2 H, *Ph*), 7.68–7.47 (m, 6 H, Sn-*Ph*), 7.42–7.28 (m, 11 H, Sn-*Ph*), 6.93–6.85 (m, 2 H, *Ph*), 4.00 (t, $^{3}J$ = 6.3 Hz, 2 H, OC$H_2$), 2.42–2.10 (m, 2 H, $OCH_2CH_2$), 1.82–1.50 (m, 2 H, SnC$H_2$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 160.0 (1 C, O*C*), 156.5 (2 C, N*C*), 155.9 (2 C, N*C*), 149.9 (1 C, NCCH*C*), 149.2 (2 C, N*C*H), 138.8 ($^{1}J_{C,Sn}$ = 493.1 Hz, 3 C, SnPh-*C*), 137.1 (6 C, SnPh-*C*H), 136.9 (2 C, NCHCH*C*H), 130.7 (1 C, Ph-*C*), 129.1 (3 C, SnPh-*C*H),128.7 (6 C, SnPh-*C*H), 128.5 (2 C, OCCH*C*H) 123.8 (2 C, NCH*C*H), 121.5 (2 C, NC*C*H), 118.4 (2 C, NC*C*H), 115.0 (2 C, OC*C*H), 70.7 ($^{3}J_{C,Sn}$ = 66.0 Hz, 1 C, O*C*$H_2$), 26.4 ($^{2}J_{C,Sn}$ =

Table 1. Crystallographic and refinement details of compounds **2**·$CH_2Cl_2$ and **3**.

| | **2**·$CH_2Cl_2$ | **3** |
|---|---|---|
| Empirical formula | $C_{42}H_{35}N_3OSn$, $CH_2Cl_2$ | $C_{60}H_{50}I_8N_6O_2Sn_2$ |
| $M_r$ [g mol$^{-1}$] | 801.34 | 2139.64 |
| Crystal system, space group | monoclinic, $P2_1$ | triclinic, $P\bar{1}$ |
| $a$, $b$, $c$ [Å] | 11.4995(6), 11.3321(4), 14.4554(7) | 8.5663(3), 10.1406(3), 18.4266(6) |
| $\alpha$, $\beta$, $\gamma$ [°] | 90, 95.501(4), 90 | 86.995(2), 78.805(1), 87.894(1) |
| $V$ [Å$^3$] | 1875.06(15) | 1567.48(9) |
| **Z** | 2 | 1 |
| $\mu$ [mm$^{-1}$] | 0.86 | 4.78 |
| Crystal size [mm] | 0.15 × 0.08 × 0.05 | 0.14 × 0.06 × 0.03 |
| $T_{min.}$, $T_{max.}$ | 0.421, 0.624 | 0.69, 0.87 |
| Measurements | 10105 | 29987 |
| Independent reflections | 6886 | 5836 |
| Observed reflections [$I > 2\sigma(I)$] | 5827 | 5158 |
| $R_{int}$ | 0.023 | 0.033 |
| $\theta_{max}$ [°] | 25.9 | 25.5 |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.028, 0.058, 0.89 | 0.028, 0.063, 1.08 |
| Parameters | 509 | 352 |
| Restraints | 124 | 0 |
| H atom treatment | constrained parameters<br>$w = 1 / [\sigma^2(F_o^2) + (0.0298P)^2]$<br>where $P = (F_o^2 + 2F_c^2)/3$ | constrained parameters<br>$w = 1 / [\sigma^2(F_o^2) + (0.0163P)^2 + 10.2837P]$<br>where $P = (F_o^2 + 2F_c^2)/3$ |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.57, –0.42 | 2.27, –1.62 |
| Absolute structure | Flack $x$ determined using 2381 values<br>$[(I+) - (I-)]/[(I+) + (I-)]$ | – |
| Absolute structure parameter | –0.036 (13) | – |

19.6 Hz, 1 C, $OCH_2CH_2$), 7.1 ($^1J_{C,Sn}$ = 390.9 Hz, 1 C, $SnCH_2$) ppm. $^{119}$Sn NMR (149 MHz, $CDCl_3$): $\delta$ = –99.3 ppm. MS (ESI$^+$): $m/z$ (%) = 718.2 (100) $[M + H]^+$.

**{[PhISn(CH$_2$)$_3$OPhttpy]$_2$}(I$_3$)$_2$ (3):** Triphenylstannane (**2**) (0.15 mg, 0.209 mmol) was dissolved in dichloromethane (7 mL) and cooled to –60 °C. A HI/$H_2O$ solution (57%, 0.1 mL, 0.758 mmol) was added and the flask was covered with aluminum foil to darken and warm it slowly to room temperature. The mixture was stirred for 2 w and the light yellow slurry was filtered and washed with EtOH to isolate the precipitate (160 mg, mmol, 72%). Attempts to recrystallize the precipitate from hot ethanol did not lead to crystalline material but layering of the (saturated) filtrate with *n*-hexane yielded yellow needles of **3**. EDX (crystals): I/Sn calcd: 4:1; found 3.89:0.96, EDX (yellow precipitate): I/Sn found: 4.1:0.9.

**Single-Crystal X-ray Diffraction Data:** $T$ = 100 K, graphite monochromator, area detector system Stoe IPDS2[27] (**2**) or Bruker D8 Quest[28] (**3**). Both structures were solved by direct methods in SHELXS97 and refined by full-matrix least-squares refinement against $F^2$ in SHELXL97[29] or SHELXL-2013[30] with anisotropic displacement parameters for the non-hydrogen atoms. Absorption corrections were performed by semi-empirical methods,[31] using multi-scanned reflections. Where possible, H atoms were inserted assuming idealized geometry and refined riding on their parent atoms with $U_{eq}$ = n·$U_{eq}$ (parent atom), where $n$ = 1.2 ($n$ = 1.5 for H atoms in methyl groups). Absolute structure determination was performed according to Persons and Flack.[32] For further details see Table 1. Selected structural parameters are listed in Table S2.

CCDC-982294 (for **2**) and -982295 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Supporting Information** (see footnote on the first page of this article): Further details on single-crystal X-ray crystallography, electrospray ionization (ESI), mass spectrometry, nuclear magnetic resonance (NMR) spectroscopy, energy dispersive X-ray (EDX) spectroscopy, and on the synthesis of **3**.

## Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) within the framework of the Research Training Group GRK1782. We additionally thank Nicholas Rau and Uwe Justus for their help in the lab.

[1] a) M. Gielen, *Appl. Organomet. Chem.* **2002**, *16*, 481–494; b) P. Yang, M. Guo, *Coord. Chem. Rev.* **1999**, *185–186*, 189–211; c) W. T. Piver, *Environ. Health Perspect.* **1973**, *4*, 61–79; d) M. Gielen, A. G. Davies, K. Pannell, E. Tiekink, in: *Tin Chemistry: Fundamentals, Frontiers, and Applications*, Wiley-VCH, Weinheim, Germany, **2008**, p. 746; e) A. Ozerianskyi, P. Švec, H. Vaňkátová, M. Vejsová, L. Česlová, Z. Padělková, A. Růžička, J. Holeček, *Appl. Organomet. Chem.* **2011**, *25*, 725–734; f) E. López-Torres, A. Medina-Castillo, J. Fernández-Sánchez, M. Mendiola, *J. Organomet. Chem.* **2010**, *695*, 2305–2310.

[2] A. Sousa-Pedrares, M. Casanova, J. García-Vázquez, M. Durán, J. Romero, A. Sousa, J. Silver, P. Titler, *Eur. J. Inorg. Chem.* **2003**, 678–686.

[3] a) A. Szorcsik, L. Nagy, M. Scopelliti, A. Deák, L. Pellerito, G. Galbács, M. Hered, *J. Organomet. Chem.* **2006**, *691*, 1622–1630; b) S. Singh, S. Bhattacharya, *Inorg. Chem. Commun.* **2012**, *24*, 144–147; c) C. Ma, J. Li, R. Zhang, D. Wang, *J. Organomet. Chem.* **2006**, *691*, 1713–1721; d) T. Basu Baul, S. Dhar, S. Pyke, R. Tiekink, E. Rivarola, R. Butcher, F. Smith, *J. Organomet. Chem.* **2001**, *633*, 7–17.

[4] a) S. Suga, T. Manabe, J. Yoshida, *Chem. Commun.* **1999**, 1237–1238; b) Z.-Y. Chai, Z.-X. Wang, *Dalton Trans.* **2009**, 8005–8012; c) M. Bouška, L. Dostál, Z. Padělková, A. Lyčka, S. Herres-Pawlis, K. Jurkschat, R. Jambor, *Angew. Chem. Int. Ed.* **2012**, *51*, 3478–3482; *Angew. Chem.* **2012**, *124*, 3535.

[5] a) D. Clive, W. Yang, *J. Org. Chem.* **1995**, *60*, 2607–2609; b) J. Sauer, D. Heldmann, G. Pabst, *Eur. J. Org. Chem.* **1999**, 313–

321; c) A. Tagne Kuate, L. Iovkova, W. Hiller, M. Schürmann, K. Jurkschat, *Organometallics* **2010**, *29*, 5456–5471; d) A. Růžička, Z. Padělková, P. Švec, V. Pejchal, L. Česlová, J. Holeček, *J. Organomet. Chem.* **2013**, *732*, 47–57; e) G. Pabst, O. Pfüller, J. Sauer, *Tetrahedron* **1999**, *55*, 5047–5066; f) I. Barbul, R. A. Varga, K. C. Molloy, C. Silvestru, *Dalton Trans.* **2013**, *42*, 15427–15436.

[6] L. Dostál, A. Růžička, J. Holeček, R. Jambor, *Inorg. Chem. Commun.* **2010**, *13*, 1470–1472.

[7] a) Z. Fard, R. Clérac, S. Dehnen, *Chem. Eur. J.* **2010**, *16*, 2050–2053; b) Z. Fard, M. Holynska, S. Dehnen, *Inorg. Chem.* **2010**, *49*, 5748–5752; c) Z. Fard, L. Xiong, C. Müller, M. Holynska, S. Dehnen, *Chem. Eur. J.* **2009**, *15*, 6595–6604; d) M. Halvagar, Z. Fard, S. Dehnen, *Chem. Commun.* **2010**, *46*, 4716–4718; e) M. Halvagar, Z. Fard, S. Dehnen, *Chem. Eur. J.* **2011**, *17*, 4371–4374.

[8] B. Barth, E. Leusmann, K. Harms, S. Dehnen, *Chem. Commun.* **2013**, *49*, 6590–6592.

[9] a) S. Thoonen, B.-J. Deelman, G. v. Koten, *J. Organomet. Chem.* **2004**, *689*, 2145–2157; b) C. Pöhlker, I. Schellenberg, R. Pöttgen, S. Dehnen, *Chem. Commun.* **2010**, *46*, 2605–2607; c) W. Caseri, *J. Organomet. Chem.* **2013**, 1–5.

[10] a) P. Harston, J. Wardell, D. Marton, G. Tagliavini, P. Smith, *Inorg. Chim. Acta* **1989**, *162*, 245–250; b) M. Mehring, C. Nolde, M. Schürmann, *Inorg. Chim. Acta* **2009**, *362*, 745–752.

[11] a) Y. Aksu, S. Aksu, H. Schumann, *Appl. Organomet. Chem.* **2007**, *21*, 521–530; b) V. Pinoie, K. Poelmans, H. Miltner, I. Verbruggen, M. Biesemans, G. Assche, B. Van Mele, J. Martins, R. Willem, *Organometallics* **2007**, *26*, 6718–6725; c) B. Zobel, A. Duthie, D. Dakternieks, E. Tiekink, *Organometallics* **2001**, *20*, 2820–2826.

[12] H. Zhou, E. Liang, X. Ding, Z. Zheng, Y. Peng, *Chem. Commun.* **2012**, *48*, 10553–10555.

[13] J. Wang, G. Hanan, *Synlett* **2005**, 1251–1254.

[14] H. Weichmann, B. Rensch, *Z. Chem.* **1989**, *29*, 184–185.

[15] J. Christoffers, T. Werner, A. Baro, P. Fischer, *J. Organomet. Chem.* **2004**, *689*, 3550–3555.

[16] D. Dakternieks, G. Dyson, K. Jurkschat, R. Tozer, E. Tiekink, *J. Organomet. Chem.* **1993**, *458*, 29–38.

[17] M. Gielen, *Bull. Soc. Chim. Belg.* **1983**, *92*, 409–410.

[18] a) T. Lockhart, W. Manders, E. Holt, *J. Am. Chem. Soc.* **1986**, *108*, 6611–6616; b) J. Holeček, A. Lyčka, *Inorg. Chim. Acta* **1986**, *118*, L15–L16.

[19] a) V. Arens, C. Dietz, D. Schollmeyer, K. Jurkschat, *Organometallics* **2013**, *32*, 2775–2786; b) L. Dostál, A. Růžička, R. Jambor, *Inorg. Chim. Acta* **2010**, *363*, 2051–2054; c) G. Reeske, G. Bradtmöller, M. Schürmann, K. Jurkschat, *Chem. Eur. J.* **2007**, *13*, 10239–10245; d) B. Kašná, L. Dostál, R. Jirásko, I. Císařová, R. Jambor, *Organometallics* **2008**, *27*, 3743–3747; e) L. Dostál, R. Jambor, A. Růžička, I. Císařová, J. Holeček, M. Biesemans, R. Willem, F. De Proft, P. Geerlings, *Organometallics* **2007**, *26*, 6312–6319; f) J. Martincová, L. Dostál, J. Taraba, A. Růžička, R. Jambor, *J. Organomet. Chem.* **2007**, *692*, 3415–3423.

[20] P. Deacon, N. Devylder, M. Hill, M. Mahon, K. Molloy, G. Price, *J. Organomet. Chem.* **2003**, *687*, 46–56.

[21] a) J. Beckmann, A. Duthie, M. Grassmann, *J. Organomet. Chem.* **2009**, *694*, 161–166; b) H. Schumann, B. Wassermann, M. Frackowiak, B. Omotowa, S. Schutte, J. Velder, S. Mühle, W. Krause, *J. Organomet. Chem.* **2000**, *609*, 189–195.

[22] Reaction of **2** with $I_2$ ($Br_2$, HBr, $Cl_2$, HCl) in $CH_2Cl_2$ under cooling, heating or at room temperature led to completely insoluble, but partly halogenated mixtures (verified by their weight) that could not be further identified.

[23] a) B. Wrackmeyer, G. Kehr, R. Boese, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1370–1372; *Angew. Chem.* **1991**, *103*, 1374; b) B. Wrackmeyer, G. Kehr, A. Sebald, J. Kümmerlen, *Chem. Ber.* **1992**, *125*, 1597–1603; c) A. Wirth, O. Moers, A. Blaschette, P. Jones, *Z. Anorg. Allg. Chem.* **1999**, *625*, 982–988; d) K. Sakamoto, Y. Hamada, H. Akashi, A. Orita, J. Otera, *Organometallics* **1999**, *18*, 3555–3557; e) K. Sakamoto, H. Ikeda, H. Akashi, T. Fukuyama, A. Orita, J. Otera, *Organometallics* **2000**, *19*, 3242–3248.

[24] C. Pettinari, A. Lorenzotti, G. Sclavi, A. Cingolani, E. Rivarola, M. Colapietro, A. Cassetta, *J. Organomet. Chem.* **1995**, *496*, 69–85.

[25] W. Gustavson, L. Principe, W. Rhee, J. Zuckerman, *Inorg. Chem.* **1981**, *20*, 3460–3468.

[26] S. Batsanov, *Inorg. Mater.* **2001**, *37*, 871–885.

[27] *X-AREA*, v. 1.56, Stoe & Cie GmbH, Darmstadt, Germany, **2011**.

[28] *APEX2*, v. 2013.10.0, Bruker-AXS Inc., Madison, WI, **2013**.

[29] G. M. Sheldrick, *SHELXTL*, v. 12.2, Bruker AXS Inc., Madison, WI, **2013**.

[30] G. M. Sheldrick, *SHELXL-2013*, University of Göttingen, Germany, **2013**.

[31] a) G. M. Sheldrick, *XPREP*, v. 2013/1, Bruker-AXS, Karlsruhe, Germany, **2013**; b) G. M. Sheldrick, *SADABS*, v. 2012/1, Bruker, Karlsruhe, Germany, **2013**.

[32] S. Parsons, H. Flack, *Acta Crystallogr., Sect. A* **2004**, *60*, s61.

Received: January 23, 2014
Published Online: ■

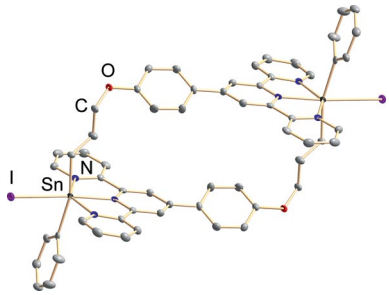
EurJIC European Journal of Inorganic Chemistry



## Tinorganyl Moieties



**Keywords:** Tin / N ligands / Halogenation




A new compound $Ph_3SnR$, comprising a 2,2′,6′,2′′-terpyridine-functionalized ligand R, has been synthesized in a five-step procedure. On attempting to halogenate this compound, a partially iodinated derivative was obtained that forms a head-to-tail connected dimer in the salt $[(PhISn(CH_2)_3OPhttpy)_2](I_3)_2$ with the terpyridine units acting as chelating ligands.