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Redistribution reaction on a six-fold coordinated Sn(IV) atom and reactions towards axially unsymmetric substituted Sn(IV) porphyrins

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ABSTRACT

Investigations of the Kocheshkov redistribution reaction were performed on the six fold coordinated tin(IV) atom using the axially coordinated Sn(IV) meso-tetra-phenylporphyrin system with axially *trans* di-chloro and *trans* di-acetylido substituted derivatives. The immobile four dentate porphyrin ligand enables the detailed investigation of these typically complex reaction systems on higher coordinated tin(IV) species. The thermally activated reaction displays an equilibrium. Further on, a series of axial unsymmetrically substituted Sn(IV) porphyrins are selectively synthesized and described.

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Introduction

The effort of organometallic Sn^{IV} compounds to undergo redistribution reactions is long known in literature for organometallic halides like the generation of $R_{4-n}SnCl_n$ (n= 1–3) from the educts R_4Sn and Cl_4Sn [1]. This so called "Kocheshkov reactions" [IPA: k ɑ dʒ ə t k o f] were subject of detailed research considering different ligands [2-4] and on corresponding reaction dynamics [3,5]. However, the ability of redistributing ligands is very manifold and takes place besides organic substituents and halides also between e.g. organic substituents and hydrides [6,5] or between halides and hydrides [7]. Regarding the reactions among organic substituents and halides, it is nowadays well established to consider these reactions as equilibria [3,5] with equilibrium constants far on the side of the mixed species [2,3]. However, these statements were mainly derived from species containing tin in the oxidation state +IV and with a coordination number of four.

The situation becomes more difficult, if the coordination number is raised to five or six, as depending on the ligand situation, the number of reaction products may increase [5]. Thus detailed investigation of one single redistribution reaction is often hindered. Nevertheless, redistribution reactions on higher coordinated molecules bearing Sn as the central atom were observed [8-12]. Overall, from these reactions is concluded, that migration on higher coordinated Sn species takes place much faster than on fourfold coordinated tin species and requires lower temperatures for the induction of migration. Further on, "reverse Kocheshkov reactions" are observed, giving de-mixed species [9].

In order to achieve coordination numbers higher than four, oligo dentate ligands were mainly used in above literature. Despite the obvious assumption, that monodentate ligands should be preferred for migration over oligo dentate ligands, as dissociation requires more energy, bidentate ligands were found to exchange too, even next to monodentate ones [9,10]. Therefore, the herein used ligand meso- tetraphenyl porphyrin, being a four dentate ligand with two covalent bonds to the metal center, was found to be a convenient system to study the redistribution reaction on higher coordinated Sn species. Sn^{IV} atoms coordinated by this system prefer the coordination number six having two additional ligands in the axial positions preferably *trans* to the porphyrin ring plane. Migration of substituents therefore takes place mainly related to the two axial ligands, enabling the investigation of a rather simple and defined redistribution reaction on a six fold coordinated Sn^{IV} species according to Fig. 1. Further on, we herein show a synthetical approach towards the selective synthesis of axially asymmetric substituted tin(IV) porphyrins. A compound class, which might gain upcoming importance due to increased solubility and thus wider applicability in e.g. opto-electronic devices.

Results and discussion

The starting compound of all performed investigations was compound (1), which is accessible by literature known methods [13]. Compound (2) is synthesized by the reaction of compound (1)

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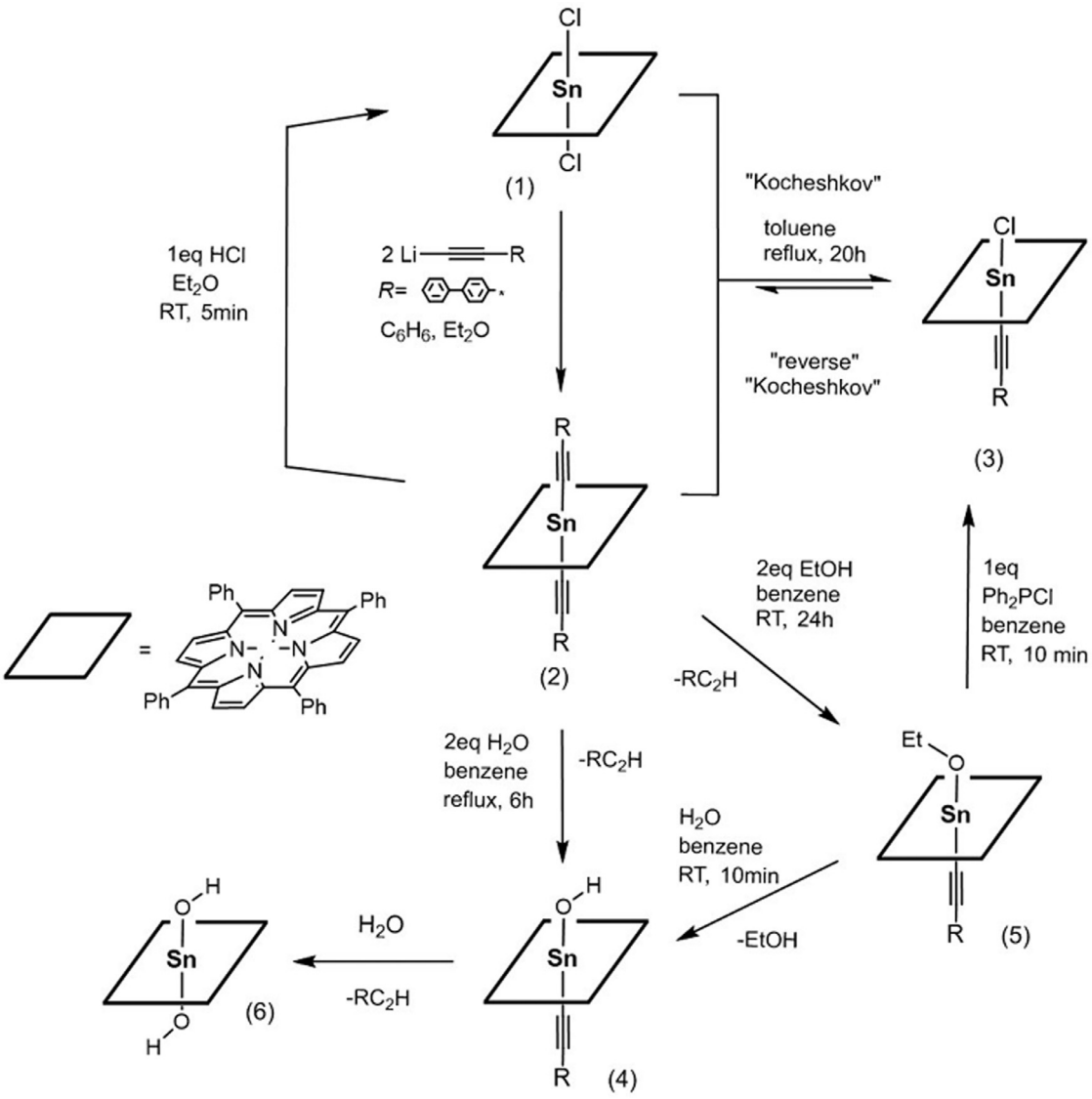

Fig. 1. Reactions to asymmetric substituted Sn(IV) porphyrins.

with two equivalents of lithiated 4-biphenylethyne as previously reported [14]. The redistribution reaction towards compound (3) was performed and investigated by reacting equimolar amounts of compounds (1) and (2) in toluene according to Fig. 1. After reflux heating for about 20 hours under inert atmosphere an equilibrium is reached giving a mixture of compounds (1), (2) and (3).

The quantitative progress of the Kocheshkov reaction was followed via ^{1}H NMR spectroscopy by the relative integrals of the β-H-atoms of compounds (1), (2) and (3) and partially by the ortho-H-atoms of the axial ligand of compound (2) and (3) as shown in Fig. 2. For a nomenclature of the hydrogen atoms see Fig. 4. Corresponding ^{1}H NMR shifts and important coupling constants are listed in Table 1.

The rate of conversion is determined by setting the relative integral of the β-H-atom of (3) in relation to the sum of the corresponding integrals of (1), (2) and (3). Applying these conversion rates over the reflux times reveals the equilibrium state for each reaction after certain reflux time. This is demonstrated in Fig. 3 for two different educt ratios of (2) to (1).

For all tested reactions (used educt ratios of (2):(1) = 3:1, 2:1, 1:1, 1:3), the equilibrium state is reached after approx. 24 hours in refluxing toluene. The corresponding equilibrium constant was

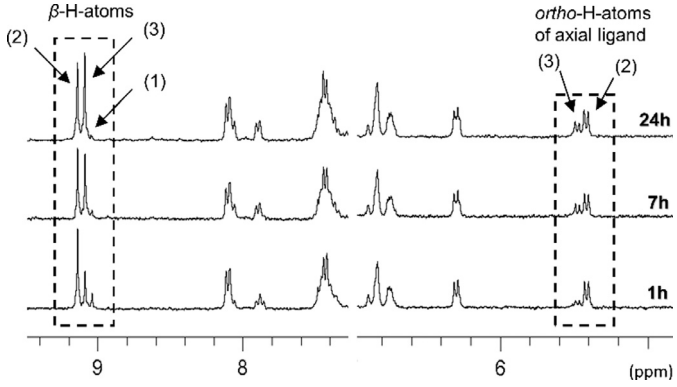

Fig. 2. ^{1}H NMR in C_6D_6 showing progress of Kocheshkov reaction over reflux time in toluene for the educt ratio of (2):(1) = 3:1.

determined with different educt ratios, and was found to be 15±3 (n=5) in refluxing toluene. Thus, the equilibrium is clearly shifted to the product side of the reaction. This is in contrast to literature, where “reverse Kocheshkov reactions” are observed [9]. Attempts

Table 1
Significant NMR parameter of RR'SnTPP in C_6D_6.

nr.	R,X	R',X	$\delta^1{}_{H\beta}$ (ppm)	$^4J^{119}{}_{Sn\text{-}}{}^1{}_{H\beta}$ (Hz)	$\delta_{o\text{-}H}{}^{TPP}$ (ppm)/(Hz)	δ_{Haxial} (ppm)/(Hz)	^{119}Sn (ppm)
(1)	Cl	Cl	9.039	14.7	d: 7.87/7.1	–	-588.6
(2)	R	R	9.14	7.75	d: 8.11/7.4	d: 6.30/8.3; d: 5.42/8.3;	-625.9
(3)	R	Cl	9.09	11.0	d:8.07/7.4; d:7.90/7.4;	d:6.29/8.5; d:5.48/8.5;	-610.4
(4)	R	OH	9.09	8.1	d:8.08/6.6; d:7.99/6.8;	d: 6.29/7.9; d: 5.44/7.9; s: -7.25;	-591.9
(5)	R	OEt	9.095	8.37	d:8.04/7.8; d:8.01/8.6;	d:6.29/8.4; d:5.44/8.3; q:-1.75/6.8; tr:-1.93/6.8	-596.8
(6)	OH	OH	9.045	9.1	d: 7.97/6.0	s: -7.11	-568.0*

* in $CDCl_3$;
R = *para-bis*phenylethynyl

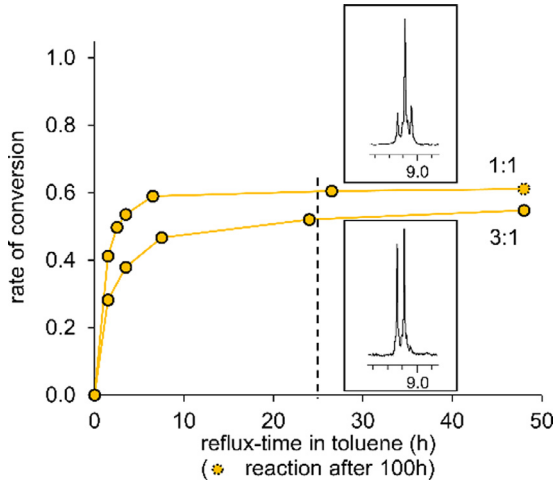

Fig. 3. Rate of conversion of Kocheshkov reaction for different educt ratios of (2):(1), inlays: ^{1}H NMR spectra of β-hydrogen region after 25 h.

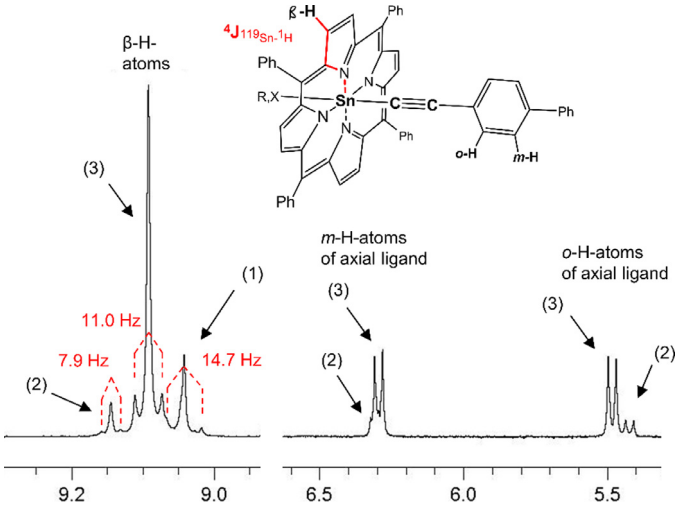

Fig. 4. Selected parts of ^{1}H NMR spectrum in C_6D_6 of filtrate with enriched (3), starting educt ratio of (2):(1) ~ 1:1.

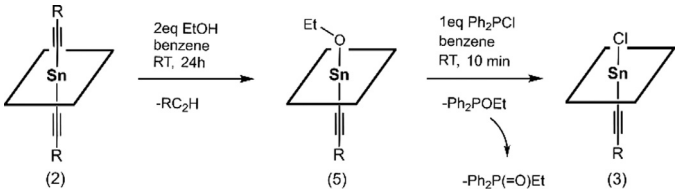

Fig. 5. Selective synthesis of compound (3).

to shift the equilibrium constant by changing temperature works for 90 °C and 120 °C giving K= 6 and 25, but fail for temperatures above 120 °C due to evolving decomposition. Shifting K at lower temperatures also failed, as keeping a previously in toluene refluxed and equilibrated reaction solution at 25 °C for 100 h, did not show significant changes. It is therefore concluded, that this reaction is a static equilibrium, with the assumed backreaction from the equilibrated state being kinetically hindered at lower temperatures.

As a proof of concept, the redistribution reaction was also tested with different axial ligands (R= phenyl or n-pentyl) and found to work as well ending up in an equilibrated state. Detailed investigations on their equilibrium constants were not performed.

Isolation of compound (3), if synthesized over the redistribution reaction of (1) and (2) is difficult due to the described equilibrium. Thus, the highest achieved purity of (3) was 75% with impurities from (1) and (2). Parts of the corresponding ^{1}H NMR spectrum displaying the β-H and the axial H region with enriched compound (3) are depicted in Fig. 4. A possible way to deal with the existence of educts as side products is the suppression of one of the two educts (1) or (2) by using an educt ratio (2):(1) of 3:1 or 1:3. This ends up in the compound ratio (2):(3):(1) of either 16:17:1 or opposite.

Beside the side products from the equilibrium, additional side products may arise from hydrolysis of compound (2) to compounds (4) and (6), thus working under inert atmosphere is strongly required. The partial hydrolysis of (2) to (4) proceeds faster, than the actual equilibrated Kocheshkov reaction. The elucidation of the hydrolyzed side products (4) and (6) can be done either by the high field shifted ^{1}H NMR signals at - 7.25 and - 7.11 ppm in C_6D_6 of the axial hydroxy groups, or by the ^4J1_H-119_{Sn} coupling constants of 8.06 and 9.05 Hz to the β-H-atom, which significantly differ from 11.0 and 14.7 Hz for compounds (3) and (1). Interestingly, the hydrolysis reaction from (2) to (4) opens up a direct way to synthesize compound (4) by reacting two equivalents of H_2O with (2) under reflux in benzene for 6 h. A similar approach is known in lit [15] for vicinal diols and can be applied for the synthesis of compound (5) by reacting 2 eq of EtOH with compound (2) in benzene. Compound (5) is sensitive towards moisture and hydrolysis within minutes to compound (4) by releasing EtOH. Attempts to allocate the reactivity of this partial hydrolysis/alcoholysis to the acidolysis reaction of compound (2) with HCl to give (3) failed, as the addition of 1 eq HCl to compound (2) yielded predominantly an equimolar mixture of compound (2) and (1). Thus, the chlorination of compound (3) with HCl is preferred over the chlorination of compound (2).

Another way of generating compound (3) is the reaction of (2) with chloroform. This is however accompanied by the generation of side products. Thus, $CDCl_3$ as the NMR solvent should be excluded. A similar reaction was recently published [14].

Finally, a selective route for the synthesis of compound (3) is given by the reaction of compound (5) with one equivalent of Ph_2PCl. (see Fig. 5) After 10 minutes, the reaction solution was worked up, yielding pure compound (3). Subsequent analysis of

Table 2
UVVIS shifts of RXSn(IV) porphyrins.

	R, X	N(0,0)		B(1,0)		Soret B(0,0)		Q(2,0)		Q(1,0)		Q(0,0)	
nr.		λ	ε	λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
(1)	Cl, Cl	338	0.03	408	0.10	429	1.00	520	0.01	563	0.03	601	0.02
(2)	R, R	343	0.06	418	0.10	440	1.00	540	0.01	582	0.03	625	0.05
(3)	R, Cl	338	0.08	412	0.11	434	1.00	531	0.02	571	0.04	611	0.04
(4)	R, OH	338	0.10	413	0.12	434	1.00	529	0.01	572	0.05	612	0.05
(5)	R, OEt	338	0.09	413	0.15	435	1.00	530	0.03	572	0.05	612	0.04

λ: wavelength (nm), ε: rel. int. (1), R= 4-bisphenylethynyl

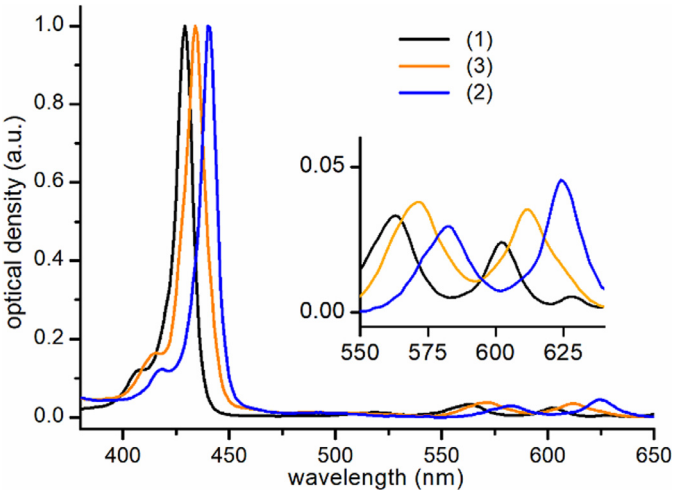

Fig. 6. UVVIS spectra of (1), (2) and (3) in C_6H_6, inlay: detailed spectra of Q-band region.

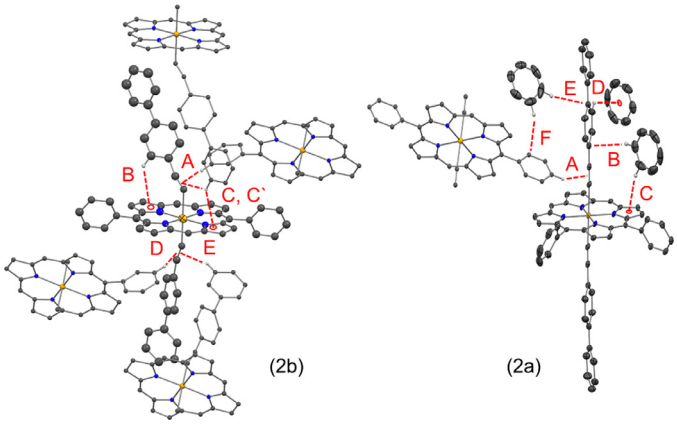

Fig. 7. Polymorphic single crystal XRD structures of compound (2) and related packing interactions of the axial ligand; left: crystals obtained by slow diffusion of benzene into chlorobenzene (2b) A= 2.54 Å, B= 3.29 Å, C= 2.74 Å, C'= 3.03 Å, D= 2.56 Å, E= 2.58 Å; right: crystals obtained by cooling of a refluxing benzene solution (2a) A= 2.69 Å, B= 2. 90 Å, C= 2.92 Å, D= 2.89 Å, E= 3.07 Å, F= 2.90 Å, hydrogen atoms and phenyl groups not involved in packing interactions partially omitted for clarity, different styles used for clarification.

the remaining extraction solution by ^{31}P-NMR (C_6D_6,121.4 MHz) revealed a strong signal at 28.9 ppm for $Ph_2P(=O)Et$ [19], which is the Arbuzov-rearrangement product of the primarily formed Ph_2POEt [20]. Compound (3) is more stable towards hydrolysis compared to (2) as evidenced by an unfinished hydrolysis reaction after 100 h with 10 eq H_2O.

Above reaction products can be analyzed by ^{119}Sn-NMR spectroscopy. The measured ^{119}Sn-NMR shifts are given in Table 1. As expected, the ^{119}Sn- NMR chemical shift of compound (3) appears nearby the mean value of the chemical shifts of (1) and (2). Representative ^{119}Sn-NMR spectra of equilibrated reaction solutions from the Kocheshkov redistribution reaction can be seen in the supporting information. In most ^{119}Sn-NMR spectra, the FWHM of (3) is significantly higher than in compound (2), displaying typical values of 40 vs. 30 Hz.

As shown in Fig. 6 the UVVIS absorption spectra of compound (3) is located in the center of the two educt spectra of (1) and (2), thus also the properties related to the optical absorption of the porphyrin ring system seem to be averaged in (3). Main UVVIS transitions also for compounds (4) and (5) are listed in Table 2.

A clear differentiation between asymmetric substituted compounds (3), (4), and (5) was not possible via UVVIS spectroscopy.

The asymmetric substituted Sn(IV) porphyrin derivatives (3), (4) and (5) were analyzed using MALDI-TOF MS. In case of compound (3), the molecular peak $[M]^+$ at m/z= 944.22 was observed including fragmentation peaks for $[M\text{-}Cl]^+$ and $[M\text{-}R]^+$ (R= p-biphenylethynyl). Compounds (4) and (5) do not show the molecular peak, but give similar fragmentation peaks for $[M\text{-}X]^+$, $[M\text{-}R]^+$ and $[M\text{-}X\text{-}R]^+$ (X= OH, OEt; R= p-biphenylethynyl).

Compound (2) shows polymorphic behavior in the solid state as demonstrated by two different single crystal XRD structures measured at equal temperature of 100 K. The two XRD structures are depicted in Fig. 7. Selected bond lengths and angles can be found in Table 3. Main differences of these two structures refer to the geometry of the axial ligand. While the geometrical situation in the structure of (2a) is symmetric, the two axial ligands are different in (2b). Therein, one axial ligand of (2b) is bent by an Sn-C≡C angle of 132.9° while the opposite one is 162.5° This is in sharp contrast to the angles observed for (2a) which are both 177.5° This behavior supports the idea of a weak Sn-C bond as reported earlier [14]. Another difference between the two structures refers to the enclosure of crystal benzene. Structure (2a) was crystallized from cooling a hot benzene solution of (2), structure (2b) was crystallized by slow evaporation of a benzene solution of (2) at room temperature. In the structure of (2a) four benzene molecules are included in the unit cell, which are located in the vicinity of the axial ligand, while (2b) does not contain any solvent molecule. A closer look to the packing interactions around the axial ligand of these two structures reveals strong CH- π interactions for (2b) between 2.7 to 2.5 Å, while comparable interactions in (2a) are above 2.7 Å.

The single crystal XRD structures of (4) and (5) can be seen in Fig. 8. Certain bond lengths and angles are depicted in Table 3. The crystals were grown by slow evaporation of benzene solutions of corresponding compounds (4) and (5). No solvent molecule is included in the unit cell of compound (4), while three benzene molecules are included in the unit cell of compound (5). Significant disorder of the para positioned phenyl ring in axial position is observed for (4) displaying 50% split positions.

The appearing Sn-O bond lengths of 2.06 Å and 2.13 Å fit to the literature known Sn-O bond length of 2.08 Å of a phenolate derivative in the axial position [15]. The C≡C bond length of 1.14 Å of compound (4) is short compared to typical 1.21 Å of compounds

Table 3
Selected bond lengths [Å] and angles [°] of (4-biphenylethynyl)XSnTPP for compounds (2), (3), (4), (5).

	(2a)	(2b)	(3)	(4)	(5)
X	4-biphenylethynyl	Cl	OH	OEt	
Sn(IV)-X	2.171(3)	2.25(4)	2.4740(12)	2.057(8)	2.13(2)
Sn(IV)-C23	2.171(3)	2.12(3),	2.171(4)	2.195(13)	2.048(19)
C23≡C24	1.206(3)	1.206(5), 1.209(5)	1.182(5)	1.141(19)	1.212(8)
Sn(IV)-N1	2.1173(18)	2.11(2)	2.107(2)	2.131(6)	2.122(17)
Sn(IV)-N2	2.1209(18)	2.082(17)	2.110(2)	2.108(8)	2.10(2)
Sn(IV)-C23≡C24	177.4(2)	163(4), 133(3)	175.3(3)	180.0	154(2)
C23-E(IV)-X	180	177(2)	178.72(8)	180.0	176.5(8)
C23-E(IV)-N1	91.44(8)	90.3(18)	93.38(11)	91.91(19)	91.3(7)
C23-E(IV)-N2	90.98(8)	92.9(18)	90.93(11)	90.7(2)	87.0(9)
C≡C-C	178.7(3)	170(4), 163(4)	178.7(4)	180.0	174(3)

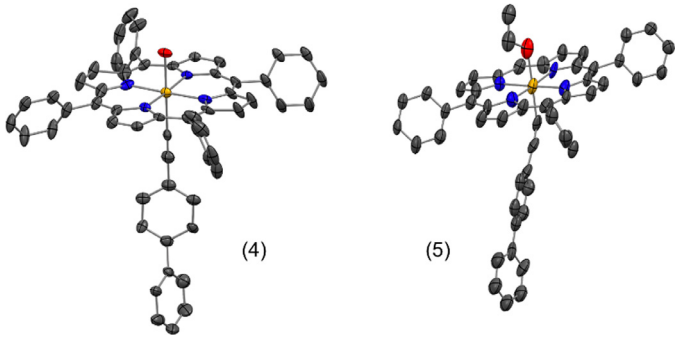

Fig. 8. Single crystal XRD structures of compound (4) and (5). Hydrogen atoms and certain phenyl groups partially omitted for clarity.

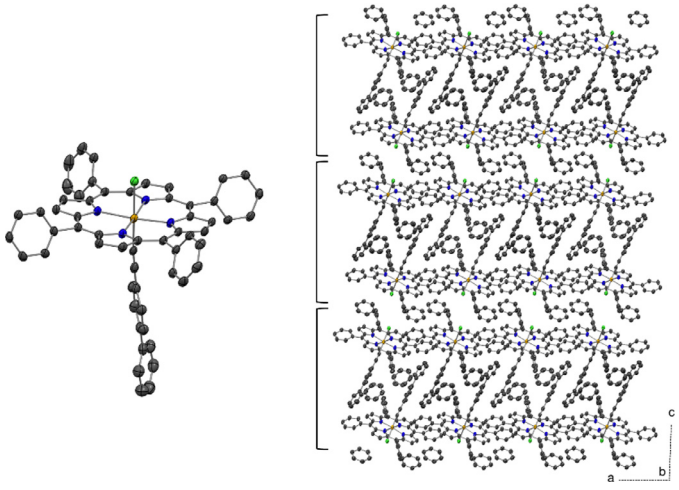

Fig. 9. Single crystal XRD structure of compound (3) and related bimolecular layered build up structure. Hydrogen atoms omitted for clarity.

(2), (5) and literature known derivatives [14,38]. However, comparison with the bond lengths 1.18 Å from compound (3) and 1.19 Å of the phenolate derivative from literature [15] may indicate a possible influence from the ligand in trans position and thus, gives rise to further investigations. Packing of (4) is in contrast to compound (2) mostly determined by close contacts of the hydrogen atoms on the phenyl ring in meso position to the porphyrin ring plane of adjacent molecules. Packing of compound (5) is rather similar to the subsequent one of compound (3).

The single crystal XRD structure of compound (3) is depicted in Fig. 9. Selected bond lengths and angles are listed in Table 3. Single crystals were grown from slow evaporation of a benzene solution of compound (3). The Sn-Cl bond length of 2.47 Å is slightly elongated compared to the literature known bond length (2.42 Å) observed for compound (1) [16], but is within the expected range for Sn-Cl bond lengths of octahedral coordinated Sn atoms with four nitrogen atoms in the equatorial plane (from 2.40 Å [17] to 2.52 Å [18]). Observed Sn-C bond lengths of 2.17 Å display typical values compared to literature [14,15,38]. Regarding the packing of compound (3), two benzene molecules are included per porphyrin molecule in the unit cell. Further on, the single porphyrin molecules are arranged in a bimolecular layered build up structure built from layers in cell directions a and b, with polar (chloride) sides on the outsides and apolar (organic) sides on the inside of each double layer. The double layers seem to be separated from each other in cell direction c by the incorporation of benzene molecules. These benzene molecules undergo several packing interactions of CH-π type and parallel displaced π- π type interaction with adjacent porphyrin molecules.

Conclusion

The axially trans substituted Sn(IV) meso-tetra phenyl porphyrins serve as a convenient system to study the Kocheshkov redistribution reaction between alkynyl ligands and chlorine atoms on a six fold coordinated Sn(IV) atom. The immobile four dentate porphyrin ligand enables the study of only two redistributing ligands, thus simplifying this typically complex reaction for higher coordinated Sn(IV) species. In the investigated system, Kocheshkov reactions with equilibrium constants of K ~15 are observed and are in contrast to literature, where “reverse Kocheshkov reactions” are discussed.

Besides the literature known partial alcoholysis [15] and the above described partial hydrolysis, the herein described Kocheshkov redistribution reaction and the selective backchlorination using chloro phosphanes, serve as new methods towards the preparation of axial unsymmetrically substituted Sn(IV) porphyrins. These axially unsymmetrically substituted porphyrins have higher solubilities compared to their symmetrically substituted educts and may therefore provide wider applicability for example in opto-electronic devices, where solubilities of components play an important role to achieve higher layer thicknesses.

Experimental:

Material and methods

All reactions have been carried out under nitrogen or Argon using common Schlenk techniques. Each flask was flame-dried before its use. Nitrogen was dried *via* a column of mole sieves (3 Å) and P_4O_{10}. Argon 5.0 was used as released from the pressure cylinder. Organic solvents were dried *via* a solvent drying system from Innovative Technology Inc. The water content was determined using Karl-Fischer titration and was found to be less than 5 ppm.

4- biphenylacetylene 99% was purchased from Sigma Aldrich and was used as received. "AcroSeal" n-BuLi, 1.6 molar in hexane was purchased from Acros organics. $TPPH_2$ 97% was purchased from ABCR GmbH & Co KG and was used as received. Deuterated solvents ($CDCl_3$, C_6D_6) were purchased from Deutero GmbH, VWR Int., dried with P_4O_{10}, distilled and stored in a flask over molecular sieves (3 Å). Elemental mass analyses were carried out using an Elementar Vario instrument by Heraeus Elementar.

NMR-measurements were performed on a Mercury 300 MHz spectrometer (Varian) at ambient temperature. Measurements of ^1H (300 MHz) were carried out using TMS (δ=0 ppm) as a reference; measurements of broad band decoupled ^{119}Sn (111.8 MHz) were related to Me_4Sn (δ=0 ppm). Due to the low concentration in the reaction solutions (around 1 – 5 mmol/l), spectra were recorded overnight. Measurements of ^{31}P (121.4 MHz) were related to 85% phosphoric acid (δ=0 ppm).

UV/VIS Spectra were acquired under inert atmosphere in quartz class cuvettes of thickness one cm at a "Cary 60 UV–VIS" from "Agilent Technologies".

MALDI TOF Spectra were recorded on a "MALDI micro MX" from "Waters". Sample preparation was done in the glovebox under argon atmosphere. The sample was dissolved in CH_2Cl_2 and crystallized on the target either with or without matrix. Used matrix materials were anthraline and DCTB. Ionization was performed using a laser with 337 nm. Mass filtration was done using TOF analyzer incl. repeller. Calibration was done using a solution of NaTFA (1 mg/ml) with PEG1000 (5 mg/ml).

XRD (standard)

All crystals suitable for single crystal X-ray diffractometry were removed from a vial or a Schlenk under N_2 and immediately covered with a layer of silicone oil. A single crystal was selected, mounted on a glass rod on a copper pin, and placed in the cold N_2 stream provided by an Oxford Cryosystems cryostream. XRD data collection was performed on a Bruker Apex II diffractometer with use of an Incoatec microfocus sealed tube Mo Kα radiation (λ=0.71073 Å), with graphite monochromator and a CCD area detector. Data collection was performed using φ and ω scans. Data reduction and cell refinement were done with Bruker SAINT. Empirical absorption corrections were applied using SADABS or TWINABS [21,22]. The structures were solved with use of the intrinsic phasing option in SHELXT and refined by the full-matrix least-squares procedures in SHELXL [23–25]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in calculated positions using standard bond lengths and angles and refined using a riding model. The space group assignments and structural solutions were evaluated using PLATON [26,27]. Electrostatic non-covalent intermolecular interactions [28-31] for presented and published compounds were based on a Cambridge Structural Database search and fall within expected ranges. Centroids and planes were determined by features of the programs Mercury [32] and Diamond [33]. All crystal structures representations were made with the program Mercury Table 4 contains crystallographic data and details of measurements and refinement for compound (2a). CCDC 1,986,147 contains the supplementary crystallographic data for compound (2a). These data can be obtained free of charge from The Cambridge Crystallographic Data center *via* www.ccdc.cam.ac.uk/data_request/cif.

XRD synchrotron

Single crystals of the axially asymmetric substituted porphyrins have been of small size with at least two dimensions being in the 10–20 µm range. These crystals diffracted poorly on the standard inhouse XRD, thus making the higher brilliance of synchrotron radiation necessary to improve diffraction. Crystal data were therefore collected at 100 K at the XRD1 and XRD2 beamlines of the Elettra Synchrotron, Trieste (Italy) [34], using a monochromatic wavelength of 0.700 Å. The data sets were integrated and corrected for Lorentz, absorption and polarization effects with the XDS package [35] The structures were solved by direct methods using SHELXT program [25] and refined using full-matrix least-squares implemented in SHELXL-2018/3 [36]. Thermal motions for all non-hydrogen atoms have been treated anisotropically for dataset of (4). Hydrogens have been included on calculated positions, riding on their carrier atoms. The Coot program was used for structure building [37]. The crystal data are given in Table 9. Crystallographic data have been deposited at the Cambridge Crystallographic Data center and allocated the deposition numbers CCDC 1,986,147, 1,985,527, 1,985,525, 1,985,528 and 1,985,526 for compounds (2a), (2b), (3), (4) and (5). These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures.

Synthesis of compounds

Compound (1) (Cl_2SnTPP) was synthesized acc. literature [13]. The known procedure and data are given below. A one necked flask is fed with 2.00 g $TPPH_2$ (3.08 mmol, 1 eq), 400 ml pyridine and 1.6 g $SnCl_2{\cdot}2H_2O$ (6.96 mmol, 1.5 eq). The violet reaction mixture is refluxed for 4 h turning into a green solution. The solution is cooled and 400 ml of distilled H_2O are added. The precipitate is isolated via centrifugation at 2000 rpm for 15 minutes and washed with 50 ml of $H_2O_{dest}/HCl_{aq}/H_2O_{dest}$. 6 molar HCl_{aq} was found to work properly. The wet precipitate was dried using the water trap with toluene and $CHCl_3$. Pure compound acc. to NMR, isolated yield: 60%; ^1H NMR(C_6D_6, 300 MHz): 9.04(s, 8H, $^4J_{SnH}$ 14.63 Hz), 7.87(d, 8H, $^3J_{HH}$ 7.03 Hz), 7.38 (m, 12H); ^{119}Sn(C_6D_6, 111.8 MHz): - 588.6 (s); UV/VIS (C_6H_6; λ(nm)/rel Int): 338/0.032, 408/0.099, 429/1.00, 520/0.008, 563/0.034, 602/0.022, HRMS ((+)-MALDI, DCTB): *m/z*= 802.16 (calcd. 802.07 for $C_{44}H_{28}N_4SnCl_2$, $[M]^+$); *m/z*= 767.18 (calcd. 767.10 for $C_{44}H_{28}N_4SnCl$, $[M\text{-}Cl]^+$),

Compound (2): E^{IV} = Sn, R= 4-biphenyl was synthesized acc. literature [14], washing solvent: small amount benzene, solubilities in benzene and chlorobenzene: ~4 mmol/l and ~9 mmol/l mp: > 285 °C (decomposition), pure compound acc. to NMR, isolated yield: 75% ^1H NMR(C_6D_6, 300 MHz): 9.14(s, 8H, $^4J_{SnH}$ 7.81 Hz), 8.11 (dd, 8H, $^3J_{HH}$ 7.62 Hz, $^4J_{HH}$ 1.36 Hz), 7.42 (m, 12H), 6.84 (m, 6H), 6.75 (dd, 4H, $^3J_{HH}$ 7.10 Hz, $^4J_{HH}$ 2.75 Hz), 6.30 (d, 2H, $^3J_{HH}$ 8.45 Hz), 5.42 (d, 2H, $^3J_{HH}$ 8.45 Hz); ^{119}Sn(C_6D_6, 111.8 MHz): - 625.9 (s), ^{119}Sn($CDCl_3$): - 627.9 (s); UV/VIS (C_6H_6; λ(nm)/ rel Int): 292/0.136, 343/0.060, 418/0.095, 440/1.00, 540/0.009, 582/0.034, 625/0.048 $C_{72}H_{46}N_4Sn \cdot 2C_6H_6$ (1085.89) found C 79.85 N 4.48 H 4.22 req C 79.64 N 5.16 H 4.27

Compound (3): R= 4-biphenyl, X=Cl:

By equilibrated redistribution reaction of compound (1) and (2): In a typical reaction for an educt ratio of 1:1, 13.3 mg of (1) (16 µmol, 1 eq) are mixed with 20.1 mg of (2) (0.016 mmol, 1 eq) and placed in a Schlenk vessel. 3 ml of chlorobenzene are added to the mixture and heated to 110 °C for 20 h. The reactions solution is evaporated to dryness and dissolved in 1.5 ml hot benzene and slowly cooled to room temperature. Filtration gives enriched compound (3) in the filtrate with a purity of 75%, being impure by 25% of a mixture of (1) and (2).

Attempts by partial acidolysis of compound (2): In a typical reaction 8.0 mg of (2) (6 µmol, 1eq) were placed in a Schlenk vessel and dissolved in 2 ml C_6H_6. One eq of HCl dissolved in Et_2O (approx. 0.06 molar) was added dropwise at 5 °C. The reaction was stirred for 1 hour. Subsequent analysis via ^1H NMR in C_6D_6 gave a product ratio for (1):(3):(2) of approx. 10:1:10.

Table 4
Crystallographic data of compounds (2), (4) and (3).

	(2a)	(2b)	(3)	(4)	(5)
Formula	$C_{84}H_{58}N_4Sn$	$C_{72}H_{44}N_4Sn$	$C_{70}H_{49}N_4ClSn$	$C_{58}H_{37}N_4OSn$	$C_{64.5}H_{46.5}N_4OSn$
Mr, g mol-1	1242.03	1085.82	1100.27	924.6	1012.24
Cryst. size, mm³	0.1×0.1×0.01	0.05×0.01×0.005	0.1×0.05×0.02	0.08×0.03×0.01	0.12×0.07×0.02
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*P 21/c*	*P 21/c*	*I 2/a*	C 2/c	*P 21/c*
crystal color	blue	blue	purple	purple/blue	purple/blue
Habit	hexagonal	rhombohedron	thin plate	blocks	thin plate
a, Å	14.0125(9)	23.555(5)	21.388(4)	16.991(3)	22.111(4)
b, Å	10.7162(7)	10.894(2)	10.825(2)	18.983(4)	11.044(2)
c, Å	21.3390(14)	20.461(4)	46.320(14)	13.539(3)	20.395(4)
α, deg	90	90	90	90	90
β, deg	96.534(4)	94.78(3)	91.85(3)	92.13(3)	93.71(3)
γ, deg	90	90	90	90	90
V, Å³	3183.5(4)	5232.2(18)	10,719(4)	4369.8(15)	4969.9(17)
Z	2	4	8	4	4
Rint	0.0776	0.1701	0.0736	0.0990	0.0673
Dcalcd, g cm-3	1.296	1.378	1.364	1.409	1.353
μ(MoKα), cm-1	0.452	0.511	0.397	0.601	0.534
Temperature(K)	100	100	100	100	100
F(000), e	1280	2224	4512	1888	2078
2θ, deg	2.40–27.0	0.85–13.96	1.54–26.29	1.585–25.96	1.818–21.857
hkl range	-17 to 17, -13 to 13, -27 to 27	-16 to 16, -7 to 7, -14 to 14	-30 to 30, -15 to 15, -66 to 66	-21 to 21, -23 to 23, -16 to 16	-23 to 23, -11 to 11, -21 to 21
Refl. meassured/independent/ observed [I>2σ(I)]	40,207/6958/4984	6475/1768/772	101,960/16,366/10,926	16,761/4336/3080	32,865/6162/2993
No. of data/params/restraints	6958/403/41	1768/218/129	16,366/589/0	4336/298/23	6162/536/86
R1, wR2 (all data)	0.0623, 0.0685	0.2878, 0.3514	0.0909, 0.1508	0.1301, 0.2354	0.2286, 0.3421
R1, wR2 (>2σ)	0.0328/ 0.0625	0.1352, 0.2736	0.0548, 0.1325	0.0966, 0.2115	0.1527, 0.2831

By selective chlorination of compound (5) with Ph_2P-Cl: In a typical reaction 9.1 mg of (5) (9.5 µmol, 1 eq) were placed in a Schlenk vessel and dissolved in 3 ml benzene. 63 µl of a stock solution of Ph_2PCl in benzene (0.15 mol/l) (9.5 µmol, 1eq) were added dropwise. The reaction was stirred for 10 min at room temperature. The reaction solution was evaporated to dryness and washed with 1.5 ml Et_2O three times. The remaining residue was dried in vacuum. Single crystals suitable for XRD diffraction were obtained by slow evaporation of a benzene solution of compound (3). solubility in benzene: ~25 mmol/l, m.p.: decomp. >300 °C, purity acc. to NMR: 97%, isolated yield: 62%

^{1}H NMR(C_6D_6, 300 MHz): 9.09 (s, 8H, $^4J_{SnH}$ 11.25 Hz), 8.07(d, 4H, $^3J_{HH}$ 7.42 Hz), 7.90 (d, 4H, $^3J_{HH}$ 7.44 Hz), 7.44 (m, 12H), 6.83 (m, 3H), 6.73 (dd, 2H, $^3J_{HH}$ 7.02 Hz, $^4J_{HH}$ 2.95 Hz), 6.29(d, 2H, $^3J_{HH}$ 8.30 Hz), 5.48(d, 2H, $^3J_{HH}$ 8.30 Hz); ^{119}Sn-NMR (C_6D_6, 111.8 MHz): -610.5 (s); UV/VIS (C_6H_6; λ(nm)/ rel Int): 338/0.080, 412/0.113, 434/1.000, 531/0.021, 571/0.038, 611/0.035, HRMS ((+)-MALDI, DCTB): *m/z*= 944.22 (calcd. 944.17 for $C_{58}H_{37}N_4SnCl$, $[M]^+$), *m/z*= 909.19 (calcd. 909.21 for $C_{58}H_{37}N_4Sn$, $[M\text{-}Cl]^+$), *m/z*= 767.10 (calcd. 767.10 for $C_{44}H_{28}N_4SnCl$, $[M\text{-}C_{14}H_9]^+$)

Compound (4): R= 4-biphenyl, X=OH, is synthesized by partial hydrolysis of compound (2). In a typical reaction 5.1 mg of (2) (0.004 mmol, 1 eq) are placed in a Schlenk vessel. 0.75 ml C_6H_6 are added. 1 eq of H_2O (0.004 mmol) is incorporated by the addition of 0.75 ml wet C_6H_6 (water content determined by KF titration: 101.9±5.5 ppm). The reaction solution is heated to 80 °C for 6 h to give an equimolar mixture of 4-biphenylethyne and compound (4) in the NMR spectra. Isolated yield: 82%, ^{1}H NMR(C_6D_6, 300 MHz): 9.09 (s, 8H, $^4J_{SnH}$ 8.06 Hz), 8.08(dd, 4H, $^3J_{HH}$ 6.9 Hz), 8.00 (dd, 4H, $^3J_{HH}$ 7.5 Hz), 7.44 (m, 12H), 6.83(m, 3H), 6.74(m, 2H), 6.30(d, 2H, $^3J_{HH}$ 7.49 Hz), 5.44(d, 2H, $^3J_{HH}$ 7.49 Hz), - 7.25 (s, 1H); ^{119}Sn-NMR (C_6D_6, 111.8 MHz): -591.9 (s); UV/VIS (C_6H_6; λ(nm)/ rel Int): 338/0.096, 413/0.122, 434/1.000, 529/0.014, 572/0.046, 612/0.046, HRMS ((+)-MALDI, DCTB): *m/z*= 909.23 (calcd. 909.21 for $C_{58}H_{37}N_4Sn$, $[M\text{-}OH]^+$), *m/z*= 749.14 (calcd. 749.14 for $C_{44}H_{28}N_4SnCl$, $[M\text{-}C_{14}H_9]^+$); *m/z*= 732.10 (calcd. 732.13 for $C_{44}H_{28}N_4Sn$, $[M\text{-}OH\text{-}C_{14}H_9]^+$)

Compound (5): R= 4-biphenyl, X=OEt: The reaction was performed by partial alcoholysis of compound (2) with two equivalents of ethanol close to literature [38]. In a typical reaction 11.8 mg of (2) (9.5 µmol, 1eq) were placed in a Schlenk vessel and dissolved in 3 ml benzene. 0.08 ml of a stock solution of ethanol in benzene (0.12 mol/l) (19 µmol, 2eq) were added dropwise. The reaction is stirred for 24 h at room temperature to give a bluish-green solution. The solution is evaporated to dryness and the hydrolyzed ligand R-C≡C-H was removed by sublimation to give a 98% pure compound according to NMR, isolated yield: 73%, m.p.: decomp. >300 °C, ^{1}H NMR(C_6D_6, 300 MHz): 9.095 (s, 8H, $^4J_{SnH}$ 8.37 Hz), 8.07(m, 8H), 7.41 (m, 12H), 6.83 (m, 3H), 6.74 (m, 2H), 6.29 (d, 2H, $^3J_{HH}$ 8.35 Hz), 5.44(d, 2H, $^3J_{HH}$ 8.30 Hz); -1.75 (q, 2H, $^3J_{HH}$ 6.81 Hz), -1.93 (t, 3H, $^3J_{HH}$ 6.81 Hz); ^{119}Sn-NMR (C_6D_6, 111.8 MHz): -596.8 (s); UV/VIS (C_6H_6; λ(nm)/ rel Int): 338/0.087, 413/0.149, 435/1.000, 530/0.030, 572/0.048, 613/0.042, HRMS ((+)-MALDI, DCTB): *m/z*= 909.10 (calcd. 909.21 for $C_{58}H_{37}N_4Sn$, $[M\text{-}OEt]^+$), *m/z*= 777.09 (calcd. 777.17 for $C_{44}H_{28}N_4SnCl$, $[M\text{-}C_{14}H_9]^+$); *m/z*= 732.07 (calcd. 732.13 for $C_{44}H_{28}N_4Sn$, $[M\text{-}OEt\text{-}C_{14}H_9]^+$)

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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REFERENCES

[1] K.A. Kocheshkov, Untersuchungen über metallorganische Verbindungen, Ber. Dtsch. Chem. Ges. 62 (1926) 996–997.
[2] D. Grant, J.R. Van Wazer, Some scrambling reactions of tetramethyltin, J. Organomet. Chem. 4 (3) (1965) 229–236.
[3] W.P. Neumann, G. Burkhardt, Organozinnverbindungen, IV. Die Komproportionierung von Zinnalkylen mit Zinnhalogeniden und die Darstellung von Alkylzinn-Trihalogeniden, Ann. Chem. 663 (1) (1963) 11–21.
[4] B. Wrackmeyer, G. Kehr, Tetra-1-Alkynyltin Compounds and Exchange Reactions with Tin Tetrachloride -^{13}C and ^{119}Sn Nuclear Magnetic Resonance Study, Main Group Metal Chem. 16 (5) (1993) 305–314.
[5] K. Moedritzer, Redistribution Equilibria of Organometallic Compounds, Adv. Organometal. Chem. 6 (1968) 171–271.
[6] W.P. Neumann, H. Niermann, Organozinnverbindungen, II. Darstellung von Organozinn-mono-, -di- und -tri-hydriden, Ann. Chem 653 (1) (1962) 164–172.
[7] W.P. Neumann, J. Pedain, Synthesen mit organo-halogenozinn-hydriden, Tetrahedron Lett. 5 (36) (1964) 2461–2465.
[8] D.P. Arnold, J. Blok, The coordination chemistry of tin porphyrin complexes, Coord. Chem. Rev. 248 (3-4) (2004) 299–319.
[9] I.A. Portnyagin, V.V. Lunin, Reverse Kocheshkov reaction – Redistribution reactions between $RSn(OCH_2CH_2NMe_2)_2Cl$ (R = Alk, Ar) and $PhSnCl_3$: Experimental and DFT study, J. Organomet. Chem. 693 (26) (2008) 3847–3850.
[10] Z. Padelkova, T. Weidlich, L. Kolarova, A. Eisner, I. Cisarova, T.A. Zevaco, A. Ruzicka, Products of hydrolysis of C,N-chelated triorganotin(IV)chlorides and use of products as catalysts in transesterification reactions", J. Organomet. Chem. 692 (25) (2007) 5633–5645.
[11] J. Beckmann, D. Dakternieks, A. Duthie, E.R.T. Tiekink, , „Hydrolysis of $(Me_3SiCH_2)PhSnCl_2$. Isomerisation of the dimeric tetraorganodistannoxane $[(Me_3SiCH_2)Ph(Cl)SnOSn(Cl)Ph(CH_2SiMe_3)]_2$, Dalton Trans. (2003) 755–759.
[12] D.V. Airapetyan, V.S. Petrosyan, S.V. Gruener, K.V. Zaitsev, D.E. Arkhipov, A.A. Korlyukov, Disproportionation reactions within the series of coordinated monoorganostannanes", J. Organomet. Chem. 747 (2013) 241–248.
[13] M.J. Crossley, P. Thordarson, R.A.S. Wu, „Efficient formation of lipophilic dihydroxotin(IV) porphyrins and bis-porphyrins, J. Chem. Soc. Perkin Trans. 1 18 (2001) 2294–2302.
[14] S. Stadlbauer, R. Fischer, M. Flock, P.W. Zach, S.M. Borisov, A. Torvisco, F. Uhlig, Structure and spectroscopic properties of porphyrinato group 14 derivatives: Part I-Phenylacetylido ligands, Z. Naturforsch. B 72 (11) (2017) 801–811.
[15] G. Du, A. Ellern, L.K. Woo, Reaction of tin porphyrins with vicinal diols, Inorg. Chem. 43 (7) (2004) 2379–2386.
[16] D.M. Collins, W.R. Scheidt, J.L. Hoard, , "Crystal structure and molecular stereochemistry of .alpha.,.beta.,.gamma.,.delta. tetraphenylporphyrinatodihlorotin(IV), J. Am. Chem. Soc. 94 (1972) 6689–6696.
[17] Daiki Kuzuhara, Wataru Furukawa, Aya Kitashiro, Naoki Aratani, Hiroko Yamada, Synthesis and Metalation of Doubly o-Phenylene-Bridged Cyclic Bis(dipyrrin)s with Highly Bent Skeleton of Dibenzoporphyrin(2.1.2.1), Chem. Eur. J. 22 (2016) 10671–10678.
[18] W.J. Belcher, P.J. Brothers, M.V. Land, C.E.F. Rickard, D.C. Ware, Tin(IV), germanium(IV) and silicon(IV) complexes of the dianion of 5, 14-dihydro-6,8,15,17-tetramethyldibenzo-[b,i][1,4,8,11]tetraazacyclotetradecine (H_2L): crystal structures of trans-$Sn(L)Cl_2$ and trans-$Sn(L)(NO_3)_2$·MeCN, J. Chem. Soc. Dalton Trans. (14) (1993) 2101–2105.
[19] E.E. Nifant'ev, I.A. Trofimtsova, L.A. Chekulaeva, E.V. Chechegoeva, V.V. Gavrilenko, , „study of reactions of phosphinous acids with triethylaluminium", Zh. Obshch. Khim. 62 (5) (1992) 1027–1031.
[20] P.-Y. Renard, P. Vayron, E. Leclerc, A. Valleix, C. Mioskowski, Lewis Acid catalyzed Room-Temperature Michaelis-Arbuzov Rearrangement, Angew. Chem. Int. Ed. 42 (21) (2003) 2389–2392.
[21] R. Blessing, An empirical correction for absorption anisotropy, Acta Crystallogr. A51 (1995) 33–38.
[22] Bruker, APEX2 and SAINT, Bruker AXS Inc., Madison, WisconsinUSA, 2012.
[23] G.M. Sheldrick, Phase annealing in SHELX-90: direct methods for larger structures, Acta Crystallogr. A46 (1990) 467–473.
[24] G.M. Sheldrick, A short history of SHELX, Acta Crystallogr. A64 (2008) 112–122.
[25] G.M. Sheldrick, "SHELXT - Integrated space-group and crystal-structure determination, Acta Crystallogr. A71 (2015) 3–8.
[26] A.L. Spek, Single-crystal structure validation with the program PLATON, J. Appl. Crystallogr. 36 (2003) 7–13.
[27] A.L. Spek, Structure validation in chemical crystallography, Acta Crystallographica Section D 65 (2009) 148–155.
[28] C.A. Janiak, A critical account on $\pi-\pi$ stacking in metal complexes with aromatic nitrogen-containing ligands, J. Chem. Soc., Dalton Trans. 21 (2000) 3885–3896.
[29] C.A. Hunter, J.K.M. Sanders, The nature of .pi.-.pi. interactions, J. Am. Chem. Soc. 112 (14) (1990) 5525–5534.
[30] E.A. Meyer, R.K. Castellano, F. Diederich, Interactions with aromatic rings in chemical and biological recognition, Angew. Chem., Int. Ed. 42 (11) (2003) 1210–1250.
[31] S.K. Nayak, R. Sathishkumar, T.N.G. Row, "Directing role of functional groups in selective generation of C-H$\cdots\pi$ interactions: In situ cryo-crystallographic studies on benzyl derivatives", CrystEngComm 12 (10) (2010) 3112–3118.
[32] C.F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, Mercury CSD 2.0 – new features for the visualization and investigation of crystal structures, J. Appl. Crystallogr. 41 (2008) 466–470.
[33] H. Putz, K. Brandenburg, Diamond - Crystal and Molecular Structure Visualization, 3.2i ed., Crystal Impact, Bonn, Germany, 2012.
[34] A. Lausi, M. Polentarutti, S. Onesti, J.R. Plaisier, E. Busetto, G. Bais, L. Barba, A. Cassetta, G. Campi, D. Lamba, A. Pifferi, S.C. Mande, D.D. Sarma, S.M. Sharma, G. Paolucci <b>, title: "Status of the crystallography beamlines at Elettra, Eur. Phys. J. Plus 130 (43) (2015) 1–8.
[35] W. Kabsch, XDS, Acta Cryst. D66 (2) (2010) 125–132.
[36] G.M. Sheldrick, "Crystal structure refinement with SHELXL, Acta Cryst. C71 (2015) 3–8.
[37] P. Emsley, B. Lohkamp, W. Scott, K. Cowtan, "Features and Development of Coot", Acta Cryst. D66 (2010) 486–501.
[38] J. Chen, L.K. Woo, Synthesis and Characterization of Alkyl- and Amidotin Porphyrin Complexes: Molecular Structure of trans-Bis (phenylacetylido)(meso-tetra-p-tolylporphyrinato)tin(IV)", Inorg. Chem. 37 (13) (1998) 3269–3275.