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A sterically congested aryltrimethylstannane – Synthesis, reactivity, transmetalation and CH–π interaction

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ABSTRACT

The synthesis of a novel sterically congested tetraorganotin compound, (4-*tert*-butyl-2,6-dimesitylphenyl)trimethylstannane (**1**), is reported and its reactivity with special focus on transmetalation studied. The reaction of compound **1** with reagents such as $HgCl_2$, $BiCl_3$ and HOTf gave (4-*tert*-butyl-2,6-dimesitylphenyl)dimethyltin chloride (**2**) and (4-*tert*-butyl-2,6-dimesitylphenyl)dimethyltin triflate (**3**), respectively, as a result of selective tin–methyl bond cleavage. Less bulky aryltrimethyltin derivatives react with $BiCl_3$ to give both tin–methyl and tin–aryl bond cleavage. Hydrolysis of compound **3** proceeds slowly to give bis-(4-*tert*-butyl-2,6-dimesitylphenyl)dimethyl stannoxane (**5**) via the intermediate (4-*tert*-butyl-2,6-dimesitylphenyl)dimethyltin hydroxide (**4**). All terphenyldimethyltin derivatives that were characterized by single crystal X-ray diffraction analysis show C–H···π interactions. Based on these results, the optimum C–H···π distance (C···centroid$_{aryl}$ distance) is suggested to be in the range 3.4 and 3.5 Å.

1. Introduction

Organotin compounds have been intensively studied and have found widespread use in organic synthesis [1]. The most prominent examples include esterification and transesterification using diorganotin compounds [2,3], hydride transfer reactions using triorganotin hydrides [4] and C–C bond coupling using tri- and tetraorganotin compounds in the presence of metal catalysts [5]. The latter reaction which is called *Stille coupling* is well established for aryl group transfer reactions using aryltrimethylstannanes in the presence of diverse Pd catalysts [6]. However, a catalyst is not always needed for C–C coupling reactions. For example, starting from aroyl chlorides even aryltrimethylstannanes serve as reagents for a simple and selective synthesis of asymmetric diaryl ketones which are otherwise difficult to prepare [7]. The method makes use of the exceptional leaving group capacity of the trimethylstannyl cation. In contrast, selective methyl group transfer under mild reaction conditions starting from organotin reagents is less common and usually affords the activation of the tin–methyl bond as for instance by catalysis or hypercoordination [8]. However, in the presence of both tin–alkyl and tin–aryl bonds in the organotin reagent selective tin–methyl bond cleavage is rarely observed and the tin–aryl bond is cleaved [3,9]. The same result is observed when organotin compounds are used as reagents for transmetalation in organometallic main group chemistry. Several organometallic arylboron, arylgallium and arylaluminium compounds were prepared by aryl group transfer starting from aryltrialkylstannanes [10,11]. Transmetalation with alkyl, allyl or vinyl group transfer is less common but was observed occasionally [11–13]. A prominent example is the preparation of bismabenzene starting from 1,1-di-*n*-butyl-1-stannacyclo-1,4-hexadiene and bismuth trichloride [14].

We are interested in synthetic strategies towards organometallic compounds of heavy main group elements and started to investigate the potential of aryltrimethylstannanes as transmetalation reagents for bismuth halides including the sterically congested (4-*tert*-butyl-2,6-dimesitylphenyl)trimethylstannane (**1**). Since the discovery of the remarkable potential of bulky terphenyl ligands to stabilise unusual coordination numbers and oxidation states an enormous variety of otherwise unstable organotin compounds was reported [15]. Main emphasis is given to compounds of low valency including metal clusters, whereas studies on tetraorganotin(IV) compounds were rarely reported. However, the first report on terphenyl substituted trimethlyltin compounds dates back to 1964 when *Seyferth* et al. reported the synthesis of 2-iodo-2′-trimethlytin-octaphenyl-biphenyl starting from 1-iodo-2-trimethyltin-tetraphenylbenzene using harsh reaction conditions (Scheme 1) [16]. The same product was obtained by the reaction of 1,2-iodo-tetraphenylbenzene with 1,2-bis-trimethyltin-tetraphenylbenzene. The latter was also used as a starting

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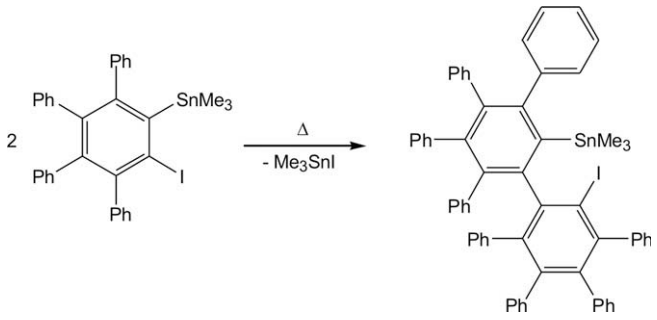


Scheme 1.

material to prepare 1-trimethlytin-2-*para*-tolyl-tetraphenylbenzene and 1-trimethlytin-2-*meta*-tolyl-tetraphenylbenzene from *para*- and *meta*-iodo-toluene, respectively, [16]. Driving force for these reactions is a loss of trimethyltin iodide. However, the reactivity of these unsymmetrical-substituted terphenyl tin compounds was not investigated.

Here, we report on the synthesis, structure and transmetalation reaction of the terphenyl-substituted organotin(IV) compound **1** and present some of its derivatives including (4-*tert*-butyl-2,6-dimesitylphenyl)dimethyltin chloride (**2**) and (4-*tert*-butyl-2,6-dimesitylphenyl)dimethyltin triflate (**3**). Both the compounds were obtained upon selective tin–methyl bond cleavage from compound **1**.

2. Experimental

2.1. General procedures and instrumentation

The commercially available starting materials Me_3SnCl, Me_4Sn, $HgCl_2$, CF_3SO_3H (Aldrich), and $BiCl_3$ (Lancaster) were used as received. Solvents were distilled from appropriate drying agents prior to use. 4-*tert*-Butyl-2,6-dimesitylphenyl magnesium bromide [17], $PhSnMe_3$, *ortho*-$MeO–C_6H_4SnMe_3$ and *ortho*-$Me–C_6H_4SnMe_3$ were prepared according to the literature procedures [18]. All the reactions were carried out under inert atmosphere by using standard vacuum-line and Schlenk-type techniques. Elemental analyses were performed on a LECO CHNS 932 instrument. ^1H, ^{13}C, ^{31}P and ^{119}Sn NMR spectra in solution were recorded at 200.1 MHz (^1H), 400.1 MHz (^1H), 599.8 MHz (^1H), 100.6 MHz (^{13}C), 111.9 MHz (^{119}Sn) and 149.2 MHz (^{119}Sn) at room temperature using the following spectrometers: Varian Mercury 200, Bruker DPX 300, Bruker DRX 400 and Varian Inova 600. Chemical shifts δ are given in ppm and were referenced against Me_4Si or Me_4Sn, respectively. IR spectra were obtained from a Bruker FTIR IFS 113v spectrometer. The FAB mass spectra were recorded on a Finnigan MAT 8230 spectrometer. Electrospray mass spectrometric analyses (ESI-MS) were recorded in the positive mode on a *Thermoquest-Finnigan* instrument using CH_3CN as the mobile phase. The compounds were dissolved in CH_3CN and then diluted with the mobile phase to give solutions of approximate concentration 0.1 mM. The samples were introduced via a syringe pump operating at 10–20 μL/min. The capillary voltage was kept at 4.5 kV, while the cone-skimmer voltage was varied between 50 and 180 V. The extraction cone voltage was −5 V. The ion source temperature was kept at 300 °C. The *m*/*z* values reported correspond to that of the most intense peaks in the corresponding isotope pattern.

2.2. X-ray crystal structure determination

Intensity data for the colourless crystals (**1**–**3**, **5**) were collected on a Nonius KappaCCD diffractometer with graphite-monochromated MoKα radiation at 173 K. Crystal decay was monitored by repeating the initial frames at the end of data collection. Analyzing the duplicate reflections there was no indication for any decay. The structures were solved by direct methods using SHELXS97 [19] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods using SHELXL97 [20]. The H atoms were placed in the geometrically calculated positions using a riding model with U_{iso} constrained at 1.2 times U_{eq} for non-methyl and 1.5 times U_{eq} for methyl groups of the carrier C atom.

2.3. Synthesis

2.3.1. (4-tert-Butyl-2,6-dimesitylphenyl)trimethylstannane (*1*)

A THF solution of 4-*tert*-butyl-2,6-dimesitylphenyl magnesium bromide, prepared from 9.0 g (20 mmol) 1-bromo-2,6-dimesityl-4-*tert*-butylbenzene and 2.0 g (80 mmol) magnesium in 60 ml THF, was added dropwise within 30 min to a THF solution (100 ml) of 5.0 g (25 mmol) Me_3SnCl. The reaction mixture was heated at reflux for 3 h. The solvent was removed under *vacuo* and the residue dissolved in 50 ml Et_2O. After the addition of an aqueous KF solution, the solid formed was filtered off and the organic phase was separated and dried with $MgSO_4$. The solvent was removed under *vacuo* and the residue crystallized twice from hexane to give 5.2 g (50% referred to 1-bromo-2,6-dimesityl-4-*tert*-butylbenzene) of compound **1** as a colourless solid. Single crystals suitable for X-ray diffraction analysis were obtained by crystallisation from *n*-heptane/Et_2O by slow evaporation of the solvent.

Anal. Calc. for $C_{31}H_{42}Sn$ (533.38): C, 69.8; H, 7.9. Found: C, 70.0; 7.9%. Mp 163–165 °C. ^1H NMR (400.1 MHz, $CDCl_3$): δ −0.60 (s, $^2J(^1H–^{117/119}Sn)$ = 53/55 Hz, 9H, Sn–CH_3); 1.26 (s, 9H, CH_3); 1.96 (s, 12H, CH_3); 2.32 (s, 6H, CH_3); 6.92 (s, 4H, H_{aryl}); 6.98 (s, 2H, H_{aryl}). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ −7.4 ($^1J(^{13}C–^{117/119}Sn)$ = 325/341 Hz, Sn–CH_3); 20.9 (CH_3); 21.1 (CH_3); 31.3 (CH_3); 34.6 (C_q); 124.5, 128.0 (2×), 136.4, 136.5, 141.7, 148.9, 152.1 (C_{aryl}). $^{119}Sn\{^1H\}$ NMR (111.9 MHz, CH_2Cl_2/D_2O-cap.): δ −51.3 ($^1J(^{119}Sn–^{13}C)$ = 341 Hz). IR (KBr-pellet, cm^{-1}): 271 w, 293 w, 348 w, 524 vst, 551 m, 665 w, 717 st, 737 m, 773 vst, 848 vst, 882 m, 933 w br, 1011 m, 1031 m, 1045 m, 1112 m, 1172 m, 1182 m, 1200 w, 1244 w, 1361 st, 1376 st, 1434 st, 1480 st, 1539 m, 1555 m, 1572 m, 1585 st, 1612 st, 1720 w, 1776 w, 2349 w, 2729 m, 2861 vst, 2914 vst, 2962 vst.

2.3.2. (4-tert-Butyl-2,6-dimesitylphenyl)dimethyltin chloride (*2*)

To a suspension of 1.13 g (3.58 mmol) $BiCl_3$ in 100 ml THF was added 1.02 g (1.19 mmol) **1** and the reaction mixture was heated 3 h at reflux. The solid material was filtered off and the solvent removed *in vacuo* to give quantitatively compound **2** as a colourless solid. Single crystals suitable for X-ray diffraction analysis were obtained by crystallisation from toluene/CH_2Cl_2 by slow evaporation of the solvent.

Anal. Calc. for $C_{30}H_{39}ClSn$ (553.79): C, 65.1; H, 7.1. Found: C, 64.8; 7.1%. Mp 175–178 °C. ^1H NMR (200.1 MHz, $CDCl_3$): δ −0.22 (s, $^2J(^1H–^{117/119}Sn)$ = 56/58 Hz, 6H, Sn–CH_3); 1.29 (s, 9H, CH_3); 2.03 (s, 12H, CH_3); 2.33 (s, 6H, CH_3); 6.96 (s, 4H, H_{aryl}); 7.10 (s, 2H, H_{aryl}). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ −0.2 (Sn–CH_3); 21.0 (CH_3); 30.9 (CH_3); 31.2 (CH_3); 34.8 (C_q); 125.3, 128.4 (2×), 136.6, 137.3, 140.1, 148.8, 154.3 (C_{aryl}). $^{119}Sn\{^1H\}$ NMR (111.9 MHz, CH_2Cl_2/D_2O-cap.): δ 81.8. IR (KBr-pellet, cm^{-1}): 272 w, 294 w, 330 st, 450 w, 524 m, 583 m, 552 m, 657 w, 722 m, 737 m, 750 m, 766 m, 793 m, 848 vst, 883 m, 925 w, 1047 m, 1114 m, 1173 m, 1201 w, 1245 st, 1362 m, 1379 m, 1439 m, 1479 m, 1542 m, 1584 m, 1612 m, 1722 w, 1777 w, 2733 m, 2862 st, 2915 st, 2961 vst, 3555 m.

2.3.3. (4-tert-Butyl-2,6-dimesitylphenyl)dimethyltin triflate (*3*)

A solution of 0.42 g (2.8 mmol) CF_3SO_3H in 25 ml toluene was added dropwise at 0 °C to a solution of 1.50 g (2.8 mmol) **2** in

30 ml toluene. The reaction mixture was stirred at room temperature for 18 h. The solvent was removed *in vacuo* and the residue dissolved in 20 ml CH_2Cl_2 and 20 ml *n*-heptane. A crystalline product (**3** · 2.5H_2O) suitable for single crystal X-ray diffraction analysis was obtained after slow evaporation of the solvent. After drying in vacuo 1.43 g (73%) of colourless, partially dehydrated **3** was isolated.

Anal. Calc. for $C_{31}H_{43}F_3O_5SSn$ (703.44): C, 52.9; H, 6.2. Found: C, 53.5; 6.0%. Mp 172 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 0.04 (s, $^2J(^1H–^{117/119}Sn)$ = 56/58 Hz, 6H, Sn–CH_3); 1.29 (s, 9H, *t*-Bu); 1.78 (s, 4H, H_2O); 1.98 (s, 12H, CH_3); 2.32 (s, 6H, CH_3); 6.96 (s, 4H, H_{aryl}); 7.16 (s, $^4J(^1H–^{117/119}Sn)$ = 22 Hz, 2H, H_{aryl}). ^{1}H NMR (400.1 MHz, CD_3CN): δ −0.20 (s, $^2J(^1H–^{117/119}Sn)$ = 68/70 Hz, 6H, Sn–CH_3); 1.30 (s, 9H, *t*-Bu); 2.00 (s, 12H, CH_3); 2.30 (s, 6H, CH_3); 3.07 (s, 4H, H_2O) 6.97 (s, 4H, H_{aryl}); 7.12 (s, $^4J(^1H–^{117/119}Sn)$ = 23 Hz, 2H, H_{aryl}); ^{3}C NMR data from ^{1}H–^{13}C–COSY (599.8 MHz, $CDCl_3$): δ 2.0 (Sn–CH_3), 21.0 (CH_3), 21.4 (CH_3), 31.3 (CH_3), 35.6 (C_q), 126.0, 128.9 (2×), 136.0, 136.7, 138.4, 139.6, 156.1 (C_{aryl}); ^{119}Sn{^{1}H} NMR (111.9 MHz, CH_2Cl_2/D_2O-cap.): δ 168.8; ^{119}Sn{^{1}H} NMR (111.9 MHz, toluene/D_2O-cap.): δ 151.5; ^{119}Sn{^{1}H} NMR (149.2 MHz, CD_3CN): δ −24.3; IR (KBr-pellet, cm^{-1}): 519 w, 554 m, 579 w, 632 st, 764 st, 850 m, 884 w, 1021 vst, 1113 w, 1234 vst, 1288 vst, 1389 m, 1479 m, 1541 w, 1586 m, 1612 m, 1658 m, 2868 m, 2961 m, 3259 st br, 3414 st br; FAB-MS: *m*/*z* (%) 519 (100, M-OTf); (+)ESMS *m*/*z* (%) 560 (65, $[C_{28}H_{33}Me_2Sn + CH_3CN]^+$), 530 (32, $[C_{27}H_{30}MeSn + CH_3CN]^+$), 519 (100, $[C_{28}H_{33}Me_2Sn]^+$), 489 (86, $[C_{27}H_{30}MeSn]^+$).

2.3.4. (4-tert-Butyl-2,6-dimesitylphenyl)dimethyltin hydroxide (**4**) and bis-(4-tert-butyl-2,6-dimesitylphenyl)dimethyl stannoxane (**5**)

To a solution of 0.50 g (5.0 mmol) Et_3N in 10 ml water was added dropwise a solution of 0.20 g (0.28 mmol) **3** in 30 ml CH_2Cl_2. The reaction mixture was stirred for 2 h. The organic phase was separated, dried with $MgSO_4$ and the solvent removed *in vacuo*. The yellow residue (0.18 g) was composed of the starting material, [Et_3NH]OTf and Ar*$SnMe_2OH$ (**4**). The following NMR data were assigned to compound **4**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ −1.00 (s, $^2J(^1H–^{117/119}Sn)$ = 27 Hz, 1H, Sn–OH), −0.12 (s, $^2J(^1H–^{117/119}Sn)$ = 56/58 Hz, 6H, Sn–CH_3); 1.28 (s, 9H, *t*-Bu); 2.00 (s, 12H, CH_3); 2.31 (s, 6H, CH_3); 6.95 (s, 4H, H_{aryl}); 7.08 (s, $^4J(^1H–^{117/119}Sn)$ = 18 Hz, 2H, H_{aryl}); ^{119}Sn{^{1}H} NMR (149.2 MHz, $CDCl_3$): δ 37.7. The residue was dissolved in a mixture of 10 ml CH_2Cl_2 and 5 ml *n*-hexane. Upon slow evaporation of the solvent a crop of crystals of compound **5** suitable for single crystal X-ray diffraction analysis was isolated. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ −0.19 (s, $^2J(^1H–^{117/119}Sn)$ = 59 Hz, 12 H, Sn–CH_3); 1.27 (s, 18H, *t*-Bu); 2.00 (s, 24H, CH_3); 2.30 (s, 12H, CH_3); 6.94 (s, 8H, H_{aryl}); 7.07 (s, $^4J(^1H–^{117/119}Sn)$ = 18 Hz, 2H, H_{aryl}); ^{119}Sn{^{1}H} NMR (149.2 MHz, $CDCl_3$): δ 44.0.

2.3.5. Transmetalation – general procedure

In a typical procedure, 0.87 g (3.6 mmol) $PhSnMe_3$ was added to a slurry of 1.1 g (3.6 mmol) $BiCl_3$ in 5 ml THF. The reaction mixture was heated at reflux for 2 h. The solvent was removed in *vacuo* and 3 ml CH_2Cl_2 was added. The solid material was filtered off and the solution was analysed by ^{119}Sn NMR. The reported yields are based on the integration of the ^{119}Sn NMR signals. Each experiment was repeated four times.

3. Results and discussion

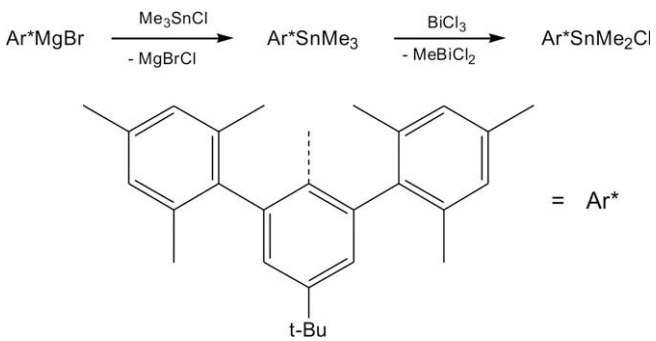
3.1. Synthesis and reactivity of (4-tert-butyl-2,6-dimesitylphenyl)trimethylstannane (**1**)

The synthesis of the title compound (4-*tert*-butyl-2,6-dimesitylphenyl)trimethylstannane (Ar*$SnMe_3$, **1**) was achieved with 49% yield starting from Ar*MgBr and Me_3SnCl. Excess Me_3SnCl is removed by treatment with potassium fluoride solution and subsequent filtration of the insoluble trimethyltin fluoride. Compound **1** was crystallised from *n*-heptane/Et_2O as well as from acetonitrile/Et_2O to give colourless crystals. Noteworthy, attempts to prepare the corresponding aryltributyl- and aryltricyclohexylstannane failed which we ascribe to steric reasons.

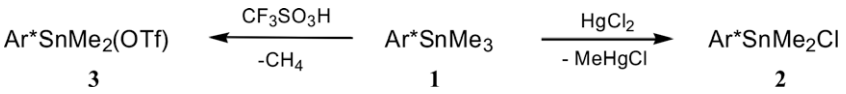
Compound **1** was reacted with $BiCl_3$ in THF at reflux in order to study whether Ar*$BiCl_2$ or $MeBiCl_2$ is formed. A colourless precipitate was observed that was soluble in DMSO-d_6 and gave a single ^{1}H NMR resonance at 1.56 ppm. Although aryl group transfer to bismuth might be expected the ^{1}H NMR spectrum was indicative for the exclusive formation of $MeBiCl_2$ [21]. Work-up of the reaction mixture followed by the crystallisation of the reaction product and subsequent characterisation of the latter including ^{1}H, ^{13}C and ^{119}Sn NMR proofed the transmetalation to occur with methyl group transfer to bismuth to give Ar*$SnMe_2Cl$ (**2**) quantitatively (Scheme 2). Compound **2** crystallized from the various mixtures of solvents (*iso*-PrOH/Et_2O; *iso*-PrOH/CH_2Cl_2; toluene/CH_2Cl_2) by slow evaporation of the solvent to give colourless crystals. The single crystal X-ray diffraction analysis confirmed the formation of Ar*$SnMe_2Cl$ (**2**). Aryl group transfer with attack at the *ipso*-carbon atom in favour of alkyl group transfer is usually observed in transmetalation reactions. However, selective tin–alkyl bond cleavage was previously shown to occur in some intramolecularly coordinated organotin compounds [22,23] and in sterically demanding aryltrialkylstannanes such as 2,2′-bis(trimethylstannyl)-1,1′-binaphthyl upon reaction with BCl_3 [13].

In order to show that methyl group transfer is a result of the bulkiness of the terphenyl ligand and not restricted to bismuth reagents compound **1** was reacted with $HgCl_2$, iodine and CF_3SO_3H. These compounds are well-known reagents for selective tin–phenyl bond cleavage in compounds of the type $Ph_{4-x}R_xSn$ (*x* = 1–3, R = alkyl) [1]. Surprisingly, compound **1** did not react with iodine. Reaction with $HgCl_2$ and CF_3SO_3H gave selective cleavage of the tin–methyl bond, thus providing Ar*$SnMe_2Cl$ (**2**) and Ar*$SnMe_2$(OTf) (**3**), respectively (Scheme 3).

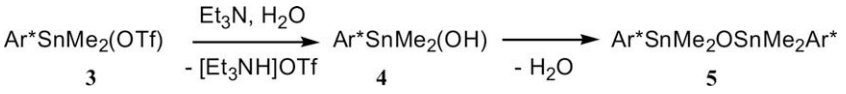
The latter was crystallized from heptane/CH_2Cl_2 by slow evaporation of the solvent in the presence of moisture to give the hydrated aqua-complex [Ar*$SnMe_2$(OTf)(H_2O)] · 1.5 H_2O (**3** · 2.5H_2O). Compound **3** is stable in air in the presence of air moisture, but the addition of Et_3N and water to a CH_2Cl_2 solution of compound **3** gave the hydrolysis product Ar*$SnMe_2$(OH) (**4**). We did not isolate pure **4**, but did obtain a mixture of compound **4**, triethylammonium triflate and starting material **3**. Upon crystallisation from CH_2Cl_2/hexane by slow evaporation of the solvent a few crystals were obtained. Surprisingly, the single crystal structure analysis showed that the condensation product [Ar*$SnMe_2$]O (**5**) was formed (Scheme 4). Thus, the bulky terphenyl ligand does not prevent the triorganotin hydroxide from condensation. Noteworthy,



Scheme 2.



Scheme 3.



Scheme 4.

the diorganotin dihydroxide $(2,6\text{-}Mes_2H_3C_6)_2Sn(OH)_2$ was reported to be stabilized by both the bulky ligand and additional OH-π interactions [24], thus preventing distannoxane formation.

3.2. Transmetalation between bismuth trichloride and organotin compounds

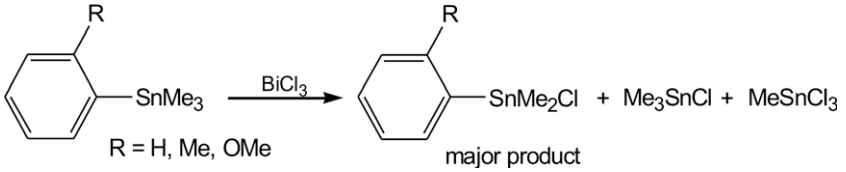
Similar to $HgCl_2$, the reaction of $BiCl_3$ with Ar^*SnMe_3 (**1**) quantitatively gave tin–methyl bond cleavage. Thus, it might be expected that $BiCl_3$ shows a similar reactivity in transmetalation reactions as it is observed for $HgCl_2$. The latter compound is a well-known reagent for selective tin–aryl bond cleavage for sterically less demanding organotin compounds. In order to test whether the less toxic $BiCl_3$ might be a potential substitute for $HgCl_2$, we examined the reaction of $BiCl_3$ with selected aryltrimethylstannanes, $ArSnMe_3$ (Ar = Ph, *ortho*-Me–Ph, *ortho*-MeO–Ph). In contrast to the reaction with $HgCl_2$, we did observe tin–methyl as well as tin–aryl bond cleavage for all organotin compounds. A typical reaction mixture contains 55–60% $ArSnMe_2Cl$, 20–25% Me_3SnCl and 15–20% $MeSnCl_3$ (Scheme 5). It is worth to note that in addition to Me_3SnCl we did observe the formation of $MeSnCl_3$ but Me_2SnCl_2 was not detected in these experiments. This is in agreement with the observation that Me_3SnCl reacts with $BiCl_3$ to give mainly $MeSnCl_3$ (93%) and only minor amounts of Me_2SnCl_2 (7%). However, Me_2SnCl_2 was observed as the main product upon the reaction of Me_4Sn with equimolar amounts of $BiCl_3$. In contrast, neither Bu_3SnCl nor Ph_3SnCl, Ph_4Sn or Ar^*SnMe_2Cl (**2**) did react with $BiCl_3$. In conclusion, $BiCl_3$ does cleave tin–methyl and tin–aryl bonds but a selective reaction as it is known for $HgCl_2$ was not observed. The presented reaction of Ar^*SnMe_3 (**1**) to give selectively Ar^*SnMe_2Cl (**2**) seems to be a rare example of selective tin–methyl bond cleavage using $BiCl_3$. We attribute the reverse reactivity with a high selectivity mainly to the bulkiness of the terphenyl ligand with its mesityl groups in ortho position to the tin-bound carbon atom. Thus, attack at the ipso carbon atom becomes less likely and tin–methyl bond cleavage is favoured. Additionally, the stability and high solubility of Ar^*SnMe_2Cl (**2**) as well as the low solubility of $MeBiCl_2$ are assumed to contribute to the observed reactivity.

3.3. Structures in the solid state

In course of our studies, the solid state structures of the tetraorganotin compound **1**, the triorganotin chloride **2**, the hydrate of the triorganotin triflate **3** and distannoxane **5** were determined.

Single crystals of compound **1** suitable for single crystal X-ray diffraction analysis were obtained from *n*-heptane/Et_2O as well as from acetonitrile/Et_2O by slow evaporation of Et_2O. The compound crystallizes in the space group $P2_1/n$ with eight discrete mononuclear molecules in the unit cell. The asymmetric unit contains two conformations of the tetraorganotin compound, **1a** and **1b**. Selected bond lengths and angles are given in the caption of Fig. 1. In conformer **1a**, two methyl groups of the Me_3Sn moiety corresponding to C(31) and C(33) lie above the π-faces of the mesityl-rings and show short $H_3C\cdots C_{aryl}$ distances in the range 3.29–4.16 Å. Thus, the C–H···π distances of the CH_3 groups to the ring centroids ($C\cdots centroid_{aryl}$ distance) amount to 3.59 and 3.54 Å, respectively. These values are close to values that are ascribed to typical attractive C–H···π interactions with distances of approximately 3.75 Å [25]. However, the tin–carbon bond distances are in the expected range and the coordination geometry at the tin atoms is very close to tetrahedral without significant distortions. For example, an average C–Sn–C angle of 109.4(2)° is observed and the largest deviation is found for C(33)–Sn(1)–C(1) with 113.74(14)°. The values for the geometrical factors $\Delta\Sigma(\vartheta_{Sn(1)})$ = 12.3° and $\Delta\Sigma(\vartheta_{Sn(2)})$ = 7.7° are also indicative for tetrahedral coordination in both conformers. The geometrical factor was originally introduced to describe structures along the pathway tetrahedron–trigonal bipyramid but might also be used to describe the deviation of a tetrahedron from its ideal geometry. The position along the pathway is given by the difference of the sums of the hypothetical equatorial and axial angles $\Delta\Sigma(\vartheta)$, which is 0° for the ideal tetrahedron and 90° for the trigonal bipyramid [23]. In conformer **1b**, only one methyl group is located directly above a π-face of the mesityl-ring and the C–H···π distance of the corresponding CH_3 (C35) group to the ring centroid amounts to 3.41 Å. The methyl groups corresponding to C(34) and C(36) show $C\text{–}H\cdots\pi_{centroid}$ distances of 3.91 and 4.15 Å, respectively. Similar to conformer **1a**, no significant distortion from a tetrahedral coordination geometry at Sn(2) is observed. Thus, despite short $H_3C\cdots C_{aryl}$ distances free rotation of the Me_3Sn group in compound **1** is expected in solution, which is evidenced by a single ^1H NMR signal for the Me_3Sn moiety in $CDCl_3$ solution.

Single crystals of compound **2** suitable for single crystal X-ray diffraction analysis were obtained from toluene/CH_2Cl_2 by slow evaporation of the solvent. The compound crystallizes in the space group $P2_1/c$ with eight discrete mononuclear molecules in the unit



Scheme 5.

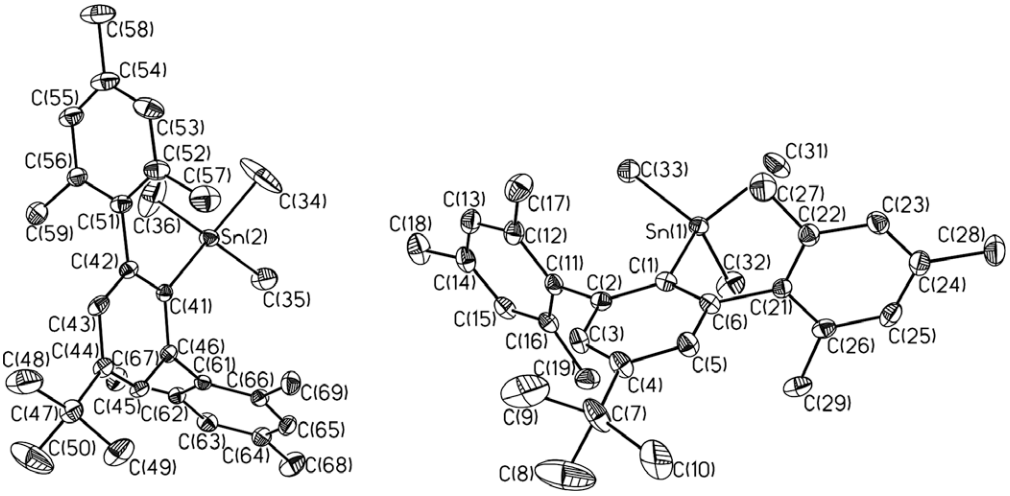


Fig. 1. General view (SHELXTL) of **1** showing 30% probability displacement ellipsoids and the atom numbering scheme of molecules **1a** (right) and **1b** (left). Selected bond distances [Å] and angles [°]: **1a** Sn(1)–C(1) 2.172(3), Sn(1)–C(31) 2.141(4), Sn(1)–C(32) 2.139(4), Sn(1)–C(33) 2.134(4), C(31)-centroid$_{C21-C26}$ 3.587, C(33)-centroid$_{C11-C16}$ 3.541; C(1)–Sn(1)–C(31) 113.64(14), C(1)–Sn(1)–C(32) 110.01(15), C(1)–Sn(1)–C(33) 113.74(14), C(31)–Sn(1)–C(32) 105.51(17), C(31)–Sn(1)–C(33) 106.93(17), C(32)–Sn(1)–C(33) 106.46(16); **1b** Sn(2)–C(41) 2.174(3), Sn(2)–C(36) 2.138(5), Sn(2)–C(35) 2.125(4), Sn(2)–C(34) 2.121(5), C(34)-centroid$_{C51-C56}$ 3.918, C(35)-centroid$_{C61-C66}$ 3.411; C(36)-centroid$_{C11-C56}$ 4.152; C(41)–Sn(2)–C(36) 111.91(17), C(41)–Sn(2)–C(35) 115.40(14), C(34)–Sn(2)–C(41) 112.54(19), C(34)–Sn(2)–C(35) 104.0(2), C(34)–Sn(2)–C(36) 108.0(3), C(35)–Sn(2)–C(36) 104.3(2).

cell. As it was observed for compound **1** the asymmetric unit contains two conformers, **2a** and **2b**, of which **2a** is shown in Fig. 2. Similar to the Me_3Sn moiety in compound **1**, the Me_2ClSn moiety in compound **2** is locked in two positions and the coordination geometry at the tin atoms might be described to be distorted tetrahedral although the average C–Sn–X angle (X = C, Cl) amounts to 109.0°. The distortion is demonstrated by the values for the geometrical factors $\Delta\Sigma(\vartheta_{Sn(1)}) = 31.1°$ and $\Delta\Sigma(\vartheta_{Sn(2)}) = 37.9°$, which are significantly larger than those of the tetraorganotin compound **1** [23]. Both the conformers of compound **2** contain two methyl groups close to the π-faces of the mesityl-rings and the Cl ligands are locked between the two bulky mesityl rings. The C–H···π distances of the CH_3 groups to the ring centroids (C ··· centroid$_{aryl}$ distance) in conformer **2a** amount to 3.44 and 3.56 Å, and in conformer **2b** to 3.52 and 3.55 Å. These short distances might be interpreted as a result of an attractive C–H···π interaction. This assumption is supported by a closer look at the C(31)/C(32)–Sn(1)–C(1) and C(34)/C(35)–Sn(2)–C(41) bond angles, which are in the range 116.8–119.0° and thus deviate strongly from an ideal tetrahedral angle. Furthermore, short CH_3 ··· Cl–Sn distances are observed with C ··· Cl distances in the range 3.62–3.95 Å, which is in the expected region reported for this type of week hydrogen bonds [26]. Noteworthy, in conformer **2a** the C ··· Cl distances amount to 3.73 and 3.79 Å (av. 3.75 Å), respectively, and in conformer **2b** to 3.62 and 3.95 Å (av. 3.79 Å). In conclusion, compound **2** shows a balanced interplay between different types of weak interactions leading to different conformations with the Cl ligand locked between the mesityl rings.

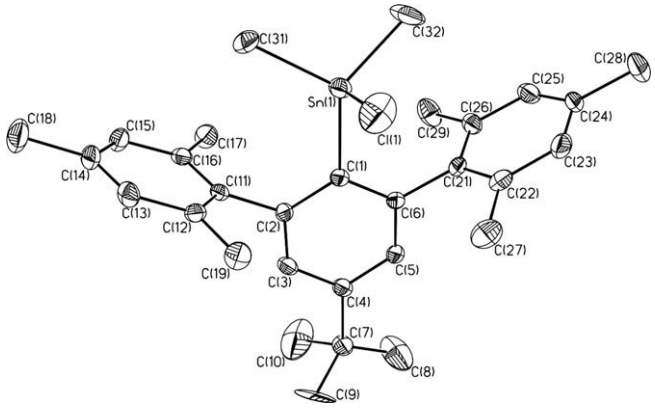


Fig. 2. General view (SHELXTL) of **2** showing 30% probability displacement ellipsoids and the atom numbering scheme. One out of two independent molecules, **2a** and **2b**, of the unit cell is shown. Selected bond distances [Å] and angles [°] of **2a**: Sn(1)–C(1) 2.160(4), Sn(1)–C(31) 2.124(4), Sn(1)–C(32) 2.128(5), Sn(1)–Cl(1) 2.3643(16), C(31)-centroid$_{C11-C16}$ 3.440, C(32)-centroid$_{C21-C26}$ 3.558; C(1)–Sn(1)–Cl(1) 106.16(12), C(31)–Sn(1)–C(32) 108.4(2), C(31)–Sn(1)–C(1) 117.23(17), C(32)–Sn(1)–C(1) 119.03(17), C(31)–Sn(1)–Cl(1) 101.29(15), C(1)–Sn(1)–Cl(1) 106.16(12).

Single crystals of the hydrated form of the organotin triflate **3** suitable for single crystal X-ray diffraction analysis were obtained from heptane/CH_2Cl_2 by slow evaporation of the solvent. The compound crystallizes in the space group Ccca with sixteen molecules in the unit cell. As a result of coordination of a water molecule, the coordination geometry at the tin atom is best described as trigonal bipyramidal with three carbon-atom-based ligands occupying the equatorial positions, and the oxygen atoms of the triflate group and the water molecule in axial positions (Fig. 3). The O(1)–Sn(1)–O(2) angle amounts to 176.16(10)° and the angles within the equatorial plane amount to 122.74(14)°, 121.79(13)° and 115.32(13)° for C(1)–Sn(1)–C(31), C(1)–Sn(1)–C(33) and C(31)–Sn(1)–C(33), respectively. Noteworthy, both methyl groups are centred above the π-faces of the mesityl-rings and the C–H···π distances of the CH_3 groups to the ring centroids (C ··· centroid$_{aryl}$ distance) amount to 3.42 and 3.46 Å. These values are among the shortest for the reported compounds in this work. However, the bond angle C(31)–Sn(1)–C(33) of 115.32(13)° might be interpreted to be the result of repulsion of the methyl groups from the π-ligand face rather than attraction. Thus, it might be concluded that the ideal C ··· centroid$_{aryl}$ distance of a $SnCH_3$ group amounts to approximately 3.4–3.5 Å.

In addition to the water molecule coordinated at the tin atom, a water molecule (O(5), site occupation 50%) is bonded to the triflate group via a strong hydrogen bond. The corresponding bond distance O(3)–O(5) amounts to 2.775(5) Å. As a result of additional hydrogen bonding using the oxygen atoms O(3) and O(4) of the triflate ligand and the oxygen atoms O(1) and O(5) of the water molecules, compound **3** forms an one-dimensional hydrogen-bonded

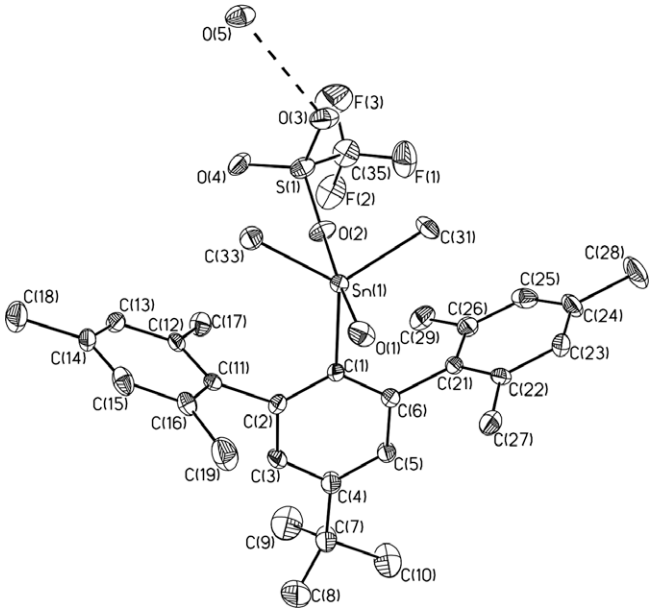


Fig. 3. General view (SHELXTL) of the hydrated form of **3** showing 30% probability displacement ellipsoids and the atom numbering scheme. The position of O(5) shows an occupation factor of 50%. Selected bond distances [Å] and angles [°]: Sn(1)–C(1) 2.131(3), Sn(1)–C(31) 2.118(4), Sn(1)–C(33) 2.114(4), Sn(1)–O(1) 2.273(3), Sn(1)–O(2) 2.351(3), C(31)-centroid$_{C21-C26}$ 3.416, C(33)-centroid$_{C11-C16}$ 3.456, O(1)–O(4′) 2.705(4), O(1)–O(5′) 2.731(4), O(3)–O(5) 2.775(5); O(1)–Sn(1)–O(2) 176.16(10), C(1)–Sn(1)–O(1) 94.70(13), C(1)–Sn(1)–O(2) 88.66(12), C(1)–Sn(1)–C(31) 122.74(14), C(1)–Sn(1)–C(33) 121.79(13), C(31)–Sn(1)–C(33) 115.32(13), C(31)–Sn(1)–O(1) 88.55(14), C(31)–Sn(1)–O(2) 88.07(13), C(33)–Sn(1)–O(1) 90.44(14), C(33)–Sn(1)–O(2) 89.36(13).

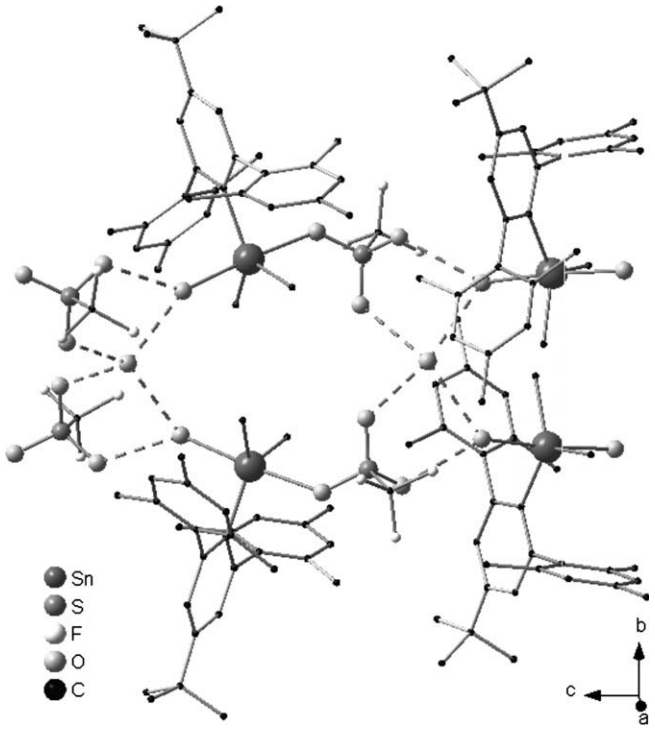


Fig. 4. View of hydrated **3** along the a-axis showing the hydrogen bond pattern that extends in the direction of the *c*-axis.

polymer (Fig. 4). The hydrogen bond distances O(1)–O(4) 2.705(4) Å and O(1)–O(5) 2.731(4) Å are indicative for strong hydrogen bonds, which demonstrates the capability of the triflate group to act as good hydrogen bond acceptor. Some additional water is found in the crystal lattice that does not form hydrogen bonds and is partially lost upon drying. The IR spectrum shows two absorption bands at 3259 cm^{-1} and 3414 cm^{-1} corresponding to the hydrogen bonded water molecules and water trapped in the crystal lattice.

Single crystals of distannoxane **5** suitable for single crystal X-ray diffraction analysis were obtained from *n*-hexane/CH_2Cl_2 by slow evaporation of the solvent. The compound crystallizes in the space group $P2_1/c$ with four discrete mononuclear molecules in the unit cell. Selected bond lengths and angles are given in the caption of Fig. 5. The coordination geometry at tin is best described as tetrahedral. This is nicely demonstrated by the values for the geometrical factors $\Delta\Sigma(\vartheta_{Sn(1)}) = 12.1°$ and $\Delta\Sigma(\vartheta_{Sn(2)}) = 8.6°$, which are close to the ideal value of 0° for tetrahedral coordination [23]. The Sn(1)–O(1)–Sn(2) angle of 127.35(13)° is comparable to the corresponding bond angle in $(Ph_3Sn)_2O$ (137.3°) [27], but deviates strongly from the linear arrangement reported for the bulky (*tert*-$Bu_3Sn)_2O$ and $[(PhCH_2)_3Sn]_2O$ [28]. Noteworthy, the analogue terphenyldimethyldisiloxane shows an O–Si–O angle of 141.9° and a slightly increased value $\Delta\Sigma$ (ϑ_{Si}) = 15.7° [29]. Similar to the other reported compounds, the methyl groups at tin are in proximity to the π-faces of the mesityl-rings and the C–H···π distances of the CH_3 groups to the ring centroids (C···centroid$_{aryl}$ distance) are in the range 3.39–3.57 Å. (Table 1)

3.4. Structures in solution

^{119}Sn chemical shifts, $^1J(^{119}Sn–^{13}C)$ and $^2J(^{119}Sn–^1H)$ coupling constants were shown to be sensitive measures for the elucidation

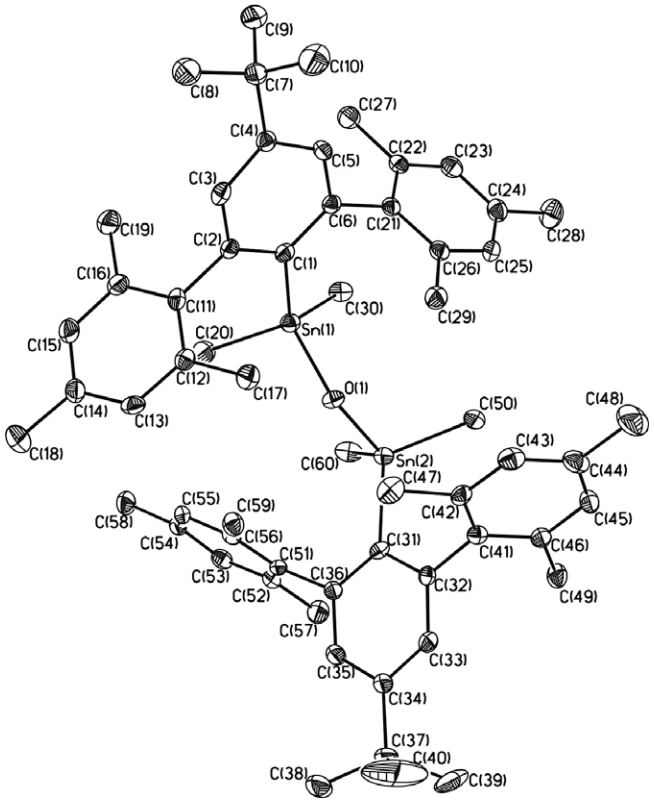


Fig. 5. General view (SHELXTL) of **5** showing 30% probability displacement ellipsoids and the atom numbering scheme. Selected bond distances [Å] and angles [°] corresponding to Sn(1): Sn(1)–C(1) 2.169(4), Sn(1)–C(20) 2.139(4), Sn(1)–C(30) 2.132(4), Sn(1)–O(1) 1.908(2), C(20)-centroid$_{C11-C16}$ 3.565, C(30)-centroid$_{C21-C26}$ 3.394; C(1)–Sn(1)–O(1) 108.59(12), C(20)–Sn(1)–C(30) 106.64(17), C(1)–Sn(1)–C(20) 114.49(15), C(1)–Sn(1)–C(30) 113.10(15), O(1)–Sn(1)–C(20) 106.76(14), O(1)–Sn(1)–C(30) 106.83(13).

Table 1
Crystallographic data for compounds **1**–**3** $2.5H_2O$ and **5**

Compound number	**1**	**2**	**3** $2.5H_2O$	**5**
Empirical formula	$C_{31}H_{42}Sn$	$C_{30}H_{39}ClSn$	$C_{31}H_{39}F_3O_3SSn\ 2.5H_2O$	$C_{60}H_{78}OSn_2$
Formula weight	533.34	553.75	712.41	1052.60
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$Ccca$	$P2_1/c$
a (Å)	17.0047(2)	18.3994(2)	22.6827(4)	13.0633(2)
b (Å)	14.1320(3)	16.9166(2)	38.1207(6)	12.3163(2)
c (Å)	24.2176(3)	18.8325(2)	16.9599(4)	34.8121(5)
β (°)	90.4415(3)	99.3756(11)		100.2137(5)
V (Å^3)	5819.57(13)	5783.44(11)	14664.9(5)	5512.21(15)
Z	8	8	16	4
φ_{calc} (g cm^{-3})	1.217	1.272	1.291	1.268
μ (mm^{-1})	0.893	0.990	0.803	0.943
Crystal size (mm^3)	0.08 × 0.05 × 0.05	0.10 × 0.07 × 0.07	0.25 × 0.23 × 0.20	0.15 × 0.15 × 0.13
θ Range (°)	3.12–27.47	3.26–27.49	3.02–25.34	3.07–25.34
Reflection collected	47107	43417	43012	40713
Independent reflection	13128	12840	6695	10041
R_{int}	0.026	0.037	0.054	0.036
Completeness to 2θ (%)	98.4	96.7	99.5	99.5
Goodness-of-fit (F^2)	1.023	0.985	0.838	0.970
R_1 [$I > 2\sigma(I)$]	0.0449	0.0504	0.0348	0.0363
wR_2 (all data)	0.1147	0.1247	0.0686	0.0863
Largest differrence in peak and hole (e Å^{-3})	0.812/−0.658	1.216/−1.410	0.385/−0.352	0.545/−0.588

of coordination numbers and geometries of organotin compounds with similar substituent patterns [30–32]. High field shift of the ^{119}Sn NMR signal and an increase of the $^2J(^{119}Sn–^1H)$ coupling constants are usually indicative for an increase in the coordination number. The ^{119}Sn and ^{1}H NMR data for compounds **1**–**5** are listed in Table 2. The ^{119}Sn NMR as well as the ^{1}H NMR signal of the $SnCH_3$ group in the bulky Ar^*SnMe_3 (**1**) (δ ^{119}Sn −51.3, δ ^{1}H −0.60) is shifted to a higher field in comparison to $PhSnMe_3$ (δ ^{119}Sn −29.4, δ ^{1}H 0.28). However, this is rather a result of an increasing coordination number at tin but a result of the anisotropic ring current effect of the mesityl groups. The $SnCH_3$ groups are close to the π-faces of the mesityl rings and thus are highly shielded. This phenomenon is observed for all of reported compounds.

In this work, the $^2J(^{119}Sn–^1H)$ coupling constant is better suited to study the coordination at the tin atom in solution. According to *Lockhart* and *Manders*, the $CH_3–Sn–CH_3$ angle in methyltin compounds can be calculated according to the empirical formula $\theta = 0.0161\ (^2J)^2 - 1.32(^2J) + 133.4$ [32]. In agreement with the solid state structural analysis, the $^2J(^{119}Sn–^1H)$ coupling constant of 55 Hz for compound **1** is in agreement with a tetrahedral coordination. Similar coupling constants are observed for compounds **2**, **4** and **5**, and thus are indicative for tetrahedral coordination at the tin atoms similar to **1**. In contrast, the organotin triflate **3** shows a solvent-dependent coordination behaviour. In $CDCl_3$, a $^2J(^{119}Sn–^1H)$ coupling constant of 58 Hz is observed which increases to 70 Hz in CD_3CN. The latter value is in agreement with an $CH_3–Sn–CH_3$ angle of 120° and indicates pentacoordination at the tin atom, whereas the former is indicative for tetracoordination. The change of coordination is also demonstrated by ^{119}Sn NMR. The ^{119}Sn chemical shift of compound **3** in non-coordinating solvents is found between 150 and 170 ppm, whereas in CD_3CN a high-field shift to −24.3 ppm is observed as a result of the coordination of acetonitrile. The strong coordination of acetonitrile is demonstrated by electrospray ionization mass spectrometry using CH_3CN as a solvent. In addition to the peak assigned to $[M–OTf]^+$, the acetonitrile adduct $[M–OTf+CH_3CN]^+$ is observed as a prominent peak.

Table 2
Selected ^{119}Sn and ^{1}H NMR data of compounds **1**–**5**[a]

Compound	δ^{119}Sn/ppm	δ^1H (CH_3)/ppm	^1J (^{1}H–^{119}Sn)/Hz
$PhSnMe_3$	−29.4 [30]	0.28 [33]	56 [33]
Ar^*SnMe_3 (**1**)	−51.3[b]	−0.60	55
Ar^*SnMe_2Cl (**2**)	81.8[b]	−0.22	58
$Ar^*SnMe_2(OTf)$ (**3**)	168.8[b]	0.04	58
	151.1[c]		
	−24.3[d]	−0.20[d]	70[d]
$Ar^*SnMe_2(OH)$ (**4**)	37.7	−0.12	60
$(Ar^*SnMe_2)_2O$ (**5**)	44.0	−0.19	59

[a] ^{1}H and ^{119}Sn NMR spectra were recorded from $CDCl_3$ solution if not otherwise stated.
[b] CH_2Cl_2/D_2O capillary.
[c] Toluene/D_2O capillary.
[d] CD_3CN.

4. Conclusion

We have prepared a novel sterically congested tetraorganotin compound, (4-*tert*-butyl-2,6-dimesitylphenyl)trimethylstannane (**1**), and its reactivity is studied with a special focus on transmetalation. The results demonstrate that compound **1** is not suitable to act as a transfer reagent for the bulky terphenyl ligand, but is suitable for a methyl group transfer. Selective tin–methyl bond cleavage with reagents such as HOTf, $HgCl_2$ and $BiCl_3$ was observed. It is well known that aryltrimethyltin compounds bearing less bulky aryl ligands show a reverse selectivity in reactions with HOTf and $HgCl_2$. However, we have shown that in the case of $BiCl_3$ the cleavage of both Sn–methyl and Sn–aryl bonds results for compounds such as $PhSnMe_3$. Thus, the reaction of Ar^*SnMe_3 (**1**) to give selectively Ar^*SnMe_2Cl (**2**) upon reaction with $BiCl_3$ seems to be a rare example of selective tin–methyl bond cleavage in favour of tin–aryl bond cleavage. The reactivity is assumed to be partially a result of the low solubility of $MeBiCl_2$, but the major reason for the selectivity is ascribed to a steric effect by the terphenyl ligand. Additionally, both methyl groups in the reaction product **2** are close to the π-faces of the mesityl-rings with an average C–H···π ring centroid distance of 3.52 Å and thus contribute to the stabilisation as well as to the high solubility of the reaction product **2**. This is assumed to additionally favour the selective tin–methyl bond cleavage in **1**.

5. Supplementary material

CCDC 670709–670711 and 670712 contain the supplementary crystallographic data for **1**–**3** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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