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Phosphanyl-substituted tin half-sandwich complexes†

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Phosphanyl-substituted tin(II) half sandwich complexes are reported. Due to the Lewis acidic tin center and Lewis basic phosphorous atom they form head-to-tail dimers. Their properties and reactivities were investigated both experimentally and theoretically. Furthermore, related transition metal complexes of these species are presented.

Introduction

Organometallic complexes exhibiting η^5-bonded cyclopentadienyl (Cp) ligands are well-known species nowadays. The most common variants are complexes with two η^5-Cp ligands, commonly referred to as metallocenes, and complexes with only one η^5-Cp ligand, usually referred to as half-sandwich complexes.[1] While many examples of such species are known for transitions metals, this structural motif can also be found in *p*-block chemistry.[2] For instance, the first example of a group 14 half-sandwich complex was cyclopentadienyltin chloride, **CpSnCl**, which was reported by Noltes *et al.* in 1972,[3] about 16 years after Fischer and Grubert had described the related metallocene parent compound stannocene, **Cp_2Sn**,[4] and a few years before Lappert *et al.* and Veith reported the first diorganostannylenes with σ-bonded substituents (Chart 1).[5] While the latter are commonly regarded as the first examples of stable diorganostannylenes, stannocene, **Cp_2Sn**, and cyclopentadienyltin chloride, **CpSnCl**, are also divalent tin(II) compounds of the general type R_2Sn, but differ significantly from "typical" stannylenes in their properties and reactivities. Among other things, the central tin atoms in **Cp_2Sn** and **CpSnCl** exhibit mostly electrophilic character but only minor nucleophilic character.[6]

Nowadays, different half-sandwich complexes of tin(II) with various cyclopentadienyl groups and different substituents bound to the tin atom are known, but noteworthy, the substitution patterns on the Cp ligands are almost exclusively limited to H atoms, or alkyl and aryl groups.[2b,3,7,8] Donor groups at the Cp ligands of tin half-sandwich complexes on the other hand are unknown as of yet.

Since low valent tin species have attracted wide attention for their applications ranging from coordination chemistry to small molecule activation and homogeneous catalysis,[9] and following our recent studies on phosphanyl-functionalized stannocenes and other main-group metallocenes,[10] we herein report the related phosphanyl-functionalized tin half-sandwich complexes, which exhibit Lewis amphiphilic character due to a Lewis acidic tin atom and a Lewis basic phosphanyl group attached to the Cp ligand.

Results

Recently, our group reported on diphosphanylstannocenes, which exhibit moderate Lewis amphiphilic character, due to Lewis basic phosphorus centres and mildly Lewis acidic tin atoms.[10] Following established procedures for the synthesis of tin(II) half-sandwich complexes,[2,7] we reacted

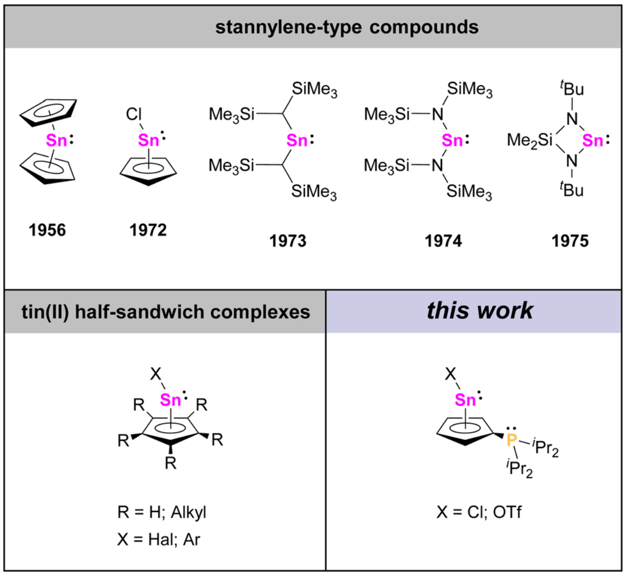

Chart 1 Overview of selected R_2Sn(II)-type compounds.

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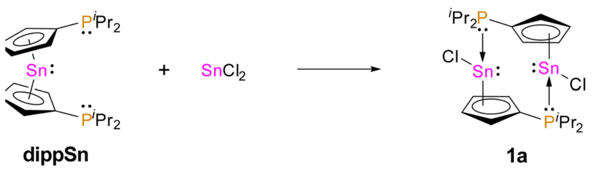
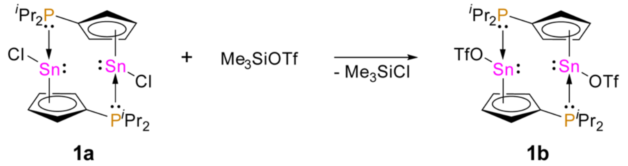
bis(diisopropylphosphanyl)stannocene, **dippSn**, with tin(II) chloride and obtained the heteroleptic system **1a** (Scheme 1). Furthermore, the corresponding triflate **1b** could be obtained, by reacting **1a** with trimethylsilyltriflate, in analogy to literature reports (Scheme 2).[11]

To gain further insight into the electronic properties of phosphanyl-functionalized half-sandwich compound **1a,b** and to assess whether the **CpSnCl** and **1a,b** do indeed possess more Lewis acidic central atoms than the related homoleptic metallocenes, we performed DFT calculations to obtain fluoride ion affinities (FIA) and global electrophilicity indices (GEI) (Fig. 1).[12]



Scheme 1 Synthesis of **1a** by the reaction of **dippSn** with $SnCl_2$.



Scheme 2 Synthesis of **1b** *via* treatment of **1a** with Me_3SiOTf.

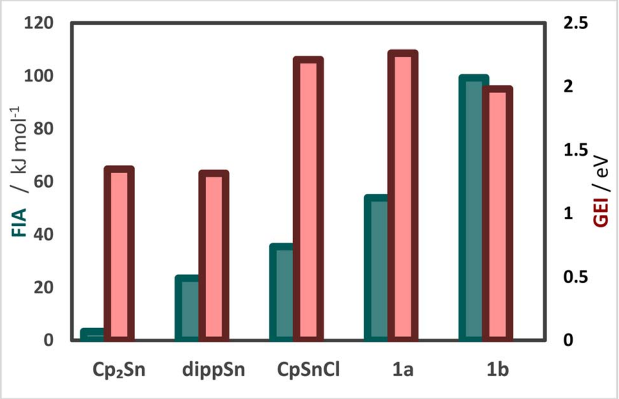


Fig. 1 Fluoride ion affinities (FIA; green), and global electrophilicity indices (GEI; red), for Cp_2Sn, **dippSn**, **CpSnCl**, **1a** and **1b** calculated at B3LYP-D3/def2-TZVP.

The results suggest that the metallocene-type compounds **Cp_2Sn** and **dippSn** possess GEIs of 1.32 to 1.35 eV, while GEIs of 1.98 to 2.26 eV are computed for **CpSnCl** and **1a,b**. Similarly, lower FIAs are computed for **Cp_2Sn** and **dippSn** than for **CpSnCl** and **1a,b**. Thus, these results suggest that **1a,b** do indeed possess a more pronounced Lewis acidity than their stannocene counterparts. To obtain experimental evidence for this, we conducted measurements following the Gutmann–Beckett method (Table 1).[13] Indeed, significantly higher $\Delta\delta^{31}$P values of 14.9 to 17.8 ppm and acceptor numbers (ANs) of 32.9 to 39.3 are obtained for **CpSnCl** and **1a,b**, than for their metallocene counterparts, **Cp_2Sn** and **dippSn**, which is in qualitative agreement to the afore discussed DFT calculations.

1a and **1b** exhibit ^{119}Sn NMR chemical shifts of δ^{119}Sn(**1a**)(CP/MAS) = −709 and δ^{119}Sn(**1b**)(CP/MAS) = −928, which is rather unusual for a tin(II) half sandwich compound (*e.g.* δ^{119}Sn(**CpSnCl**)(CP/MAS) = −1580).[14] Moreover, the solid state ^{31}P{^{1}H} NMR spectra, exhibit signals at δ^{31}P(**1a**)(CP/MAS) = 4.3 and δ^{31}P(**1b**)(CP/MAS) = 19.2, accompanied by $^{117/119}$Sn satellites with coupling constants of $^1J_{PSn}$ = 950 Hz (**1a**), $^1J_{PSn}$ = 1460 Hz (**1b**), clearly reflecting an Sn–P bonding interaction. To gain further insight into the structures of **1a** and **1b**, we determined the crystal structures *via* X-ray diffraction. **1a** crystallized in the monoclinic space group $P2_1/c$ and **1b** in the triclinic space group $P\bar{1}$, each with one formula unit ($(({}^iPr_2PC_5H_4)SnX)$) per asymmetric unit. Interestingly, due to its Lewis amphiphilic character and inability for intramolecular quenching, **1a,b** form head-to-tail dimers with Sn–P contacts of 279.08(13) pm (**1a**) and 279.58(4) pm (**1b**) (Fig. 2 and 3). Compared to related compounds, these Sn–P bonds are relatively long ($[(TMS_2N)_2Sn(Cl)PPh]_2$: d(Sn–P) = 257.06(6) pm (ref. 15)). Furthermore, the Cp rings in **1a** and **1b** are bound in what may best be described as a heavily distorted η^5 coordination. Although the Sn–C^{Cp} bonds are relatively unequal (**1a**: 243.56(44) to 315.68(43) pm; **1b**: 245.73(18) to 300.45(19) pm), the C–C bonds within the Cp rings are fairly uniform (**1a**: 138.81(57) to 141.65(64) pm; **1b**: 139.48(24) to 142.84(22) pm), indicating a certain degree of aromaticity.

The Sn–Cl bond length in **1a** is 247.54(12) pm, which is considerably shorter than in **CpSnCl** (324 to 326 pm[16]), but this is related to the different structure of **CpSnCl** in the solid-state.

Table 1 ^{31}P NMR chemical shifts and acceptor numbers (AN) of triethylphosphine oxide and corresponding adducts with Cp_2Sn, **dippSn**, **CpSnCl**, and **1a,b**

Compound	$\delta^{31}P^a$ (ppm) ($\Delta\delta^{31}P = \delta^{31}P_{sample} - 46.2$)	AN ($2.21 \times (\delta^{31}P_{sample} - 46.2)$)
Et_3PO	46.2	0
Cp_2Sn·$OPEt_3$	49.4 ($\Delta\delta^{31}P = 3.4$)	7.5
dippSn·$OPEt_3$	46.7 ($\Delta\delta^{31}P = 0.5$)	1.1
CpSnCl·$OPEt_3$	61.1 ($\Delta\delta^{31}P = 14.9$)	32.9
1a·$OPEt_3$	61.8 ($\Delta\delta^{31}P = 15.6$)	34.5
1b $OPEt_3$	64.0 ($\Delta\delta^{31}P = 17.8$)	39.3

[a] C_6D_6; r.t.

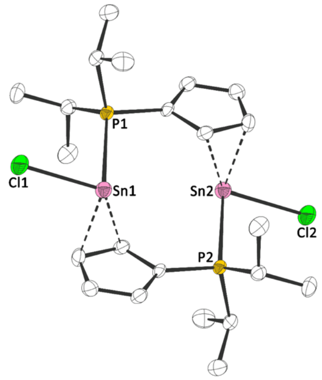


Fig. 2 Molecular structure of **1a** in the crystal (displacement ellipsoids at 50% probability level, hydrogen atoms omitted for clarity). Selected bond lengths [pm]: Sn–Cl: 247.54(2); Sn–P: 279.08(2).

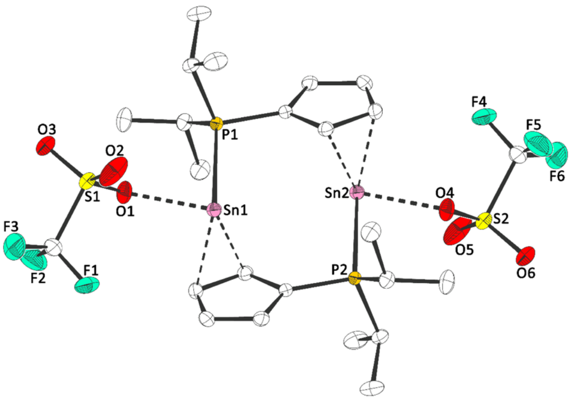


Fig. 3 Molecular structure of **1b** in the crystal (displacement ellipsoids at 50% probability level, hydrogen atoms omitted for clarity). Selected bond lengths [pm]: Sn–O: 233.48(14); Sn–P: 279.58(4).

Noteworthy, the ^{31}P NMR chemical shifts in solution are very similar to the ones observed in the solid-state ($\delta^{31}\mathrm{P}(\mathbf{1a})(\mathrm{CD_2Cl_2}) = 3.6$ and $\delta^{31}\mathrm{P}(\mathbf{1b})(\mathrm{CD_2Cl_2}) = 19.8$), suggesting the dimeric structures may be persistent in solution. Dimeric/oligomeric structures are not uncommon for tin(II) half-sandwich halides in the solid state, although **CpSnCl** forms a chloro-bridged polymer.[16] To investigate the dimerization energy of **1a**, we conducted DFT calculations (Fig. 4).

These calculations clearly suggest that a head-to-tail dimer with dative Sn–P bonds is preferred over a chloro-bridged structure and that the overall dimerization energy is 167.7 kJ mol^{-1}. This is in line with the assumption that **1a** and **1b** exist predominantly as dimers in solution at room temperature.

Inspection of the frontier orbitals reveals that the LUMO has a large coefficient at the tin atom in the shape of a p orbital, which is typical for stannylene-type compounds. The HOMO corresponds to the lone-pair at the phosphorous atom, in-line with the compounds Lewis amphiphilicity and its head-to-tail dimerization, while the lone-pair at the tin atom is lower in energy and corresponds to the HOMO-3 (Fig. S25†).[17]

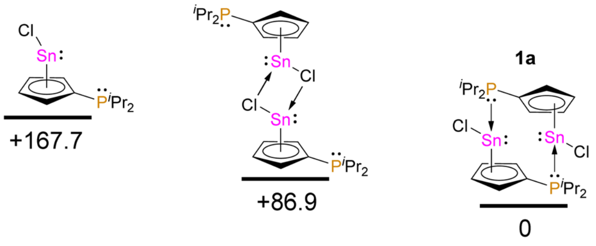
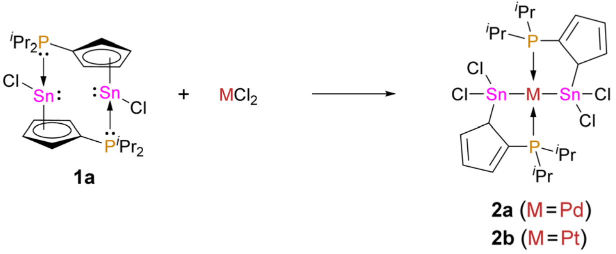


Fig. 4 Relative energy differences between monomeric **1a**, related chloro-bridged dimer, and P–Sn dimer, **1a**, calculated at B3LYP-D3/def2-SVP (energies in kJ mol^{-1}).

As many phosphines and tetrylenes are potent ligands for metal fragments and the latter can undergo oxidative addition reactions, we probed the reactivity of **1a** towards metal halides and reacted it with palladium dichloride and platinum dichloride (Scheme 3). In both cases, an oxidative addition reaction at the low valent tin centres takes place and the corresponding stannylide complexes **2a,b** were obtained. Storage of solutions of **2a,b** at 253 K afforded red (**2a**) and orange (**2b**) crystals, suitable for single crystal X-ray diffraction analysis. Both compounds crystallize in the monoclinic space group *C*2/*c* with half a formula unit ((${}^i\mathrm{Pr_2PC_5H_4})\mathrm{SnCl_2M_{0.5}}$) per asymmetric unit (Fig. 5). The structures show two stannylide ligands per metal centre coordinated in a bidentate square-planar fashion with Sn–[M] bond lengths of 256.34(4) pm ([M] = Pd)/257.02(4) pm ([M] = Pt) and P–[M] bond length of 233.48(4) pm ([M] = Pd)/232.58(10) pm ([M] = Pt). This is in-line with bond lengths found in related complexes ($[\mathrm{ClPd(SnCl_2Ph)(PPh_2Py)}]_2$]:[18] 252.49(3) pm; $[\mathrm{Pt(Sn(CH_3)_2(\mu\text{-}C_2H_4)(PPh_2))_2}]$:[19] 259.73(5) to 260.47(5) pm). Two short and three long C–C bonds within the Cp rings in **2a,b** indicate a diene-type situation, with η^1/σ bound tin atoms. The coordination geometry of the group 10 metal is distorted square planar (**2a**: Sn–Pd–P: 82.2°, 97.7°; **2b**: Sn–Pt–P: 82.1°, 97.8°).

With the aim of increasing the Lewis acidity of the tin centre, we explored the possibility to generate a (diisopropylphosphanyl)-cyclopentadienyl tin cation. However, treatment of **1a** with lithium and sodium salts of weakly coordinating anions (*e.g.* lithium hexafluorophosphate and sodium tetrakis-(pentafluorophenyl)borate) to abstract the chloride and obtain the corresponding stannyliumylidene were unsuccessful and led to complex mixtures of products. We therefore investigated the



Scheme 3 Synthesis of **2a,b** by the reaction of **1a** with (COD)PdCl$_2$ and PtCl$_2$.

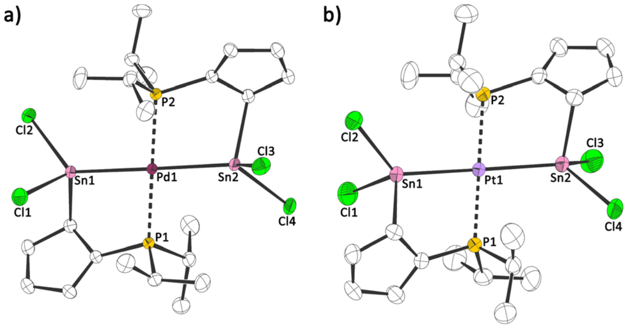


Fig. 5 Molecular structures of (a) **2a** and (b) **2b** in the crystal (displacement ellipsoids at 50% probability level, hydrogen atoms omitted for clarity). Selected bond lengths [pm] and angles [°]: (a): Sn–Pd: 256.34(1); P–Pd: 233.48(1); Sn–Pd–P: 82.185(1); Sn–Pd–P: 97.735(1); (b): Sn–Pt: 257.02(1); P–Pt: 232.58(1); Sn–Pd–P: 82.131(1); Sn–Pd–P: 97.824(1).

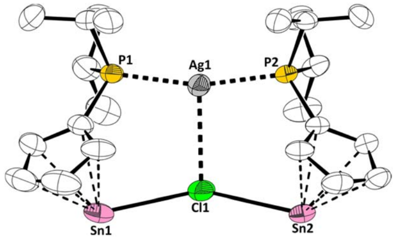
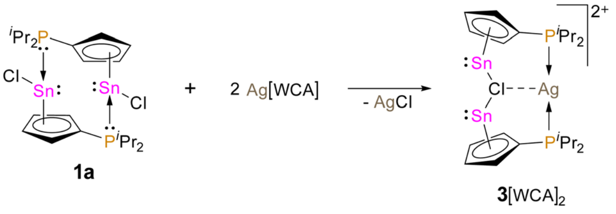


Fig. 6 Molecular structure of **3** in the crystal (displacement ellipsoids at 50% probability level, hydrogen atoms and anions omitted for clarity). Selected bond lengths [pm]: Sn–Cl: 283.66(18)/285.26(19); P–Ag: 238.49(13)/238.57(15); Ag–Cl: 285.03(17); Sn–Cp$^{\text{centriod}}$: 223.51(5)/224.50(4).

possibility of using a silver tetrakis(perfluoro-*tert*-butoxy) aluminate salt as chloride abstraction agent. This strategy was reported to be successful for the generation of a cyclopentadienyltin cation, by Krossing *et al.*[20] Thus, we reacted **1a** with silver tetrakis(perfluoro-*tert*-butoxy)aluminate in dichloromethane and indeed a chloride abstraction and precipitation of silver chloride was observed, along with the arise of a new resonance in the ^{119}Sn{^{1}H} NMR spectrum at δ^{119}Sn NMR = −2122 (Scheme 4).

Storage of the reaction solution at 253 K resulted in the formation of colorless crystals suitable for single crystal X-ray diffraction. Most interesting, the solid-state structure did not reveal the targeted cation, but a complex with two (diisopropylphosphanyl)cyclopentadienyl tin cation units complexing a silver chloride moiety (Fig. 6). The Sn–Cp bonding in silver complex **3** can best be described as distorted η^5, with relatively uniform C–C bond lengths within the Cp ring (138.81(13) to 143.69(74) pm), indicating a certain degree of aromaticity. The Sn–Cl bonds measure 283.66(18) and 285.26(19) pm which is significantly longer than in **1a** (247.54(2) pm), in-line with the Sn–Cl–Sn multi-centre bond, but shorter than Sn–Cl contacts in **CpSnCl** (324 to 326 pm (ref. 7*a*)). The P–Ag bonds in **3** are 238.49(13) and 238.57(15) pm, which is slightly shorter than in comparable complexes ([(Ph$_3$P)$_2$AgCl]:[16] 246.7(2)/247.2(2) pm; [(Ph$_3$P)$_3$AgCl]:[21] 252.0(1)/255.2(1)/255.6(1) pm). Most interestingly, the Ag–Cl distance in **3** measures 285.03(17) pm, which is significantly longer than what is found in "traditional" silver chloride phosphine complexes ([(Ph$_3$P)$_3$AgCl]:[21] 255.2(1) pm; [(Ph$_3$P)$_2$AgCl]:[16] 259.6(2) pm), indicating a rather weak Ag–Cl bonding interaction. This elongation results from the unique bonding motive in **3**, in which the chloride atom exhibits a formal coordination number of three, as it is bonded to the two tin atoms in addition to the silver centre, giving it a distorted trigonal planar geometry (Ag–Cl–Sn: 100.7°, 103.3°; Sn–Cl–Sn: 151.1°). Similarly, the silver atom also exhibits a distorted trigonal planar coordination environment (P–Ag–Cl: 98.8°, 96.3°; P–Ag–P: 164.8°). The structure of **3** is maintained in solution, as the ^{31}P{^{1}H} NMR spectrum shows two doublet which arises from coupling with the ^{107}Ag and ^{109}Ag nuclei ($^{1}J_{^{31}\text{P}^{107}\text{Ag}} = 471$ Hz; $^{1}J_{^{31}\text{P}^{109}\text{Ag}} = 544$ Hz). However, prolong stirring of a solution of **3**[WCA]$_2$ in benzene-d_6 led to decomposition.



Scheme 4 Synthesis of **3**[WCA]$_2$ by the reaction of **1a** with Ag[WCA] (WCA = Al(OC(CF$_3$)$_3$)$_4$).

Conclusions

We were able to synthesize the first phosphanyl substituted tin(II) half-sandwich complexes, **1a,b**, which properties differ significantly from previously reported **CpSnCl**. In the solid state, head-to-tail dimers with Sn–P bonds are observed, which are maintained in solution. Transition metal complexes **2a** and **2b** could be synthesized by oxidative addition reactions, which both exhibit a square planar geometry at the central transition metal atom in the solid state. By the reaction of **1a** with silver tetrakis(perfluoro-*tert*-butoxy)aluminate, a cationic silver chloride complex, **3**, with two tin half-sandwich moieties was obtained.

Conflicts of interest

There are no conflicts to declare.

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