



Full paper/Mémoire

Dative P→Sn interactions in *ortho*-phenylene phosphine-stannanesTzu-Pin Lin^a, Pauline Gualco^b, Sonia Ladeira^c, Abderrahmane Amgoune^b, Didier Bourissou^{b,*}, François P. Gabbaï^a^a Department of Chemistry, Texas A&M University, College Station, 77843–3255 Texas, USA^b University of Toulouse, UPS, CNRS, LHFA UMR 5069, LHFA, 118, route de Narbonne, 31062 Toulouse, France^c Structure fédérative Toulousaine en chimie moléculaire, FR 2599, 118, route de Narbonne, 31062 Toulouse cedex 9, France

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ABSTRACT

Monophosphine and diphosphine-stannane compounds **1** and **2** are shown spectroscopically, structurally and theoretically to present rare intramolecular P→Sn interactions.

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R É S U M É

La présence d'interactions P→Sn intramoléculaires est démontrée spectroscopiquement, structuralement et théoriquement au sein des composés monophosphine- et diphosphine-stannane **1** et **2**.

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1. Introduction

The ability of tin (IV) to form compounds with coordination numbers greater than 4 through donor-acceptor interactions with Lewis bases has been largely explored over the last decades. The ensuing hypervalent derivatives have attracted considerable interest as models for the intermediate/transition-state structures of nucleophilic substitutions at tetracoordinate group 14 centers [1]. Most of these stannane adducts involve hard *N*- or *O*-based donors, and comparatively, little is known with soft phosphine donors. About ten *P*-adducts have been structurally authenticated with SnX₄ and RSnX₃ com-

pounds (X = halogen) [2], but only two (adducts **I** and **II**) with the less Lewis acidic R₃SnX moieties are currently known (Fig. 1) [3,4]. High-field shifts of the ¹¹⁹Sn NMR resonance signals compared to the related tetracoordinated tin compounds and short P–Sn distances are diagnostic for the presence of P→Sn interactions that are favored in both compounds by rather flexible linkers, resulting in unstrained 5-membered ring structures.

Our interest in the chemistry of ambiphilic compounds [5,6] has led us to synthesize main group compounds combining both donor and acceptor groups. As part of this effort, we observed that phosphine-boranes based on the *ortho*-phenylene backbone (type **A**, Fig. 2) sometimes display an intramolecular P–B interaction leading to the formation of a strained four membered-ring (Fig. 2) [7].

In this article, we seek to determine if related donor-acceptor interactions could be observed in *ortho*-phenylene-based phosphine-stannane derivatives (type **B**, Fig. 2),

* Corresponding author.

E-mail addresses: dbouriss@chimie.ups-tlse.fr (D. Bourissou), gabbaï@mail.chem.tamu.edu (F.P. Gabbaï).

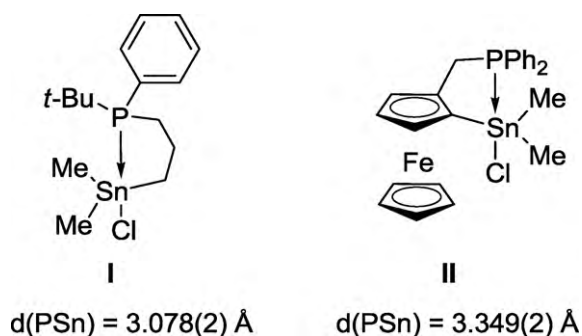
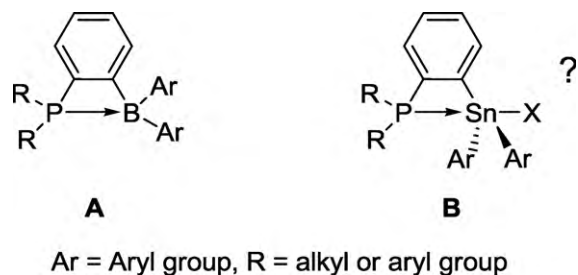
Fig. 1. Adducts **I** and **II**.

Fig. 2. Type A phosphine-boranes.

despite the weaker Lewis acidity of the tin(IV) derivatives vs. boranes (Fig. 3).

2. Results and discussion

Reaction of *ortho*-(Ph₂P)C₆H₄Li [6d,8] with Ph₂SnCl₂ in Et₂O afforded *ortho*-(Ph₂P)C₆H₄(SnPh₂Cl) (**1**) which was isolated as a colorless solid in 29% yield. This compound

has been characterized by multinuclear NMR spectroscopy and elemental analysis. The phosphorus center gives rise to a ³¹P NMR resonance at –1.0 ppm (*J*_{Sn–P} = 18.1 Hz) which can be compared to the value of –4 ppm observed for Ph₃P. Interestingly, the ¹¹⁹Sn NMR resonance appears as a singlet at –101.7 ppm, a chemical shift which is distinctly upfield from that observed for Ph₃SnCl (–45 ppm) [9]. This situation is reminiscent of that encountered in the known *ortho*-(*i*-Pr₂P)C₆H₄)₂SnPhCl (**2**) [10] which gives rise to a ¹¹⁹Sn NMR resonance at –126.4 ppm. In fact, the ¹¹⁹Sn NMR chemical shifts of **1** and **2** approach those reported for hypervalent tin species adducts such as [2-(Me₂NCH₂)C₆H₄]SnPh₂Cl (–176.9 ppm) [11] or ClPh₃Sn-pyridine (–219 ppm) [12]. These spectroscopic observations can be reconciled by invoking the presence of an intramolecular P→Sn interaction in **1** and **2**. Because the rigidity of the *ortho*-phenylene backbone as well as the diverging orientation of the phosphine and stannane groups in **1** and **2** are not necessarily consistent with the formation of such P→Sn dative interactions, we resorted to X-ray crystallography.

Examination of the structure of **1** indicates that the P(1) and Sn(1) atoms are separated by 3.125(4) Å. This separation, which is well within the sum of the Van der Waals radii of the two elements (4.2 Å) [13], is commensurate with the presence of a dative interaction. In line with this argument, we note that the C(6)–C(1)–Sn(1) (117.9(1)°) and C(1)–C(6)–P(1) (113.1(1)°) angles are both smaller than 120°. The P(1)–Sn(1)–Cl(1) angle (159.7(1)°) and the sum of the C_{eq}–Sn(1)–C_{eq} angles of 350.3° suggest that the coordination geometry at tin is best described as trigonal bipyramidal. Altogether, the structure of **1** is reminiscent of that of compound **I** which possesses an intramolecular P→Sn dative interaction of 3.079(2) Å. The structure of **2** has also been determined. Inspection of the

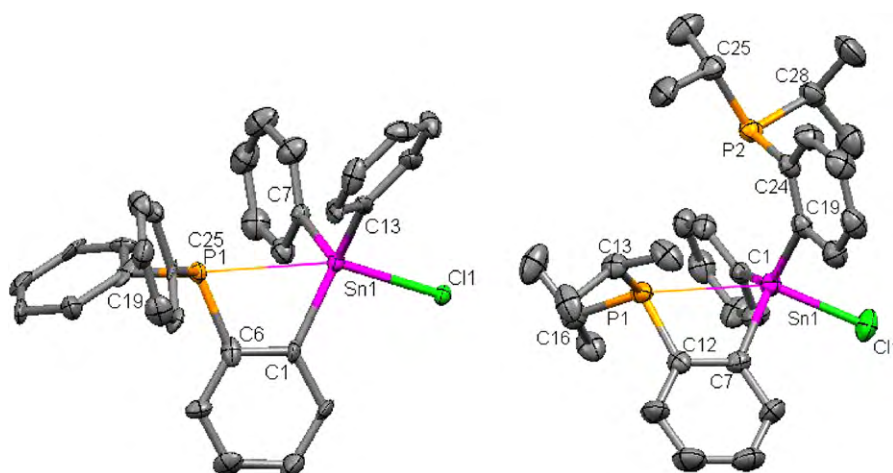


Fig. 3. Crystal structure of **1** (left) and **2** (right) (H-atom omitted for clarity, ellipsoids drawn at 50% probability). Selected bond lengths(Å) and angles(°) for **1** are as follows: Sn(1)–C(13) 2.122(16), Sn(1)–C(1) 2.131(16), Sn(1)–C(7) 2.132(13), Sn(1)–Cl(1) 2.512(3), Sn(1)–P(1) 3.125(4), P(1)–C(19) 1.816(15), P(1)–C(6) 1.850(18), P(1)–C(25) 1.861(14), C(13)–Sn(1)–C(1) 118.8(6), C(13)–Sn(1)–C(7) 117.2(5), C(1)–Sn(1)–C(7) 114.4(5), C(13)–Sn(1)–Cl(1) 99.2(4), C(1)–Sn(1)–Cl(1) 101.1(4), C(7)–Sn(1)–Cl(1) 101.1(4), C(19)–P(1)–C(6) 104.8(7), C(19)–P(1)–C(25) 103.7(6), C(6)–P(1)–C(25) 105.3(7), C(1)–C(6)–P(1) 113.1(13), C(6)–C(1)–Sn(1) 117.9(12), P(1)–Sn(1)–Cl(1) 159.7(1). Selected bond lengths(Å) and angles(°) for **2** are as follows: C(1)–Sn(1) 2.132(4), C(7)–Sn(1) 2.155(4), C(19)–Sn(1) 2.153(4), Cl(1)–Sn(1) 2.4499(10), C(12)–P(1) 1.832(4), C(13)–P(1) 1.865(4), C(16)–P(1) 1.855(4), C(24)–P(2) 1.833(4), C(25)–P(2) 1.855(4), C(28)–P(2) 1.881(4), P(1)–Sn(1) 3.120(1), P(2)–Sn(1) 3.528(1), C(12)–C(7)–Sn(1) 117.1(3), C(7)–C(12)–P(1) 113.5(3), C(1)–Sn(1)–C(7) 114.98(13), C(1)–Sn(1)–C(19) 134.42(13), C(7)–Sn(1)–C(19) 106.91(13), C(1)–Sn(1)–Cl(1) 96.31(10), C(7)–Sn(1)–Cl(1) 96.08(10), C(19)–Sn(1)–Cl(1) 96.35(10), C(12)–P(1)–C(16) 103.80(17), C(12)–P(1)–C(13) 105.13(18), C(16)–P(1)–C(13) 104.16(17), P(1)–Sn(1)–Cl(1) 153.92(3).

Table 1
Experimental and computed bond lengths (Å) and angles (°) for **1–3**.

	1 X-Ray	1 Density Functional Theory	2 X-Ray	2 Density Functional Theory	3 Density Functional Theory
P1-Sn	3.125(4)	3.294	3.1206(9)	3.235	3.231
P2-Sn	–	–	3.528(1)	3.601	–
Sn-Cl	2.512(3)	2.505	2.450(1)	2.536	2.511
Sn-C-C	117.9(1)	118.6	117.1(3)	117.7	117.4
P-C-C	113.1(1)	115.9	113.3(3)	114.7	115.1
P-Sn-Cl	159.7(1)	155.2	153.9(1)	153.3	156.3
$\sum C_{eq}\text{-Sn-}C_{eq}$	350.32	349.8	356.31	356.4	350.6

structure indicates that the P(1)–Sn(1) distance (3.120(1) Å) is very similar to that observed in **1**. The second phosphorus atom remains far away from tin (P(2)–Sn(1) = 3.528(1) Å). This dichotomy can be assigned to the presence of a P(1)–Sn(1) dative interaction which closely resembles that observed in **1**. This resemblance can be further ascertained by the similarity of the C(12)–C(7)–Sn(1) (117.1(3)°) and C(7)–C(12)–P(1) (113.5(3)°) and P(1)–Sn(1)–Cl(1) angle (153.92(3)°). The sum of the $C_{eq}\text{-Sn(1)-}C_{eq}$ angles of 356.31° is also close to that observed in **1**.

In order to better understand the nature of the P–Sn interaction present in these compounds, their gas phase

structures have been optimized using Density Functional Theory (DFT) methods (functional: BP86 [14]; mixed basis set: P, Sn, Cl: Stuttgart RLC ECP [15]; F: 6–31 g(d'); C, H: 6–31 g(d)). The optimized geometries, which are close to those experimentally determined (Table 1), were subjected to natural bond orbital (NBO) analyses which identified a $lp(P)\rightarrow p(Sn)$ donor-acceptor interaction (Fig. 4). Moreover, a deletion calculation carried out by zeroing the Kohn-Sham matrix elements corresponding to the $lp(P)\rightarrow p(Sn)$ interaction in **1** and **2** shows that this interaction contributes to the stability of the molecule by $E_{del}(P\rightarrow Sn) = 18.9$ kcal/mol in the case of **1** and

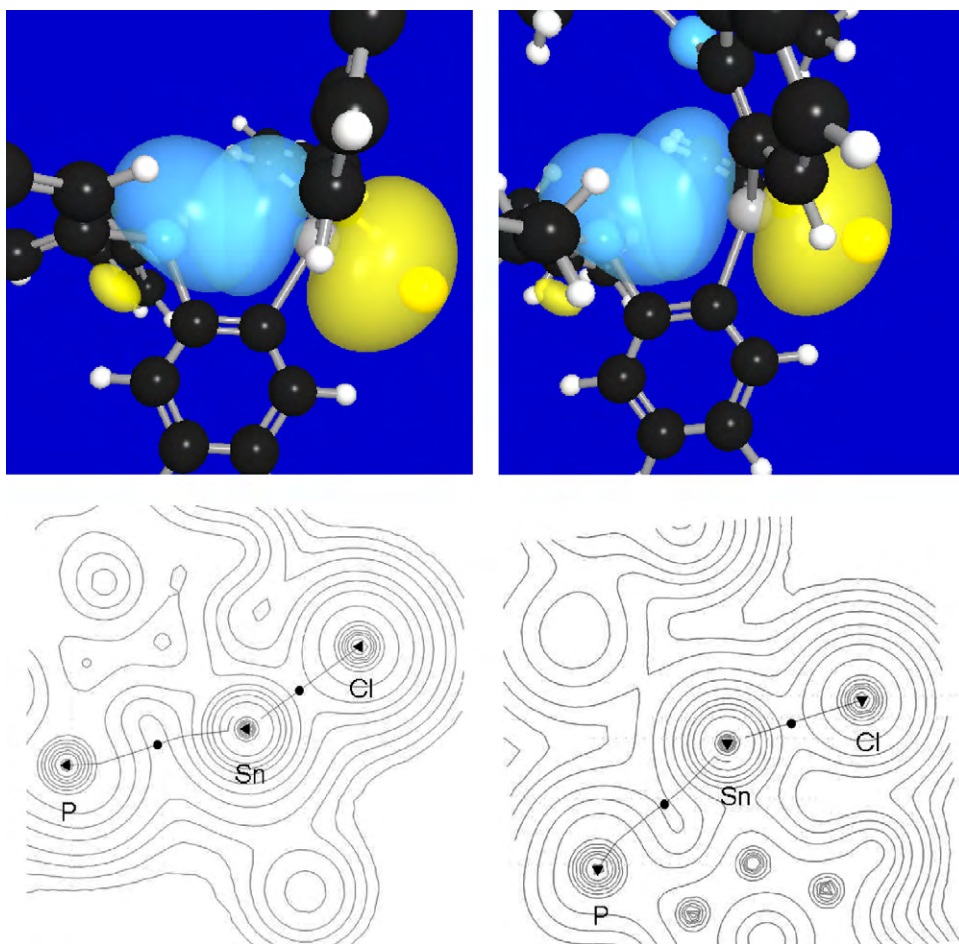
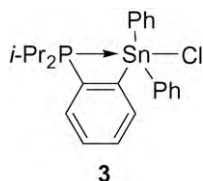


Fig. 4. Top: NBO contour plots showing the $lp(P)\rightarrow p(Sn)$ donor-acceptor interactions involved in **1** (left) and **2** (right). Bottom: Atom-In-Molecule electron density maps for **1** and **2** in the P–Sn–Cl plane showing the relevant bond paths and bond critical points.

$E_{\text{del}}(\text{P}\rightarrow\text{Sn}) = 24.4$ kcal/mol in the case of **2** (Fig. 4). In turn, the tin center of these derivatives experiences significant electron donation from the phosphorus. The difference in $E_{\text{del}}(\text{P}\rightarrow\text{Sn})$ between **1** and **2** is indicative of the increased donicity of the di(iso-propyl)phosphine moiety of **2**. This view is confirmed by a computational study of the model compound *ortho*-(*i*-Pr₂P)C₆H₄(SnPh₂Cl) (**3**), the di(iso-propyl)phosphine analog of **1**, which affords E_{del} (**3**) = 22.8 kcal. The donor-acceptor interaction between the phosphorus and tin atoms of these compounds was further ascertained by application of the Atom-In-Molecule (AIM) method [16]. This method, which allows for straightforward topological analysis of the electron density of a given compound, confirmed the presence of a bond path connecting the tin and phosphorus atoms of **1**, **2** and **3**. The values of the density at the P-Sn bond critical point of **1**, **2** and **3** are respectively equal to 0.017, 0.019 and 0.018 e/bohr³. Although these values are very close to one another, the higher densities observed in the case of **2** and **3** can also be correlated to the increased donicity of the di(iso-propyl)phosphine moiety.



3. Conclusion

The results reported here evidence that, despite the rigidity of the *ortho*-phenylene backbone, the phosphine and stannane groups of **1** and **2** are engaged in an intramolecular P→Sn dative interaction.

4. Experimental section

4.1. General considerations

Ph₂SnCl₂ and *n*-BuLi were purchased from Aldrich. *ortho*-(Ph₂P)C₆H₄Li **1** [6d,8] and **2** [10] was prepared according to the reported procedures. Solvents were dried by passing through an alumina column (CH₂Cl₂) or refluxing under N₂ over Na/K (Et₂O and *n*-hexane). NMR spectra were recorded on Varian Unity Inova 400 FT NMR (399.59 MHz for ¹H, 161.75 MHz for ³¹P, 149.00 MHz for ¹¹⁹Sn) spectrometers at ambient temperature. Chemical shifts are given in ppm, and are referenced to residual ¹H and ¹³C solvent signals and external H₃PO₄ (³¹P) and SnMe₄ (¹¹⁹Sn).

4.2. Synthesis of compound **1**

To a 15 mL Et₂O solution of 2-bromophenyl-diphenylphosphine (1250 mg, 3.66 mmol) was added a *n*-hexane solution of *n*-BuLi (2.2 M, 1.83 mL, 4.03 mmol) at 0 °C. After stirring at room temperature for 20 min, this mixture was transferred into a 5 mL Et₂O solution of Ph₂SnCl₂ (1.39 g, 4.03 mmol) at –78 °C. The reaction was allowed to warm

up slowly (in 1 h) and stir for overnight. Next day, the solvent was removed under reduced pressure. The product was extracted with CH₂Cl₂ (3 × 10 mL), and the solution was filtrated through celite. After evaporating CH₂Cl₂, the resulting white solid was washed with hexane (3 × 10 mL) to afford **1** as crude product (0.60 g, 28.7% yield). Further recrystallization in CH₂Cl₂ at –30 °C afforded colorless crystals of **1** suitable for crystallographic measurements. ¹H NMR (CDCl₃) δ = 7.05 (t, 4H, ³J_{H-H} = 8.5 Hz), 7.18–7.36 (m, 15H), 7.74 (d, 4H, ³J_{H-H} = 7.8 Hz), 8.24 (d, 1H, ³J_{H-H} = 7.6 Hz). ³¹P{¹H} NMR (CDCl₃) δ = –1.0 (³J_{Sn-P} = 18.1 Hz). ¹¹⁹Sn{¹H} NMR (CDCl₃) δ = –101.7 (bs).

4.3. X-ray measurements

The crystallographic measurements were performed at 110(2) K for **1** and 133(2) K for **2** using a Bruker APEX-II CCD area detector diffractometer (Mo-K_α radiation). A specimen of suitable size and quality was selected and mounted onto a nylon loop for **1** and glass fiber for **2**. Semi-empirical absorption corrections were employed [17]. The structures were solved by direct methods (SHELXS-97 [18] or SHELXTL [19]) and refined using the least-squares method on F² [20].

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-788735 (**1**) and 788736 (**2**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223_336_033; or deposit@ccdc.cam.ac.uk).

4.4. Computational details

DFT calculations were performed using Gaussian program [21]. Structural optimizations of **1–3** were carried out using BP86 functional. C, H were treated with 6-31G(d) basis set; F were treated with 6-31G(d') basis set; P, Cl, Sn were treated with Stuttgart RLC ECP basis set [15]. NBO calculations were carried out using Gaussian program with the same functional and basis set. The topology of the electron density of **1–3** was obtained by performing a single point calculation on the optimized structure using different basis set (6-31G(d) for C, H; 6-31G(d') for F; 6-31G+(d) for P, Cl; cc-PVDZ-pp for Sn). AIM analysis was carried out in AIM2000 program [22].

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