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First organotin complex of a phosphonic diamide RP(O)(NHR)₂

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Abstract

Diorganotin dichloride-phosphonic diamide complex, $[Ph_2SnCl_2(tBuP(O)(NH^iPr)_2)_2]$ (**1**), is prepared by the addition of two equivalents of $^tBuP(O)(NH^iPr)_2$ to one equivalents of Ph_2SnCl_2 either in the presence or absence of triethylamine. Compound **1** is a rare example of an all-*trans* $SnA_2B_2C_2$ complex that contains H-bonded six-membered rings which are made up of six different main group elements.
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1. Introduction

Organotin compounds and their complexes with electron-donor molecules have been studied in detail by various physicochemical methods in last four decades. Much of the interest in such complexes arises from their biological and catalytic activity [1]. Phosphoryl-containing compounds have, in particular, been used as effective complexation agents in organotin chemistry [2]. Previous work, using both ^{31}P NMR spectroscopic and calorimetric studies, has indicated that organotin chlorides form predominantly 1:1 adducts in solution, with evidence of 1:2 and other adducts for both R_2SnCl_2 and $RSnCl_3$ [1c,3]. A variety of 1:1 and 1:2 adducts of triphenylphosphine oxide with diorganotin(IV) dihalides are known in the literature [4]. On the other hand, organophosphonic amides $R_2P(O)(NHR)$ and $RP(O)(NHR)_2$ have not so far been studied as ligands in organotin chemistry. Unlike phosphine oxides, phosphonic amides can coordinate tin through P=O group and also further react with Sn–X bonds through the N–H group, thus offering possibilities for the preparation of tin complexes with Sn–N linkages stabilized by Sn–O coordination.

Tin complexes of phosphonic amides assume further importance due to the recent reports where a series of chiral-phosphoramides were shown to catalyze the enantioselective allylation of allyltrichlorosilanes [5]. To elucidate the relationship between the catalyst structure and its selectivity and reactivity, it is necessary to have a clear understanding of the phosphoramide · Lewis acid complex structure. Unfortunately, the complexation of phosphoramides to chlorosilanes is very weak [5]. However, phosphoramide can bind much better to tin through its phosphoryl oxygen and hence we have investigated the reaction of Ph_2SnCl_2 and $PhSnCl_3$ with a phosphonic diamide. The results obtained on the synthesis and structure of the first example of a organotin-phosphonic diamide complex, with a rare H-bonded six-membered ring with six different main group elements, are presented herein.

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2. Results and discussion

2.1. Synthesis and spectral characterization

The six coordinate tin compound, [Ph$_2$SnCl$_2$(^{t}Bu-P(O)(NH^{i}Pr)$_2$)$_2$] (**1**), was initially synthesized by the reaction of either Ph$_2$SnCl$_2$ with ^{t}BuP(O)(NH^{i}Pr)$_2$ in presence of Et$_3$N (Scheme 1). In spite of using an HCl scavenger, no reaction has been observed between Sn–Cl bonds and the N–H protons of the phosphoramide to result in Sn–N linkages. This is probably both due to the steric congestion around the nitrogen as well as a decreased acidity of the N–H protons.

The reaction between PhSnCl$_3$ and ^{t}BuP(O)(NH^{i}Pr)$_2$ does not yield the expected 1:2 product [PhSnCl$_3$(^{t}Bu-P(O)(NH^{i}Pr)$_2$)$_2$], but once again results in the formation of **1** (Scheme 1). Obliviously, a disproportionation of PhSnCl$_3$ to Ph$_2$SnCl$_2$ and SnCl$_4$ has taken place during the course of the reaction, thus leading to the formation of **1**. A similar aryl transfer in the case of PhSnCl$_3$ has been observed previously [6].

Since the formation of **1** either from Ph$_2$SnCl$_2$ or PhSnCl$_3$ did not involve the participation of Et$_3$N, the synthesis of **1** was repeated in the absence of Et$_3$N in order to optimize the conditions for the preparation of **1** and also to improve the yield of the reaction. For examples, stirring a 1:2 toluene solution of Ph$_2$SnCl$_2$ and ^{t}BuP(O)(NH^{i}Pr)$_2$ at room temperature followed by warming the mixture to 50 °C for 2 h resulted in quantitative formation of **1**. Single crystals of **1** were obtained from the reaction mixture in about 85% yield by cooling the solution overnight at 5 °C.

Compound **1** has been characterized by elemental analysis, IR, and NMR (^{1}H, ^{31}P and ^{119}Sn NMR) spectroscopy and single crystal X-ray diffraction studies. The IR spectrum displays vibration bands for all structural linkages expected for this compound [7]. For example, the characteristic P=O absorption for the compound was observed at 1092 cm^{-1}. The N–H stretching vibrations result in the two different strong absorptions at 3337 and 3268 cm^{-1} probably indicating two types of the –NH groups in the complex. Absorptions observed at 2967 and 3053 cm^{-1} are readily assignable to aliphatic and aromatic C–H stretching vibrations, respectively.

The ^{1}H NMR spectral data obtained for **1** are suggestive of the expected structure of this molecule. The protons of the *tert*-butyl group on phosphorous appear as a phosphorous coupled doublet at δ 1.04 ppm ($^3J_{PH}$ = 15 Hz). The two isopropyl groups (NH^{i}Pr) of the phosphonamide are non-equivalent and hence appear as two different doublets
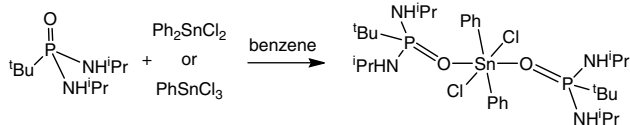
at δ 1.06 and 1.08 ppm ($^3J_{HH}$ = 6.5 Hz), due to the coupling of the methine (CH) proton. The corresponding signals of the CH protons of the isopropyl group appear as two overlapping septets observed at δ 3.26–3.38 ppm ($^3J_{HH}$ = 6.5 Hz). An apparent triplet (which is actually two overlapping doublets) is observed at δ 2.08 ppm, due to the presence of two different types of N–H protons in the molecules ($^2J_{PH}$ = 11.5 Hz). The appearance of two different N–H doublets is an indication of two different types of hydrogen bonding interaction for these moieties (vide infra). The aryl protons show multiplets in the region δ 7.30–7.50 to 8.00–8.01 ppm. The ^{31}P NMR spectrum of **1** shows a singlet (δ 36.45 ppm) which is only slightly downfield shifted from the value observed for the parent ligand ^{t}BuP(O)(NH^{i}Pr)$_2$ (δ 35.5 ppm). The decoupled ^{119}Sn{^{31}P} NMR spectrum of **1** yields a single resonance at δ 86.92 ppm. For comparison, free Ph$_2$SnCl$_2$ shows a signal in ^{119}Sn NMR at −32.0 ppm [6].

2.2. Molecular structure of 1

The title compound crystallizes in orthorhombic space group *Pnca* with the asymmetric part of the unit cell composed of one phenyl group, one ^{t}BuP(O)(NH^{i}Pr)$_2$ group, one chlorine atom and one-half of the metal. A view of the molecular structure as ORTEP is shown in Fig. 1. As shown in Fig. 1, the central tin atom is surrounded by two phenyl groups (Sn–C(1), 2.146(2); Sn–C(5), 2.134(2) Å), two chloride ions (Sn–Cl, 2.5842(5) Å) and two ^{t}BuP(O)(NH^{i}Pr)$_2$ moiety (Sn–O, 2.193(1) Å) in an
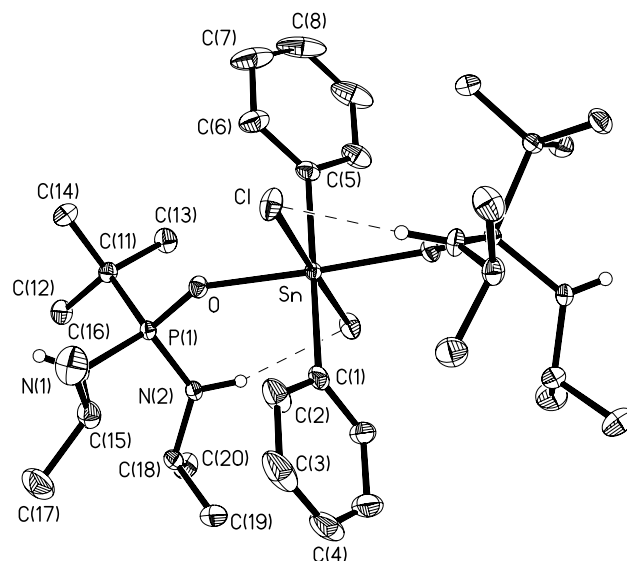
Fig. 1. ORTEP of [Ph$_2$SnCl$_2$(^{t}BuP(O)(NH^{i}Pr)$_2$)$_2$] at 50% probability level. Selected bond distances (Å) and angles (°): Sn–O 2.193(1), Sn–Cl 2.5842(5), Sn–C(1) 2.146(2), Sn–C(5) 2.134(2), P(1)–N(1) 1.632(1), P(1)–N(2) 1.636(1), P(1)–O 1.515(1); O–Sn–O1′ 177.40(5), Cl′–Sn–Cl 177.76(2), O–Sn–Cl′ 92.16(3), O–P(1)–N(2), 107.99(5), O–P(1)–C(11) 108.36(6), C(1)–Sn–O 91.30(2), O–P(1)–N(1) 115.66(6), C(5)–Sn–C(1) 180.0, N(1)–P(1)–N(2) 106.81(6), C(1)–Sn–Cl 91.121(8), C(5)–Sn–O 88.70(2), N(1)–P(1)–C(11) 105.53(6), O–Sn–Cl 87.79(3), N(2)–P(1)–C(11) 112.61(6), C(5)–Sn–Cl 88.879(8), P(1)–O–Sn 144.62(6).
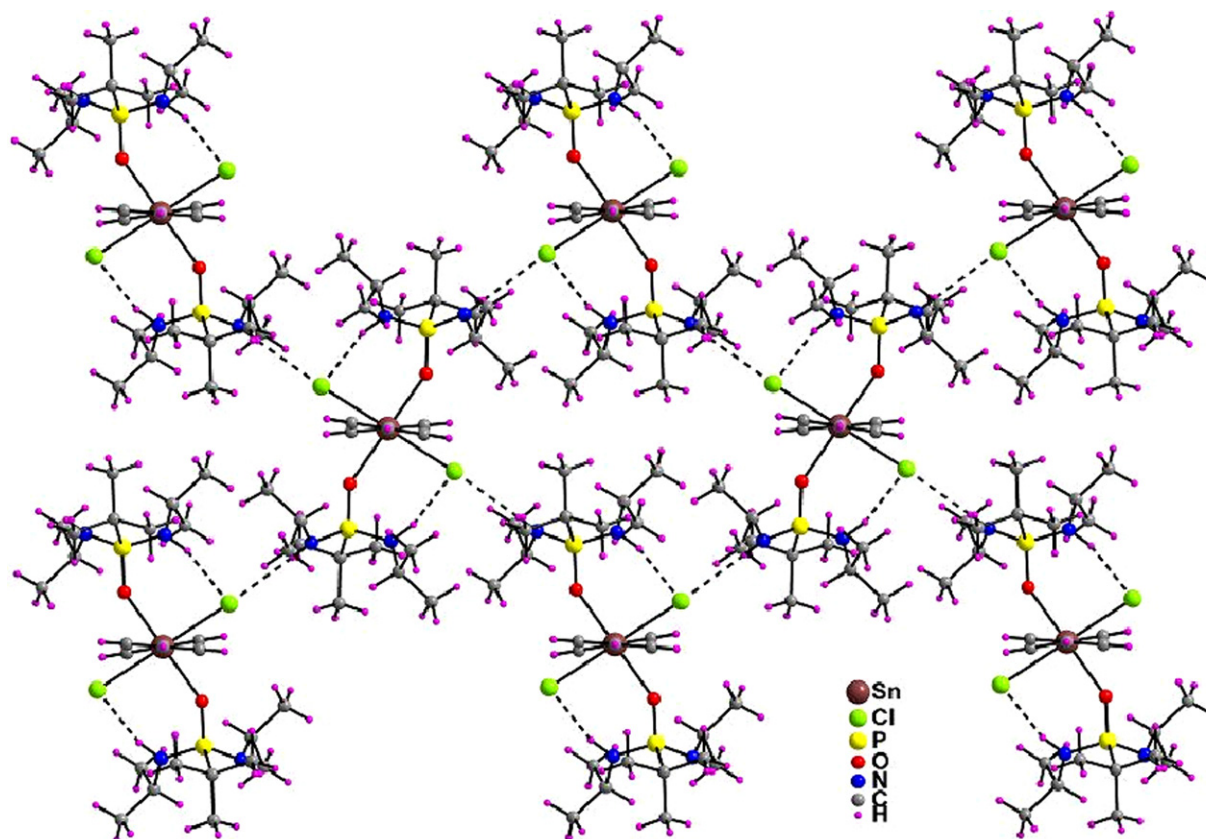

Scheme 1. Synthesis of **1**.

Fig. 2. Formation of 2-D sheets in **1** through intramolecular N–H···Cl hydrogen bonding.

octahedral geometry. The same types of ligands on the central metal are *trans* to each other, thus producing an all-*trans* structure. The *trans* angles found around the metal are in the range of 177.40–180.00°, while the *cis* angles are in the range of 87.79–91.12°. As a result of coordination to the tin metal, as expected, the P=O distance (P(1)–O, 1.515(1) Å) in this compound is longer than that found in the parent ^{t}BuP(O)(NH^{i}Pr)$_2$ (1.489(2) Å) [8]. Other bond distances are comparable to the values found for similar linkages in the literature [7].

The presence of Sn–Cl and N–H moieties leads to the formation of interesting intra- and inter-molecular hydrogen bonding. One of the two N–H linkages on each ^{t}Bu-P(O)(NH^{i}Pr)$_2$ moiety is involved in hydrogen bonding with chlorine atom of the same molecule. This N–H···Cl hydrogen bond completes the formation two spirocyclic six-membered rings around tin as depicted in Fig. 1. The architecture of these two six-membered rings is remarkable due to the fact that they are made up of as many as six different elements coming from as many as five different groups of the main group (group 1 (H), group 14 (Sn), group 15 (N, P), group 16 (O), group 17 (Cl)). It is of further interest to note that at least three different types of bonding (covalent, coordinate and hydrogen) are represented within these six-membered rings, with formal bond order ranging from fractional to two with varying degrees of multiple bonding. The existence of such six-membered rings, to our best knowledge, is unknown in the literature.

Thus the title compound represents a rare inorganic ring system involving main group elements. The other N–H group on each phosphonic diamide is involved in intermolecular hydrogen bonding with the chlorine of a neighboring molecule. This leads to the formation of sheet-like 2-D structure as shown in Fig. 2. The non-participation of the second N–H group in hydrogen bonding is also reflected both in IR and ^{1}H NMR spectroscopy (vide supra).

3. Conclusion

A phosphonic diamide has been used as a ligand in organotin chemistry. The organotin phosphonamide complex [Ph$_2$SnCl$_2$ (^{t}BuP(O)(NH^{i}Pr)$_2$)$_2$] has been synthesized from two different precursor halides and the product has been structurally characterized. The presence of reactive Sn–Cl and N–H linkages offer further possibilities in using molecules of type **1**, albeit with smaller substituents on nitrogen and phosphorus, as precursors for tin–amide complexes stabilized by phosphoryl coordination. Work on this direction is currently underway.

4. Experimental

4.1. Synthesis of **1**

Phosphonic diamide ^{t}BuPO(NH^{i}Pr)$_2$ (440 mg, 2 mmol) was dissolved in toluene (50 mL), and Ph$_2$SnCl$_2$ (344 mg,

1 mmol) in 15 mL of toluene was added at room temperature and stirred for overnight to obtain small amount white precipitate which got dissolved on warming solution at 50 °C. The solution was stirred at 50 °C for 2 h. Colorless X-ray diffraction quality crystals of **1** were obtained after 12 h at 5 °C. Yield: 0.636 g (85%). Mp. 145–147 °C. Anal. Calc. for $C_{32}H_{60}N_4P_2O_2SnCl_2$: C, 49.00; H, 7.71; N, 7.14. Found: C, 48.46; H, 7.47; N, 7.07%. IR (KBr, cm^{-1}): 3337 (s), 3268 (s), 3053 (w), 2967 (s), 2870 (m), 1469 (s), 1431 (s), 1262 (m), 1131 (s), 1092 (vs), 1057 (vs), 1020 (vs), 903 (w), 880 (w), 803 (m), 732 (m), 696 (m), 653 (w), 569 (w), 537 (w), 456 (w). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.04 (d, CH_3 of ^tBu, 18H, $^3J_{PH} = 15$ Hz), 1.06–1.08 (d, CH_3 of ^iPr, 24H, $^3J_{HH} = 6.5$ Hz), 2.08 (dd, NH, 4H, $^2J_{PH} = 11.5$ Hz), 3.26–3.38 (doublet of septet, CH, 4H, $^3J_{HH} = 6.5$ Hz), 7.30–7.50 (m, Ph, 6H), 8.00–8.01 (d, Ph, 4H). ^{31}P NMR (121 MHz, $CDCl_3$) δ (ppm): 36.45. ^{119}Sn NMR (112 MHz, $CDCl_3$) δ (ppm): 86.92.

4.2. Crystal data for 1

$C_{32}H_{60}Cl_2N_4O_2P_2Sn$, orthorhombic, space group *Pnca*, $a = 14.208(3)$ Å, $b = 14.799(3)$ Å, $c = 19.296(5)$ Å, $V = 4057.5(16)$ Å^3, $Z = 4$, $d_{calc} = 1.284$ mg m^{-3}, $\lambda = 0.71073$ Å, $\mu = 0.871$ mm^{-1}, 36 120 reflections, 6491 unique ($R_{int} = 0.0553$), $R_1 = 0.0253$, $wR_2 = 0.0597$ [$I > 2\sigma(I)$]. Data were collected on a Bruker diffractometer CCD system.

Acknowledgements

Appendix A. Supplementary material

CCDC 621084 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.12.044.

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