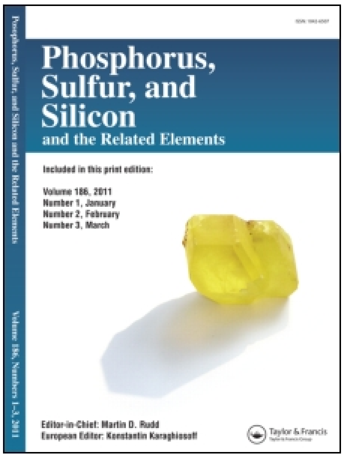

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Hypercoordination in Organotin Chemistry – A Novel O,C,O-Coordinating Ligand

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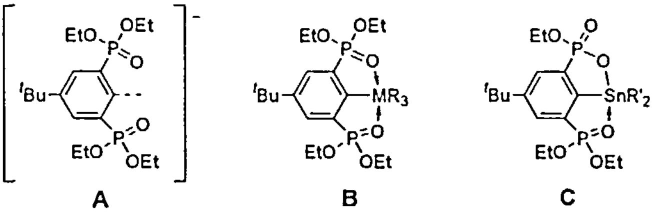
Recent results are reported on the application of the novel O,C,O-coordinating pincer ligand $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}tert\text{-}Bu\text{-}C_6H_2\}^-$ (A) for the synthesis of hypercoordinate organotin(IV) compounds $ASnR_3$ (R = Ph, Cl), heteroleptic stannylenes ASnR (R = Cl, CH_2SiMe3) and intramolecularly coordinated 1,2,5-oxaphosphastannolanes.

Keywords: silicon; phosphorus; tin; hypercoordination; stannylenes

INTRODUCTION

Hypercoordinate compounds of the heavier group 14 elements silicon and tin have been intensively studied during the last decades because of their biological activity, their enhanced reactivity, and their stereochemical nonrigidity. In particular, the use of ligands with intramolecular donor sites led to the stabilization of highly reactive compounds such as silylenes and stannylenes, as well as organo-silicon and -tin cations. In the case of intramolecularly coordinated compounds amino substituted aryl ligands are the most intensively investigated ligand systems[1-5]. Recently, we reported on the synthesis and structure of some intramolecularly coordinated organosilicon and organotin derivatives of type B containing the novel O,C,O-coordinating ligand $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}tert\text{-}Bu\text{-}C_6H_2\}^-$ A. Here we present the application of the pincer-ligand A in the synthesis of various intramolecularly penta- and hexacoordinated organotin compounds including heterocycles of type C (CHART 1).



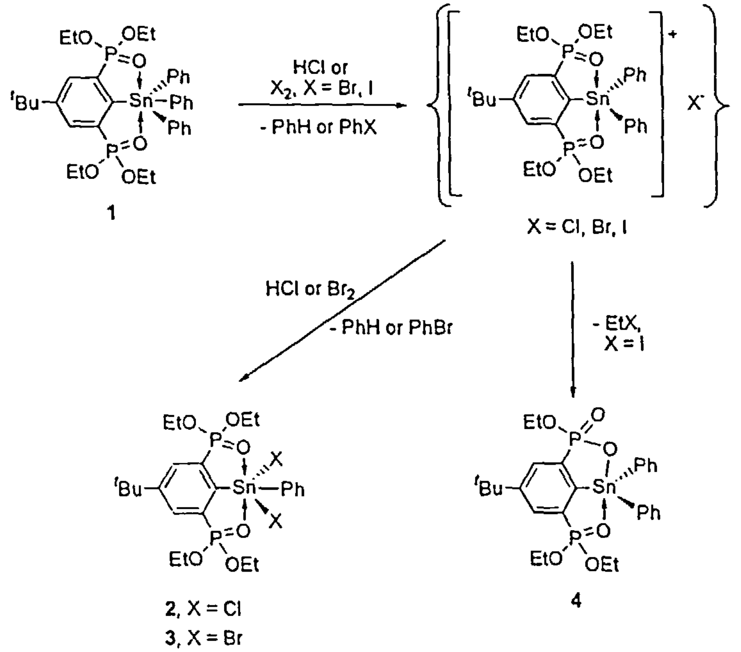
M = Si, Sn
R = Alkyl, aryl, halogen

R' = Ph or Cl

CHART 1

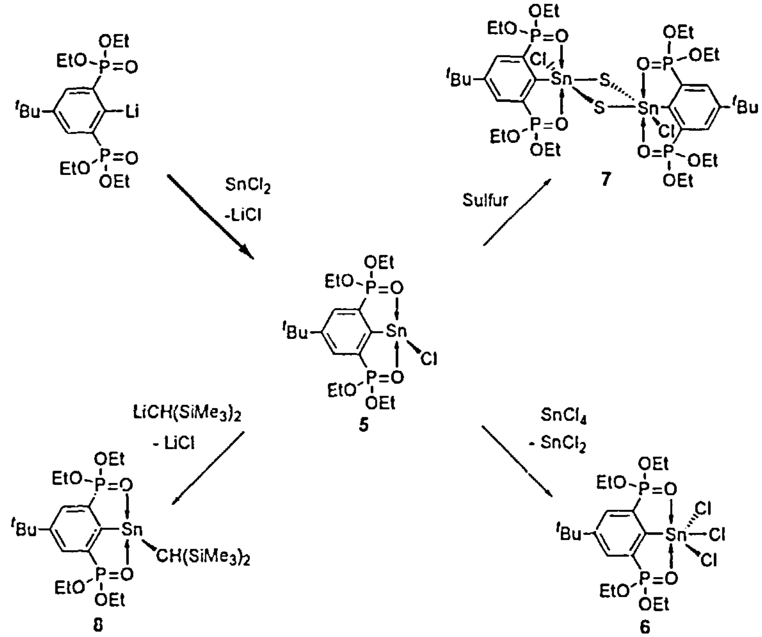
RESULTS AND DISCUSSION

Hypercoordinate organotin compounds. The hypercoordinate tetraorganotin compound $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}tert\text{-}Bu\text{-}C_6H_2\}SnPh_3$ (**1**) has been prepared by the reaction of $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}tert\text{-}Bu\text{-}C_6H_2\}Li$ with Ph_3SnCl[6]. Treatment of this compound with two mole equivalents of HCl or Br_2 provided $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}tert\text{-}Bu\text{-}C_6H_2\}SnX_2Ph$ (**2**, X = Cl; **3**, X = Br), whereas the reaction with elemental iodine led to the heterocyclic compound **4**[7] (SCHEME 1).



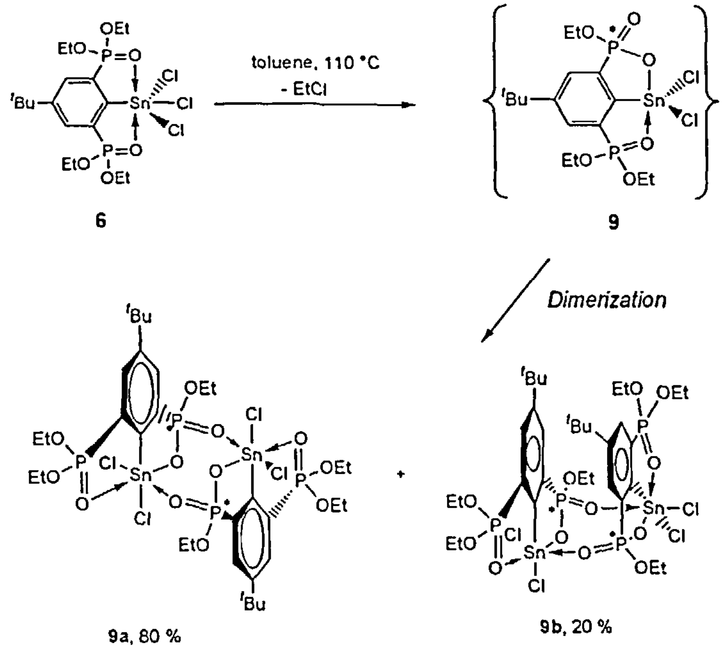
SCHEME 1

The monoorganotin trichloride {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnCl$_3$ (6) was synthesized by oxidation of the heteroleptic stannylene {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnCl (5) with SnCl$_4$. The stannylene 5 reacts with elemental sulfur to give the stannathione [{2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}Sn(Cl)S]$_2$ (7), whereas the reaction with (Me$_3$Si)$_2$CHLi provided the heteroleptic stannylene {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnCH(SiMe$_3$)$_2$ (8) (SCHEME 2).



SCHEME 2

Hypercoordinate organotin heterocycles. The ease in which the heterocycle 4 was synthesized implies that the hexacoordinate trichloride 6 should also undergo intramolecular cyclization to provide a dichloro substituted oxaphosphastannolane. This reaction occurs indeed by simply heating compound 6 in toluene at reflux for several hours. The dihalogenated 1,2,5-oxaphosphastannolane 9 formed in this reaction dimerizes as a result of an intermolecular O–Sn coordination to give the diastereomeric mixture of 9a and 9b (SCHEME 3).



SCHEME 3

This was indicated by observation of four ^{31}P NMR signals at δ = 11.95 [$J(^{31}\text{P}-^{119/117}\text{Sn})$ = 316/301 Hz, $J(^{31}\text{P}-^{119/117}\text{Sn})$ = 137/125 Hz] (9a), δ = 13.12 [$J(^{31}\text{P}-^{119/117}\text{Sn})$ = 304 Hz] (9b), δ = 25.17 [$J(^{31}\text{P}-^{119/117}\text{Sn})$ = 334/320 Hz] (9a), δ = 25.14 [($J(^{31}\text{P}-^{119/117}\text{Sn})$ = 324 Hz] (9b) with an integral ratio of 4:1:4:1. Compound 9a was isolated and completely characterized.

Molecular Structures of 4 and 9a. The molecular structures of the compounds 4 and 9a are shown in FIGURES 1 and 2.

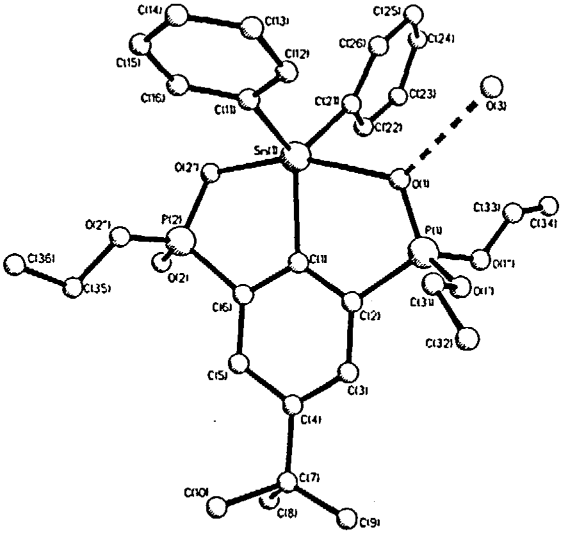


FIGURE 1 Molecular structure of the 1,2,5-oxaphosphastannolane **4**.

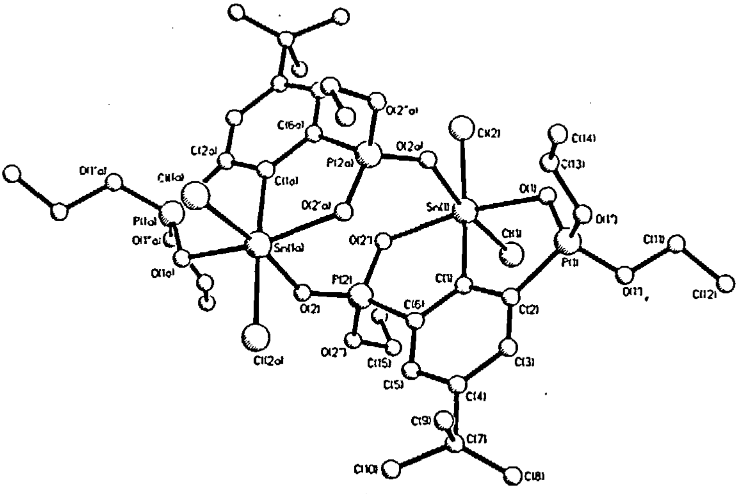


FIGURE 2 Molecular structure of the 1,2,5-oxaphosphastannolane **9a**.

In the heterocyclic compound **4** the tin center adopts a slightly distorted trigonal bipyramidal configuration with O(1) and O(2') in axial and C(1), C(11), and C(21) in equatorial positions. The O(1)–Sn(1)–O(2') angle amounts to 160.2(2)°. In the crystal lattice a polymeric chain structure is observed as result of the incorporation of water molecules. In the IR spectrum of compound **4** two different ν(P=O) bands of 1172 cm^{-1} and 1242 cm^{-1} are observed, which are in line with P(1)–O(1) and P(2)–O(2) bond distances of 1.488(4) and 1.463(6) Å, respectively, and which demonstrate the presence of both a strongly coordinating and a non-coordinating P=O group.

As a result of both inter- and intramolecular interactions the coordination geometries of the tin centers in dimeric **9a** can be described as distorted octahedra with *cis*-angles in the range between 81.78(9)° and 97.97(7)° and *trans*-angles of 172.8(1)° for C(1)–Sn(1)–Cl(2), 173.98(8)° for Cl(1)–Sn(1)–O(2a), and 161.78(9)° for O(1)–Sn(1)–O(2'), respectively. In comparison with the O–Sn bond lengths of the monomeric 1,2,5-oxaphosphastannolane **4** the corresponding O–Sn bond lengths in **9a** are shortened, the dative bond O(1)–Sn(1) in **9a** amounts to 2.204(3) Å. The almost equal O(2')–Sn(1) and O(2a)–Sn(1) bond lengths of 2.147(3) Å and 2.140(3) Å, respectively, are even shorter, and lie in the typical range of a O–Sn single bond (2.15 Å). They show the phosphonyl group to act as a bidentate bridging ligand. Since the Lewis acidity of the tin atom in **9a** is greater than that of the tin atom in **4**, the tin center in compound **9a** displays a distorted octahedral coordination as result of a dimerization. The results of the IR spectroscopic measurements are in agreement with the X-ray data. The

ν(P=O) for the dative bonded phosphonyl group was found at 1168 cm^{-1}. Furthermore, a strong absorption at 1139 cm^{-1} is assigned to the bidentate bridging phosphonyl group.

CONCLUSION

We have shown the use of the new O,C,O-coordinating ligand $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}tert\text{-}Bu\text{-}C_6H_2\}^-$ in the synthesis of various hypercoordinate organotin compounds. The high donor capacity and the rigidity of the ligand frame make this O,C,O-coordinating ligand an ideal substituent for the intramolecular donor-stabilization of highly reactive compounds.

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