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Bis- and tris-phosphinostannane gold complexes featuring Au → Sn dative interactions: Synthesis, structures, and DFT calculations

Tzu-Pin Lin, François P. Gabbaï *

Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, United States

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ABSTRACT

As part of our interest in the coordination chemistry of heavy Group 14 elements, we have synthesized complexes of general formula $[(o\text{-}(Ph_2P)C_6H_4)_2SnClPh]AuX$ (X = Cl (**2**-Cl), X = Br (**2**-Br), and X = I (**2**-I)) in which the chlorostanane unit acts as a σ-acceptor ligand toward gold. The existence of a Au → Sn dative bond is evidenced by a trigonal bipyramidal geometry about the tin atom as well as a distorted square planar geometry about the gold center. While the measured Au–Sn bond distances are crystallographically indistinguishable in this series, theoretical investigations reveal that the strength of the Au → Sn interaction increases in the order **2**-I < **2**-Br < **2**-Cl. These results suggest that the Au → Sn interaction is affected by the ligands around gold. Lastly, we also report the tripodal complex $[(o\text{-}(Ph_2P)C_6H_4)_3SnCl]AuSnCl_3$ (**4**) in which the gold atom is concomitantly coordinated to a Z-type tin ligand and an X-type tin ligand.

1. Introduction

The interactions between ligands and transition metals have been an essential subject in inorganic chemistry. Other than the commonly known L-type (two-electron donors) and X-type ligands (one-electron donors), Z-type ligands (two-electron acceptors) have begun to surface in the past decade [1]. Capable of drawing a pair of d-electrons away from a metal, Z-ligands affect the electronic structures of transition metals, leading to interesting properties and reactivity [2]. While a large fraction of the earlier work focused on boron containing Z-ligands [1d,1f,1g,2a], recent efforts have shown that that other Lewis acidic main group elements can also be considered [3].

Among these, group 14-based systems have drawn special attention because of the saturated nature of the group 14 acceptor that achieves hypervalence upon interaction with the metallobasic transition metal atom. Examples of such complexes include transition metal silane, germane, and stannane complexes characterized by dative M → E bonds (E = Si, Ge, Sn) [4]. Some representative examples of such complexes are shown in Chart 1. In addition to the metallastannatrane and metallasilatrane of type **I** in which the M → Si/Sn interaction is supported by four rigid 2-mercapto-1-methylimidazolide buttresses [4a-d], several groups including ours have described derivatives which feature two or three *o*-phosphino-phenylene buttresses as in the case of complexes of type **II** and **III** [4e-k]. These recent results demonstrate that heavy Group

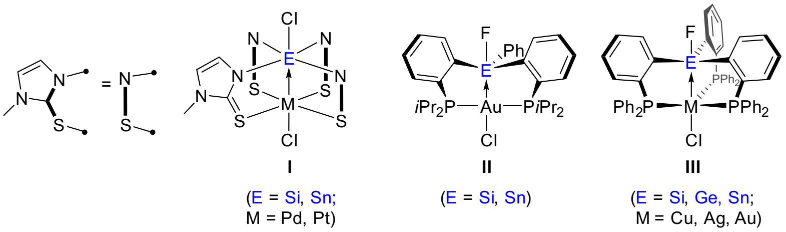

Chart 1. Selected examples of transition metal silane, germane, and stannane complexes.

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* Corresponding author.

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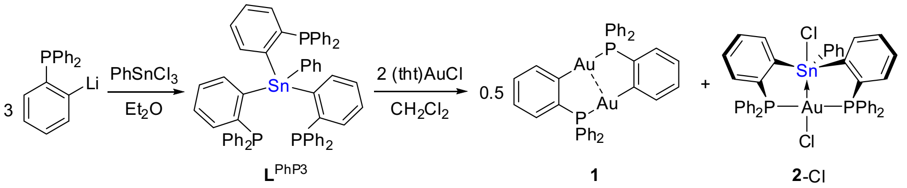
14 Lewis acids can coordinate to electron-rich late transition metals as σ-accepting ligands. To better understand the parameters governing the strength of the Au → Sn interactions in such complexes, we herein report the synthesis of new *bis*- and *tris*-phosphinostannane gold complexes. The strength of the Au → Sn interactions in these complexes have been evaluated using DFT methods.

2. Results and discussions

The reaction of *ortho*-lithio-diphenylphosphinobenzene with $PhSnCl_3$ in Et_2O afforded the *tris*-phosphinostannane ligand $(o\text{-}(Ph_2P)C_6H_4)_3SnPh$, hereafter referred to as $\mathbf{L}^{PhP3}$, in moderate yield (Scheme 1). The ^{31}P NMR spectrum of this ligand displays one resonance at δ−2.51 flanked by two satellites resulting from coupling with the tin nuclei ($^3J_{Sn\text{-}P} = 28.5$ Hz). Accordingly, the ^{119}Sn NMR resonance of $\mathbf{L}^{PhP3}$ (Fig. 1a) is split into a quartet (−144 ppm, $^3J_{Sn\text{-}P} = 28.5$ Hz). The ^{119}Sn chemical shift of $\mathbf{L}^{PhP3}$ is very close to that observed for Ph_4Sn (−128 ppm) [5], suggesting the unchanged tetrahedral geometry at the tin center and the absence of P → Sn interactions. This view is supported by the crystallographically measured Sn–P separations (Sn–P(1) 3.408(3) Å, Sn–P(2) 3.457(3) Å, Sn–P(3) 3.494(3) Å) in $\mathbf{L}^{PhP3}$ which could only be consistent with rather weak P → Sn interactions (Fig. 2). We note that $(o\text{-}(Ph_2P)C_6H_4)_3SnF$ has been described previously [6]. This compound features shorter P → Sn interactions (3.366(1) Å) because of the greater acidity of the fluorostannane moiety and the greater Lewis basicity of the di-*iso*-propylphosphino groups. Shorter P → Sn contacts (3.125(4) Å) have also been reported in $(o\text{-}(Ph_2P)C_6H_4)SnClPh_2$ which again possesses a more Lewis acidic chlorostannane unit and a less congested structure allowing for a closer approach of the Lewis base and Lewis acid [7].

Ligand $\mathbf{L}^{PhP3}$ reacted cleanly with (tht)AuCl (tht = tetrahydrothiophene) to afford complex **2**-Cl as well as the known gold derivative **1** [8] isolated as a byproduct of the reaction (Scheme 1). The stability of the latter, which features a short aurophilic interaction of 2.8594(3) Å, provides the thermodynamic driving force for the transmetallation reaction. The yield of **2**-Cl could be optimized by addition of two equivalents of (tht)AuCl. Complex **2**-Cl has been fully characterized. The ^{31}P NMR resonance of **2**-Cl which features the expected tin satellites ($^3J_{117/119Sn,P} = 78/80$ Hz), appears at 56 ppm confirming the symmetrical coordination of the phosphorus atoms to gold. The ^{119}Sn NMR resonance of **2**-Cl (Fig. 1b) appears as a triplet at -86 ppm ($^3J_{Sn,P} = 80$ Hz) which is comparable to the value reported for $[(o\text{-}(iPr_2P)C_6H_4)_2SnClPh]AuCl$ (−80 ppm, $^3J_{Sn,P} = 67.7$ Hz) [4e]. This ^{119}Sn chemical shift of **2**-Cl is, however, distinctly upfield from that of Ph_3SnCl (−45 ppm) [5], in line with an increase in the coordination number of the tin atom. These spectroscopic features strongly suggest the presence of a Au → Sn interaction.

As shown in Fig. 3, the Au-Sn distance (2.9069(6) Å) measured in complex **2**-Cl is shorter than the sum of the van der Waals radii



Scheme 1. Synthesis of $\mathbf{L}^{PhP3}$ and **2**-Cl.

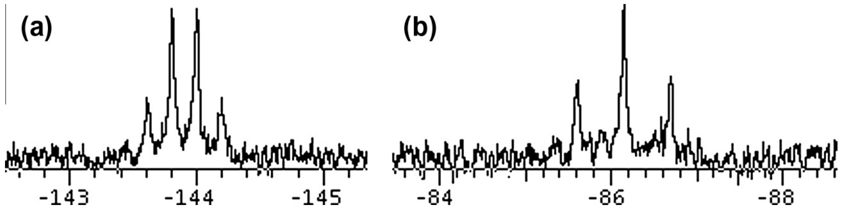


Fig. 1. (a) ^{119}Sn NMR spectrum of $\mathbf{L}^{PhP3}$ in $CDCl_3$ and (b) ^{119}Sn NMR spectrum of **2**-Cl in CD_2Cl_2.

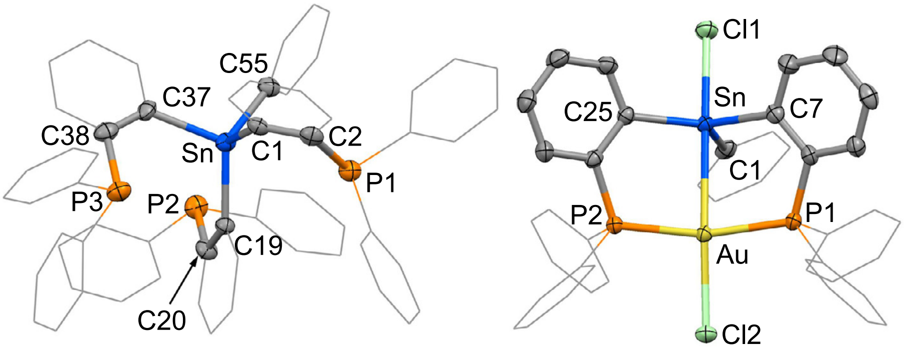


Fig. 2. Molecular structures of $\mathbf{L}^{PhP3}$ (left) and **2**-Cl (right) in the crystal. Ellipsoids are given at the 50% probability level. Some of the phenyl rings are drawn as thin lines. Hydrogen atoms and the solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg) for $\mathbf{L}^{PhP3}$: Sn–P(1) 3.408(3), Sn–P(2) 3.457(3), Sn–P(3) 3.494(3), C(19)–Sn–C(55) 124.6(3), C(1)–C(2)–P(1) 117.6(6), C(19)–C(20)–P(2) 116.5(6), C(37)–C(38)–P(3) 118.4(7), C(2)–C(1)–Sn 121.2(6), C(20)–C(19)–Sn 124.2(6), C(38)–C(37)–Sn 124.2(7). Selected bond lengths (Å) and angles (deg) for **2**-Cl: Au–P(2) 2.3052(9), Au–P(1) 2.3113(10), Au–Cl(2) 2.5539(10), Au–Sn 2.9069(6), Sn–C(1) 2.145(4), Sn–C(7) 2.175(4), Sn–C(25) 2.182(3), Sn–Cl(1) 2.5010(10), P(2)–Au–P(1) 165.48(3), Cl(2)–Au–Sn 165.90(2), Cl(1)–Sn–Au 177.93(3), C(1)–Sn–C(7) 110.01(14), C(1)–Sn–C(25) 126.15(14), C(7)–Sn–C(25) 123.66(13).