Bis- and Tris-phosphinostannane Gold Complexes Featuring Au→Sn Dative Interactions: Synthesis, Structures, and DFT Calculations

*Tzu-Pin Lin and François P. Gabbaï**

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

ABSTRACT: As part of our interest in the coordination chemistry of heavy Group 14 elements, we have synthesized complexes of general formula $[(o-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4)_2\text{SnClPh}]\text{AuX}$ ($\text{X} = \text{Cl}$ (**2-Cl**), $\text{X} = \text{Br}$ (**2-Br**), and $\text{X} = \text{I}$ (**2-I**)) in which the chlorostannane unit acts as a σ -acceptor ligand toward gold. The existence of a $\text{Au} \rightarrow \text{Sn}$ dative bond is evidenced by a trigonal bipyramidal tin as well as a distorted square planar gold center. While the measured Au-Sn bond distances are crystallographically indistinguishable in this series, theoretical investigations reveal that the strength of the $\text{Au} \rightarrow \text{Sn}$ interaction increases in the order **2-I** < **2-Br** < **2-Cl**. These results suggest that the $\text{Au} \rightarrow \text{Sn}$ interaction is affected by the ligands around gold. Lastly, we also report the tripodal complex $[(o-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4)_3\text{SnCl}]\text{AuSnCl}_3$ (**4**) in which the gold atom is concomitantly coordinated to a Z-type tin ligand and an X-type tin ligand.

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 other Lewis acidic main group elements can also be considered [3].

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

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 $M \rightarrow E$ bonds ($E = \text{Si, Ge, Sn}$) [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 $M \rightarrow \text{Si/Sn}$ interaction is supported by four rigid 2-mercapto-1-methylimidazolidine 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 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.

RESULTS AND DISCUSSIONS

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

The reaction of *ortho*-lithio-diphenylphosphinobenzene with PhSnCl_3 in Et_2O afforded *tris*-phosphinostannane ligand (*o*-(Ph_2P) C_6H_4) $_3\text{SnPh}$; hereafter referred to as $\mathbf{L}^{\text{PhP3}}$) 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 ($^3J_{\text{Sn-P}} = 28.5$ Hz). Accordingly, the ^{119}Sn NMR resonance of $\mathbf{L}^{\text{PhP3}}$ (Figure 1a) is split into a quartet (-144 ppm, $^3J_{\text{Sn-P}} = 28.5$ Hz). The ^{119}Sn chemical shift of $\mathbf{L}^{\text{PhP3}}$ 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 $\mathbf{L}^{\text{PhP3}}$ which could

only be consistent with rather weak P→Sn interactions (Figure 2). We note that (*o*-(Ph₂P)C₆H₄)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*-(Ph₂P)C₆H₄)SnClPh₂ 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 **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 ³¹P NMR resonance of **2**-Cl which features the expected tin satellites (³*J*_{117/119Sn,P} = 78/80 Hz), appears at 56 ppm confirming the symmetrical coordination of the phosphorus atoms to gold. The ¹¹⁹Sn NMR resonance of **2**-Cl (Figure 1b) appears as a triplet at -86 ppm (³*J*_{Sn,P} = 80 Hz) which is comparable to the value reported for [(*o*-(*i*Pr₂P)C₆H₄)₂SnClPh]AuCl (-80 ppm, ³*J*_{Sn,P} = 67.7 Hz) [4e]. This ¹¹⁹Sn chemical shift of **2**-Cl is, however, distinctly upfield from that of Ph₃SnCl (-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.

Figure 1. (a) ^{119}Sn NMR spectrum of $\text{L}^{\text{PhP}3}$ in CDCl_3 and (b) ^{119}Sn NMR spectrum of **2-Cl** in CD_2Cl_2 .

Figure 2. Molecular structures of $\text{L}^{\text{PhP}3}$ (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 $\text{L}^{\text{PhP}3}$: 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).

As shown in Figure 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 (4.35 Å) [9], and only slightly exceeds the sum of

the covalent radii (2.75 Å) [10]. The Sn-Cl(1) bond length (2.5010(10) Å) in complex **2-Cl** significantly surpasses those of tetra-coordinate organoaryl tin compounds (2.32 Å in Ph₃SnCl) [11], and is close to the value of 2.62 Å reported for penta-coordinate stannate [Ph₃SnCl₂][−] [12]. Moreover, the tin coordination geometry is that of an essentially undistorted trigonal bipyramid as shown by the linearity of the Cl(1)-Sn-Au angle of 177.93(3)° and the sum of the C_{eq}-Sn-C_{eq} angles of 359.8° (hereafter denoted as Σ_{C-Sn-C}). The molecular structures of complex **2-Cl** unambiguously indicate the coordination of the stannane moiety to the gold center. The heavier Group 14 element behaves here as a Lewis acid *via* the low-lying σ*(Sn-Cl) orbital. The Au→Sn interaction in the gold(I) complex **2-Cl** results in an unusual distorted square planar geometry at the gold center (P(1)-Au-P(2) = 165.48(3)° and Sn-Au-Cl(2) = 165.90(2)°), a situation reminiscent of that observed in the related gold-borane complex [(*o*-(*i*Pr₂P)C₆H₄)₂BPh]AuCl.[13] The Au-Cl distance of 2.5539(10) Å is longer than that in (Ph₃P)₂AuCl (2.500(4) Å) [14] and [(*o*-(*i*Pr₂P)C₆H₄)₂BPh]AuCl (2.524(1) Å) [13]. Taken collectively, the structure of **2-Cl** is analogous to that of the previously characterized fluorostannane-gold analogue which features a Au→Sn bond of 2.891(2) Å [4e].

Scheme 2. Synthesis of complexes **2-Br** and **2-I**.

Figure 3. Molecular structures of complex **2-Br** (left) and **2-I** (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 molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **2-Br**: Au-Br 2.6395(8), Au-P(1) 2.3028(16), Au-P(2) 2.3061(16), Au-Sn 2.9015(6), Sn-C(1) 2.148(7), Sn-C(25) 2.167(6), Sn-C(7) 2.182(6), Sn-Cl 2.4930(16), P(1)-Au-P(2) 164.83(6), Br-Au-Sn 165.08(2), Cl-Sn-Au 177.38(5), C(1)-Sn-C(25) 110.6(3), C(1)-Sn-C(7) 126.7(3), C(25)-Sn-C(7) 122.4(2). Selected bond lengths (Å) and angles (deg) for **2-I**: Au-I 2.7983(5), Au-P(1) 2.3109(14), Au-P(2) 2.3160(14), Au-Sn 2.9201(5), Sn-C(1) 2.157(6), Sn-C(25) 2.172(6), Sn-C(7) 2.189(6), Sn-Cl 2.4879(15), P(1)-Au-P(2) 163.69(5), I-Au-Sn 167.601(15), Cl-Sn-Au 177.34(5), C(1)-Sn-C(25) 110.0(2), C(1)-Sn-C(7) 128.6(2), C(25)-Sn-C(7) 121.0(2).

When TBABr (*n*-tetrabutylammonium bromide) or TBAI (*n*-tetrabutylammonium iodide) is added to the reaction mixture of $\mathbf{L}^{\text{PhP}_3}$ and (tbt)AuCl, the gold-bromide and gold-iodide complexes **2-Br** and **2-I** are isolated (Scheme 2). The *in situ* halide metathesis reactions suggest that the gold center has a stronger affinity for softer halide which seems to contradict the fact Au-X bond energy of trivalent gold complexes of general formula $(\text{Ph}_3\text{P})\text{Au}(\text{4-Me-C}_6\text{H}_4)(\text{CF}_3)(\text{X})$ decreases in the following order $\text{X} = \text{Cl} > \text{Br} > \text{I}$.^[15] This apparent dichotomy can be reconciled by noting that the formation of **2-Br** and **2-I** from **2-Cl** does not involve homolytic cleavage of the Au-X bond but instead halide exchange. As such, the formation **2-Br** and **2-I** from **2-Cl** is not solely guided by the thermodynamic stability of the Au-X bond. The

solvation of the free halides in the reaction mixture will also influence the fate of these reactions as explained several decades ago for other soft metal halide complexes.[16] Examination of the crystal structures of both complexes (Figure 3) shows that the Au-Sn distance (2.9015(6) Å for **2-Br**, 2.9201(5) Å for **2-I**). While the Au-Sn distance of **2-Br** is essentially identical to that **2-Cl**, a measurable increase is noted for the iodide complex **2-I**. This small change originates from the decreased *trans* influence of the iodide anion, leading to a reduction of the gold atom metallobasicity. A more accentuated version of this effect is known for complexes such as (*o*-*i*Pr₂P-(C₆H₄))₃B)AuCl [17] and [(*o*-(Ph₂P)C₆H₄)₂SbF₃]AuCl [18] which undergo a rather drastic lengthening of the transannular Au→B and Au→Sb, respectively, bond upon abstraction of the chloride anion. The tin center in both **2-Br** and **2-I** adopts an undistorted trigonal bipyramid as indicated by the Cl(1)-Sn-Au angles (177.38(5)° for **2-Br**, 177.34(5)° for **2-I**) and the Σ_{C-Sn-C} values (359.7° for **2-Br**, 359.6° for **2-I**). The NMR spectroscopic features ($\delta(^{31}\text{P})$ 56.0; $\delta(^{119}\text{Sn})$ -83, $^3J_{\text{Sn-P}} = 78$ Hz for **2-Br** and $\delta(^{31}\text{P}) = 55.9$; $\delta(^{119}\text{Sn})$ -83, tin satellites not detected for **2-I**) show little change when compared to those of **2-Cl** and as such merit no further comments.

Scheme 3. Synthesis of complexes **3** and **4**.

As a part of these studies, we have also been able to prepare the mono-phosphinostannane ligand $\mathbf{L}^{\text{Ph}_2\text{PCl}}$. As shown in Scheme 3, reaction of this ligand with (tht)AuCl and TBABr in dry CH_2Cl_2 afforded the known compound **2**-Br as well as a new compound **3** characterized by a ^{31}P NMR resonance at 65 ppm. The structure of this new compound has been elucidated by X-ray crystallography (Figure 4). It features two 1-dichlorophenylstannyl-2-diphenylphosphino-benzene ligands bound to a single gold-chloride moiety. Interestingly, the gold-bound chlorine atom interacts with the two neighboring tin atoms, resulting in an unusual T-shaped geometry as indicated by the Au-Cl(1)-Sn and Sn-Cl(1)-Sn' angles of $84.93(5)^\circ$ and $169.86(9)^\circ$, respectively. The concomitant interaction of the two tin atoms with the chloride anion is reminiscent of the Sn-Cl-Sn motifs formed when bidentate tin-based Lewis acids such as $o\text{-C}_6\text{H}_4(\text{SnClMe}_2)_2$ bind chloride anions [19]. However, the bonds formed between the bridging chloride and the two symmetrically equivalent tin atoms (Sn-Cl(1) 2.8793(9) Å) are much longer than those observed in $[o\text{-C}_6\text{H}_4(\text{SnClMe}_2)_2\text{Cl}]^-$ (2.5267(11) and 2.4762(11) Å) [19]. This lengthening is explained by the fact that the chloride anion is also interacting with the gold center through a Au-Cl bond of 2.860(3) Å which, as expected, appears elongated when compared to that in $(\text{Ph}_3\text{P})_2\text{AuCl}$ (2.500(4) Å) [14]. The lengthening of the Au-Cl bond is to be correlated to a widening of the P-Au-P angle ($156.73(8)^\circ$) which is much larger than in $(\text{Ph}_3\text{P})_2\text{AuCl}$ ($132.1(1)^\circ$) [14]. Last, a parallel can be drawn between the structure of **3** and that of a Al-Cl-Al bridged intermediate formed when $t\text{Bu}_2\text{Al}(\text{PhHC=})\text{CMes}_2\text{P-Au-PMes}_2\text{C(=CHPh)AlCl}t\text{Bu}_2$ undergoes intramolecular chloride exchange [20].

Figure 4. Molecular structure of complex **3** in the crystal (left), including a top view along the Cl(3)-Sn-Cl(1)-Sn'-Cl(3)' axis (right). 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): Au-P 2.2936(17), Au-Cl(1) 2.860(3), Sn-Cl(1) 2.8793(9), Sn-Cl(2) 2.334(2), Sn-Cl(3) 2.428(2), Au-Cl(1)-Sn 84.93(5), Sn-Cl(1)-Sn' 169.86(9), Cl(3)-Sn-Cl(1) 173.49(7), P-Au-P' 156.73(8).

The concomitant formation of **2-Br** and **3** indicates the occurrence of uncontrollable exchange reactions at tin. In fact, yet another derivative (**4**) can be isolated upon recrystallization of mixtures of **2-Br** and **3** from CH₃CN/CH₂Cl₂ (9/1). Complex **4** was characterized by elemental analysis and ESI-Mass spectrometry. An examination of the solid-state structure of **4** reveals that this new compound features a tris-phosphino-chlorostannane ligand (*o*-(Ph₂P)C₆H₄)₃SnCl; referred to as **L**^{P³Cl}) coordinated to a Au-SnCl₃ unit (Figure 5). The Au-Sn(2) bond distance (2.718(1) Å) approaches the sum of covalent radii of gold and tin (2.75 Å) and is slightly shorter than that measured in (PPh₃)₃AuSnCl₃ (2.7523(2) Å) [21]. The shortening of this bond may be correlated to the fact that of the Sn(1) tin atom engages the gold center in dative Au→Sn

interaction of 3.087(1) Å in a direction directly trans from the trichlorostannate ligand. The Au→Sn interaction in **4** is longer and thus weaker than that in **2-Cl** (2.9069(6) Å). In line with this argument, the Sn(1)-Cl(1) distance (2.435(2) Å) measured in **4** is slightly shorter than that in **2-Cl** (2.5010(10) Å). As a result of the Au→Sn dative interaction, the Sn(1) atom adopts a nearly perfect trigonal bipyramidal geometry as indicated by the Au-Sn(1)-Cl(1) angle of 177.01(5)° and the $\Sigma_{\text{C-Sn-C}}$ value equal to 358.6°. Moreover, the gold atom displays an unusual pentacoordination geometry approaching that of a trigonal bipyramidal (Sn(2)-Au-Sn(1) = 175.61(2)°, $\Sigma_{\text{P-Au-P}}$ = 348.2°). Altogether, the structure of **4** is unique in that the gold atom is concomitantly coordinated to a Z-type tin ligand and an X-type tin ligand. We also note that the geometries around Sn and Au in complex **4** are similar to the fluorostannane gold complex (Chart 1, **III**). However, the Au→Sn distance is longer in **4** (3.087(1) Å) than in **III** (2.9686(3) Å).

Figure 5. Molecular structure of complex **4** in the crystal (left), including a top view along the Sn(2)-Au-Sn(1)-Cl(1) axis (right). 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): Au-P(3) 2.404(2), Au-P(1) 2.410(2), Au-P(2) 2.412(2), Au-Sn(2) 2.7181(12), Au-Sn(1) 3.0873(13), Sn(2)-Cl(2) 2.392(2), Sn(2)-Cl(3) 2.410(2), Sn(2)-Cl(4) 2.413(2), Sn(1)-C(37) 2.151(8), Sn(1)-C(19) 2.169(8), Sn(1)-C(1) 2.174(8), Sn(1)-Cl(1) 2.435(2), P(1)-Au-P(2) 113.94(7), P(3)-Au-P(1) 116.59(7), P(3)-Au-P(2) 117.69(8), Sn(2)-Au-Sn(1) 175.61(2), C(37)-Sn(1)-C(19) 117.3(3), C(37)-Sn(1)-C(1) 118.5(3), C(19)-Sn(1)-C(1) 122.8(3), Cl(1)-Sn(1)-Au 177.01(5).

In order to better understand the unusual Au→Sn interactions present in complexes **2-Cl**, **2-Br**, **2-I**, and **4**, DFT calculations have been carried out using the ADF program [22]. BP86 functional [23] and a TZP all-electron basis sets [24] were used in all cases. To account for relativistic effects, a method of Zero Order Regular Approximation (ZORA) [25] has been applied. The optimized geometries are close to those observed experimentally (Table 1), thus suggesting the adequacy of this computational method. The Au→Sn bonding situation was then assessed by an Electron Localization Function (ELF) analysis [26] which was shown to be particularly useful in describing chemical bonds [27] including in complexes involving Z-ligands bound to gold [28]. In all cases, one localization domain on gold, which can be correlated to a lone pair of d-electrons, is clearly pointing toward the tin atom (Figure 6a, see SI for the ELF plots of **2-Br** and **2-I**). Therefore, the plots of ELF indicate the presence of a Au→Sn dative bond. Interestingly, a similar donor-acceptor situation could be envisioned in the Au-SnCl₃ ionic bond (complex **4**) where the electron localization around tin is directing toward gold. Further insights into these Au-Sn bonds are derived from a Boys localization analysis [29] which reveals a polarized bonding orbital for **2-Cl** (Au: 87%, Sn: 2%) and **4** (Au: 90%, Sn: 1%) (Figure 6b, see SI for the Boys plots of **2-Br** and **2-I**). Accordingly, the Boys orbital calculated for the Au-SnCl₃ bond in **4** bears a significant contribution from tin (Au: 9%, Sn: 75%), suggesting the polar nature of the Au-SnCl₃ ionic bond.

Table 1. Selected bond lengths and angles (in Å and deg, respectively) for complexes **2-Cl**, **2-Br**, **2-I**, and **4** as determined crystallographically and optimized computationally.

	2-Cl		2-Br		2-I		4	
	X-Ray	DFT	X-Ray	DFT	X-Ray	DFT	X-Ray	DFT
Au-Sn	2.9069(6)	3.005	2.9015(6)	3.016	2.9201(5)	3.046	3.087(1)	3.154
Au-X ^a	2.554(1)	2.589	2.6395(8)	2.717	2.7983(5)	2.899	2.718(1)	2.852
Sn-Cl	2.501(1)	2.535	2.493(1)	2.537	2.488(1)	2.528	2.435	2.520
Au-Sn-Cl	177.93(3)	179.27	177.38(5)	178.80	177.34(5)	179.69	177.01(5)	179.46
Σ C-Sn-C	359.8	359.5	359.7	359.5	359.6	359.3	358.6	359.4

^aX = Cl for **2-Cl**; X = Br for **2-Br**; X = I for **2-I**; X = SnCl₃ for **4**.

Figure 6. (a) ELF plots for **2**-Cl (left) and **4** (right). The maps are drawn in the plane containing two central heavy atoms and the tin-bound chloride. (b) Plots of the Au-Sn Boys localized orbital (at 0.03 isovalue) for **2**-Cl (left) and **4** (right). Hydrogen atoms are omitted for clarity.

Aside from the qualitative view, the topology of the electron density of the ADF optimized structures was subjected to an Atoms-In Molecules (AIM) [30] analysis using the Dgrid program [31]. This analysis reveals a straight bond path connecting the gold and tin atom in **2**-Cl with an electron density $\rho(r)$ of 0.0343 e bohr⁻³ at the bond critical point (BCP) (Figure 7). Analogous calculations previously carried out on [(*o*-(*i*Pr₂P)C₆H₄)₂SnClPh]AuCl [4e] afforded electron density of 0.0356 e bohr⁻³. This difference suggests that the increase Lewis basicity of the di-*iso*-propylphosphino moiety of [(*o*-(*i*Pr₂P)C₆H₄)₂SnClPh]AuCl strengthens the Au→Sn interaction. Furthermore, the *trans* influence of the gold-bound halide is noticeable as the electron density (ρ_e) at Au→Sn BCP slightly decreases on going from **2**-Cl (0.0343 e bohr⁻³) to **2**-Br (0.0336 e bohr⁻³) and **2**-I (0.0317 e bohr⁻³) (Table 2). This trend is consistent with the calculated Au→Sn bond length which increases in the order **2**-Cl (3.005 Å) < **2**-Br (3.016 Å) < **2**-I (3.046 Å). These results are in line with the reported *trans* influence for halides in square-planar Pt^{II} complexes [32]. The tris-phosphinostannane gold complex **4** possesses the weakest Au→Sn interaction among all as indicated by the electron density at BCP of Au→Sn(1) linkage (0.0263 e bohr⁻³). This value can also be correlated to the longer calculated Au→Sn(1) distance of 3.154 Å (vs 3.005 Å in **2**-Cl). It is also interesting to note that the electron densities calculated at the Au→Sn BCP in **2**-Cl, **2**-Br, and **2**-I (0.0343-0.0317 e bohr⁻³) are only slightly lower than that of the Au-SnCl₃ ionic bond in **4** (0.0464 e bohr⁻³). This comparison attests to the strength of the Au→Sn interactions. Further insights into the Au-Sn bonds are derived from the Laplacian value ($\nabla^2\rho_e$) at the BCP which determines whether the electron density is locally concentrated

($\nabla^2\rho_e < 0$) or depleted ($\nabla^2\rho_e > 0$).[33] As shown in Table 2, the positive Laplacian sign at the BCPs suggests the polar nature of the Au-Sn, Sn-Cl, and Au-X bonds.

Table 2. Calculated electron density (ρ_e , e bohr⁻³) and Laplacian ($\nabla^2\rho_e$, e bohr⁻⁵) at the (3, -1) BCPs.

	2-Cl		2-Br		2-I		4	
	ρ_e	$\nabla^2\rho_e$	ρ_e	$\nabla^2\rho_e$	ρ_e	$\nabla^2\rho_e$	ρ_e	$\nabla^2\rho_e$
Au-Sn	0.0343	0.0428	0.0336	0.0416	0.0317	0.0399	0.0263	0.0344
Au-X ^a	0.0563	0.1510	0.0510	0.1143	0.0452	0.0810	0.0464	0.0602
Sn-Cl	0.0584	0.1165	0.0582	0.1161	0.0590	0.1183	0.0604	0.1207

^aX = Cl for **2-Cl**; X = Br for **2-Br**; X = I for **2-I**; X = SnCl₃ for **4**.

Figure 7. Calculated electron-density maps for complexes **2-Cl** (left) and **4** (right) with relevant bond paths and bond critical points. Hydrogen atoms and the diphenyl substituents at phosphorus are omitted for clarity.

CONCLUSION

In summary, we show that bis- and tris-phosphino-chlorostannane ligands can coordinate

to gold ions, with the tin center acting as a Z-ligand. The Au→Sn interaction present in these complexes results in unusual square planar (**2-Cl**, **2-Br**, **2-I**) and trigonal bipyramidal (**4**) geometries at gold reminiscent of the trivalent state. According to the DFT calculations, the Au→Sn interaction in **2-Cl** is weaker than that in the *iso*-propylphosphino analogue [(*o*-(*i*Pr₂P)C₆H₄)₂SnClPh]AuCl. Furthermore, we show that the Au→Sn interaction is also affected by the gold-bound halide as the electron density at the BCP increases from 0.0317 e bohr⁻³ (**2-I**) to 0.0336 e bohr⁻³ (**2-Br**) and 0.0343 e bohr⁻³ (**2-Cl**). Hence, these results indicate that the strength of the Au→Sn dative interaction is influenced by the ligands surrounding gold. Finally, we also describe a complex (**4**) in which the gold atom is interacting simultaneously with a Z-type tin ligand and an X-type tin ligand. The structural and computational results obtained for **4** shows that the X-type tin ligand forms a stronger interaction with the gold center.

EXPERIMENTAL SECTION

General considerations. Trichlorophenylstannane, TBABr, and TBAI (TBA = *n*-tetrabutylammonium) were purchased from Aldrich and used as received. *Ortho*-lithio-diphenylphosphinobenzene,[34] ligand **L**^{Ph₂PCl},[35] and (tht)AuCl[36] were prepared according to the reported procedures. Solvents were dried by passing through an alumina column (MeCN and CH₂Cl₂) or refluxing under N₂ over Na/K (Et₂O). NMR spectra were recorded on Varian Unity Inova 400 FT NMR (399.57 MHz for ¹H, 100.47 MHz for ¹³C, 161.75 MHz for ³¹P, 149 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 85% H₃PO₄ and neat Me₄Sn.

Synthesis of ligand L^{PhP3} . A solution of trichlorophenylstannane (120mg, 0.397 mmol) was added to a solution *ortho*-lithio-diphenylphosphinobenzene in ether (10 mL). After stirring for 10 min, the brown residue was extracted with CH_2Cl_2 (3 x 10 mL) and filtered over Celite. The solvent was removed to afford a brown solid, which was washed with hexane (3 x 10 mL) to afford L^{PhP3} as a light yellow solid (260 mg, 66.8 % yield). 1H NMR (399.57 MHz, $CDCl_3$): δ 6.85 (t, 12H, $^3J_{H-H} = 7.6$ Hz), 6.92 (t, 3H, $^3J_{H-H} = 7.6$ Hz), 7.05 (t, 15H, $^3J_{H-H} = 7.2$ Hz), 7.14 (t, 6H, $^3J_{H-H} = 7.6$ Hz), 7.25 (t, 3H, $^3J_{H-H} = 7.6$ Hz), 7.34 (d, 3H, $^3J_{H-H} = 7.6$ Hz), 7.53 (d, 2H, $^3J_{H-H} = 6.8$ Hz, $^3J_{Sn-H} = 50.3$ Hz), 7.77 (d, 3H, $^3J_{H-H} = 7.6$ Hz, $^3J_{Sn-H} = 50.7$ Hz); ^{13}C NMR (100.47 MHz, $CDCl_3$): δ 127.46, 127.55, 127.67, 127.87 (d, $J_{P-C} = 6.0$ Hz), 128.75, 129.012 (s, $J_{Sn-C} = 50.4$ Hz), 133.09 (d, $J_{P-C} = 17.5$ Hz), 134.95 (s, $J_{Sn-C} = 46.6$ Hz), 137.94 (d, $J_{P-C} = 1.2$ Hz, $J_{Sn-C} = 38.2$ Hz), 138.36 (d, $J_{P-C} = 11.4$ Hz), 139.63 (d, $J_{P-C} = 20.6$ Hz, $J_{Sn-C} = 64.8$ Hz), 144.08 (d, $J_{P-C} = 3.0$ Hz, $J_{Sn-C} = 46.6$ Hz), 144.48 (d, $J_{P-C} = 6.1$ Hz, $J_{Sn-C} = 18.2$ Hz), 154.60 (d, $J_{P-C} = 69.4$ Hz, $J_{Sn-C} = 12.3$ Hz); ^{31}P NMR (161.75 MHz, $CDCl_3$): δ -2.51 (s, $^3J_{Sn-P} = 28.5$ Hz); ^{119}Sn NMR (149 MHz, $CDCl_3$): δ -144 (q, $^3J_{Sn-P} = 28.5$ Hz). Anal. Calcd for $C_{60}H_{47}P_3Sn$: C, 73.56; H, 4.84. Found: C, 72.68; H, 5.08.

Synthesis of complex 2-Cl. Solid (tht)AuCl (26.2 mg, 0.082 mmol) was added to a solution of L^{PhP3} (40 mg, 0.041 mmol) in dry CH_2Cl_2 (3 mL) at room temperature. The reaction was allowed to stir for 15 min. Slow vapor diffusion of Et_2O into the resulting solution resulted in the crystallization of both **2-Cl**-0.5 CH_2Cl_2 and **1** (28.7 mg) over 24 hours. Based on elemental

analysis, it was determined that **2**-Cl-0.5CH₂Cl₂ and **1** had formed and crystallized in a 2:1 ratio resulting in a 47.3% yield for this reaction. ¹H NMR of **2**-Cl (399.57 MHz, CD₂Cl₂): δ 6.47-6.57 (m, 4H), 6.85 (t, 1H, ³J_{H-H} = 7.2 Hz), 7.29-7.52 (m, 20H), 7.70-7.76 (m, 6H), 8.86 (d, 2H, ³J_{H-H} = 7.7 Hz, ³J_{Sn-H} = 63.9 Hz); ¹³C NMR (100.47 MHz, CD₂Cl₂): δ 129.87, 130.75, 131.19 (t, *J*_{P-C} = 5.78 Hz), 131.94, 133.43, 133.67 (d, *J*_{P-C} = 9.50 Hz), 134.26, 134.37, 135.64 (t, *J*_{P-C} = 7.36 Hz), 136.25 (t, *J*_{P-C} = 6.54 Hz), 136.38, 154.16, 167.67 (one of the quaternary carbon resonances is not detected); ³¹P NMR (161.75 MHz, CD₂Cl₂): δ 56.2 (s, ³J(^{117/119}Sn,P) = 78/80 Hz); ¹¹⁹Sn NMR (149 MHz, CD₂Cl₂): δ -86 (t, ³J_{Sn-P} = 80 Hz). Anal. Calcd for C₁₂₁H₉₆Au₄Cl₆P₆Sn₂ (**2**-Cl-0.5CH₂Cl₂ : **1** = 2 : 1): C, 48.87; H, 3.25; Cl, 7.15. Found: C, 48.76; H, 3.01; Cl, 7.56.

Synthesis of complex 2-Br. Solid (tht)AuCl (42.5 mg, 0.133 mmol) was added to a solution of **L**^{PhP3} (65 mg, 0.066 mmol) in dry CH₂Cl₂ (3 mL). After stirring for 10 min, solid *n*-tetrabutylammonium bromide (32.1 mg, 0.100 mmol) was added to the reaction mixture. Slow vapor diffusion of Et₂O into the resulting solution resulted in the crystallization of both **2**-Br-0.5CH₂Cl₂ and **1** (58 mg) over 24 hours. Based on the different crystal morphologies of **2**-Br-0.5CH₂Cl₂ and **1**, isolation of the crystals of **2**-Br-0.5CH₂Cl₂ was carried out under a microscope, affording a pure sample of **2**-Br-0.5CH₂Cl₂ (22 mg) in 30.9% yield. ¹H NMR of **2**-Br (399.57 MHz, CD₂Cl₂): δ 6.48-6.58 (m, 4H), 6.85 (t, 1H, ³J_{H-H} = 7.1 Hz), 7.28-7.56 (m, 20H), 7.69-7.77 (m, 6H), 8.86 (d, 2H, ³J_{H-H} = 7.8 Hz, ³J_{Sn-H} = 64.6 Hz); ¹³C NMR (100.47 MHz, CD₂Cl₂): δ 129.87, 130.70, 131.12 (t, *J*_{P-C} = 5.78 Hz), 133.41, 133.66 (d, *J*_{P-C} = 9.89 Hz), 134.25, 134.37,

135.64 (t, $J_{\text{P-C}} = 7.56$ Hz), 136.25 (t, $J_{\text{P-C}} = 5.81$ Hz), 136.37, 154.03, 167.59 (two of the quaternary carbon resonances are not detected); ^{31}P NMR (161.75 MHz, CD_2Cl_2): δ 56.0 (s, $^3J_{\text{Sn-P}} = 78$ Hz); ^{119}Sn NMR (149 MHz, CD_2Cl_2): δ -83 (bs). Anal. Calcd for $\text{C}_{42.5}\text{H}_{34}\text{AuBrCl}_2\text{P}_2\text{Sn}$ (2-Br-0.5 CH_2Cl_2): C, 47.57; H, 3.19. Found: C, 47.25; H, 3.33.

Synthesis of complex 2-I. Solid (tht)AuCl (42.5 mg, 0.133 mmol) was added to a solution of L^{PhP_3} (65 mg, 0.066 mmol) in dry CH_2Cl_2 (3 mL). After stirring for 10 min, solid *n*-tetrabutylammonium iodide (36.8 mg, 0.100 mmol) was added to the reaction mixture. Slow vapor diffusion of Et_2O into the resulting solution resulted in the crystallization of both 2-I-0.5 CH_2Cl_2 and **1** (47 mg) over 24 hours. Based on elemental analysis, it was determined that 2-I-0.5 CH_2Cl_2 and **1** had formed and crystallized in a 2:1 ratio resulting in a 44.9% yield for this reaction. ^1H NMR of 2-I (399.57 MHz, CD_2Cl_2): δ 6.49-6.59 (m, 4H), 6.86 (t, 1H, $^3J_{\text{H-H}} = 7.1$ Hz), 7.28-7.62 (m, 20H), 7.69-7.77 (m, 6H), 8.86 (d, 2H, $^3J_{\text{H-H}} = 7.7$ Hz, $^3J_{\text{Sn-H}} = 64.3$ Hz); ^{13}C NMR (100.47 MHz, CD_2Cl_2): δ 129.76, 130.73, 131.04 (t, $J_{\text{P-C}} = 5.22$ Hz), 131.94, 133.32, 133.68 (d, $J_{\text{P-C}} = 8.28$ Hz), 134.11, 134.25, 135.55 (t, $J_{\text{P-C}} = 6.14$ Hz), 136.12 (t, $J_{\text{P-C}} = 6.14$ Hz), 136.39, 154.09, 167.41 (one of the quaternary carbon resonances is not detected); ^{31}P NMR (161.75 MHz, CD_2Cl_2): δ 55.9 (bs); ^{119}Sn NMR (149 MHz, CD_2Cl_2): δ -83 (bs). Anal. Calcd for $\text{C}_{121}\text{H}_{96}\text{Au}_4\text{Cl}_4\text{I}_2\text{P}_6\text{Sn}_2$ (2-I-0.5 CH_2Cl_2 : **1** = 2 : 1): C, 46.04; H, 3.07. Found: C, 46.53; H, 3.59.

Synthesis of complexes 3 and 4. To a CH₂Cl₂ solution (10 mL) of ligand **L**^{Ph₂PCl} (83 mg, 0.146 mmol) was added solid (tht)AuCl (46.7 mg, 0.146 mmol) and TBABr (47.0 mg, 0.146 mmol) in the glove box at room temperature. After stirring for 30 min, the reaction mixture was filtrated through Celite. Slow vapor diffusion of Et₂O into the resulting solution at -40 °C resulted in the crystallization of both **2**-Br-0.5CH₂Cl₂ and **3**-CH₂Cl₂-0.5Et₂O (39 mg) over 24 hours. Complex **3** has been characterized by ³¹P NMR (161.75 MHz, CD₂Cl₂) at 64 ppm. Further recrystallization of the mixture of **2**-Br and **3** from dry MeCN/CH₂Cl₂ (9/1) afforded 5 mg of **4**-CH₂Cl₂ in the form of colorless single crystals which are insoluble in organic solvents such as CD₂Cl₂. Anal. Calcd for C₅₅H₄₄AuCl₆P₃Sn₂ (**4**-CH₂Cl₂): C, 45.72; H, 3.07. Found: C, 46.55; H, 3.14. HRMS(ESI⁺): m/z calculated for C₅₄H₄₂AuClP₃Sn⁺ 1135.0870, found 1135.0908.

Crystallographical measurements. The crystallographic measurements were performed at 110(2) K using a Bruker APEX-II CCD area detector diffractometer (Mo-K_α radiation, λ = 0.71073 Å) for **L**^{PhP₃}, **2**-Br-0.5CH₂Cl₂, **2**-I-0.5CH₂Cl₂, **3**-CH₂Cl₂-0.5Et₂O, and **4**-CH₂Cl₂; and a Siemens SMART-CCD area detector diffractometer (Mo-K_α radiation, λ = 0.71073 Å) for **2**-Cl-0.5CH₂Cl₂. In each case, a specimen of suitable size and quality was selected and mounted onto a nylon loop. The structures were solved by direct methods, which successfully located most of the nonhydrogen atoms. Semi-empirical absorption corrections were applied.[37] Subsequent refinement on F² using the SHELXTL/PC package (version 6.1)[38] allowed location of the remaining non-hydrogen atoms.

Computational details. All electrons structural optimizations were carried out on complexes **2-Cl**, **2-Br**, **2-I**, and **4** using the ADF program (2008.01).[22b, 22c, 39] All calculations were carried out using the BP86[23] functional with all electron a TZP[24] basis set for all atoms. These calculations were performed using the Zero Order Regular Approximation (ZORA).[25] The topology of the electron density of the ADF optimized structures was subjected to an Atom-In-Molecule (AIM)[30] analysis using the Dgrid program (version 4.4).[31] Visualization of the geometry (including bond paths and bond critical points) as well as of the electron density map was carried with the Material Studio program (version 4.4). Electron localization function (ELF)[26] plots and the Boys localized orbitals[29b-d] were visualized in ADF program.

Supporting Information

Appendix A. Supplementary data CCDC 1481793-1481798 contains the supplementary crystallographic data for complexes **L^{PhP3}**, **2-Cl**, **2-Br**, **2-I**, **3**, and **4**. 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.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation (CHE-1300371), the Welch Foundation (A-1423), Texas A&M University (Arthur E. Martell Chair of Chemistry). We also acknowledge Dr. Lisa Pérez for her help with the theoretical calculations.

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