

# Synthesis of Heteropolynuclear Complexes Using New Tin(IV) Dimers. X-ray Structure of $[\text{AuSnCl}(\text{tBu})_2(\text{SC}_6\text{H}_4)(\text{PPh}_3)]$

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$\text{Li}_2(\text{SC}_6\text{H}_4)$  reacts with  $[\text{SnR}_2\text{Cl}_2]$  affording the dinuclear derivatives  $[\{\text{SnR}_2(\text{SC}_6\text{H}_4)\}_2]$  ( $\text{R} = \text{Me}, \text{tBu}, \text{Ph}$ ) (**1a–c**). The reaction of these dimer derivatives with various  $[\text{AuClL}]$  breaks the tin-sulfur bonds, affording the heterobimetallic complexes  $[\text{AuSnClR}_2(\text{SC}_6\text{H}_4)\text{L}]$  ( $\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{CH}_2\text{PPh}_3$ ) (**2–4**). The synthesis of  $[\text{Au}\{\text{SnClMe}_2(\text{SC}_6\text{H}_4)\}_2]$  (**5**) is carried out in a similar way. The lithiated product  $\text{Li}_2(\text{SC}_6\text{H}_4)$  can react with  $[\text{AuCl}(\text{PPh}_3)]$ , giving  $[\text{Au}_2(\text{SC}_6\text{H}_4)(\text{PPh}_3)_2]$  (**6**). The molecular structure of the complex  $[\text{AuSnCl}(\text{tBu})_2(\text{SC}_6\text{H}_4)(\text{PPh}_3)]$  (**2b**) has been established by X-ray diffraction and shows a tetrahedral tin center and a linear gold(I) atom bridged by the “C–S” bidentate ligand.

## Introduction

The synthesis of heteronuclear complexes has attracted much attention in the last two decades, with the expectation that new reactivity patterns might emerge from the combination of disparate metals in a single species.<sup>1</sup> The early–late complexes are the most studied, with examples of transition/main group metal derivatives being less abundant.<sup>2</sup> On the other hand, thiolate metal complexes are particularly interesting, not only because they are an important class of heteronuclear complexes but also due to their participation in central components of the active sites of enzymes such as ferredoxin and nitrogenase,<sup>3</sup> their relevance to metal-catalyzed hydrodesulfurization,<sup>4</sup> and their applications as fungicides,<sup>5</sup> electrical conductors,<sup>6</sup> and inorganic

pharmaceuticals.<sup>7</sup> There are relevant examples of the latter in gold thiolate chemistry because of antiarthritic and anticancer activity.<sup>8</sup>

The transmetalation reaction of dithiolate groups from tin to gold has been successfully carried out in very mild conditions by our group;<sup>9</sup> in contrast, the C–Sn bond usually is not easily broken, and the transfer of organic groups to gold requires some palladium catalyst (Stille reaction).<sup>10</sup> The differences in reactivity conditions to transfer S or C ligand ends from tin to other metals should be a clean way for the preparation of heteronuclear complexes. If the ligand contains the two ends, S and C, simultaneously, the partial transfer of the ligand should afford complexes with the ligand bridging two metal centers.

We have selected a heterodifunctional S,C-donor ligand ( $\text{SC}_6\text{H}_4^{2-}$ ) bonded to a tin center as a reagent in a synthetic strategy to form heterodinuclear Sn–Au derivatives by partial transfer of the thiolate end ligand to the gold center, whereas the *ortho*-carbon remains bonded to the tin atom. In this paper, we report the synthesis of the tin(IV) dimer compounds  $[\{\text{SnR}_2(\text{SC}_6\text{H}_4)\}_2]$  ( $\text{R} = \text{Me}, \text{tBu}, \text{Ph}$ ). From the former, several heteropolynuclear Au(I)–Sn(IV) complexes have been obtained, and in the case of  $[\text{AuSnCl}(\text{tBu})_2(\text{SC}_6\text{H}_4)(\text{PPh}_3)]$ , characterization by X-ray diffraction shows a heterometallic *ortho*-metalated species.

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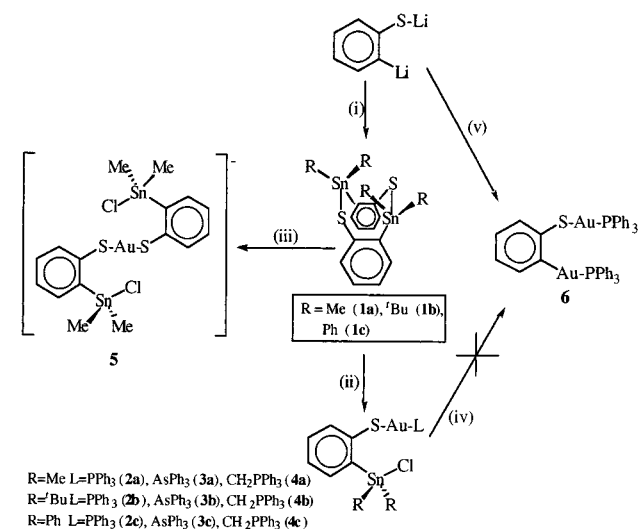
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Scheme 1<sup>a</sup>

<sup>a</sup> Key: (i) [SnR<sub>2</sub>Cl<sub>2</sub>]. (ii) 2[AuClL]. (iii) PPN[AuCl<sub>2</sub>]. (iv) Δ, [AuCl(PPh<sub>3</sub>)]. (v) 2[AuCl(PPh<sub>3</sub>)].

Table 1. Mass Spectral Data<sup>a</sup> for Complexes 1a–c

complex	[M] <sup>+</sup>	[M – R] <sup>+</sup>	[M – 2R] <sup>+</sup>	[M – 3R] <sup>+</sup>	[M – 4R] <sup>+</sup>
<b>1a</b> dimer	515 (21)	499 (67)		469 (14)	
monomer	259 (52)	243 (46)	229 (53)		
<b>1b</b> dimer	683 (6)	625 (28)	569 (7)	511 (7)	455 (16)
monomer	343 (100)				
<b>1c</b> dimer	763 (22)	685 (100)	609 (12)		
monomer	381 (40)	305 (76)	229 (60)		

<sup>a</sup> *m/z*, relative intensity in parentheses.

## Results and Discussion

As starting material for the synthesis of tin complexes, we selected lithium 2-lithiobenzenethiolate, Li<sub>2</sub>(SC<sub>6</sub>H<sub>4</sub>), which can be obtained by reaction of benzenethiolate and LiBu in a 1.2 ratio and isolated as a white oil.<sup>11</sup> It reacts smoothly with equimolecular amounts of dialkyl- or diaryldihalotin(IV) complexes, affording [{SnR<sub>2</sub>(SC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>] (R = Me (**1a**), t-Bu (**1b**), Ph (**1c**)) as white solids (eq i, Scheme 1). Two different formulations are possible for our complexes **1a–c**, as monomer with a five-atom metallacycle with the group SC<sub>6</sub>H<sub>4</sub> acting as a chelate group, or as a dinuclear derivative with the orthometalated groups doubly bridging. The mass spectra (LSIMS<sup>+</sup>) of these compounds show peaks corresponding to both protonated monomer [SnR<sub>2</sub>(SC<sub>6</sub>H<sub>4</sub>) + H]<sup>+</sup> and dimer [Sn<sub>2</sub>R<sub>4</sub>(SC<sub>6</sub>H<sub>4</sub>)<sub>2</sub> + H]<sup>+</sup>, with no peaks for higher nuclearities. Other peaks that come from these monomers and dimers by the loss of several organic groups (methyl, *tert*-butyl or phenyl) (Table 1) are present. Although some associative processes are not completely out of the question, the elevated intensities of the dimer formulation and the peaks that come from these suggest that these tin complexes are dinuclear.

The <sup>1</sup>H NMR spectra show signals corresponding to inequivalent groups bonded to tin. In the methyl derivative (**1a**), the presence of two signals from these groups with the corresponding satellites from the active nuclei of tin (<sup>119</sup>Sn and <sup>117</sup>Sn) is the final proof for the dimer formulation of complexes **1**. In a monomer compound, the organic groups have to be equivalent, but in

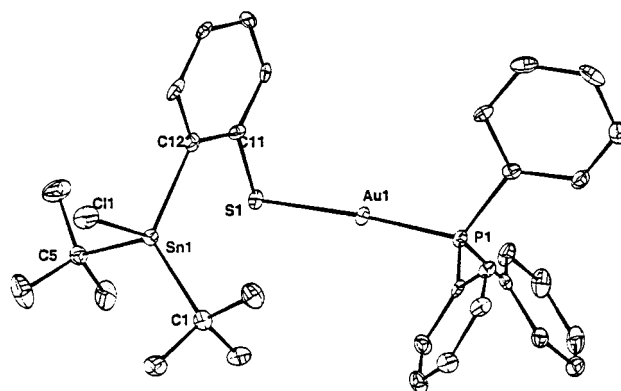


Figure 1. Molecule of **2a** in the crystal. Displacement parameter ellipsoids represent 50% probability surfaces. H atoms are omitted for clarity.

the dimer the eight-membered ring which is formed makes two different groups, *endo* and *exo*, inequivalent (Scheme 1).

The reaction of halogold(I) complexes [AuClL] (L = PPh<sub>3</sub>, AsPh<sub>3</sub>, CH<sub>2</sub>PPh<sub>3</sub>) with the tin compounds **1a–c** transfers only the thiolate unit to gold, thus breaking the dimer. Heterodinuclear derivatives are obtained: [AuSnClR<sub>2</sub>(SC<sub>6</sub>H<sub>4</sub>)L] (R = Me, L = PPh<sub>3</sub> (**2a**), AsPh<sub>3</sub> (**3a**), CH<sub>2</sub>PPh<sub>3</sub> (**4a**); R = t-Bu, L = PPh<sub>3</sub> (**2b**), AsPh<sub>3</sub> (**3b**), CH<sub>2</sub>PPh<sub>3</sub> (**4b**); R = Ph, L = PPh<sub>3</sub> (**2c**), AsPh<sub>3</sub> (**3c**), CH<sub>2</sub>PPh<sub>3</sub> (**4c**)) (eq ii, Scheme 1). The IR spectra of these gold–tin complexes show the lack of the characteristic<sup>12</sup> ν(Au–Cl) ≈ 350 cm<sup>–1</sup> band, suggesting that the thiolate group has been transferred. The mass spectra (LSIMS<sup>+</sup>) do not show peaks corresponding to the molecular ion, but [M – Cl]<sup>+</sup> and [M – R]<sup>+</sup> are present, the former being more abundant than the latter. The <sup>1</sup>H NMR spectra of the methyl complexes show only one signal corresponding to this group, so now the organic residues bonded to the tin center are equivalent. The <sup>31</sup>P{<sup>1</sup>H} NMR show singlets at 37.9, 37.8, and 37.4 ppm for **2a–c**, respectively. These data are in accordance with the existence of a S atom *trans* to the phosphorus in a linear coordination of gold(I) (e.g., at 35.6 ppm in [Au<sub>2</sub>(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>],<sup>13</sup> 36.3 ppm in [Au<sub>2</sub>(S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>C–H<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>],<sup>13</sup> and 36.5 ppm in [Au<sub>2</sub>(C<sub>3</sub>S<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sup>14</sup>). in contrast with a coordination of the bridging SC<sub>6</sub>H<sub>4</sub> group through the carbon to the gold center (e.g., 44.9 ppm in [Au(mes)PPh<sub>3</sub>]<sup>15</sup> and 42.7 ppm in [Au(C<sub>6</sub>F<sub>5</sub>)PPh<sub>3</sub>]). Complexes **4a–c** show singlets at around 30.5 ppm.

The molecular structure of **2a** was determined by an X-ray study and is shown in Figure 1. Selected bond lengths and angles are given in Table 2. The (SC<sub>6</sub>H<sub>4</sub>)<sup>2–</sup> ligand is bridging both metals centers, with the S atom bonded to the gold and the carbon to the tin center. The gold atom is in a linear coordination typical for gold(I) complexes, with S–Au–P = 176.56(11)°. Unlike other (phosphine)gold(I) thiolate complexes, there are no intermolecular short gold–gold contacts in the lattice, probably because the bulkiness of this thiolate–tin ligand prevents further contacts between gold atoms.

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**Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2a**

Au(1)–P(1)	2.259(3)	Au(1)–S(1)	2.306(3)
Sn(1)–C(12)	2.152(11)	Sn(1)–C(5)	2.180(11)
Sn(1)–C(1)	2.185(12)	Sn(1)–Cl(1)	2.442(3)
S(1)–C(11)	1.795(10)		
P(1)–Au(1)–S(1)	176.6(1)	C(12)–Sn(1)–C(5)	113.8(4)
C(12)–Sn(1)–C(1)	122.3(4)	C(5)–Sn(1)–C(1)	117.9(4)
C(12)–Sn(1)–Cl(1)	96.5(3)	C(5)–Sn(1)–Cl(1)	100.2(4)
C(1)–Sn(1)–Cl(1)	98.0(3)	C(111)–P(1)–C(121)	107.3(5)
C(111)–P(1)–Au(1)	111.4(4)	C(121)–P(1)–Au(1)	110.8(4)
C(131)–P(1)–Au(1)	117.7(4)	C(11)–S(1)–Au(1)	98.7(3)
C(12)–C(11)–S(1)	117.0(8)	C(11)–C(12)–Sn(1)	116.4(8)
C(3)–C(12)–Sn(1)	125.7(9)	C(3)–C(1)–Sn(1)	107.7(9)
C(2)–C(1)–Sn(1)	108.1(8)	C(4)–C(1)–Sn(1)	112.0(7)
C(8)–C(5)–Sn(1)	111.2(8)	C(6)–C(5)–Sn(1)	108.0(8)
C(7)–C(5)–Sn(1)	109.9(8)		

The Au–P bond length is 2.259(3) Å, very similar to those found in [Au(SR)PPh<sub>3</sub>] (R = Ph,<sup>16</sup> 2,4,6-C<sub>6</sub>H<sub>2</sub>(iPr)<sub>3</sub>,<sup>16</sup> C<sub>17</sub>H<sub>15</sub>NSO<sub>2</sub>)<sup>17</sup> derivatives, which lie in the range 2.2566(14)–2.260(3) Å. The Au–S distance is 2.306(3) Å, in the range of the latter complexes [2.284(2)–2.3229(13) Å]. The tin(IV) is tetracoordinated in an irregular tetrahedral disposition, C(12)–Sn–C(5) = 113.8(4)°, C(12)–Sn–C(1) = 122.3(4)°, C(5)–Sn–C(1) = 117.9(4)°, C(12)–Sn–Cl = 96.5(3)°, C(5)–Sn–Cl = 100.2(3)°, and C(1)–Sn–Cl = 98.0(3)°. The bond lengths Sn–C are similar at *ca.* 2.17 Å, in accordance with normal Sn(IV)–C distances.<sup>18</sup> There is a short interaction between the sulfur and the tin center (2.920 Å), which can be responsible for the distorted geometry around this metal, but there is no interaction between the tin and the gold center (Sn...Au = 4.63 Å).

A tin–gold–tin trinuclear complex can be obtained by this kind of process. The reaction of PPN[AuCl<sub>2</sub>] and [{SnMe<sub>2</sub>(SC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>}] in a 1:1 ratio gives the complex PPN[Au{SnClMe<sub>2</sub>(SC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>}] (**5**) (eq iv, Scheme 1). The IR spectrum of the new trinuclear compound shows the lack of the characteristic signal  $\nu$ (Au–Cl), and in the mass spectrum (LSIMS<sup>–</sup>) there is a peak corresponding to the anion [M – PPN]<sup>–</sup> at *m/z* 781 (85%). The acetone solution of this complex shows a conductivity value, 124 Ω<sup>–1</sup> cm<sup>2</sup> mol<sup>–1</sup>, in agreement with a formulation as a 1:1 electrolyte.<sup>19</sup>

It is noteworthy that the mass spectra of **2a–c** show a signal at *m/z* 1026 assignable to an [Au<sub>2</sub>(SC<sub>6</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> ion. Complexes of this kind could be obtained if the transfer of the SC<sub>6</sub>H<sub>4</sub> ligand was complete from the tin to the gold centers. So we tried the reaction between **2a–c** with [AuCl(PPh<sub>3</sub>)] in a 1:1 ratio in chloroform at reflux with the presence of catalytic amounts of [PtCl<sub>2</sub>(NCPH)<sub>2</sub>], but no reaction occurred. [Au<sub>2</sub>(SC<sub>6</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (**6**) can be obtained by reaction of the ortholithiated thiophenol with [AuCl(PPh<sub>3</sub>)] in a 1:2 ratio. Complex **6** shows in the mass spectrum the parent peak at *m/z* 1026 (12%), and the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows, at room temperature, two sharp singlets at 37.2 and 41.5 ppm. The former could be assigned to the phos-

phorus *trans* to the S atom and the latter, at lower field, to the one *trans* to the C atom. Complex **6** is one of the few examples of *ortho*-metalated gold complexes.<sup>20</sup>

## Experimental Section

The starting materials Li<sub>2</sub>(SC<sub>6</sub>H<sub>4</sub>),<sup>11</sup> [AuClL] (L = PPh<sub>3</sub>,<sup>21</sup> AsPh<sub>3</sub>,<sup>22</sup> CH<sub>2</sub>PPh<sub>3</sub>),<sup>23</sup> and PPN[AuCl<sub>2</sub>]<sup>24</sup> were prepared as described previously. All other reagents were commercially available.

The C, H, N, S analyses were carried out on a Perkin-Elmer 2400 microanalyzer. Conductivities were measured in approximately 5 × 10<sup>–4</sup> mol dm<sup>–3</sup> acetone solutions with a Jenway 4010 conductimeter. The infrared spectra were recorded (4000–200 cm<sup>–1</sup>) on a Perkin-Elmer 599 spectrophotometer, using Nujol mulls between polyethylene sheets. The NMR spectra were recorded on a Bruker ARX 300 spectrometer, in CDCl<sub>3</sub>. Chemical shifts are cited relative to SiMe<sub>4</sub> (<sup>1</sup>H) or 85% H<sub>3</sub>PO<sub>4</sub> (external <sup>31</sup>P). Mass spectra were recorded on a VG Autospec LSIMS using 3-nitrobenzyl alcohol as matrix.

**Synthesis of [SnR<sub>2</sub>(SC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>] [R = Me (**1a**), 'Bu (**1b**), Ph (**1c**)].** Lithium 2-lithiobenzenethiolate was prepared as described previously from thiophenol (0.788 g, 7.2 mmol), TMDA (2.38 cm<sup>3</sup>, 15.9 mmol), and *n*-butyllithium (1.015 g, 15.9 mmol). Solid Li<sub>2</sub>(SC<sub>6</sub>H<sub>4</sub>) was isolated by filtration under nitrogen, washed with dry hexane (2 × 15 cm<sup>3</sup>), and dissolved in dry THF (10 cm<sup>3</sup>) precooled to –78 °C. The solution was then treated dropwise during 45 min with [SnCl<sub>2</sub>R<sub>2</sub>] [R = Me (1.090 g, 5 mmol), 'Bu (1.519 g, 5 mmol), Ph (1.719 g, 5 mmol)] dissolved in dry THF (15 cm<sup>3</sup>). The mixture was warmed to room temperature overnight; the solution was acidified with dilute chloridic acid and then concentrated in vacuum, and the residue was taken up in dichloromethane. The solution was washed with water and dried with MgSO<sub>4</sub> and active carbon, the solvent was evaporated to 5 cm<sup>3</sup>, and hexane (20 cm<sup>3</sup>) was added, resulting in the precipitation of white complexes. Yield (%): **58** (**1a**), **74** (**1b**), **47** (**1c**).

Data for **1a** are as follows. Anal. Calcd: C, 37.4; H, 3.9; S, 12.5. Found: C, 36.85; H, 3.8; S, 11.85.  $\Lambda_M$ : 4 Ω<sup>–1</sup> cm<sup>2</sup> mol<sup>–1</sup>. <sup>1</sup>H NMR:  $\delta$  = 7.50 and 7.24 (m, 8H, SC<sub>6</sub>H<sub>4</sub>), 0.45 (s, <sup>2</sup>J<sub>Sn–H</sub> = 57.1 Hz, 3H, Me) 0.41 (s, <sup>2</sup>J<sub>Sn–H</sub> = 51.6 Hz, 3H, Me).

Data for **1b** are as follows. Anal. Calcd: C, 49.3; H, 6.5; S, 9.4. Found: C, 49.3; H, 6.05; S, 8.8.  $\Lambda_M$ : 4 Ω<sup>–1</sup> cm<sup>2</sup> mol<sup>–1</sup>. <sup>1</sup>H NMR:  $\delta$  = 7.77, 7.32, 7.13, and 7.07 (m, 8H, SC<sub>6</sub>H<sub>4</sub>), 1.35 (s, <sup>3</sup>J<sub>Sn–H</sub> = 40.3 Hz, 18H, 'Bu).

Data for **1c** are as follows. Anal. Calcd: C, 56.75; H, 3.7; S, 8.4. Found: C, 56.25; H, 3.65; S, 8.1.  $\Lambda_M$ : 3 Ω<sup>–1</sup> cm<sup>2</sup> mol<sup>–1</sup>. <sup>1</sup>H NMR:  $\delta$  = 7.86–6.88 (m, 28H, SC<sub>6</sub>H<sub>4</sub> and Ph).

**Synthesis of [AuSnClR<sub>2</sub>(SC<sub>6</sub>H<sub>4</sub>)L] [R = Me, L = PPh<sub>3</sub> (**2a**), AsPh<sub>3</sub> (**3a**), CH<sub>2</sub>PPh<sub>3</sub> (**4a**); R = 'Bu L = PPh<sub>3</sub> (**2b**), AsPh<sub>3</sub> (**3b**), CH<sub>2</sub>PPh<sub>3</sub> (**4b**); R = Ph, L = PPh<sub>3</sub> (**2c**), AsPh<sub>3</sub> (**3c**), CH<sub>2</sub>PPh<sub>3</sub> (**4c**)].** To a dichloromethane solution (20 cm<sup>3</sup>) of **1a** (0.026 g, 0.1 mmol), **1b** (0.034 g, 0.1 mmol), or **1c** (0.038 g, 0.1 mmol) was added [AuClL] [L = PPh<sub>3</sub> (0.049 g, 0.1 mmol), AsPh<sub>3</sub> (0.054 g, 0.1 mmol), or CH<sub>2</sub>PPh<sub>3</sub> (0.051 g, 0.1 mmol)]. After 1 h of stirring, the solutions were concentrated in vacuo, and the addition of hexane afforded the precipitation of the new complexes as white, pale yellow (**3a**, **4c**), or pink solids

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(4b). Yield (%): 75 (2a), 48 (3a), 67 (4a), 82 (2b), 49 (3b), 68 (4b), 71 (2c), 51 (3c), 62 (4c).

Data for 2a are as follows. Anal. Calcd: C, 41.55; H, 3.35; S, 4.25. Found: C, 41.35; H, 3.25; S, 3.95.  $\Lambda_M$ :  $3 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta = 37.9$  (s).  $^1\text{H}$  NMR:  $\delta = 7.69$  and  $7.20$  (m, 4H,  $\text{SC}_6\text{H}_4$ ),  $7.52\text{--}7.44$  (m, 15H,  $\text{PPh}_3$ ),  $0.96$  (s,  $^2J_{\text{Sn-H}} = 65.3$  Hz, 6H, Me). Mass spectrum,  $m/z$  (relative intensity):  $[\text{M} - \text{Cl}]^+ = 717$  (35),  $[\text{M} - \text{R}]^+ = 737$  (19).

Data for 3a are as follows. Anal. Calcd: C, 39.25; H, 3.15; S, 4.05. Found: C, 39.0; H, 2.9; S, 4.15.  $\Lambda_M$ :  $7 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .  $^1\text{H}$  NMR:  $\delta = 7.68$  and  $7.20$  (m, 4H,  $\text{SC}_6\text{H}_4$ ),  $7.43$  (m, 15H,  $\text{AsPh}_3$ ),  $0.97$  (s,  $^2J_{\text{Sn-H}} = 63.6$  Hz, 6H, Me). Mass spectrum,  $m/z$  (relative intensity):  $[\text{M} - \text{Cl}]^+ = 761$  (59),  $[\text{M} - \text{R}]^+ = 782$  (30).

Data for 4a are as follows. Anal. Calcd: C, 42.35; H, 3.55; S, 4.2. Found: C, 42.0; H, 3.4; S, 3.9.  $\Lambda_M$ :  $37 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta = 30.7$  (s).  $^1\text{H}$  NMR:  $\delta = 7.63\text{--}7.47$  (m, 15H,  $\text{-PPh}_3$ ),  $7.11$  and  $7.01$  (m, 4H,  $\text{SC}_6\text{H}_4$ ),  $1.95$  (d,  $^2J_{\text{P-H}} = 12.2$  Hz, 2H,  $\text{-CH}_2\text{-}$ ),  $0.96$  (s,  $^2J_{\text{Sn-H}} = 65.1$  Hz, 6H, Me). Mass spectrum,  $m/z$  (relative intensity):  $[\text{M} - \text{Cl}]^+ = 729$  (31),  $[\text{M} - \text{R}]^+ = 749$  (30).

Data for 2b are as follows. Anal. Calcd: C, 46.0; H, 4.45; S, 3.85. Found: C, 45.9; H, 4.35; S, 3.7.  $\Lambda_M$ :  $2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta = 37.4$  (s).  $^1\text{H}$  NMR:  $\delta = 7.77$  and  $7.13$  (m, 4H,  $\text{SC}_6\text{H}_4$ ),  $7.49\text{--}7.46$  (m, 15H,  $\text{PPh}_3$ ),  $1.46$  (s,  $^2J_{\text{Sn-H}} = 52.6$  Hz, 18,  $\text{'Bu}$ ). Mass spectrum,  $m/z$  (relative intensity):  $[\text{M} - \text{Cl}]^+ = 801$  (27),  $[\text{M} - \text{R}]^+ = 779$  (15).

Data for 3b are as follows. Anal. Calcd: C, 43.7; H, 4.25; S, 3.65. Found: C, 43.15; H, 4.4; S, 4.0.  $\Lambda_M$ :  $7 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .  $^1\text{H}$  NMR:  $\delta = 7.74$  and  $7.13$  (m, 4H,  $\text{SC}_6\text{H}_4$ ),  $7.57\text{--}7.46$  (m, 15H,  $\text{AsPh}_3$ ),  $1.46$  (s,  $^3J_{\text{Sn-H}} = 48.8$  Hz, 18,  $\text{'Bu}$ ). Mass spectrum,  $m/z$  (relative intensity):  $[\text{M} - \text{R}]^+ = 846$  (11).

Data for 4b are as follows. Anal. Calcd: C, 46.65; H, 4.65; S, 3.75. Found: C, 46.35; H, 4.25; S, 3.7.  $\Lambda_M$ :  $36 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta = 30.5$  (s).  $^1\text{H}$  NMR:  $\delta = 7.69\text{--}7.47$  (m, 15H,  $\text{-PPh}_3$ ),  $7.00$  and  $6.90$  (m, 4H,  $\text{SC}_6\text{H}_4$ ),  $1.98$  (d,  $^2J_{\text{P-H}} = 12.2$  Hz, 2H,  $\text{-CH}_2\text{-}$ ),  $1.35$  (s,  $^3J_{\text{Sn-H}} = 52.5$  Hz, 18,  $\text{'Bu}$ ). Mass spectrum,  $m/z$  (relative intensity):  $[\text{M} - \text{Cl}]^+ = 815$  (47),  $[\text{M} - \text{R}]^+ = 793$  (9).

Data for 2c are as follows. Anal. Calcd: C, 49.35; H, 3.35; S, 3.65. Found: C, 49.35; H, 3.35; S, 3.5.  $\Lambda_M$ :  $2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta = 37.4$  (s).  $^1\text{H}$  NMR:  $\delta = 8.07\text{--}7.22$  (m, 29H). Mass spectrum,  $m/z$  (relative intensity):  $[\text{M} - \text{Cl}]^+ = 842$  (28),  $[\text{M} - \text{R}]^+ = 800$  (16).

Data for 3c are as follows. Anal. Calcd: C, 47.0; H, 3.2; S, 3.5. Found: C, 46.75; H, 2.65; S, 3.85.  $\Lambda_M$ :  $3 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .  $^1\text{H}$  NMR:  $\delta = 8.05\text{--}6.90$  (m, 29H). Mass spectrum,  $m/z$  (relative intensity):  $[\text{M} - \text{Cl}]^+ = 885$  (51),  $[\text{M} - \text{R}]^+ = 843$  (41). Data for 4c are as follows. Anal. Calcd: C, 49.95; H, 3.4; S, 3.6. Found: C, 49.55; H, 3.45; S, 3.4.  $\Lambda_M$ :  $49 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta = 30.7$  (s).  $^1\text{H}$  NMR:  $\delta = 8.04\text{--}6.99$  (m, 29H),  $1.73$  (d,  $^2J_{\text{P-H}} = 12.0$  Hz, 2H,  $\text{-CH}_2\text{-}$ ). Mass spectrum,  $m/z$  (relative intensity):  $[\text{M} - \text{Cl}]^+ = 855$  (20),  $[\text{M} - \text{R}]^+ = 813$  (12).

**Synthesis of  $[\text{Au}\{\text{SnClMe}_2(\text{SC}_6\text{H}_4)_2\}_2]$  (5).** To a dichloromethane solution (20  $\text{cm}^3$ ) of 1a (0.026 g, 0.1 mmol) was added  $\text{PPN}[\text{AuCl}_2]$  (0.040 g, 0.05 mmol). After 1 h of stirring, the solution was concentrated in vacuum, and the addition of hexane afforded the precipitation of the new complex as a white solid. Yield: 43%. Anal. Calcd: C, 47.3; H, 3.8; S, 4.85. Found: C, 47.7; H, 4.2; S, 5.15.  $\Lambda_M$ :  $117 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .  $^1\text{H}$  NMR:  $\delta = 7.64\text{--}7.42$  and  $7.04$  (m, 8H,  $\text{SC}_6\text{H}_4$ ),  $0.88$  (s,  $^2J_{\text{Sn-H}} = 65.6$  Hz, 12H, Me).

**Synthesis of  $[\text{Au}_2(\text{SC}_6\text{H}_4)(\text{PPh}_3)_2]$  (6).** Lithium 2-lithiobenzenethiolate was prepared as described previously from thiophe-

nol (0.788 g, 7.2 mmol), TMDA (2.38  $\text{cm}^3$ , 15.9 mmol), and *n*-butyllithium (1.015 g, 15.9 mmol). Solid  $\text{Li}_2(\text{SC}_6\text{H}_4)$  was isolated by filtration under nitrogen, washed with dry hexane ( $2 \times 15 \text{ cm}^3$ ), and dissolved in dry THF (40  $\text{cm}^3$ ) precooled to  $-78^\circ\text{C}$ . Then  $[\text{AuCl}(\text{PPh}_3)]$  (4.947 g, 10 mmol) was added slowly. The mixture was warmed to room temperature overnight; the solution was acidified with dilute chloridic acid and then was concentrated in vacuum, and the residue was taken up in dichloromethane. The solution was washed with water and dried with  $\text{MgSO}_4$  and active carbon; evaporation of the solvent to 5  $\text{cm}^3$  and addition of diethyl ether (20  $\text{cm}^3$ ) resulted in the precipitation of white complex. Anal. Calcd: C, 49.15; H, 3.35; S, 3.1. Found: C, 49.7; H, 3.35; S, 3.2.  $\Lambda_M$ :  $4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .  $^1\text{H}$  NMR:  $\delta = 7.76$ ,  $7.09$ ,  $6.99$ , and  $6.84$  (m, 4H,  $\text{SC}_6\text{H}_4$ ),  $7.61\text{--}7.32$  (m, 30H,  $\text{PPh}_3$ ).

**X-ray determination of  $[\text{AuSnCl}(\text{'Bu})_2(\text{SC}_6\text{H}_4)(\text{PPh}_3)]$ .** Single crystals were grown by diffusing hexane into a dichloromethane solution of 2a at room temperature. A colorless prism 0.18 mm  $\times$  0.16 mm  $\times$  0.16 mm was used. The diffraction experiments were carried out on a Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating-anode generator and using Mo K $\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) at 150 K, following procedures described elsewhere.<sup>25</sup> In total, 12 761 reflections were collected in the  $\theta$  range  $1.96\text{--}25.10^\circ$  ( $-11 \leq h \leq 0$ ,  $-12 \leq k \leq 0$ ,  $-30 \leq l \leq 0$ ;  $0 \leq h \leq 11$ ,  $0 \leq k \leq 12$ ,  $0 \leq l \leq 25$ ). The structure was determined using the PATT instruction of SHELXS 86,<sup>26</sup> refined by full-matrix least-squares on  $F_o^2$ , using the program SHELXL 93.<sup>27</sup> Unfortunately, no additional  $\psi$  data were collected, and, due to the high absorption coefficient, all data used were corrected for Lorentz-polarization factors, and subsequently for absorption ( $\mu = 5.6 \text{ mm}^{-1}$ ), using the program DIFABS.<sup>28</sup> For  $Z = 4$ , we found an orthorhombic system [ $a = 10.0780(10) \text{ \AA}$ ,  $b = 11.1730(10) \text{ \AA}$ ,  $c = 28.167(2) \text{ \AA}$ ] and space group  $P2_12_12_1$ . The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included in idealized positions. Refinement proceeds to  $R = 0.0310$ ,  $wR = 0.0964$ , and the goodness of fit on  $F^2$  was 1.054 for 4852 data and 340 parameters, and  $R = 0.0382$ ,  $wR = 0.0974$  for all data. In the final Fourier synthesis, the electron density fluctuates in the range  $1.196$  to  $-0.622 \text{ e \AA}^{-3}$ .

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**Supporting Information Available:** Description of the crystal structure determinations, including tables of crystal data, data collection, and solution and refinement parameters, hydrogen coordinates, bond distances and angles, and thermal parameters (5 pages). Ordering information is given on any current masthead page.

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