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Tris(amido)tingold Complexes in Different Oxidation States. First Structural Characterization of a Sn−Au−Au−Sn Linear Chain

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The reaction of $[\mathrm{MeSi}\{\mathrm{Me_2SiN(Li)}(p\text{-tol})\}_3(\mathrm{Et_2O})_2]$ with $\mathrm{SnCl_2}$ in a 1:1 molar ratio leads the tris(amido)stannate $[\mathrm{MeSi}\{\mathrm{Me_2SiN}(p\text{-tol})\}_3\mathrm{SnLi(Et_2O)}]$ (**1**), which further reacts with neutral $[\mathrm{AuCl(PPh_3)}]$ and anionic $[\mathrm{PPN}][\mathrm{AuCl_2}]$, $\mathrm{PPN}[\mathrm{AuRCl}]$ ($\mathrm{R} = \mathrm{C_6F_5}$, mes), and chlorogold(I) complexes yielding $[\mathrm{Au}(\mathrm{MeSi}\{\mathrm{Me_2SiN}(p\text{-tol})\}_3\mathrm{Sn})(\mathrm{PPh_3})]$ (**2**) and $[\mathrm{PPN}][\mathrm{Au}(\mathrm{MeSi}\{\mathrm{Me_2SiN}(p\text{-tol})\}_3\mathrm{Sn})_2]$ (**3**) and $[\mathrm{Au}(\mathrm{MeSi}\{\mathrm{Me_2SiN}(p\text{-tol})\}_3\mathrm{Sn})(\mathrm{R})]$ ($\mathrm{R} = \mathrm{C_6F_5}$, **4**; R = mes, **5**), respectively. The reaction of **1** with the dinuclear gold(II) derivative $[\mathrm{Au_2(CH_2PPh_2CH_2)_2Cl_2}]$ in a 1:2 ratio affords $[\mathrm{Au_2(CH_2PPh_2CH_2)_2}(\mathrm{MeSi}\{\mathrm{Me_2SiN}(p\text{-tol})\}_3\mathrm{Sn})_2]$ (**6**) . In a similar way but starting from $\mathrm{PPN}[\mathrm{Au(C_6F_5)_3Cl}]$ and reacting with **1** in a 1:1 ratio, the Au(III) complex $[\mathrm{PPN}][\mathrm{Au}(\mathrm{MeSi}\{\mathrm{Me_2SiN}(p\text{-tol})\}_3\mathrm{Sn})(\mathrm{C_6F_5})_3]$ (**7**) has been obtained. X-ray crystal structure analyses were performed for compounds **2** and **6**, establishing the Sn−Au bonds [$d(\mathrm{Au{-}Sn}) = 2.5651(13)$ and 2.6804(13) Å, respectively). Compound **6** has a nearly linear Sn−Au-Au−Sn array and features the first examples of tin−gold(II) bonds.

Introduction

Since the publication of the seminal work of Nyholm and Lewis[1−3] in 1964, a great number of homo- and heteronuclear gold complexes containing direct metal−metal bonds have been described. Most of them are either clusters with the gold having a formal oxidation state between 0 and 1 or, alternatively, polynuclear complexes containing up to six $\mathrm{Au(PR_3)}$ units in the molecule, being gold(I) derivatives.[4] In contrast to these results there are only a few examples of heteronuclear complexes with gold−metal bonds in which the gold center is in the oxidation states II and III, $[\mathrm{Au_2Pt}(\mu\text{-C,S-CH_2PPh_2S})_4\mathrm{Cl_2}]$ being the only example which was characterized by an X-ray diffraction study.[5]

We have recently shown that thermally stable tripodal tris(amido)metalates of the group 14 elements can act as metal building blocks[6] in the synthesis of heterometallic systems containing unsupported metal−metal bonds. The stability of the tris(amido)metalates toward oxidation enabled their coupling not only with early and late transition metal complex fragments but equally with those of the monovalent coinage metals. In a first exploratory study[7] the tris(amido)metalates $\mathrm{H_3CC(CH_2NSiMe_3)_3MLi(THF)_2}$ ($\mathrm{M} = \mathrm{Ge, Sn}$) were successfully employed in the preparation of heteronuclear gold−tin and −germanium derivatives $[\mathrm{Q}][\{\mathrm{H_3CC(CH_2NSiMe_3)_3M}\}\mathrm{Au}]$ ($\mathrm{M} = \mathrm{Ge, Sn}$; $\mathrm{Q} = \mathrm{BzPPh_3, PPh_4}$) but were found to be unsuitable for coupling with organometallic gold(I) complexes.

In view of the previously observed additional stabilization which an aryl-ligand periphery may confer on the (amido)metal derivatives, we prepared a highly robust tris(amido)stannate, $[\mathrm{MeSi}\{\mathrm{Me_2SiN}(p\text{-tol})\}_3\mathrm{SnLi(OEt_2)}]$, which contains a totally silicon-based ligand framework. First evidence for its suitablity in stabilizing otherwise elusive metal−Sn−heterobimetallics, leading, among other bimetallic combinations, to the first structural characterization of an Ag−Sn bond,[8] prompted us to a systematic study with gold precursors in the oxidation state +I as well as its higher oxidation states +II and +III.

Experimental Section

All manipulations were performed under an inert-gas atmosphere of dried nitrogen in standard (Schlenk) glassware which was flame-dried with a Bunsen burner prior to use. Solvents were dried according to standard procedures and saturated with $\mathrm{N_2}$. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze−pump−thaw" cycles and dried over 4-Å molecular sieves.

NMR spectra were recorded on a Varian UNITY 300 spectrometer {^{1}H (300 MHz), ^{13}C NMR (75.4 MHz), ^{31}P NMR (121.4 MHz), and ^{19}F NMR (282.2 MHz)} using tetramethylsilane, $\mathrm{H_3PO_4}$ (85%, external), and $\mathrm{CFCl_3}$ as references. The ^{29}Si and ^{7}Li NMR and some of the ^{31}P NMR spectra were recorded on a Bruker AC 200 spectrometer equipped

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with a B-VT-2000 variable-temperature unit with tetramethylsilane and LiI (H$_2$O, 1 M) as references. Elemental analyses were carried out using a Perkin-Elmer 2400 microanalyzer.

[MeSi{Me$_2$SiN(Li)(*p*-tol)}$_3$(Et$_2$O)$_2$],[9] AuClPPh$_3$,[10] PPN[AuCl$_2$],[11] PPN[Au(C$_6$F$_5$)Cl)],[12] PPN[Au(mes)Cl],[13] [Au$_2$(CH$_2$PPh$_2$CH$_2$)$_2$Cl$_2$],[14] and PPN[Au(C$_6$F$_5$)$_3$Cl][10] were prepared as previously reported. All other chemicals used were commercially available and used without further purification.

Preparation of Compounds. [MeSi{Me$_2$SiN(*p*-tol)}$_3$SnLi(OEt$_2$)] (1). To a stirred solution of 491 mg (0.75 mmol) of [MeSi{Me$_2$SiN(Li)(*p*-tol)}$_3$(Et$_2$O)$_2$] in 30 mL of diethyl ether which was cooled at −60 °C was added 143 mg (0.75 mmol) of SnCl$_2$. After being warmed to room temperature, the reaction mixture was allowed to react for another 8−10 h. The Et$_2$O was removed by vacuum distillation, and the oily residue was dissolved in 20 mL of *n*-hexane and filtered through Celite (removal of LiCl). Concentration of the solution to ca. 2 mL and subsequent cooling to −30 °C gave **1** as pale yellow crystals. Yield: 62%. ^{1}H NMR (C$_6$D$_6$, 295 K): δ 0.27 (s, SiMe), 0.53 (s, SiMe$_2$), 0.61 (t, $^3J_{HH}$ = 7.0 Hz, Li[O(CH$_2$C*H*$_2$)]), 2.18 (s, C*H*$_3$C$_6$H$_4$), 2.97 (q, Li[O(C*H*$_2$CH$_2$)]), 6.99 (d, $^3J_{HH}$ = 8.2 Hz, H^{2,6} of tol), 7.08 (d, H^{3,5} of Tol). {^{1}H}^{13}C NMR (C$_6$D$_6$, 295 K): δ −14.6 (SiMe), 4.2 (SiMe$_2$), 20.8 (*C*H$_3$C$_6$H$_4$), 128.5, 129.8, 130.3, 150.4 (C^{2,6}, C^{3,5}, C^4, C^1 of Tol). {^{1}H}^{7}Li NMR (C$_6$D$_6$, 295 K): δ −0.84 (reference LiI (1M) external). Anal. Calcd for C$_{32}$H$_{52}$LiN$_3$OSi$_4$Sn: C, 52.45; H, 7.15; N, 5.73. Found: C, 52.64; H, 7.42; N, 5.92.

[MeSi{Me$_2$SiN(*p*-tol)}$_3$SnAu(PPh$_3$)] (2). To a solution of 367 mg (0.50 mmol) of **1** in toluene at room temperature was added 247 mg (0.50 mmol) of AuClPPh$_3$. After being stirred for 1 h, the solution was filtrated through Celite. The solvent was removed by distillation in vacuo, and the residues were washed with *n*-pentane. Drying of the residue in vacuo gave **2** as a pale yellow solid. Yellow crystals may be obtained by cooling the toluene solution at −30 °C. Yield: 92%. ^{1}H NMR (C$_6$D$_6$, 295 K): δ 0.33 (s, 3H, SiMe), 0.72 (s, 18H, SiMe$_2$), 2.14 (s, 9H, CH$_3$ *p*-tol), 6.82 (d, 6H, $^3J_{HH}$ = 8.1 Hz, H^{2,6}, *p*-tol), 6.93 (m, 15H, Ph), 7.23 (d, 6H, H^{3,5} *p*-tol). ^{31}P{^{1}H} NMR (toluene-*d*$_8$, 295 K): δ 47.9. ^{31}P{^{1}H} NMR (toluene-*d*$_8$, 215 K): 51.6 [^2J($^{119/117}$Sn−^{31}P) = 2579/2449 Hz). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 295 K): δ −14.2 (SiMe), 3.8 [SiMe$_2$], 20.9 (*C*H$_3$C$_6$H$_4$), 127.7, 127.8, 129.6, 151.2 (*p*-tol, C^{2,6}, C^4, C^{3,5}, C^1), 127.4, 129.1 (d, J_{PC} = 11.0 Hz), 130.3 (d, J_{PC} = 29.0 Hz), 131.1 (br), 134.6 (d, J_{PC} = 14.4 Hz) (Ph, C^4, C^{3,5}, C^{2,6}, C^1). ^{29}Si{^{1}H} NMR (C$_6$D$_6$, 295 K): δ 0.1, −88.0. Anal. Calcd for C$_{46}$H$_{57}$AuN$_3$Si$_4$PSn: C, 49.73; H, 5.17; N, 3.78. Found: C, 50.14; H, 5.44; N, 3.91.

[PPN][(MeSi{Me$_2$SiN(*p*-tol)}$_3$Sn)$_2$Au] (3). To a stirred solution of **1** (733 mg, 1 mmol) in diethyl ether was added 403 mg (0.5 mmol) of solid PPN[AuCl$_2$] at 0 °C. After 1 h, the resulting yellow mixture was warmed to room temperature. Stirring for another 6−7 h, filtration through Celite, and subsequent removal of the solvent gave a pale yellow residue. After washing with *n*-pentane (2 × 10 mL) and drying in vacuo complex, **3** was obtained as a pale yellow solid. Yield: 50%. ^{1}H NMR (C$_6$D$_6$, 295 K): δ 0.13 (s, 6H, SiMe), 0.36 (s, 36H, SiMe$_2$), 2.18 (s, 18H, CH$_3$, *p*-tol), 6.59 (m, 24H, H, *p*-tol), 7.46, 7.63 (m, 30H, Ph PPN). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 295 K): δ 21.8. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 295 K): δ −14.7 (SiMe), 3.1 (SiMe$_2$), 20.4 (CH$_3$, *p*-tol), 150.7, 128.7, 124.2, 126.0 (*p*-tol), 129.5, 129.6, 131.9, 132.1, 133.9 (PPN). Anal. Calcd for C$_{92}$H$_{114}$AuSi$_8$N$_7$P$_2$Sn$_2$: C, 54.20; H, 5.65; N, 4.80. Found: C, 54.65; H, 5.60; N, 5.10.

PPN[MeSi{Me$_2$SiN(*p*-tol)}$_3$SnAuR] (R = C$_6$F$_5$ (4), mes (5)). To stirred solutions of 733 mg (1 mmol) of **1** in Et$_2$O at 0 °C was added 938 mg (1 mmol) of PPN[Au(C$_6$F$_5$)Cl] or 890 mg (1 mmol) of PPN[Au(mes)Cl] for the preparation of **4** or **5**, respectively. After the reaction mixtures were allowed to reach ambient temperature, they were stirred for 1 h. After filtration through Celite the solutions were concentrated to 5 mL and stored at −30 °C. Over a period of several hours, **4** and **5** were obtained as crystalline colorless solids.

[PPN][MeSi{Me$_2$SiN(*p*-tol)}$_3$SnAu(C$_6$F$_5$)] (4). Yield: 42%. ^{1}H NMR (C$_6$D$_6$, 295 K): δ 0.29 (s, 3H, SiMe), 0.57 (s, 18H, SiMe$_2$), 2.15 (s, 9H, CH$_3$, *p*-tol), 6.86 (m, 30H, Ph PPN), 7.03 (m, 12H, H, *p*-tol). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 295 K): δ 47.5. ^{13}C{^{1}H} (C$_6$D$_6$, 295 K): δ −14.1 (SiMe), 3.9 (SiMe$_2$), 20.7 (CH$_3$, *p*-tol), 151.6, 129.3, 125.7, 129.4 (*p*-tol), 129.5, 129.6, 129.7, 132.0, 132.1, 132.2 (PPN), 136.2, 138.7, 145.3, 149.8 (C$_6$F$_5$). ^{19}F NMR: δ −116.2 (m, 2F, *o*-F), −169.9 (t, J_{FF} = 23.0 Hz, 1F, *p*-F), −170.8 (m, 2F, *m*-F). Anal. Calcd for C$_{71}$H$_{72}$AuN$_4$Si$_4$F$_5$P$_2$Sn: C, 54.45; H, 4.65; N, 3.55. Found: C, 54.35; H, 4.55; N, 3.40.

[PPN][MeSi{Me$_2$SiN(*p*-tol)}$_3$SnAu(mes)] (5). Yield: 32%. ^{1}H NMR (C$_6$D$_6$, 295 K): δ 0.39 (s, 3H, SiMe), 0.72 (s, 18H, SiMe$_2$), 2.03 (s, 9H, CH$_3$, *p*-tol), 2.08 (s, 3H, *p*-CH$_3$ mes), 2.34 (s, 6H, *o*-CH$_3$ mes), 6.70 (s, 2H, H, mes), 7.08 (m, 12H, H, *p*-tol), 6.99, 7.19 (m, 30H, Ph PPN). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 295 K): δ 21.5. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 295 K): δ −13.9 (SiMe), 4.0 (SiMe$_2$), 20.8 (CH$_3$, *p*-tol), 152.2, 129.2, 125.7, 130.1 (*p*-tol), 21.4 (*p*-CH$_3$, mes), 26.7 (*o*-CH$_3$, mes), 126.2, 128.0, 128.4, 131.7 (mes), 129.6, 129.7, 129.8, 132.0, 132.1, 134.2 (PPN). Anal. Calcd for C$_{74}$H$_{83}$AuN$_4$Si$_4$P$_2$Sn: C, 58.55; H, 5.50; N, 3.70. Found: C, 58.45; H, 5.40; N, 4.20.

[(MeSi{Me$_2$SiN(*p*-tol)}$_3$Sn)$_2$Au$_2$(CH$_2$PPh$_2$CH$_2$)$_2$] (6). To a stirred solution of 265 mg (0.362 mmol) of **1** in diethyl ether at 0 °C was added 161 mg (0.181 mmol) of [Au$_2$(CH$_2$PPh$_2$CH$_2$)$_2$Cl$_2$]. The color of the mixture changed to green and part of [Au$_2$(CH$_2$PPh$_2$CH$_2$)$_2$Cl$_2$] (yellow) remained insoluble. The reaction mixture was stirred at room temperature for 12 h, and the color changed to bright, deep red whereas the yellow solid disappeared. The LiCl was allowed to settle (about 4 h), and the clear red solution was transferred to another Schlenk tube. The solution was concentrated to ca. 2 mL by removal of the solvent in vacuo and then cooled at −30 °C. After several days, compound **6** was obtained as orange-red crystals. Yield: 70%. ^{1}H NMR (C$_6$D$_6$, 295 K): δ 0.24 (s, 6H, SiMe), 0.57 (s, 36H, SiMe$_2$), 0.90 (d, 8H, CH$_2$−P, $^2J_{PH}$ = 11.1 Hz), 2.15 (s, 18H, CH$_3$, *p*-tol), 6.77 (m, 20H, Ph), 6.91 (m, 24H, H, *p*-tol). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 295 K): δ 47.5 [^3J($^{119/117}$Sn−^{31}P)= 350/332 Hz]. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 295 K): δ −14.5 (SiMe), −3.4 (d, *CH$_2$−P*, $^1J_{PC}$ = 45.5 Hz), 3.6 (SiMe$_2$), 20.8 (CH$_3$, *p*-tol), 151.5, 129.7, 129.0, 126.8 (*p*-tol), 128.6 (d, *o*-C PPh$_2$ $^2J_{PC}$ = 11 Hz), 130.1 (d, *m*-C, PPh$_2$, $^3J_{P-C}$ = 9.2 Hz), 131.2 (s, br, *p*-C, PPh$_2$) 136.1 (d, *ipso*-C, PPh$_2$, $^1J_{PC}$ = 72 Hz). Anal. Calcd for C$_{84}$H$_{112}$Au$_2$N$_6$Si$_8$P$_2$: C, 53.5; H, 6.00; N, 4.45. Found: C, 53.15; H, 5.90; N, 4.80.

[PPN][MeSi{Me$_2$SiN(*p*-tol)}$_3$SnAu(C$_6$F$_5$)$_3$] (7). To a solution of 367 mg (0.5 mmol) of **1** in diethyl ether at room temperature was added 636 mg (0.5 mmol) of PPN[Au(C$_6$F$_5$)$_3$Cl]. After being stirred for 2 h, the mixture reaction was filtered through Celite. The resulting solution was concentrated to ca. 2 mL, and subsequent cooling at −30 °C led to the precipitation of **7** as pale yellow crystals. Yield: 43%. ^{1}H NMR (C$_6$D$_6$, 295 K): δ 0.27 (s, 3H, SiMe), 0.60 (s, 18H, SiMe$_2$), 2.22 (s, 9H, CH$_3$, *p*-tol), 7.05 (m, 24H, H, *p*-tol), 6.98−7.07, 7.16−7.24 (m, 30H, Ph PPN). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 295 K): δ 21.6. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 295 K): δ −14.2 (SiMe), 3.8 (SiMe$_2$), 20.6 (CH$_3$, *p*-tol), 150.9, 129.2, 125.3, 130.1 (*p*-tol), 129.5, 129.6, 129.7, 132.0, 132.1, 132.2 (PPN), 136.2, 138.7, 145.3, 149.8 (C$_6$F$_5$). ^{19}F NMR (C$_6$D$_6$, 295 K): δ −114.4 (m, 4F, *o*-F), −120.2 (m, 2F, *o*-F), −161.3 (t, J_{FF} = 20.8 Hz, 1F, *p*-F), −161.8 (t, J_{FF} = 20.5 Hz, 2F, *p*-F), −163.3 (m, 2F, *m*-F), −164.2 (m, 4F, *m*-F). Anal. Calcd for C$_{82}$H$_{72}$AuSi$_4$N$_4$P$_2$F$_{15}$Sn: C, 47.20; H, 3.50; N, 2.70. Found: C, 46.80; H, 3.45; N, 2.90.

X-ray Crystallographic Study of 2 and 6. Data Collection for 2 and 6. Crystals of **2** and **6** were mounted in Lindemann capillaries under argon and in an inert oil on a glass fiber, respectively. X-ray diffraction data were collected using a Siemens P4 diffractometers with graphite-monochromated Mo Kα radiation. Unit cell parameters were determined from least-squares analysis of 46 (**2**) and 64 (**6**) automatically-centered reflections in the θ-range 3−12.5°. Data were collected using a θ−2θ scan mode with a scan speed of 10 deg min^{-1}, and three reference reflections monitored after every 97 reflections during data collection showed no evidence of crystal decomposition. A semi-empirical absorption correction, based on ψ-scans, was applied to the data. Further details are listed in Table 1.

Structure Solution and Refinement for 2 and 6. The structures of **2** and **6** were solved by direct methods and Patterson methods, respectively, and were refined on F^2.[15] All non-hydrogen atoms were assigned anisotropic displacement parameters in the final cycles of full-matrix refinement, with the exception of one tolyl methyl carbon atom in **2** which was disordered over two sites of equal occupancy (C(271)

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(15) SHELXTL-PC version 5.03, Siemens Analytical X-Rax, Madison, WI, 1994.

Table 1. Crystal Data and Structure Refinement for **2** and 6

	compound	
	2	**6**
empirical formula	$C_{51}H_{69}AuN_3PSi_4Sn$	$C_{84}H_{112}Au_2N_6P_2Si_8Sn_2$
fw	1183.08	2123.77
temp (K)	293	173
cryst size (mm)	0.48 × 0.44 × 0.40	0.40 × 0.30 × 0.25
cryst system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
unit cell dimenss		
a (Å)	12.945(3)	12.923(4)
b (Å)	14.772(4)	20.274(7)
c (Å)	15.971(6)	18.255(6)
α (deg)	77.18(2)	−
β (deg)	74.28(2)	104.70(1)
γ (deg)	73.63(2)	−
V (Å^3)	2785.4(13)	4626(3)
Z	2	2
D_{calc} (Mg m^{-3})	1.411	1.525
μ(Mo Kα) (mm^{-1})	3.227	3.877
F(000)	1192	2116
$2\theta_{max}$ (deg)	59.6	45.0
reflcs collcd	19480	7047
indepdt reflcns	9794	5958
R_{int}	0.0716	0.110
max/min transm	0.7577/−0.2997	0.583/−0.461
data/restraints/params	9771/0/550	5958/306/479
goodness-of-fit on F^2	1.060	0.894
$R1$, w$R2^a$	0.0674, 0.1553 [$I > 2\sigma(I)$]	0.049, 0.120 [$I > 2\sigma(I)$]
max $\Delta\rho$ (e Å^3)	3.187	1.70

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

and C(272)) and the atoms of a severely disordered *n*-pentane molecule in **2**. Hydrogen atoms were included in idealized positions. The only features significantly greater than 1 e Å^{-2} in the final difference-Fourier maps are in close proximity to the metal atoms. Further details of the refinements are given in Table 1.

Results and Discussion

In view of the failure to extend the previously established heterobimetallic chemistry with Au(I) using the tris(amido)-metalates $H_3CC(CH_2NSiMe_3)_3MLi(THF)_2$ (M = Ge, Sn)[7] to heteroleptic Au(I) complexes or higher valent Au species, a more robust and readily accessible type of metalate was clearly desirable. The reaction of the tripodal lithium amide [MeSi{Me$_2$SiN(Li)(*p*-tol)}$_3$(Et$_2$O)$_2$][9] containing a totally silicon-based ligand framwork with SnCl$_2$ affords the tris(amido)stannate [MeSi{Me$_2$SiN(*p*-tol)}$_3$SnLi(Et$_2$O)] (**1**), which on the basis of its analytical and spectroscopic data is thought to have a structure similar to those reported for $H_3CC(CH_2NSiMe_3)_3SnLi(THF)_2$.[7,16] As in the latter, rapid migration of the (Et$_2$O)Li$^+$ unit generates NMR spectral patterns consistent with an effective 3-fold symmetry of the stannate anion.

The stannate **1** reacts with various gold halide complexes affording the respective tin−gold heteronuclear compounds (see Scheme 1) by salt metathesis and formation of the metal−metal bond. Taking this approach, gold(I) complexes have been obtained upon reaction of 1 or 2 molar equiv of the stannate with [AuCl(PPh$_3$)] or [PPN][AuCl$_2$], respectively. The tin− or ditin−gold species [MeSi{Me$_2$SiN(*p*-tol)}$_3$SnAu(PPh$_3$)] (**2**) and [PPN][(MeSi{Me$_2$SiN(*p*-tol)}$_3$Sn)$_2$Au] (**3**) are formed in good yield. The formation of the new complexes can be monitored by ^{1}H NMR spectroscopy as well as, in the case of **2**, by ^{31}P{^{1}H} NMR spectroscopy. A broad ^{31}P NMR resonance at δ 47.9 is observed for **2** in toluene-d_8 at 295 K. Upon lowering of the temperature to 215 K the signal sharpens and is shifted to δ 51.6. Associated with it are two sets of satellites [$^2J(^{119/117}Sn-^{31}P)$ = 2579/2449 Hz) which are attributed to $^{119/117}$Sn-^{31}P coupling (Figure 1). This provides direct spectroscopic evidence for the presence of a covalent Au−Sn bond.

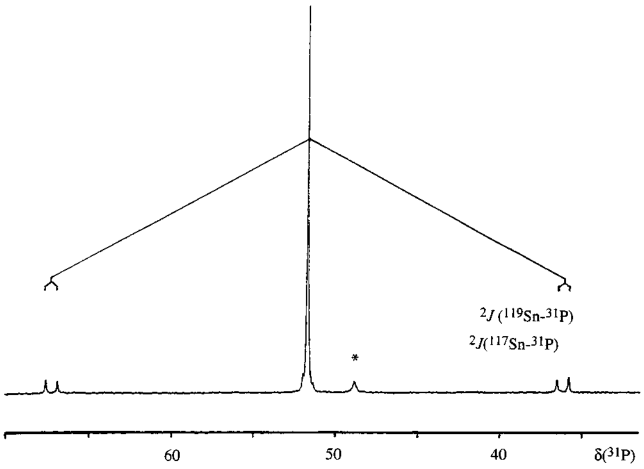

Figure 1. ^{31}P NMR spectrum of **2** recorded in d_8-toluene at 215 K displaying the $^{119/117}$Sn satellites: $^2J(^{119/117}Sn-^{31}P)$ = 2579/2449 Hz (asterisk = unidentified impurity).

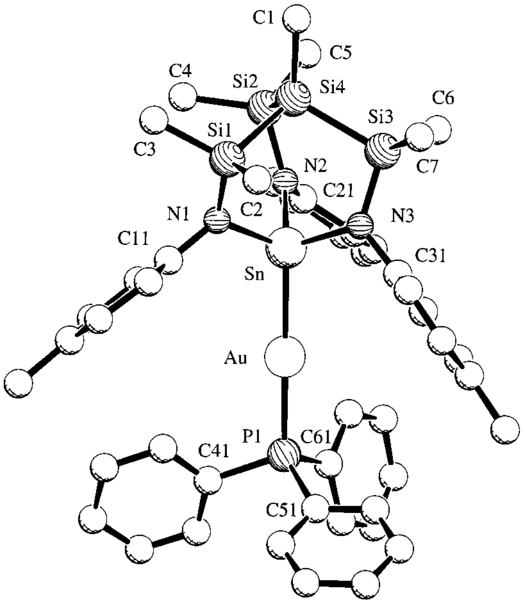

Figure 2. Molecular structure of **2** in the crystal. H atoms are omitted for clarity.

In order to elucidate the details of the structural arrangement in **2** an X-ray diffraction analysis was carried out which firmly establishes the Au−Sn bond. The molecular structure is shown in Figure 2, and the principal bonds lengths and interbond angles are listed in Table 2.

The crystal structure confirms the conclusions drawn from the spectroscopic data. The molecular structure features the tris(amido)stannate cage previously established for related lithium stannates in which the tin atom occupies one of the three-connected vertices. It is directly bonded to the Ph$_3$PAu unit [d(Au−Sn) = 2.5651(13) Å, the gold atom adopting an essentially linear geometry [<(Sn−Au−P(1)) = 179.9(1)°] as expected for monovalent gold. This Sn−Au distance is slightly shorter than that found for [Au$_8$(PPh$_3$)$_7$(SnCl$_3$)][SnCl$_6$][17] (2.625(3) Å) and considerably shorter than those in the tricoordinate Au(I)

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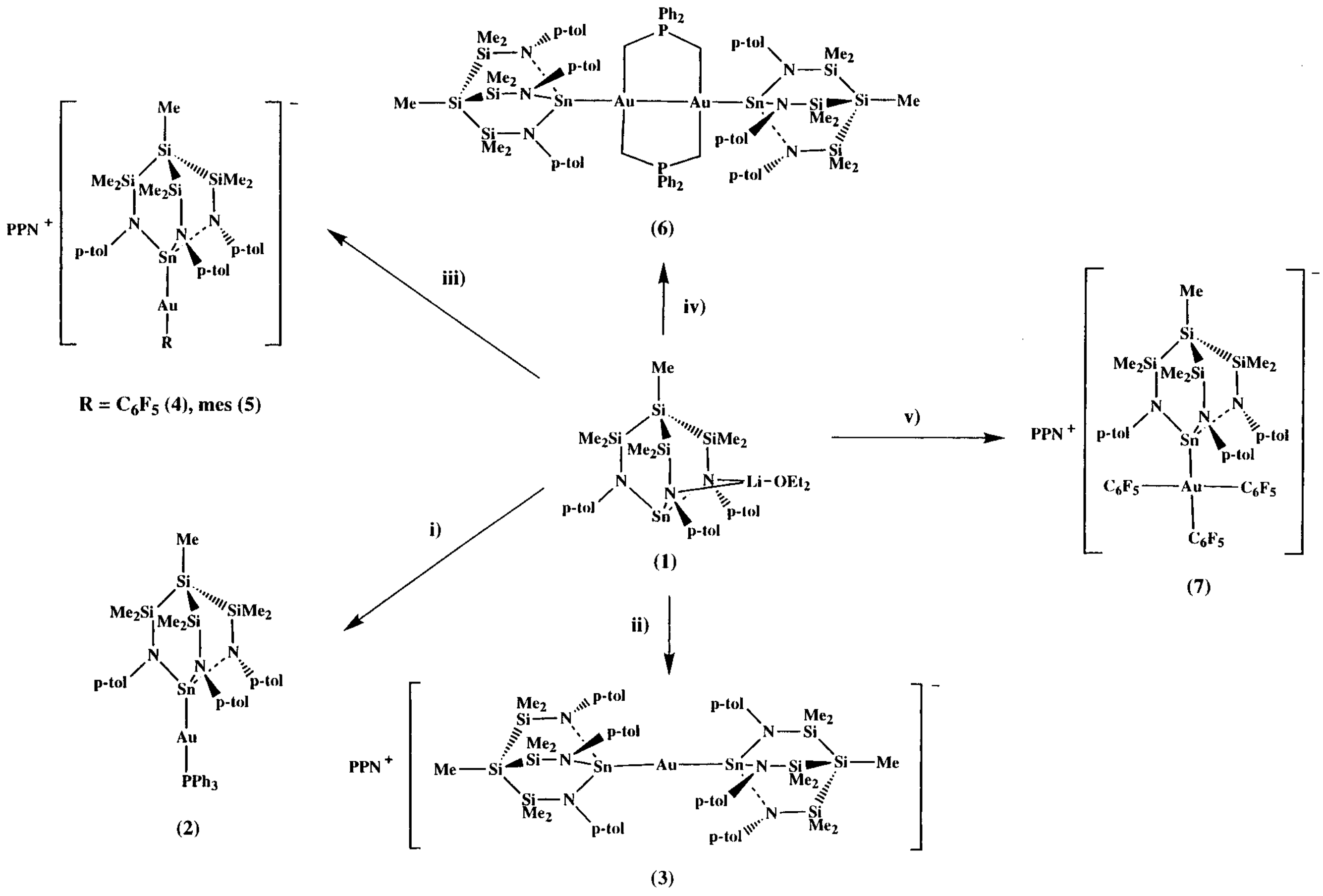
Scheme 1. Synthesis of the Au−Sn Heterobimetallic Complexes **2**−**7** Using the Tripodal Tris(amido)stannate **1** as a Tin Building Block



i) $[AuCl(PPh_3)]$, (1:1); ii) $PPN[AuCl_2]$, (2:1); iii) PPN[AuRCl], (1:1); iv) $[Au_2(CH_2PPh_2CH_2)_2Cl_2]$, (2:1); v) $PPN[Au(C_6F_5)_3Cl]$, (1:1)

complex $[(PMe_2Ph)_2AuSnCl_3]$[18] (2.881(1) Å) as well as the polynuclear compound $[Au_4(PPh_3)_4(\mu_2\text{-}SnCl_3)_2]$[19] (2.8150(7), 2.9725(8) Å) for which the authors proposed a weak Sn−Au interaction. The peripheral tolyl groups adopt the characteristic "lamp shade" arrangement previously established for metal complexes containing this tridentate amido ligand.[9,20]

Similar reactions with organometallic aurate(I) salts of the type PPN[AuRCl] {R = C_6F_5 or 2,4,6- trimethylbenzene (mes)} afforded, again by salt metathesis, the corresponding tin−gold derivatives $[MeSi\{Me_2SiN(p\text{-tol})\}_3SnAu(R)]$ (R = C_6F_5, **4**; R = mes, **5**) (reaction iii, Scheme 1). The analytical and spectroscopic data are consistent with linearly configurated organometallic gold(I) complex anions, and the organic groups remain bonded to the gold(I) center as may be deduced from the ^1H and ^{19}F NMR spectra.

As gold(II) starting material we chose $[Au_2(CH_2PPh_2CH_2)_2Cl_2]$,[14] and upon reaction with **1** in a 1:2 molar ratio in diethyl ether (reaction iv) the tetranuclear complex $[(CH_2PPh_2CH_2)_2(MeSi\{Me_2SiN(p\text{-tol})\}_3Sn)_2Au_2]$ (**6**) was obtained. This formulation is consistent with the analytical and spectroscopic data obtained. Particularly noteworthy is the presence of $^{119/117}Sn$ satellites in the ^{31}P NMR spectrum providing indirect evidence for the metal−metal bond formation [$^3J(^{119/117}Sn-^{31}P)$ = 350/332 Hz]. Other gold(II) complexes tested in similar reactions, such as $[(CH_2PPh_2CH_2)_2Au_2(C_6F_5)Cl]$, gave product mixtures which could not be separated.

In order to establish the molecular structure of the compound **6** and provide the first structural evidence for a Sn−Au(II) bond, a single-crystal X-ray structure analysis of the complex was carried out. The molecular structure of **6** is shown in Figure 3, and the principal bonds lengths and interbond angles are listed in Table 3. The compound consists of a gold(II) eight-membered diaurocycle adopting a chair conformation, linked to two tripodal tris(amido)tin fragments. This generates a nearly linear Sn−Au−Au−Sn unit linked by covalent metal−metal bonds. The molecule has a crystallographic center of symmetry which lies at the midpoint of the Au(II)−Au(II) vector.

The Sn−Au bond length is 2.6804(13) Å and thus significantly longer than the Sn−Au distance in the gold(I) derivative $[MeSi\{Me_2SiN(p\text{-tol})\}_3SnAu(PPh_3)]$ (**2**) discussed above [2.5651(13) Å]. This may be a consequence of the steric repulsion between the periphery of the tripodal amido ligand and the bis(ylide) ligands coordinated to the Au_2 unit.

The coordination geometry of the gold(II) centers is square-planar as usually exhibited in gold(II) derivatives with gold−gold bonds. The Au(II)−Au(II) distance is 2.7492(13) Å, one of the longest found for these type of gold(II) complexes, the only species with a longer Au−Au bond being $[\{(C_6F_5)Au(CH_2PPh_2CH_2)_2Au\}Au(C_6F_5)_2][Au(C_6F_5)_4]$[21] (2.755(1) Å). It should be pointed out that noncovalently bonded Au(I)···Au(I) dimers may have metal−metal contacts as short as 2.776(1)[22] and 2.769(1) Å.[23] However, given the formulation of the dinuclear complex, the existence of a covalent gold−gold bond is beyond

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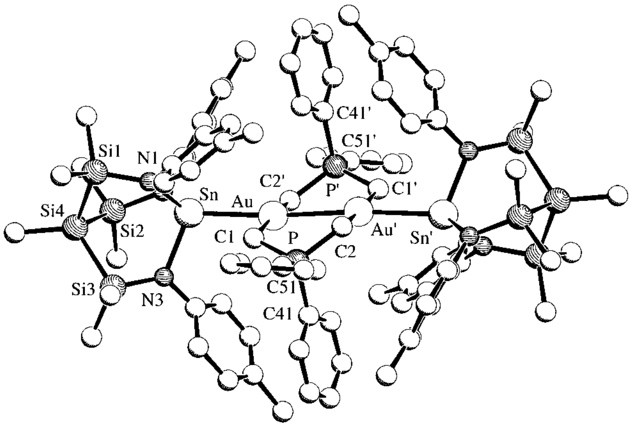

Figure 3. Structure of complex **6** in the crystal. H atoms are omitted for clarity.

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

Au−Sn	2.5651(13)	Au−P(1)	2.323(3)
Sn−N(2)	2.074(10)	Sn−N(1)	2.070(9)
Sn−N(3)	2.104(10)	P(1)−C(41)	1.827(14)
P(1)−C(51)	1.839(12)	P(1)−C(61)	1.845(13)
Si(4)−Si(3)	2.324(5)	Si(4)−Si(1)	2.347(5)
Si(3)−N(3)	1.726(10)	Si(4)−Si(2)	2.347(5)
Si(1)−N(1)	1.744(11)	Si(2)−N(2)	1.739(10)
Si(3)−N(3)	1.726(10)	C(1)−Si(4)	1.882(14)
C(2)−Si(1)	1.879(14)	C(3)−Si(1)	1.876(14)
C(4)−Si(2)	1.88(2)	C(5)−Si(2)	1.89(2)
C(6)−Si(3)	1.885(14)	C(7)−Si(3)	1.885(13)
N(1)−C(11)	1.42(2)	N(2)−C(21)	1.44(2)
N(3)−C(31)	1.41(2)		

P(1)−Au−Sn	179.91(9)	N(2)−Sn-N(1)	103.4(4)
N(2)−Sn−N(3)	101.7(4)	N(1)−Sn−N(3)	101.7(4)
N(2)−Sn−Au	116.2(3)	N(1)−Sn−Au	113.7(3)
N(3)−Sn−Au	118.0(3)	Si(1)−Si(4)−Si(2)	104.5(2)
Si(3)−Si(4)−Si(1)	103.0(2)	Si(3)−Si(4)−Si(2)	104.6(2)
N(1)−Si(1)−Si(4)	103.2(4)	N(2)−Si(2)−Si(4)	102.6(4)
N(3)−Si(3)−Si(4)	103.4(4)	C(2)−Si(1)−Si(4)	110.4(5)
C(3)−Si(1)−Si(4)	113.0(6)	C(4)−Si(2)−Si(4)	112.0(6)
C(5)−Si(2)−Si(4)	110.9(5)	C(6)−Si(3)−Si(4)	111.6(5)
C(7)−Si(3)−Si(4)	111.7(6)	C(1)−Si(4)−Si(3)	113.8(6)
C(1)−Si(4)−Si(2)	114.8(5)	C(1)−SiI4)−Si(1)	114.8(5)
N(1)−Si(1)−C(3)	110.9(7)	N(1)−Si(1)−C(2)	112.5(6)
N(2)−Si(2)−C(4)	111.2(7)	N(2)−Si(2)−C(5)	110.8(7)
N(3)−Si(3)−C(6)	114.0(6)	N(3)−Si(3)−C(7)	110.0(6)
C(3)−Si(1)−C(2)	106.9(7)	C(4)−Si(2)−C(5)	109.2(9)
C(6)−Si(3)−C(7)	106.3(7)	C(41)−P(1)−Au	111.9(5)
C(51)−P(1)−Au	114.1(4)	C(61)−P(1)−Au	111.3(4)
C(41)−P(1)−C(51)	104.5(6)	C(41)−P(1)−C(61)	108.5(6)
C(51)−P(1)−C(61)	106.3(6)	Si(1)−N(1)−Sn	120.5(5)
Si(2)−N(2)−Sn	121.6(6)	SEi(3)−N(3)−Sn	120.2(5)
C(11)−N(1)−Si(1)	121.9(8)	C(11)−N(1)−Sn	116.2(8)
C(21)−N(2)−Si(2)	121.9(8)	C(21)−N(2)−Sn	116.5(7)
C(31)−N(3)−Si(3)	123.3(8)	C(31)−N(3)−Sn	115.4(7)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **6**

Au−Sn	2.6804(13)	Au−Au′	2.7492(13)
Au−C(2′)	2.104(13)	Au−C(1)	2.112(12)
P−C(1)	1.779(14)	P−C(2)	1.795(13)
P−C(41)	1.835(12)	P−C(51)	1.856(11)
Sn−N(1)	2.126(9)	Sn−N(2)	2.108(10)
Sn−N(3)	2.148(11)	Si(1)−N(1)	1.747(10)
Si(2)−N(2)	1.761(10)	Si(3)−N(3)	1.730(11)
Si(1)−Si(4)	2.364(5)	Si(2)−Si(4)	2.372(5)
Si(3)−Si(4)	2.375		

C(1)−Au−C(2′)	172.6(5)	C(1)−Au−Sn	92.0(4)
C(2′)−Au−Sn	85.2(4)	C(2′)−Au−Au′	93.6(4)
C(1)−Au−Au′	89.8(4)	Sn−Au−Au′	174.62(3)
C(1)−P−C(2)	107.5(6)	C(1)−P−C(41)	108.9(6)
C(2)−P−C(41)	111.5(6)	C(1)−P−C(51)	112.2(6)
C(2)−P−C(51)	110.0(6)	C(41)−P−C(51)	106.8(5)
Au−C(1)−P	113.8(7)	Au′−C(2)−P	113.4(7)
N(2)−Sn−N(1)	101.7(4)	N(2)−Sn−N(3)	99.4(4)
N(1)−Sn−N(3)	102.2(4)	N(2)−Sn−Au	124.7(3)
N(1)−Sn−Au	116.4(3)	N(3)−Sn−Au	109.1(3)

doubt and the Au−Au bond length should be viewed in comparison to the metal−metal distances in dinuclear Au(I) species having a related ligand shell such as the diaurocyclic complex $[Au_2(CH_2PPh_2CH_2)_2]$[14] (2.977(1) Å) as well as the shortest intermetallic distance in metallic gold which is 2.884 Å. The distances Au−C and C−P in the diaurocycle framework are very close to those found in other cyclic gold(II) derivatives with the same bis(ylide) ligand $(CH_2PPh_2CH_2)$.[24,25]

As a gold(III) precursor material, we selected the organoaurate derivative $PPN[Au(C_6F_5)_3Cl)]$ which is known to be chemically very stable and from which the chloride atom can be easily displaced.[10] The reaction of this anionic complex with **1** in a 1:1 ratio afforded (reaction v in Scheme 1) the heteronuclear gold(III) derivative $[PPN][MeSi\{Me_2SiN(p\text{-tol})\}_3SnAu(C_6F_5)_3]$ (**7**) as established analytically and spectroscopically. The ^{19}F NMR spectrum is in accordance with a tris(pentafluorophenyl)-aurate(III) derivative displaying six signals in a 4:2:2:1:4:2 ratio which is consistent with the existence of two mutually trans C_6F_5 groups and another trans to the tin fragment.

Conclusion

In conclusion, the tripodal tris(amido)stannate with the silicon framework and the aryl periphery may be employed as a versatile "ligand" in gold chemistry, giving tin−gold complexes which are stable at room temperature. Remarkably, this behavior does not appear to be confined to monovalent gold complexes but is particularly apparent in higher valent gold species. It has produced the coordination environments typical for the different oxidation states, i.e. linear for gold(I) and square planar for gold(II) and -(III). The peripheral tolyl groups bonded to the amido-nitrogen atoms shield the tin−gold bond with respect to further reactions but do not seem to sterically impose atypical coordination geometries at the Au center.

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Supporting Information Available: Two X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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