Ligand Exchange and Molecular Aggregation of an Ag−Sn Heterobimetallic Complex: First Structural Characterization of an Ag−Sn Bond

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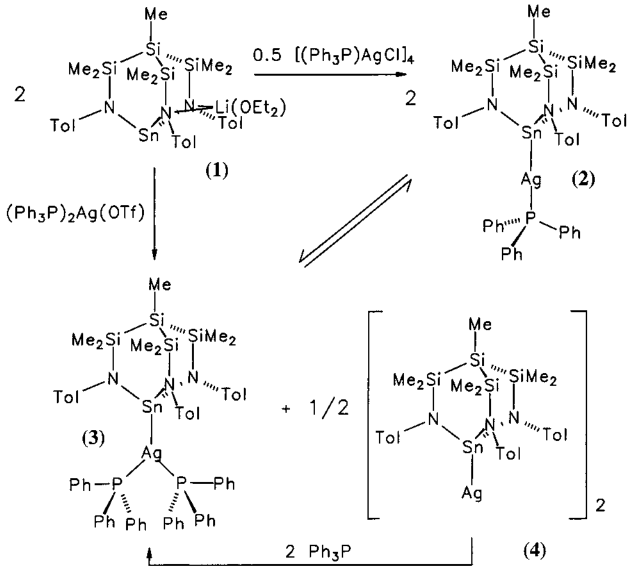
The coordination chemistry of the coinage metals is characterized by considerable variations on going from the lighter to the heavier elements. This concerns both the preferred oxidation states and the coordinations numbers, the latter being particularly evident for the oxidation state +I.[1] We recently studied the properties of Au−Sn and Au−Ge heterobimetallic complexes by using tripodal triamidometalates as building blocks in their synthesis and generating the metal−metal bonds by salt metathesis of the gold(I) halide complexes.[2]

Our development of stable tripodal triamidostannates as anionic Sn(II) nucleophiles that resist oxidation by the salts of transition metals[3,4] has facilitated the extension of our previous studies in Au(I) chemistry[2] to the lighter congeners. Ag−Sn heterobimetallic compounds are particularly rare, the only known molecular species containing an Ag−Sn bond being $(Ph_3P)_3AgSnCl_3$.[5] While this compound has been the object of several spectroscopic studies,[6] there is no direct structural proof for an Sn−Ag bond to date. Since stannous chloride finds applications in photography as a reduction sensitizer for silver halide emulsions,[7] a more detailed investigation of such Ag(I)−Sn(II) systems is of general interest.

Scheme 1. Synthesis of **2** and the phosphine redistribution equilibrium involving **2**−**4**



Reaction of a stirred solution of the lithium triamidostannate $MeSi\{SiMe_2N(p\text{-}Tol)\}_3SnLi(OEt_2)$ (**1**) with 0.25 molar equiv of $[(Ph_3P)AgCl]_4$ in toluene yields a colorless, microcrystalline solid for which analytical and spectroscopic data are consistent with a formulation as $C_{46}H_{57}AgN_3PSi_4Sn$ (**2**) and a structure as proposed in Scheme 1.[8] Although the ^1H- and ^{13}C-NMR spectra recorded within the temperature range 195−320 K appear to indicate the presence of a single component in solution (slight exchange broadening is noted at 190 K), a variable-temperature ^{31}P-NMR study revealed the presence of an equilibrium between different species in solution. On lowering of the temperature, the broad phosphine signal observed at ambient temperature (δ 14.5, 295 K) resolves into two pairs of doublets at the lowest temperature studied (centered at δ 13.3 and 15.1, 215 K). Each pair of doublets arises from $^{119}Ag-^{31}P$ and $^{117}Ag-^{31}P$ coupling and indicates discrete complexes containing $(R_3P)_nAg$ units. The pair of doublets centered at δ 15.1 displays Ag−P coupling characteristic of linear two-coordinate Ag(I) complexes [$^1J(^{119}Ag-$

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[8] (a) Compound **1** was prepared as previously reported for related triamidostannates [3] (yield 41%). Data for **1** are as follows. ^1H-NMR (C_6D_6, 295 K): δ 0.27 (s, $SiCH_3$), 0.53 (s, $Si(CH_3)_2$), 0.61 (t, $^3J_{HH} =$ 7.0 Hz, $Li[O(CH_2C\mathit{H}_2)]$), 2.18 (s, $C\mathit{H}_3C_6H_4$), 2.97 (q, $Li[O(C\mathit{H}_2CH_2)]$), 6.99 (d, $^3J_{HH} = 8.2$ Hz, $H^{2,6}$ of Tol), 7.08 (d, $H^{3,5}$ of Tol). $\{^1H\}^{13}C$-NMR (C_6D_6, 295 K): δ −14.6 ($SiCH_3$), 4.2 ($Si(CH_3)_2$), 20.8 ($\mathit{C}H_3C_6H_4$), 128.5, 129.8, 130.3, 150.4 ($C^{2,6}$, $C^{3,5}$, C^4, C^1 of Tol). $\{^1H\}^7Li$-NMR (C_6D_6, 295 K): δ −0.84 (reference LiI (1 M) external). Anal. Calcd for $C_{32}H_{52}LiN_3OSi_4Sn$: C, 52.45; H, 7.15; N, 5.73. Found: C, 52.64; H, 7.42; N, 5.92. (b) The equilibrium mixture of **2**−**4** gives only a single set of NMR data at 295 K, and the ^1H- and ^{13}C-NMR spectra recorded at 190 K are essentially identical. ^1H-NMR (C_6D_6, 295 K): δ 0.41 (s, $SiCH_3$), 0.79 (s, $Si(CH_3)_2$), 2.06 (s, $C\mathit{H}_3C_6H_4$), 6.74 (d, $^3J_{HH} = 8.2$ Hz, $H^{2,6}$ of Tol), 6.88 (m, PPh_3) 7.17 (d, $H^{3,5}$ of Tol). $\{^1H\}^{13}C$-NMR (C_6D_6, 295 K): δ −14.1 ($SiCH_3$), 3.9 ($Si(CH_3)_2$), 20.8 ($\mathit{C}H_3C_6H_4$), 125.5 ($C^{2,6}$ of Tol), 127.4 (br, C^4 of Ph), 128.7 (d, $^2J_{PC} = 38.9$ Hz), $C^{2,6}$ of Ph), 129.6, 130.4 ($C^{3,5}$, C^4 of Tol), 1131.4 (d, $^1J_{PC} = 29.0$ Hz, C^1 of Ph), 134.0 (d, $^3J_{PC} = 25.2$ Hz, $C^{3,5}$ of Ph), 152.2 (C^1 of Tol). $\{^1H\}^{31}P$-NMR (toluene-d_8, 295 K): δ 14.53 (br). That components **2** and **3** are present could only be inferred from the low-temperature ^{31}P-NMR data obtained in toluene-d_8 at 215 K: δ 13.3 [$^1J(^{117}Ag-^{31}P) = 258.7$ Hz, $^1J(^{119}Ag-^{31}P) = 298.6$ Hz, $^2J(^{117/119}Sn-^{31}P) = 716.0/750.3$ Hz, **3**], 15.1 [$^1J(^{117}Ag-^{31}P) = 399.7$ Hz, $^1J(^{119}Ag-^{31}P) = 481.3$ Hz, $^2J(^{117/119}Sn-^{31}P) = 1321.9/1383.3$ Hz, **2**].

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^{31}P) = 431.3, $^{1}J(^{117}$Ag$-^{31}$P) = 399.7 Hz].[10] In addition, the presence of $^{117/119}$Sn satellites associated with this multiplet [appearing as doublets of doublets with $^{2}J(^{117/119}$Sn$-^{31}$P) = 1321.9/1383.3 Hz] indicates the existence of direct Ag$-$Sn bonds in MeSi{SiMe$_2$N(*p*-Tol)}$_3$SnAg(PPh$_3$) (**2**). The second phosphine-containing species in solution generates a pair of doublets centered at δ 13.3. These signals have characteristics similar to those arising from **2** although reduced Ag$-$P and Sn$-$P coupling constants indicate an increase in coordination number,[11] consistent with the presence of a tricoordinate Ag(I) complex, MeSi{SiMe$_2$N(*p*-Tol)}$_3$SnAg(PPh$_3$)$_2$ (**3**) [$^{1}J(^{119}$Ag$-^{31}$P) = 298.6, $^{1}J(^{117}$Ag$-^{31}$P) = 258.7, $^{2}J(^{117/119}$Sn$-^{31}$P) = 716.0/750.3 Hz].

Since **3** is the product of a ligand redistribution, it follows that an additional phosphine-free species is generated in solution. This component was isolated as large colorless single crystals by slow fractional crystallization from a solution of **2**$-$**4** in toluene. While the analytical data, consistent with a formulation of [MeSi{SiMe$_2$N(*p*-Tol)}$_3$SnAg]$_n$,[12] indicated the absence of phosphine in this component, single-crystal *X*-ray analysis established a dimeric structure corresponding to [MeSi{SiMe$_2$N(*p*-Tol)}$_3$SnAg]$_2$ (**4**) (Figure 1).[13]

The X-ray structure of **4** shows a centrosymmetric dimeric molecular unit featuring two Sn atoms each coordinated by a triamido tripod ligand. Each Sn atom links to an Ag atom through an Sn$-$Ag bond [*d*(Sn$-$Ag) 2.6567(7) Å]. Two Ag centers in the complex are in close proximity; the distance *d*(Ag$-$Ag′) = 2.6544(11) Å is among the shortest ever observed in Ag(I) aggregates[14] and may indicate a significant d$^{10}-$d^{10} attraction. In **4**, the ligand periphery plays an “active” role[15] and facilitates the dimerization of the silver stannate units. These monomer units are linked by η^2-coordination of one tolyl group of each tripodal amido ligand to the silver atom of the opposite unit [*d*(Ag$-$C(25′)) = 2.604(5), *d*(Ag$-$C(26′)) = 2.374(4) Å]; the asymmetry of the η^2-coordination in the complex is typical of an arene$-$Ag(I) interaction.[16] In addition, the tolyl groups adopt mutual edge-to-face orientations so that a total of six $\pi-\pi$ interactions (ring centroid$-$centroid 5.1$-$5.5 Å) encircle the Ag$_2$Sn$_2$ core of the complex. This arrangement is reminisicent of the centrosymmetric sextuple phenyl embraces identified as a supramolecular motif in {Ph$_4$P$^+$}$_2$ complexes[17] and may contribute to the stability of the dimer.

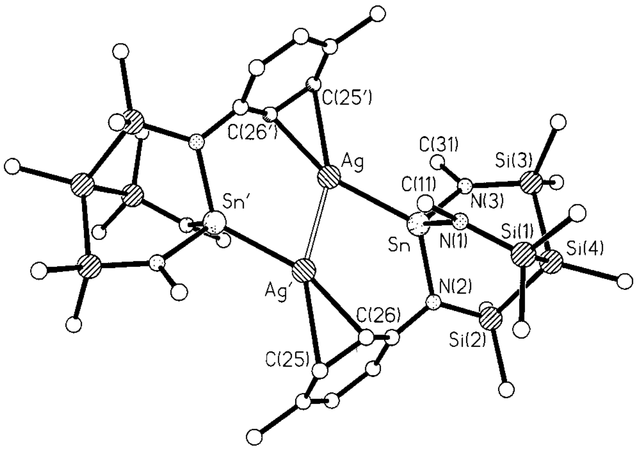

Figure 1. Molecular structure of **4** in the crystal. Peripheral tolyl groups not coordinated to Ag are omitted for clarity. Selected bond lengths (Å) and interbond angles (deg): Sn$-$Ag 2.6567(7), Sn$\cdots$Ag′ 3.2220(9), Sn$-$N(1) 2.097(4), Sn$-$N(2) 2.112(4), Sn$-$N(3) 2.100(3), Ag$-$C(25′) 2.604(5), Ag$-$C(26′) 2.375(4); Sn$-$Ag$-$C(25′) 129.47(11), Sn$-$Ag$-$C(26′) 161.92(11).

The characterization of **4** by ^{13}C-NMR spectroscopy in solution was hampered by its fairly rapid decomposition (with concomitant precipitation of Ag metal) on dissolution. The ^{1}H-NMR data are virtually identical to those obtained from the mixture of **2** and **3** with the obvious exception of absent resonances due to the phosphine ligand. Further support for the equilibrium shown in Scheme 1 derives from the observation that addition of 1 molar equiv (per equivalent of Ag) of Ph$_3$P to the solution converts both **2** and **4** to **3**, which may subsequently be isolated and characterized. The tricoordinate Ag(I) complex **3** could also be obtained by reacting the lithium stannate **1** with 1 molar equiv of (Ph$_3$P)$_2$Ag(O$_3$SCF$_3$) (Scheme 1).

In conclusion, this study has established unique behavior for these Sn$-$Ag complexes and provides the first direct structural evidence for an Ag$-$Sn bond.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the EPSRC, Wacker Chemie AG, and Professor H. Werner (Würzburg) for support of this work.

Supporting Information Available: A view of the structure of **4** showing the girdle of interacting tolyl groups in the dimer and a variable-temperature series of ^{31}P-NMR spectra of the reaction mixture of **2**$-$**4** (2 pages). An X-ray crystallographic file, in CIF format, for compound **4** is available on the Internet only. See any current masthead page for ordering and access information.

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(12) Data for **3** are as follows. Anal. Calcd for C$_{64}$H$_{72}$AgN$_3$P$_2$Si$_4$Sn: C, 59.86; H, 5.65; N, 3.27. Found: C, 59.69; H, 5.45; N, 3.44. ^{1}H-NMR (C$_6$D$_6$, 295 K): δ 0.35 (s, SiCH$_3$), 0.75 (s, Si(CH$_3$)$_2$), 2.02 (s, CH_3C$_6$H$_4$), 6.70 (d, $^3J_{HH}$ = 8.2 Hz, H^{2,6} of Tol), 6.85 (m, PPh$_3$), 7.21 (d, H^{3,5} of Tol). ^{31}P-NMR (toluene-d_8, 215 K): δ 13.3 [$^1J(^{117}$Ag$-^{31}$P) = 258.7 Hz, $^1J(^{119}$Ag$-^{31}$P) = 298.6 Hz, $^2J(^{117/119}$Sn$-^{31}$P) = 716.0/750.3 Hz]. Data for **4** are as follows. Anal. Calcd for C$_{56}$H$_{84}$Ag$_2$N$_6$Si$_8$Sn$_2$: C, 44.28; H, 5.57; N, 5.53. Found: C, 44.09; H, 5.62; N, 5.82. ^{1}H-NMR (C$_6$D$_6$, 295 K): δ 0.40 (s, SiCH$_3$), 0.77 (s, Si(CH$_3$)$_2$), 2.06 (s, CH_3C$_6$H$_4$), 6.73 (d, $^3J_{HH}$ = 8.2 Hz, H^{2,6} of Tol), 7.15 (d, H^{3,5} of Tol). The apparent C_{3v} symmetry of **4** in solution indicates that the compound either dissociates into 3-fold symmetrical halves or undergoes rapid intramolecular dynamic processes generating the observed higher symmetry on the NMR time scale. The instability of **4** in solution has impeded further investigations.

(13) Crystal data for **4**: C$_{56}$H$_{84}$Ag$_2$N$_6$Si$_8$Sn$_2$, M = 1519.14, triclinic, $P\bar{1}$ (No. 2), a = 11.183(3) Å, b = 12.615(3) Å, c = 13.815(3) Å, α = 74.582(7)°, β = 70.088(11)°, γ = 81.480(14)°, V = 1763.1(7) Å^3, Z = 1, F(000) = 768, D_c = 1.431 g cm^{-3}. The structure was solved by direct methods and refined on F^2 for 6179 unique absorption-corrected data (R_{int} 0.0211, T_{max} 0.7142, T_{min} 0.6091) out of a total of 7216 data collected. Refinement converged at R_1 [$I > 2\sigma(I)$] = 0.0389, wR_2 (all data) = 0.1058.

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