# Novel $Sn^{II}-Ag^{I}$ Reactions from $Sn[CH(SiMe_3)_2]_2$ and AgX (X = NCS, CN, NCO, or I): $Sn^{II}-Ag^{I}$ or $Sn^{IV}X_2$ Complexes

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*Summary: Treatment of $Sn(CHR_2)_2$ with the appropriate $Ag^{I}$ compound in $Et_2O$ at ca. 25 °C yielded the heterobimetallic Sn−Ag complexes $[(Ag(SCN)\{Sn(CHR_2)_2\}(thf))_2]$ (Ag−Sn′, Ag′−Sn) (**1**) and $(1/n)[(Ag(CN)\{Sn(CHR_2)_2\})_n]$ (**2**) and the oxidative adducts $Sn(CHR_2)_2X_2$ (X = NCO (**3**), I (**4**)). **1** (Ag−Sn = 2.598(1) Å) and **3** have been characterized by X-ray studies, and **1** and **2** provide the first examples of $^{119}Sn-^{109}Ag$ and $^{119}Sn-^{107}Ag$ coupling in their $^{119}Sn\{^1H\}$ NMR spectra (R = $SiMe_3$).*

Recently we reported the metathetical exchange reaction between AgNCO and $Sn(NR'_2)_2$, which gave $[\{Ag(\mu-NR'_2)\}_4]$ ($NR'_2$ = $NR_2$ or $NC(Me)_2(CH_2)_3CMe_2$, R = $SiMe_3$).[1]

We now show that from the tin(II) alkyl $Sn(CHR_2)_2$, isoelectronic with $Sn(NR_2)_2$, and (i) AgNCS or AgCN or (ii) AgNCO or AgI two quite different reaction types were observed (Scheme 1). Type i is of special interest in that the products were simple adducts, being heterobimetallic compounds containing a Ag−Sn bond: $[(Ag(SCN)\{Sn(CHR_2)_2\}(thf))_2]$ (*Ag*−*Sn*′, *Ag*′−*Sn*) (**1**) and $(1/n)[(Ag(CN)\{Sn(CHR_2)_2\})_n]$ (**2**; thf = $OC_4H_8$). Type ii reactions, in contrast, were oxidative addition−redox reactions, giving rise to metallic silver and the dialkyltin(IV) compounds $Sn(CHR_2)_2X_2$ (X = NCO (**3**) I (**4**)). Complexes **1** and **2** may be placed in the family of transition-metal complexes of carbenes $:CN(R)(CH_2)_2NR$[2a] and $:CN(R)(CH)_2NR$[2b] or their heavier group 14 element (M) congener $:MX_2$.[3]

The colorless, crystalline complexes **1**−**4** were obtained in good yield (Scheme 1) from $Sn(CHR_2)_2$[4] and AgX (X = NCS, CN, NCO, or I, respectively) in diethyl ether in the absence of light at ambient temperature and for **1** by subsequent recrystallization from thf. **2**−**4**, unlike **1**, were soluble in hydrocarbons; **1** was soluble in thf, pyridine, or chloroform. Complexes **1**−**4** gave satisfactory microanalyses, multinuclear NMR spectra, and MS data;[5] for **1**−**3**, IR and $^{119}Sn$ Mössbauer spectral data were also collected,[5] while single-crystal X-ray diffraction studies established the molecular structures of **1** and **3**.[6]

Crystalline **1** is a centrosymmetric dimer, comprising a central SnNCSAgSnNCSAg macrocycle. Each tin and silver is also bonded to two $CHR_2$ ligands and one thf ligand, respectively (Figure 1). The three-coordinate silver is in a planar and the four-coordinate tin in a distorted-tetrahedral environment (average bond angle at tin is *ca.* 108°).

The most interesting feature of the structure of **1** is the presence of the Ag−Sn covalent bond of length 2.598(1) Å. A single previous example of a more complicated compound, the $Ag^{I}$ stannate(II) species **5**, having such a bond has very recently been established

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(5) Mössbauer spectral data (at 90 K; isomer shift (IS) relative to $Ca^{119}SnO_3$): for **1**, IS = 1.81 mm $s^{-1}$, QS = 3.44 mm $s^{-1}$; for **2**, IS = 1.86 mm $s^{-1}$, QS = 3.57 mm $s^{-1}$; for **3**, IS = 1.22 mm $s^{-1}$, QS = 2.52 mm $s^{-1}$. Mass spectral data (EI, 70 eV; $[M]^+$ = parent molecular ion; fragments and $m/z$ ($z = 1$) (relative intensity, %)): for **1**, $[M/2 - C_4H_8O - Ag]^+$ 496 (55), $[M/2 - C_4H_8O - Ag - S]^+$ 464 (26); for **2**, $[M/2 - Ag]^+$ 464 (12); for **3**, $[M - Me]^+$ 507 (100); for **4**, $[M - Me]^+$ 677 (30); $[M - I]^+$ 565 (25). IR spectral data (Nujol, $cm^{-1}$): for **1**, 2114 $\nu(NCS)$; for **2**, 2161 $\nu(CN)$; for **3**, 2241, 2223 $\nu_{as}(NCO)$. NMR spectral data: $^1H$ NMR at 250 MHz and 298 K in $CDCl_3$ (i) or Py-$d_5$ (ii) for **1** and $C_6D_6$ for **2**−**4**; $^{13}C\{^1H\}$ NMR at 62.86 MHz and 298 K in Py-$d_5$ for **1**, $C_6D_6$ for **2**, and PhMe + $C_6D_6$ for **3** and **4**; $^{29}Si\{^1H\}$ NMR at 39.76 MHz and 298 K in THF with $C_6D_6$ for **1** and PhMe with $C_6D_6$ for **2**−**4**; $^{119}Sn\{^1H\}$ NMR at 74.63 MHz and 228 K in THF with $C_6D_6$ for **1** and at 298 K in PhMe with $C_6D_6$ for **2**−**4**). NMR for **1**: $^1H$ NMR $\delta$ (i) −0.17 (CH, s), 0.17 ($CH_3$, s), 0.20 ($CH_3$, s), 1.83 ($CH_2$, m), 3.72 ($CH_2$, m), (ii) 0.04 (CH, s), 0.36 ($CH_3$, s), 1.61 ($CH_2$, m), 3.64 ($CH_2$, m); $^{13}C\{^1H\}$ NMR $\delta$ 4.04 (s, $CH_3$), 12.11 (s, CH), 25.80 (s, $CH_2$), 67.81 (s, $CH_2$), 141.27 (s, NCS); $^{29}Si\{^1H\}$ NMR $\delta$ 0.35; $^{119}Sn\{^1H\}$ NMR $\delta$ 250 (dd) $[^1J(^{119}Sn-^{109}Ag)$ = 4632 Hz, $^1J(^{119}Sn-^{107}Ag)$ = 4063 Hz]. NMR for **2**: $^1H$ NMR $\delta$ 0.04 (CH, s), 0.05 (CH, s), 0.38 ($CH_3$, s), 0.44 ($CH_3$, s); $^{13}C\{^1H\}$ NMR $\delta$ 3.97 (s, $CH_3$), 4.45 (s, $CH_3$), 13.91 (s, CH), 14.22 (s, CH), 164.9 (s, CN); $^{29}Si\{^1H\}$ NMR $\delta$ −0.07, 1.52; $^{119}Sn\{^1H\}$ NMR $\delta$ 288 (dd) $[^1J(^{119}Sn-^{109}Ag)$ = 2951 Hz, $^1J(^{119}Sn-^{107}Ag)$ = 2558 Hz]. NMR for **3**: $^1H$ NMR $\delta$ −0.07 (CH, s), 0.15 ($CH_3$, s); $^{13}C\{^1H\}$ NMR $\delta$ 2.60 (s, $CH_3$) $[^1J(^{13}C-^{29}Si) = 50$ Hz, $^3J(^{13}C-^{117/119}Sn) = 24$ Hz], 14.01 (s, CH) $[^1J(^{13}C-^{119}Sn = 285$ Hz, $^1J(^{13}C-^{117}Sn) = 275$ Hz], 120.2 (s, NCO); $^{29}Si\{^1H\}$ NMR $\delta$ 1.98 $[^1J(^{29}Si-^{13}C) = 50$ Hz]; $^{119}Sn\{^1H\}$ NMR $\delta$ −47. NMR for **4**: $^1H$ NMR $\delta$ 0.90 (CH, s), 0.32 ($CH_3$, s); $^{13}C\{^1H\}$ NMR $\delta$ 3.39 (s, $CH_3$) $[^1J(^{13}C-^{29}Si) = 52$ Hz, $^3J(^{13}C-^{117/119}Sn) = 26$ Hz], 17.34 (s, CH) $[^1J(^{13}C-^{119}Sn = 146$ Hz, $^1J(^{13}C-^{117}Sn) = 140$ Hz]; $^{29}Si\{^1H\}$ NMR $\delta$ 2.72; $^{119}Sn\{^1H\}$ NMR $\delta$ −218.

(6) Crystal data: for **1**, $C_{19}H_{46}AgNOSSi_4Sn$, $M_r = 675.55$, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.403(3)$ Å, $b = 12.186(5)$ Å, $c = 15.032(4)$ Å, $\alpha = 109.88(3)°$, $\beta = 105.20(3)°$, $\gamma = 94.64(3)°$, $U = 1535.4(9)$ Å$^3$, $F(000) = 688$, $Z = 2$, $D_c = 1.46$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 1.69 mm$^{-1}$, specimen 0.40 × 0.20 × 0.15 mm, 5405 unique reflections for $2 < \theta < 25°$, R1 = 0.032 for 4575 reflections with $|F^2| > 2\sigma(F^2)$, w$R$2 = 0.074 for all data, $S = 1.082$; for **3**, $C_{16}H_{38}N_2O_2Si_4Sn$, $M_r = 521.5$, monoclinic, space group $P2_1/c$ (No. 14), $a = 11.504(9)$ Å, $b = 29.546(10)$ Å, $c = 8.101(4)$ Å, $\beta = 109.00(6)°$, $U = 2604(3)$ Å$^3$, $F(000) = 1080$, $Z = 4$, $D_c = 1.33$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 1.18 mm$^{-1}$, specimen 0.30 × 0.30 × 0.20 mm, 4560 unique reflections for $2 < \theta < 25°$, R1 = 0.061 for 3514 reflections with $|F^2| > 2\sigma(F^2)$, wR2 = 0.178 for all data, $S = 1.046$. Other conditions: data at $T = 173$ K, Enraf-Nonius CAD-4 diffractometer, absorption correction, structural solution by heavy-atom methods, full-matrix least-squares refinement on $F^2$ using SHELXL-93 with non-hydrogen atoms anisotropic.

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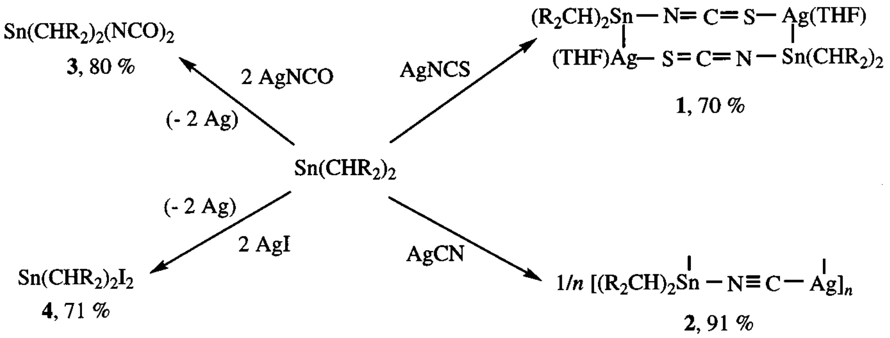
**Scheme 1**



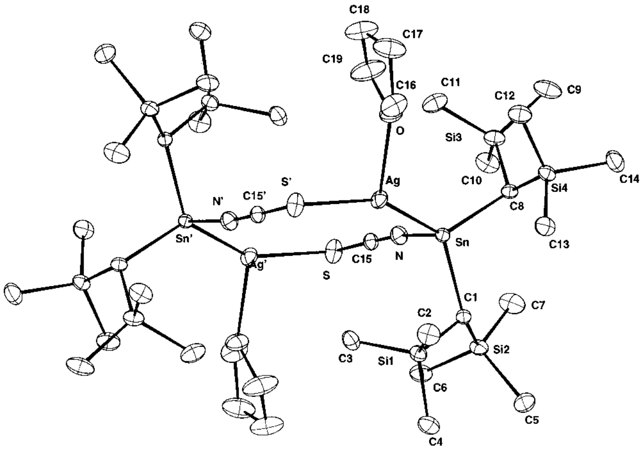
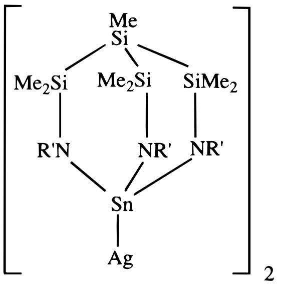
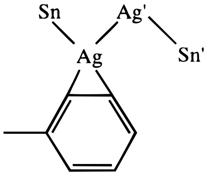


**Figure 1.** ORTEP drawing of complex **1** showing 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Ag−Sn, 2.598(1); Ag−O, 2.499(3); Sn−N, 2.188(4); Ag−S′, 2.505(1); Sn−C(8), 2.180(4); Sn−C(1), 2.194(4); S−C(15), 1.625(4); N−C(15), 1.143(5); N−Sn−Ag, 104.68(10); C(8)−Sn−Ag, 122.21(1); C(1)−Sn−Ag, 121.82(10); S′−Ag−Sn, 149.86(4); N−C(15)−S, 176.8(4); C(15)−N−Sn, 167.6(3); O−Ag−S′, 87.16(9); O−Ag−Sn, 122.51(8); C(8)−Sn−N, 99.43(14); C(8)−Sn−C(1), 106.86(14); C(15)−S−Ag′, 99.3(2).

by Gade and co-workers.[7] In **5** (which decomposed on dissolution), each Sn is bonded to three nitrogens as well as silver (Sn−Ag = 2.6567(7), Sn···Ag′ = 3.2220(9) Å) and each Ag (see **5a**) has additional close contacts to the 2- and 3-carbon atoms of a 4-tolyl group and to the neighboring Ag (Ag···Ag′ = 2.6544(11) Å). Some bond lengths and angles of **1** may be compared with those in $Sn(NCS)(NR_2)$ (which also has close intermolecular Sn···S contacts of *ca.* 3.18 Å): Sn−N = 2.250(6) Å, N−C = 1.140(8) Å, C−S = 1.618(7) Å and Sn−N−C = 168.2(3)° and N−C−S = 178.5(6)°.[8] The Ag−S distance of 2.505(1) Å is significantly longer than the 2.382(3) Å in $[\overline{AgSP(Ph)_2C(H)_2AgSP(Ph)_2CH_2}]$.[9] The C−Sn−C angle of 106.86(14)° in **1** may be compared with the values of 98 and 109.2(2)° in $[Cr(CO)_5\{Sn(CHR_2)_2\}]$[10] and $[Sn(CHR_2)_2]_2$,[4] respectively.



**5** (R′ = $C_6H_4Me$-4)[7]



**5a**

Crystalline **1** and **2** may be regarded as silver(I) complexes having either the stannylene $Sn(CHR_2)_2$ or the stannate(II) $[Sn(CHR_2)_2X]^-$ (X = NCS, CN) as ligand; *cf.* ref 2 for a review of related transition-metal complexes. The $^{119}$Sn Mössbauer spectra for **1** and **2**[5] are indicative of an intermediate situation, as evidenced by comparison with data on $[Pt(Cl)\{Sn(CHR_2)_2Cl\}(PEt_3)\{Sn(CHR_2)_2\}]$: IS = 1.73 and 2.05 mm $s^{-1}$ and QS = 2.66 and 4.23 mm $s^{-1}$ for the stannate and stannylene ligand, respectively.[11]

The $^{1}$H, $^{13}C\{^{1}H\}$, and $^{29}Si\{^{1}H\}$ NMR spectra of complex **2** in $C_6D_6$ showed sharp doublets for the diastereotopic $SiMe_3$ groups, while the $^{119}Sn\{^{1}H\}$ spectrum revealed a pair of doublets centered at $\delta$ 288 due to well-resolved $^{1}J(^{119}Sn-^{109}Ag)$ and $^{1}J(^{119}Sn-^{107}Ag)$ of 2951 and 2558 Hz, respectively.[5] A solution of **1** in thf + $C_6D_6$ showed two broad signals at 313 K which were resolved into a pair of doublets at 228 K centered at $\delta$ 250 with $^{1}J(^{119}Sn-^{109}Ag) = 4632$ Hz and $^{1}J(^{119}Sn-^{107}Ag) = 4063$ Hz; the variable-temperature data indicate the presence of a fluxional process. As far as we are aware, these are the first examples of observation of $^{1}J(^{119}Sn-^{107,109}Ag)$. Both the naturally occurring isotopes of silver, $^{107}$Ag (51.82%) and $^{109}$Ag (48.18% abundant), have $I = {}^{1}/_{2}$. The difference in magnitudes of the couplings for **1** and **2** is attributed,[12] by analogy with $^{1}J(^{31}P-^{107,109}Ag)$ data, to the effects of the different anionic ligands.

The NCO group in complex **3** was identified by the characteristic IR bands at 2241 and 2223 $cm^{-1}$ and by $\delta(^{13}C\{^{1}H\})$ at 120.2 in the NMR spectrum.[5] The $^{119}Sn\{^{1}H\}$ NMR spectral chemical shifts of $\delta$ −47 and −218 for **3** and **4**, respectively, are unexceptional for tin(IV) compounds.

Crystalline **3** is a monomer (Figure 2), the large deviations from tetrahedral bond angles being caused

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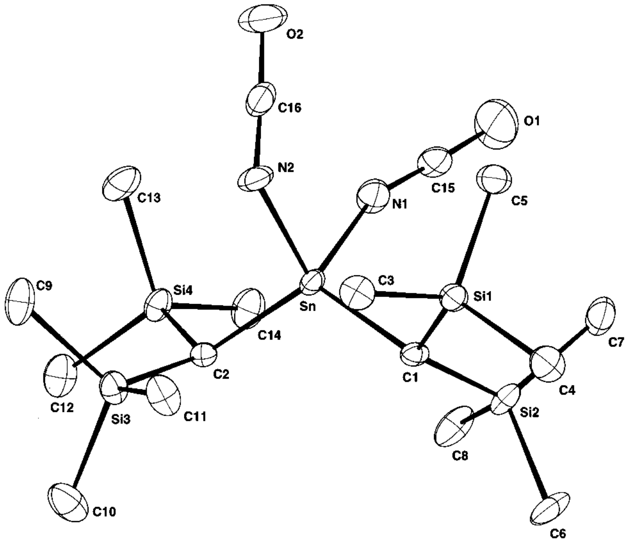

**Figure 2.** ORTEP drawing of complex **3** showing 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Sn−N(1), 2.059(7); Sn−N(2), 2.065(6); Sn−C(2), 2.106(6); Sn−C(1), 2.132(7); O(1)−C(15), 1.175(10); O(2)−C(16), 1.196(9); N(1)−C(15), 1.139(10); N(2)−C(16), 1.173(9); N(1)−Sn−N(2), 94.6(3); N(1)−Sn−C(2), 111.2(3); N(2)−Sn−C(2), 107.2(3); N(1)−Sn−C(1), 109.6(3); N(2)−Sn−C(1), 111.7(3); C(2)−Sn−C(1), 119.7(2); C(15)−N(1)−Sn, 153.0(6); C(16)−N(2)−Sn, 128.0(6); Si(1)−C(1)−Sn, 115.1(3); Si(2)−C(1)−Sn, 109.7(3); O(1)−C(15)−N(1), 177.6(9); O(2)−C(16)−N(2), 176.5(9).

by the bulky $CHR_2$ ligands. The C−Sn−C (119.7(2)°) and N−Sn−C (107.2(3)−111.7(3)°) angles may be compared with those found in $SnCl(CHR_2)_3$ (112.5(3) and 116.8(3)°)[13] and $SnBr(NR_2)_3$ (115.5(1)°),[14] respectively. Compound **3** appears to be the first X-ray-characterized organotin bis(isocyanate); the difference in the two bond angles at nitrogen is striking, and the values suggest that the formal nitrogen lone pairs are to some extent stereochemically active, rather than showing N−Sn $\pi$-bond character. X-ray data on $Ph_3Sn(NCO)$,[15a] $Ph_3Sn(ONC_5H_5)(NCO)$,[15b] and $[Me_2(HO)Sn(NCO)]_n$[15c] are available.

As previously noted,[7] $Sn^{II}-Ag^{I}$ systems are of wider interest because of the role of $SnCl_2$ in photography as a reduction sensitizer for silver halide emulsions. The formation therein of Sn−Ag complexes (*cf.* **1**, **2**, and **5**) and thereafter of redox (cf. **3** or **4**) or ligand exchange (*cf.*[1] the $SnCl_2/AgNR_2$ system) reactions are plausible outcomes. The reactions of various silver(I) salts with further divalent tin(II) substrates and divalent C, Si, Ge, and Pb compounds clearly warrant investigation.

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**Supporting Information Available:** Tables giving full details of the crystal structure analyses, crystallographic data, atomic coordinates, bond lengths, bond angles, anisotropic displacement factors, and torsion angles for **1** and **3** (14 pages). Ordering information is given on any current masthead page.

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