# Synthesis and Crystal Structure of an Unprecedented Tin(II)−Tin(II) Donor−Acceptor Complex, R$^N_2$Sn→SnCl$_2$ [R^N = CH(SiMe$_3$)C$_9$H$_6$N-8]

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The redistribution reaction of SnCl$_2$ with homoleptic tin(II) compounds SnR$_2$ [R = CH(SiMe$_3$)$_2$] leading to SnR$_2$Cl$_2$ and Sn, or to (R′SnCl)$_n$ [R′ = C(SiMe$_3$)$_2$C$_5$H$_4$N-2, *n* = 1 or R′ = N(SiMe$_3$)$_2$, *n* = 2], have been reported by Lappert and co-workers.[1,2] The reaction mechanism was proposed to involve transition state **A** for R$^-$ capable of functioning in a bridging mode, such as [C(SiMe$_3$)$_2$C$_5$H$_4$N-2]$^-$ and transition state **B** if R$^-$ is a nonfunctioning ligand such as [CH(SiMe$_3$)$_2$]$^-$.
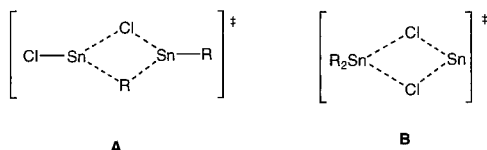

We have performed similar reactions between SnX$_2$ (X = F, Cl, Br, I) and SnR$^N_2$ [R^N = CH(SiMe$_3$)C$_9$H$_6$N-8] under different experimental conditions. The final products obtained after refluxing the reaction mixture for 2 h were SnR$^N_2$X$_2$ [X = F (**6**), Cl (**7**), Br (**8**), I (**9**)] and tin metal (Scheme 1). The mechanism for the reaction seems to match the route involving transition state **A**. However, when the reaction was performed under a milder condition with neither reflux nor heating, the reaction products R$^N_2$Sn→SnCl$_2$ (**1**) and R^{N}SnBr (**4**) were isolated respectively for reactions of SnR$^N_2$ with SnCl$_2$ and SnBr$_2$. Further refluxing of **1** and **4** has led to the formation of the final products SnR$^N_2$X$_2$ and Sn. In view of the solid state structure of **1**, we suggest that the redistribution reaction of SnR$^N_2$ and SnCl$_2$ proceeds *via* the "head-to-head" approach of SnR$^N_2$ and SnCl$_2$ to form the donor−acceptor complex **1**, which is a preliminary intermediate to the (μ-Cl)$_2$ bridging transition state as proposed earlier.[1] The complex R$^N_2$Sn→SnX$_2$ will then undergo ligand−halogen exchange to form another intermediate compound, R^{N}SnX, which can proceed to SnR$^N_2$X$_2$ at higher temperature *via* transition state **A**. Alternatively, at higher temperature the redistribution reaction may proceed *via* transition state **B** with the dissociation of the Sn−Sn interaction. In the present case, the vacant orbitals are conceivably occupied by the nitrogen lone pairs from the quinolyl ligands. Hence, SnR$^N_2$ behaves as a Lewis base and favors formation of a donor−acceptor type complex by donating a lone pair from its sp^2 orbital to the vacant p$_z$ orbital of the Lewis acid SnCl$_2$. The bonding involved differs from the donor−acceptor double bond as described for R$_2$Sn=SnR$_2$. On the basis of the structural data, compound **1** is best represented as a donor−acceptor complex (**1a**) with a single bond linking the tin atoms or in terms of valence bond structure **1b** with a Sn−Sn bond order that slightly exceeds 1.

Compound **1** is the first example of a stable donor−acceptor complex between two tin centers that has been structurally characterized. Other known examples of dimeric stannylene
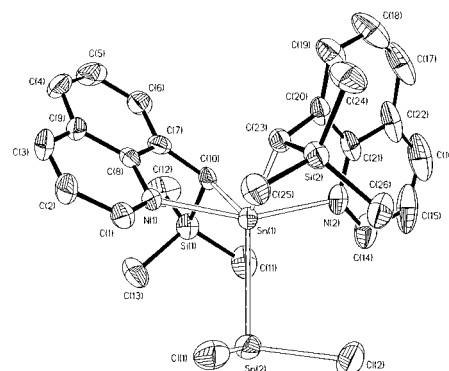
Figure 1. Molecular structure of **1** showing the atom-labeling scheme. The thermal ellipsoids are shown at 35%. Selected bond distances (Å) and angles (deg): Sn(1)−Sn(2) 2.961(1), Sn(1)−N(1) 2.400(6), Sn(1)−N(2) 2.421(7), Sn(1)−C(10) 2.200(8), Sn(1)−C(23) 2.203(8), Sn(2)−Cl(1) 2.468(3), Sn(2)−Cl(2) 2.440(4); Sn(2)−Sn(1)−N(1) 99.4(1), Sn(2)−Sn(1)−N(2) 102.0(2), N(1)−Sn(1)−N(2) 158.6(2), Sn(2)−Sn(1)−C(10) 119.6(2), N(1)−Sn(1)−C(10) 75.7(2), N(2)−Sn(1)−C(10) 92.2(3), Sn(2)−Sn(1)−C(23) 140.4(2), N(1)−Sn(1)−C(23) 89.7(2), N(2)−Sn(1)−C(23) 74.9(3), C(10)−Sn(1)−C(23) 100.1(3), Sn(1)−Sn(2)−Cl(1) 91.8(1), Sn(1)−Sn(2)−Cl(2) 96.3(1), Cl(1)−Sn(2)−Cl(2) 94.5(1), Sn(1)−C(10)−C(7) 109.6(5), Sn(1)−C(23)−C(20) 108.1(6).
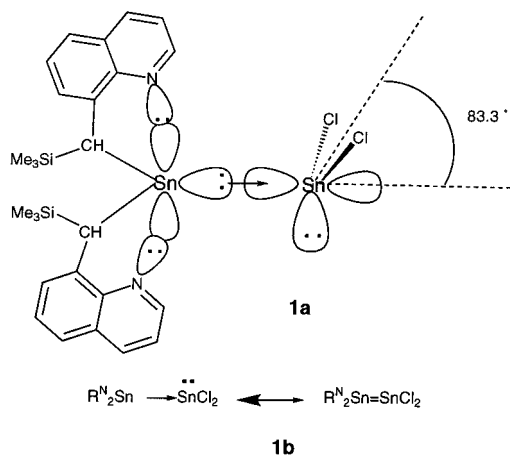
compounds are R$_2$Sn=SnR$_2$ and Ar$_2$Sn−SnAr$_2$ [Ar = C$_6$H$_2$-(CF$_3$)$_3$-2,4,6].[3,4]

The single-crystal X-ray structure of **1** with selected bond distances and angles are shown in Figure 1.[7] The alkyl ligand R^N is bonded in a C,N-chelate fashion to the Sn(1) atom which adopts a pentacoodinate square-pyramidal geometry. The Sn-(1) atom is bonded directly to Sn(2) of the SnCl$_2$ fragment with a Sn−Sn distance of 2.961(1) Å, which is significantly longer
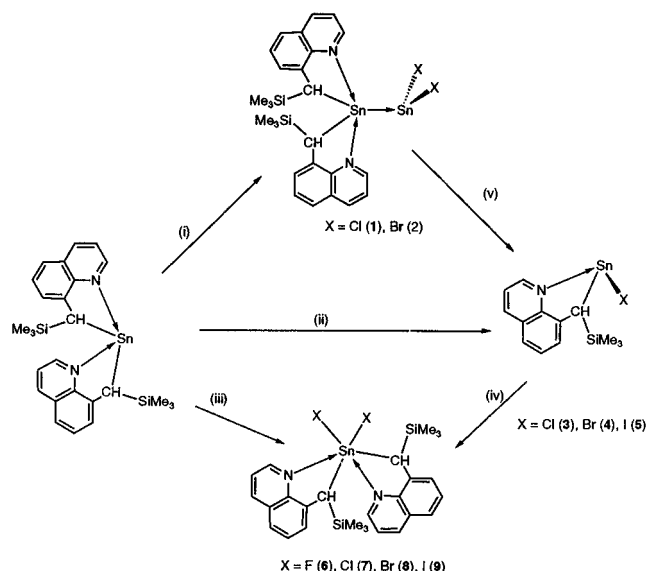
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(7) Crystal data for **1**: C$_{26}$H$_{32}$Cl$_2$N$_2$Si$_2$Sn$_2$, FW = 737.0, monoclinic, space group *P*2$_1$/*c* (No. 14); *a* = 11.054(2), *b* = 18.916(2), and *c* = 15.239-(2) Å; β = 106.61(1)°; *V* = 3053.3(7) Å^3, *Z* = 4, *F*(000) = 1456, D$_c$ = 1.603 mg m^{-3}; μ = 1.907 mm^{-1}, 2θ_{max} = 50°, *N* = 5376, *N*$_o$ = 2933, *R* = 0.040, w*R* = 0.042. A selected single crystal was sealed in a Lindemann glass capillary under dinitrogen and X-ray intensities were measured on an MSC/Rigaku AFC7 diffractometer using monochromatized Mo K$_\alpha$ radiation (λ = 0.71073 Å, 50 kV, 150 mA) from a rotating anode generator. Computations were performed using SHELXTL-PLUS program package (Sheldrick, 1985, 1990) on a PC 486 computer. The structure was solved by direct methods and refined by full-matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were placed in their idealized positions and included in structure vector calculations with assigned isotropic temperature factors.

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Scheme 1[a]

[a] Reagents and conditions: (i) SnX_2, THF, 25 °C, 30 min; (ii) SnX_2, THF, 25 °C, >2 h; (iii) SnX_2, THF, reflux; (iv) THF, reflux; (v) THF, 25 °C, >2.5 h.

than the similar distance of 2.768 Å in [{$(Me_3Si)_2CH$}$_2$Sn=Sn-{$CH(SiMe_3)_2$}$_2$] (**10**) and much shorter than the distance of 3.639 Å in Ar_2Sn—$SnAr_2$ (**11**).[3,4] The fold angle (defined as the angle between the Sn—Sn vector and the $SnCl_2$ plane) is 83.3° which is about twice as large as the fold angles of 41° in **10** and 46° in **11**. This is presumably due to the less-bulky chlorine atoms. The plane containing C(10),Sn(1),C(23) is nearly perpendicular (92.9°) to the plane of Cl(1),Sn(2),Cl(2), which is consistent with the bonding model as described in **1a**. The Sn—C distance of 2.202 (av) Å and Sn—N distance of 2.411 Å are significantly shorter than the corresponding distances of 2.263 (av) and 2.506 Å in the parent compound SnR^N_2.[5] This is presumably a consequence of reduced electron density at the Sn(1) center due to donation of its lone pair electrons to $SnCl_2$. The Sn—Cl distances of 2.468(3) and 2.440(4) Å in **1** are shorter than the Sn—Cl distance of 2.78 Å in the layer structure of anhydrous tin(II) chloride.[6] However, it is comparable to the Sn—Cl distance of 2.459(9) Å in the $SnCl_2$ complex [{Ph_2P-$(CH_2)_4Ph_2IrCl(CO)$}$_2${μ^2-$SnCl_2$}][8] and the average Sn—Cl distances in the $SnCl_3^-$ complexes [SnL^1_2]$^{2+}$[$SnCl_3^-$]$_2$ [L^1 = 1,4,7,10,13-pentaoxacyclopentadecane] [2.500(2) Å],[9] [SnL^2-Cl]$^+$[$SnCl_3^-$] [L^2 = 18-crown-6] [2.481(4) Å],[10] [$Mo(dmpe)_2$-Cl_2][$SnCl_3^-$] [2.453(3) Å],[11] [AgL^3][$SnCl_3^-$] [L^3 = 2,11-bis-((diphenylphospino)methyl)benzo[c]phenanthrene] [2.498(3) Å].[12]

The ^{119}Sn NMR spectrum of **1** in THF/benzene-d_6 displayed two singlet signals at δ 1264.44 and −637.19, respectively. The peak at δ 1264.44 is assigned to Sn(1) of the SnR^N_2 fragment

in **1**, which is more downfield than the signal of δ 141.73 for the starting compound SnR^N_2.[5] This downfield shift is a consequence of reduction of electron density at Sn(1) center due to its donor bonding to $SnCl_2$. Some π-backbonding from the lone pair of Sn(2) to vacant d orbital of Sn(1) is also possible. With reference to the ^{119}Sn NMR chemical shift of $SnCl_2$ (δ −388) reported in the literature, the signal at δ −637.19 in **1** is assigned to Sn(2) of the $SnCl_2$ fragment.[13] Furthermore, we have carried out ^{119}Sn NMR experiments to monitor the the reaction of SnR^N_2 with $SnCl_2$ in THF solution and found that a peak at δ 327.02 emerged in addition to the peaks due to **1**, after 2 h. This peak is assignable to R^NSnCl, when compared with the reported chemical shifts for $R'SnCl$ (δ 350.6)[1] and those of R^NSnBr (δ 353.67) and R^NSnI (δ 386.03) in this work. In the similar experiment with SnR^N_2 and $SnBr_2$, peaks at δ 1425.45 and −504.66 assignable to R^N_2Sn→$SnBr_2$ and at δ 353.67 due to R^NSnBr were observed. However, attempts to isolate the pure form of R^N_2Sn→$SnBr_2$ has not been successful.

The stability of R^NSnX (**3−5**) is attributed to the sterically hindered *N*-functionalized alkyl ligand R^N. Compounds of similar nature such as $R'SnX$ [X = Cl, N(SiMe_3)_2$] and Me_2-Si(NBu^t)H(NBu^t)SnX (X = Cl, Br, I) had been reported.[2,14] In contrast, the tricoordinate silylene $R''MeSi$: [R'' = 8-(dimethylamine)-1-naphthyl] generated by thermal degradation has only been trapped as a pentacoordinate 1,2-disilacyclobut-3-ene.[15] Compounds **4−9** have been characterized by elemental analysis, NMR and mass spectroscopies, and X-ray crystallography, and the results will be reported in elsewhere.

Supporting Information Available: Crystal structure analysis details for **1**, tables listing data collection and processing parameters, atomic coordinates, bond distances and angles, and thermal parameters (10 pages). See any current masthead page for ordering and Internet access instructions.

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(16) *Preparation of R^N_2Sn→$SnCl_2$* (**1**). A solution of SnR^N_2 (0.61 g, 1.11 mmol) in THF (ca 80 mL) was added slowly to a solution of $SnCl_2$ (0.21 g, 1.11 mmol) in THF (ca. 50 mL) at room temperature. The yellow mixture was stirred at room temperature for 30 min. It was then concentrated *in vacuo* to ca. 30 mL and kept at −30 °C for 2 days to afford yellow crystals of the title compound, 0.29 g yield (70%); mp 225−258 °C. Anal. Found: C, 42.29; H, 4.30; N, 3.69. Calcd. for $C_{26}H_{32}Si_2N_2Sn_2Cl_2$: C, 42.37; H, 4.38; N, 3.80. ^{1}H NMR (C_6D_6, 250 MHz): δ 0.29 (s, 18H), 1.41, (s, 2H), 6.56−6.65 (m, 2H), 6.71−6.74 (m, 2H), 6.91−6.98 (m, 4H), 7.35−7.46 (m, 2H), 8.28−8.29 (m, 1H), 9.33−9.35 (m, 1H). ^{119}Sn NMR (THF/C_6D_6, 186.5 MHz): δ −637.19 (s), 1264.44 (s). *Preparation of $SnBr(R^N)$* (**2**). A solution of SnR^N_2 (0.93 g, 1.70 mmol) in THF (ca. 80 mL) was added slowly to a solution of $SnBr_2$ (0.47 g, 1.70 mmol) in THF (ca. 50 mL) at room temperature. The resulting orange mixture was stirred for 18 h at room temperature. It was concentrated *in vacuo* to ca. 30 mL and stored at room temperature and orange crystals were obtained (0.65 g, 93%); mp 185−6 °C (dec.). Anal. Found: C, 37.51; H, 3.90; N, 3.42. Calcd. for C_{13}-$H_{16}SiNSnBr$: C, 37.81; H, 3.91; N, 3.39. ^{1}H NMR (C_6D_6, 250 MHz): δ −0.10 (s, 9H), −0.05 (s, 9H), 2.47 (s, 2H), 6.34 (dd, J = 8.4, 4.8 Hz, 2H), 6.84 (d, J = 7.8 Hz, 2H), 7.23 (d, J = 7.4 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 7.91 (d, J = 4.3 Hz, 2H). ^{119}Sn NMR (THF/C_6D_6, 186.5 MHz): δ 353.67 (s).