Sn–Sn Bonding

DOI: 10.1002/anie.200704635

$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Sn]_2$: An Intramolecularly Coordinated Diorganodistannyne**

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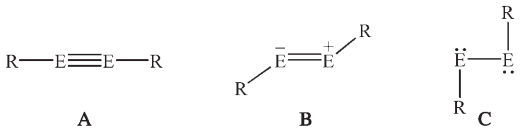
Dedicated to Professor Jaroslav Holecek on the occasion of his 75th birthday

Investigation on the nature of chemical bonding remains a central focus of fundamental research, as recently substantiated in a special issue of the *Journal of Computational Chemistry*[1] with an accompanying commentary in *Chemical and Engineering News*.[2] A valuable strategy for increasing the understanding of intramolecular binding forces is the investigation of heavy carbene analogues (R_2E), their transition-metal complexes ($L_nM{=}ER_2$), and compounds that contain multiple bonds between heavier main-group elements ($R_2E{=}ER_2$,[3–7] $RE{\equiv}ER$,[8–19] and $L_nM{\equiv}ER$;[20–22] E = Si, Ge, Sn, Pb). A recent review article by P. P. Power nicely outlines the past computational and experimental understanding of the bonding between Group 14 elements.[23] In recent years, the $RE{\equiv}ER$ and $L_nM{\equiv}ER$ compounds have attracted greater interest, with the synthesis of $[\{(Me_3Si)_2CH\}_2(i\text{Pr})SiSi]_2$[12] completing the series of heavier Group 14 element analogues of alkynes.[8–19]

The two general synthetic methods for the preparation of $RSn{\equiv}SnR$ and $RPb{\equiv}PbR$ compounds are a) the reduction of heteroleptic stannylenes RSnCl with alkali metals and b) the reaction of RPbBr with $LiAlH_4$.[8] Interestingly, in the first case a mixture consisting of mono- and dianions, $[RSnSnR]^-$ and $[RSnSnR]^{2-}$, and of the neutral species RSnSnR was obtained.[16]

An essential structural difference between alkynes ($RC{\equiv}CR$) and their heavier Group 14 analogues ($RE{\equiv}ER$; E = Si, Ge, Sn, Pb) is the *trans*-bent geometry of the latter in contrast to the linear geometry of the former (Scheme 1). Moreover, there is an ongoing debate[24–27] on whether the Group 14 compounds exhibit a true triple bond (**A**), a double bond (**B**), or a single bond whose geometry is strongly *trans*-bent (**C**). On the basis of a solid-state ^{29}Si NMR study, a silicon analogue favors the existence of a triple bond.[28] UV/Vis absorptions and molecular orbital calculations suggest that Ar′MMAr′compounds (M = Ge, Sn; $Ar' = C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-}i\text{Pr}_2)_2$) possess multiple bonds in solution.[27]



Scheme 1. Canonical formulas for compounds of the type REER.

The successful synthesis of the compounds mentioned above is related to the employment of rather bulky substituents such as a variety of substituted aryl and organosilyl groups, giving rise to kinetic stabilization. An alternative concept for the stabilization of, for instance, reactive heavy carbene analogues is the use of intramolecularly coordinating "built-in" ligands. Prominent representatives of these are N,C,N- and O,C,O-coordinating pincer-type ligands, which have been employed for the synthesis of heteroleptic stannylenes such as $\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnCl$,[29] $[2,6\text{-}\{P(O)(OR)_2\}_2\text{-}4\text{-}t\text{Bu-}C_6H_2]SnCl$ (R = Et, *i*Pr),[30,31] and $\{2,6\text{-}(ROCH_2)_2C_6H_3\}SnCl$ (R = Me, *t*Bu).[32]

From systematic studies on the reactivity of these compounds and their transition-metal complexes, we report here the synthesis of the organotin(I) species $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Sn]_2$ and discuss, on the basis of single-crystal X-ray diffraction analysis and MO calculations, the influence of intramolecular N→Sn coordination on the Sn–Sn bond.

The reaction of $\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnCl$[29] with $K[s\text{Bu}_3BH]$ in THF at 0 °C provided a dark red solution (Scheme 2). After the solvents had been removed in vacuo, the residue was recrystallized from *n*-hexane to give dark red, air- and moisture-sensitive crystals which turned out to be $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Sn]_2$ cocrystallized with KCl (**1**·KCl).

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[**] We are grateful to the Ministry of Education of the Czech Republic (projects VZ0021627501 and LC523), Dortmund University, and Hamilton College. This project was supported in part by the NIH grant 1R15A115524-01 and by NSF grants CHE-0116435 and CHE-0521063 as part of the MERCURY high-performance computer consortium (http://mercury.chem.hamilton.edu). We thank George C. Shields for helpful discussions concerning the molecular orbital calculations and an anonymous reviewer for valuable comments.

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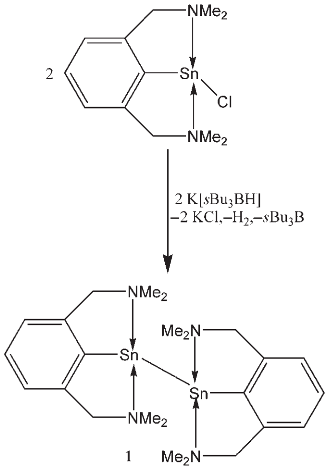


Scheme 2. Synthesis of **1**.

The presence of potassium in the crystals was unambiguously proven by flame analysis.

It is likely that the reduction of {2,6-$(Me_2NCH_2)_2C_6H_3$}SnCl proceeds via intermediate formation of the corresponding organotin(II) hydride {2,6-$(Me_2NCH_2)_2C_6H_3$}SnH, which, in turn, reductively eliminates hydrogen gas and gives the ditin compound **1**. From organotin(IV) hydrides it is well known that amines catalyze tin–tin bond formation under liberation of hydrogen.[33] Attempts at isolating {2,6-$(Me_2NCH_2)_2C_6H_3$}SnH were not successful. Crystals of **1**·KCl are stable at ambient temperature, and their solutions are stable below −30 °C.

The molecular structure of **1**·KCl is shown in Figure 1. The unit cell contains two nearly identical crystallographically independent molecules; our following discussion will focus on the parameters of one of these molecules. The Sn(1)−Sn(2) bond length of 2.9712(12) Å lies between those of the parent compounds Ar′SnSnAr′ (2.668(1) Å) and Ar*SnSnAr* (3.066(1) Å; Ar′ = C_6H_3-2,6-$(C_6H_3\text{-}2,6\text{-}i\mathrm{Pr}_2)_2$, Ar* = C_6H_2-2,6-$(C_6H_3\text{-}2,6\text{-}i\mathrm{Pr}_2)_2$-4-$SiMe_3$).[9,15]

The intramolecular Sn−N bond lengths vary between 2.585(9) Å for Sn(2)−N(3) and 2.631(9) Å for Sn(1)−N(1), and are similar to the Sn−N bond lengths of 2.525(8) and 2.602(8) Å reported for the heteroleptic organostannylene {2,6-$(Me_2NCH_2)_2C_6H_3$}SnCl.[29] Apparently, the Lewis acidity of the tin atoms in the latter compound and in compound **1**·KCl is rather similar. The C(1)-Sn(1)-Sn(2) and C(21)-Sn(2)-Sn(1) angles have values of 94.3(3) and 94.1(3)°, which are smaller than the corresponding angles of 125.24(7)° in Ar′SnSnAr′ and 99.25(14)° in Ar*SnSnAr*,[9,15] but similar to the corresponding Ar*PbPbAr* angle of 94.26(4)°.[8] By analogy, our reported C-Sn-Sn angles suggest that the Sn−Sn bond is a single bond in compound **1**·KCl. Furthermore, the angles are almost identical to the C(1)-Sn-Cl angle of 95.0(3)° in the heteroleptic organostannylene {2,6-$(Me_2NCH_2)_2C_6H_3$}SnCl,[29] which indicates that the s character of the lone pair is rather similar in both compounds. An interesting structural feature of compound **1**·KCl is the C(1)-Sn(1)-Sn(2)-C(21) torsion angle of 82.7(4)°, a smaller value than the corresponding angle in Ar*SnSnAr*.

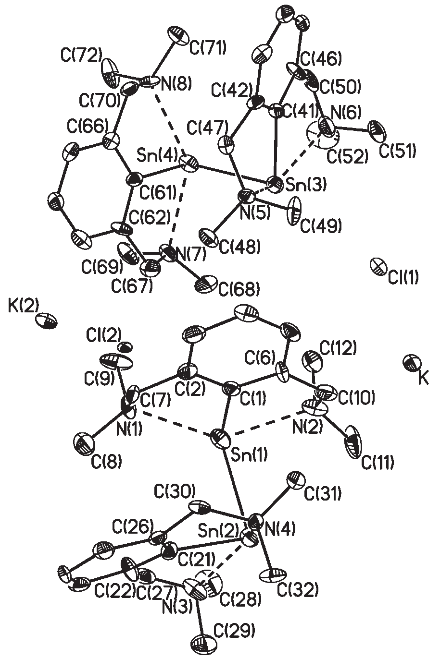


Figure 1. Molecular structure of **1**·KCl (two crystallographically independent molecules; thermal ellipsoids: 30%). Selected bond lengths [Å], bond angles [°], and torsion angles [°] of one molecule: Sn(1)-Sn(2) 2.9712(12), Sn(1)-N(1) 2.631(9), Sn(1)-N(2) 2.593(10), Sn(2)-N(3) 2.585(9), Sn(2)-N(4) 2.612(7), Sn(1)-C(1) 2.180(11), Sn(2)-C(21) 2.193(10); C(1)-Sn(1)-Sn(2) 94.3(3), C(21)-Sn(2)-Sn(1) 94.1(2), N(1)-Sn(1)-N(2) 138.6(3), N(3)-Sn(2)-N(4) 138.8(3), C(1)-Sn(1)-Sn(2)-C(21) 82.7(4).

The resolved structure of **1**·KCl showed four peaks of residual electron density. Placing potassium and chlorine on these positions gave a satisfying refinement of the structure, in which KCl is part of an infinite ···K···Cl···Sn-Sn···K···Cl··· chain with Sn···K, Sn···Cl, and K···Cl separations of 4.298(4)/4.264(4), 4.295(4)/4.293(4), and 2.977(5)/2.963(5) Å, respectively.

The ^{119}Sn NMR spectrum ([D$_8$]toluene, 186.5 MHz) of **1**·KCl revealed a broad resonance at $\delta = 612$ ppm ($\nu_{1/2}$ 97 Hz) for which, however, no ^{119}Sn-^{117}Sn coupling could be detected. At 230 K the signal broadened further ($\nu_{1/2}$ 225 Hz) and was shifted to $\delta = 582$ ppm. This is the first detection of such a signal for distannyne-type compounds RSnSnR. The observation of a ^{119}Sn NMR resonance might be related to the fact that the chemical shift anisotropy (CSA) of the tin atom is lowered by coordination of the nitrogen atoms.[17] The UV/Vis spectrum of **1**·KCl in *n*-hexane shows an absorption at $\lambda_{max} =$ 367 nm and a shoulder at 436 nm but no absorption at all at higher wavelengths, which is, according to the arguments given by Takagi and Nagase,[27] in line with a Sn−Sn single bond for compound **1**·KCl.

Gas-phase MO calculations were performed using the B3PW91 and BHandHLYP density functional theory as implemented within the Gaussian 03 software package.[34] Consistent with other theoretical studies on similar systems,[35] the LANL2DZ basis set was used in all calculations for all atoms, with the addition of two Sn basis functions (exponents of 0.253 and 0.078) to improve the orbital space description of the Sn atoms.[27] This resulted in 364 basis functions, composed of 900 primitive functions. All calculations reported here are for the neutral species with spin multiplicity of 1, unless otherwise noted. The molecule of **1** in the crystal structure reported above has near C_2 symmetry; thus, we performed calculations on both geometries with C_1 and C_2 symmetry. Frequency calculations were performed to verify that the optimized geometries are minima on the potential-energy surface and to provide vibrational frequencies. NBO analysis was performed to provide a chemical interpretation of the molecular orbitals, which includes calculating the natural populations for each atom and the Wiberg bond index matrix. Gas-phase geometry optimization of the C_1 crystal structure converges towards the C_2 geometry; thus, the remaining discussion will focus on the C_2 geometry.

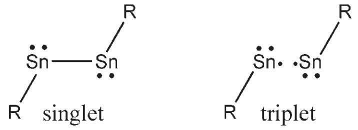
DFT calculations with the B3PW91 and BHandHLYP functionals reproduce the crystal bond lengths and angles well (Table 1). The computed C1-Sn1-Sn2-C21 torsion angle (93.2° with B3PW91, 91.0° with BHandHLYP), which defines the relative orientations of the tin fragments, is in notable disagreement with the experimental value of 82.7°. This discrepancy can be rationalized by the presence of crystal-packing forces in the X-ray structure, distorting the structure away from the gas-phase geometry. The optimized B3PW91 and BHandHLYP Sn–Sn separations are 3.045 and 3.036 Å, respectively, which are similar to the Sn–Sn bond length computed with B3PW91 for related structures believed to possess a Sn–Sn single bond.[27] The highest occupied NBO is a bonding orbital that is centered about the Sn–Sn bond. The bond index for this bond is 0.91, further supporting that this bond is a single bond. Both C-Sn-Sn angles are computed to be 97.9° (B3PW91) and 97.7° (BHandHLYP), values that are in good agreement with the experimental values of 94.1(3) and 94.3(3)°. As recently outlined by Power, the general trend for these molecules is to have the C-E-E angle decrease towards 90° as the E–E bond order decreases towards one.[23] Both the experimental and computed geometries are consistent with this trend.

Table 1: Comparison of experimental and computed bond distances, bond angles, and torsion angles.

	1·KCl	B3PW91	BHandHLYP	B3PW91 (1e$^-$ reduced)
Symmetry:		C_2	C_2	C_2
Sn(1)-Sn(2)	2.9712(12)	3.045	3.036	3.337
Sn(1)-N(1)	2.59338	2.586	2.594	2.626
Sn(1)-N(2)	2.63097	2.630	2.639	2.645
Sn(2)-N(3)	2.61195	2.630	2.639	2.645
Sn(2)-N(4)	2.58473	2.586	2.594	2.626
C(1)-Sn(1)-Sn(2)	94.3(3)	97.9	97.7	98.5
C(21)-Sn(2)-Sn(1)	94.1(3)	97.9	97.7	98.5
C(1)-Sn(1)-Sn(2)-C(21)	82.7(4)	93.2	91.0	−90.4

The lowest unoccupied orbital obtained from the optimized wavefunction is antibonding, located between the two tin atoms and delocalized over the aromatic rings. Geometry optimization of the one-electron-reduced species (multiplicity of two, charge of −1) resulted in a lengthening of the Sn–Sn bond by 0.29 Å to 3.34 Å, with a nominal effect on the C-Sn-Sn angle. This result is consistent with experimental data for the one-electron reduction of Ar′SnSnAr′ and Ar*SnSnAr*, which show an increase in Sn–Sn bond length of approximately 0.13–0.15 Å.[16] However, Power and co-workers provide a different reason for the increase in the Sn–Sn bond length of these molecules, which is due to an increase in p-orbital character that occurs as a result of a narrowing of the C-Sn-Sn angle bending.[16]

Calculations were also performed on the neutral species with a multiplicity of three, resulting in a break in the Sn–Sn bond. With a multiplicity of one, the two bonding electrons in the highest occupied NBO described above (one from each tin atom) have opposite spins and can occupy the same orbital. When the molecule has a multiplicity of three, the two electrons have the same spin, and according to the Pauli exclusion principle they are disallowed from occupying the same bonding orbital (Scheme 3). Without the presence of both electrons in this bonding orbital, the molecule dissociates into two identical fragments, which further supports the belief that the Sn–Sn bond is a single bond.



Scheme 3. Left: Formation of the Sn–Sn bond when **1** possesses a spin multiplicity of one. Right: When the molecule possesses a spin multiplicity of three, no Sn–Sn bond can be formed.

The natural populations analysis performed as part of the NBO algorithm reveals that the partial atomic charges on the four nitrogen atoms (−0.56 au) and those on the two tin atoms (0.54 au) are nearly equal and opposite in magnitude, thus indicating a favorable attraction between these atoms. The lack of significant covalent-bond character is supported by a bond index value of 0.15 for the Sn···N interactions. Both of these analysis techniques suggest that the attraction between the nitrogen atoms and the tin atoms arises mainly from electrostatic forces.

In conclusion, it appears that not only the use of bulky substituents such as 2,6-disubstituted aryl groups but also intramolecular N→Sn interactions can give rise to the stabilization of diorganodistannynes RSnSnR. Apparently, electron density from the Lewis basic nitrogen atoms is transferred into empty p orbitals at the tin atoms and stabilizes the configuration of the latter. We are currently investigating what role the identity of the donor atom (P=O, O, P=S, S, P) plays in stabilizing diorganodistannynes.

Experimental Section

1: At 0 °C a 1 M THF solution (1.5 mL) of K[sBu$_3$BH] was added under magnetic stirring to a solution of [2,6-($\mathrm{Me_2NCH_2}$)$_2$-$\mathrm{C_6H_3}$]SnCl (0.5 g, 1.5 mmol) in THF. The reaction mixture was stirred an additional hour at this temperature. Then the solution was allowed to warm to room temperature and stirred further for 3 h. After the solvent had been removed in vacuo, the residue thus obtained was suspended in hexane (40 mL), and the suspension was stirred for 10 min. After the solid had been filtered, the filtrate was concentrated to a volume of about 10 mL. Storage of this solution overnight at $-30\,^{\circ}C$ gave 0.09 g (20 % yield) deep red crystals of **1**·KCl (m.p. 123 °C, decomp). ^{1}H NMR (C_6D_6, 500.18 MHz): $\delta = 2.28$ (br s, 12 H, NCH_3), 3.29 (s, 2 H, CH_2), 3.61 (s, 2 H, CH_2), 6.90–6.99 ppm (complex pattern, 3 H, C_6H_3); ^{13}C NMR (C_6D_6, 125.77 MHz): $\delta = 47.5$ (NCH_3), 68.6 (CH_2N), 122.9, 123.9, 144.0 ppm (SnC_6H_3), (C(1) not found); ^{119}Sn NMR (C_6D_6, 186.49 MHz): $\delta = 612$ ppm; UV/Vis (*n*-hexane): λ_{max} [nm] (ε [$L\,mol^{-1}\,cm^{-1}$]) 367 (4300), 436 (shoulder).

Crystal structure analysis of a deep red crystal of **1**·KCl ($0.22 \times 0.20 \times 0.16\ mm^3$) was performed on a Nonius-Kappa CCD diffractometer at 173(1) K. Crystal data for **1**·KCl: $C_{24}H_{38}N_4Sn_2 \cdot 0.63\,KCl$, $M = 666.93\ g\,mol^{-1}$, triclinic, space group $P\bar{1}$, $a = 12.0368(11)$, $b = 14.010(2)$, $c = 17.608(8)$ Å, $\alpha = 112.459(5)$, $\beta = 99.898(9)$, $\gamma = 90.052(8)^{\circ}$, $V = 2696.0(1)$ Å^3, $Z = 4$, $\mu(Mo_{K\alpha}) = 2.031\ mm^{-1}$, 31 814 independent reflections ($\theta_{min} = 3.14^{\circ}$, $\theta_{max} = 25.41^{\circ}$), 4998 with $I \geq 2\sigma(I)$, $R_1 = 0.065$, $wR2$ (all data) = 0.1941; residual electron density (max./min.): 1.590/−0.790 e Å^3. After merging symmetry-equivalent reflections and absorption correction with the program SCALEPACK ($T_{min} = 0.662$, $T_{max} = 0.737$) an internal *R* value of 0.052 was obtained. The occupancies of the potassium and chloride ions (K(1), K(2), Cl(1), Cl(2)) were refined at 0.628(6). CCDC-6661781 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Received: October 8, 2007
Published online: January 22, 2008

Keywords: Group 14 elements · intramolecular coordination · main-group elements · NMR spectroscopy · organotin compounds

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