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Coordination Chemistry

Side-On Coordinated Distannene: An Unprecedented Nickel(0) Complex**

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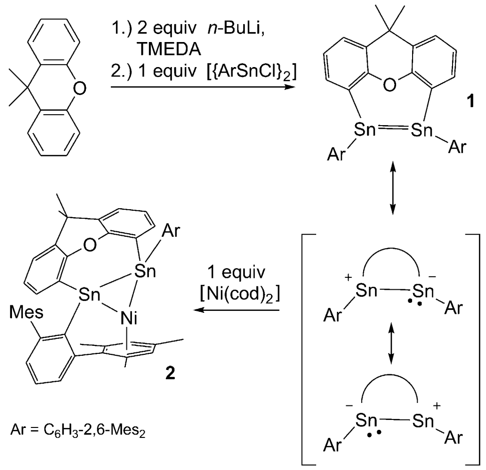
In 2011, our group reported the tripodal tin ligand $[Sn(Sn_2B_{10}H_{10})_3]^{4-}$ featuring the tin atoms incorporated in distanna-*closo*-dodecaborate clusters.[1] To broaden our research on polypodal tin ligands, we turned toward tin organyl species with tin in the oxidation state +II. Dipodal ligands with tin(II) and the smaller congeners germanium(II) and silicon(II) with base stabilization at the Group 14 atom have been reported by Hahn, Driess, and Jurkschat.[2] A rich chemistry of low-valent Group 14 elements without intramolecular donor stabilization was facilitated by introduction of extremely bulky ligands.[3] Especially the *m*-terphenyl ligands introduced by Power and co-workers facilitated the isolation of compounds which exhibit unusual reactivity.[4] Our idea was to combine tin(II) atoms protected by terphenyl ligands with rigid linking moieties known from pincer ligand chemistry to create a bis(stannane-diyl) pincer ligand.[5] The incorporation of the heavy carbene analogous diorganyl tin(II) donor sites into pincer ligands might contribute to the discovery of more compounds with intriguing reactivity because of the quite different σ-donor and π-acceptor properties of tin(II) compared to carbenes.

The reaction of 4,5-dilithio-9,9-dimethylxanthene[6] with one equivalent of $[\{ArSnCl\}_2]$ ($Ar = 2,6\text{-}Mes_2C_6H_3$, $Mes = 2,4,6\text{-}Me_3C_6H_2$)[7] yields the deep blue–green-colored compound **1**, which against our expectation can be described as a distannene rather than a bis(stannane-diyl) (Scheme 1).[3a–c] Compound **1** is of importance because it is a rare example of a distannene revealing tin–tin coupling in ^{119}Sn solution NMR spectroscopy, which provides an unambiguous proof for direct tin–tin bonding (see below). Distannene **1** is highly soluble in hydrocarbon and in ether solvents, giving intensely blue-colored solutions, and it is extremely sensitive toward oxygen and water. The reaction of distannene **1** with $[Ni(cod)_2]$ in hexane yields an intensely green-colored solution of product **2**, which gives a greenish, almost black solid when the solvent is removed. We expected the product to reveal a similar coordination as the stannane-diyls reported by Hahn and Veith, with the two tin(II) atoms coordinating separately to the nickel(0).[2a,8] Furthermore, a bis(silane-diyl) nickel complex has been reported that coordinates with separate silicon(II) atoms.[9] Again, unexpectedly, we found the distannene to stay rather intact after coordination, exhibiting a form of side-on coordination of the *trans*-bent distannene **1** to the nickel atom (Scheme 1), which to our knowledge is unprecedented for transition-metal compounds.[10] Side-on coordination of homonuclear multiply bonded Group 14 element compounds is known for silicon, which exhibit structures that are quite similar to η^2-alkenes.[11] For germanium, only the compound $[Ar'GeGeAr']$ ($Ar' = 2,6(2,6\text{-}iPr_2C_6H_3)_2C_6H_3$), an analogue of an alkyne, was reported to act as a π-electron donor.[4d]



Scheme 1. Synthesis of distannene **1** and reaction to form the nickel complex **2**.

Figure 1 shows the molecular structure of compound **1** in the solid state.[12] The xanthene backbone can be described as folded along the O112–C105 axis by an angle of 141.7° [138.8°] facilitating the tin–tin distance of 3.0009(7) Å [3.0559(15) Å]. The folding of the xanthene moiety is a rather common feature in 4,5-disubstituded polydentate ligands with a xanthene backbone.[6,13] Nevertheless, the distance between the 4,5-substituents is exceptionally short (to the best of our knowledge, the shortest distance reported in the CSD (version 5.33, November 2011) is 3.398 Å.[13b]). This clearly hints at a bonding interaction between the two tin moieties. Considering the lone pair of electrons at each of the tin(II) atoms, a bond order of up to two is conceivable. Compared to other tin–tin distances, the Sn1–Sn10 distance of compound **1** is longer than most of the reported data for $[R_2SnSnR_2]$, covering a range of 2.768(1) to 2.910(1) Å,[3b,c] with only one example containing a longer tin–tin contact of 3.639(1) Å.[14] In contrast to alkenes, the heavier Group 14 element analogues reveal distortions from planarity or even constitutional differences.[3,15] The distannene **1** is best described as a *trans*-bent structure twisted about the Sn1–

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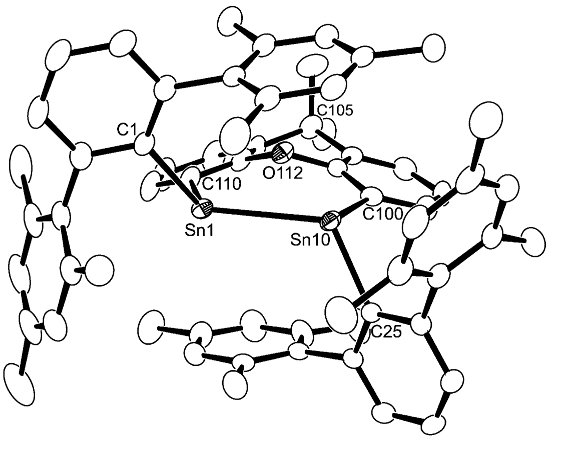


Figure 1. Molecular structure of distannene **1** (ellipsoids set at 50% probability) in the solid state. All hydrogen atoms and the minor disorder[12] are omitted for clarity. Selected bond lengths [Å] and angles [°] (corresponding values of the minor disorder are given in square brackets): Sn1–Sn10 3.0009(7) [3.0559(15)], Sn1–C1 2.195(3) [2.226(3)], Sn1–C110 2.216(4) [2.194(9)], Sn10–C25 2.213(3) [2.195(3)], Sn10–C100 2.210(5) [2.200(12)]; C1-Sn1-C110 100.45(14) [101.5(3)], C25-Sn10-C100 93.67(14) [94.8(3)].

Sn10 axis with an almost planar arrangement of the two tin atoms Sn1 and Sn10 and the two carbon atoms C100 and C110 of the xanthene. The C110-Sn1-Sn10-C100 torsion angle amounts to −2.7° [−19.3°].

A single molecule of the distannene **1** exhibits C_1 symmetry in solid state, but solution NMR data reveal higher symmetry on the NMR timescale at room temperature. In the ^{119}Sn NMR spectrum, only one singlet at 862 ppm with ^{117}Sn satellites is observed. The chemical shift lies in the range of reported chemical shifts of distannenes [R_2SnSnR_2] with R = $CH(SiMe_3)_2$ (735 and 750 ppm,[16] see below) and R = Trip (427.3 ppm)[17] and other probably dimeric [R_2Sn] compounds with R = 2-*t*Bu-4,5,6-Me_3C_6H (1329 ppm)[3f] and R = 2,6-$Mes_2C_6H_3$ (635 ppm),[7] respectively. Monomeric stannane-diyls [RR′Sn] reveal remarkably more deshielded resonances at 2315 ppm (R,R′ = $CH(SiMe_3)_2$, at 102 °C)[18] and 2323 ppm (R-R′ = $(SiMe_3)_2C(CH_2)_2C(SiMe_3)_2$),[19] respectively, but also quite similar or even more shielded resonances depending on the substituents; for example, R,R′ = 2,4,6-$(CF_3)_3C_6H_2$ (723 ppm),[14a] R,R′ = $(SiMe_3)_2N$ (766 ppm), and R = $(SiMe_3)_2N$, R′ = 4-Me-2,6-(tBu)$_2C_6H_2O$ (277 ppm).[20] The integration ratios of the ^{117}Sn satellites in distannene **1** are indicative for a symmetric distannene,[21] and the $^1J(^{119}\text{Sn-}^{117}\text{Sn})$ coupling constant of 3330 ± 30 Hz is very similar to the two reported examples of [R_2SnSnR_2] compounds with a Sn–Sn coupling in solution NMR of 3317 Hz, 1784 Hz (R = $CH(SiMe_3)_2$; two resonances at 735 and 750 ppm at −90.7 °C that are probably due to different isomers with different coupling constants)[16] and 2930 Hz (Trip = 2,4,6-iPr$_3C_6H_2$).[17] However, ^{119}Sn CP/MAS data of [$Sn_2\{CH(SiMe_3)_2\}_4$] exhibit a somewhat smaller $^1J(^{119}\text{Sn-}^{117}\text{Sn})$ coupling constant of 1340 ± 10 Hz.[18] The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of distannene **1** indicate chemical equivalence of all of the four mesityl groups as well as chemical equivalence consistent with C_2 or C_s symmetry of the xanthene moiety. Broad signals[22] for the mesityl CH_3 and mesityl H at 26 °C suggest that dynamic processes of the organic moieties are the reason for the observed high symmetry in solution NMR spectroscopy.

The most intriguing question arising from distannene **1** is the question of the nature of the tin–tin bonding.[3a–c,23] DFT calculations on distannene **1** are given in detail in the Supporting Information. Our calculations at the revPBE-D3/TZP level confirm the geometric structure of distannene **1** and reproduce the ^{119}Sn NMR chemical shift and the ^{119}Sn–^{117}Sn coupling constant surprisingly well.[24] In contrast to alkenes, the shape of the calculated HOMO suggests that less π bonding between the two tin atoms is present. Instead, the HOMO seems to have more nonbonding character, with most electron probability density equally contributed on both tin atoms.

Compared to the distannene **1**, the Sn1–Sn2 distance of 3.0592(3) Å in the nickel complex **2** is basically the same, and the Sn–C distances, the C-Sn-C angles, and the torsion angle C11-Sn1-Sn2-C1 of −19.9° remain essentially unchanged after coordination (Figure 2). Only the Sn1-Sn2-C17 angle of 137.89(7)° is widened compared to the corresponding angles in compound **1** (118.37(7)° and [122.87(7)°], respectively). The nickel atom coordinates almost perpendicularly to the least-squares plane through C11-Sn1-Sn2-C1 as is described by the angle between the normal of that plane and the normal of the plane through Sn1-Ni1-Sn2, which amounts to 78.38(5)°, and points slightly away from the xanthene backbone. Thus the coordination of the two SnR_2 moieties toward the nickel atom differs significantly. That at Sn2 can be seen as side-on coordinated, with the Sn2–Ni1 vector oriented along the same axis as the formally vacant $5p_z$ orbital at Sn2,

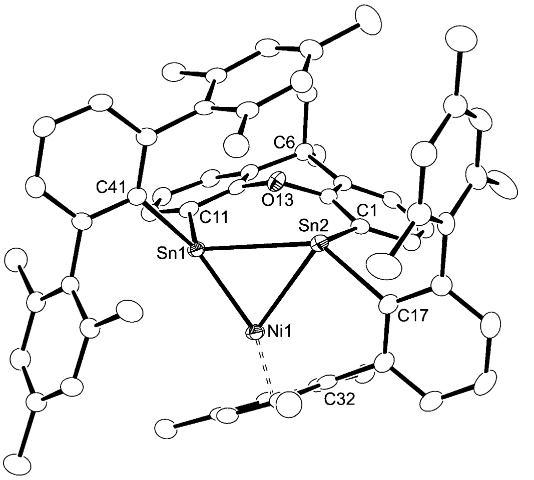
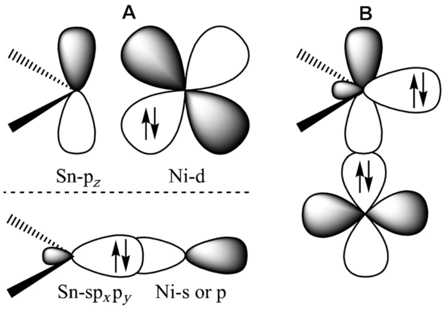


Figure 2. Molecular structure of the nickel complex **2** (ellipsoids set at 50% probability) in the solid state.[12] All hydrogen atoms and solvent molecules are omitted for the sake of clarity. Selected bond lengths [Å] and angles [°]: Sn1–Sn2 3.0592(3), Sn1–Ni1 2.4085(4), Sn2–Ni1 2.6939(4), Sn1–C41 2.185(3), Sn1–C11 2.194(3), Sn2–C17 2.203(3), Sn2–C1 2.214(3), Ni1–C range of 2.093(3)–2.202(3); Sn1-Ni1-Sn2 73.454(11), Ni1-Sn1-Sn2 57.547(10), Sn1-Sn2-Ni1 48.999(10), C11-Sn1-C41 100.73(10), C1-Sn2-C17 94.23(10).

whereas the SnR$_2$ moiety at Sn1 is oriented with the Sn1–Ni1 vector lying in the C11-Sn1-C41 plane. Several examples for side-on coordination of the smaller congeneric disilenes that show structures that are between π-coordination with planar disilenes and metallacyclopropanes with *cis*-bend disilenes are known.[11] To the best of our knowledge, no transitionmetal complexes containing *trans*-bent disilenes have been reported. Furthermore, elongations of the silicon–silicon bond for disilenes of up to 5% have been observed upon coordination. In consideration of the disorder in the crystal structure of distannene **1**, no exact quantification for an alteration of the tin–tin bond length on coordination can be stated, but at most an elongation smaller than 2% might be estimated.

The difference between the coordination geometries of Sn1 and Sn2 is underlined by the large difference of the tin–nickel bond lengths of 0.2845(8) Å. The absolute value of the shorter Sn1–Ni1 bond length of 2.4085(4) Å is rather inconspicuous but the remarkably longer Sn2-Ni1 distance of 2.6930(3) Å is exceptionally long for mononuclear nickel complexes with tin ligands,[25] hinting at an unusual bonding situation.

To give a possible interpretation for the differences depicted above within a simple valence bond picture, two limiting cases for the orientation of the R$_2$Sn···Ni coordination are considered. Within this consideration, we assume the lone pair of tin(II) to occupy the 5 sp$_x$p$_y$ hybrid orbital and the 5p$_z$ orbital, which is perpendicular to the R-Sn-R plane, to be vacant. In the first case, the Sn···Ni vector lies within the R-Sn-R plane (**A**).



For this arrangement the lone pair on tin can be considered to be capable of σ-donation to the transition metal and perhaps the vacant 5p$_z$ orbital of tin can accept a π back-donation from the transition metal. In the second case, the Sn···Ni vector lies perpendicular to the R-Sn-R plane and is aligned with the 5p$_z$ orbital (**B**). In that case, the tin can be expected to be merely capable of acting as σ acceptor into the vacant 5p$_z$ orbital. The lone pair in the 5sp$_x$p$_y$ hybrid orbital probably remains rather uninvolved owing to its orientation. In the nickel complex **2**, the observed orientation of the SnR$_2$ moiety at Sn1 accords well to case **A** and the orientation at Sn2 accords well to case **B**. The given interpretation of the orientations is consistent with the large difference in the tin–nickel bond lengths as a shorter bond would be expected when the 5sp$_x$p$_y$ orbital is involved in bonding, as observed for Sn1 according to case **A**.

Considering the description of the bonding in *trans*-bent distannenes within a simple valence bond model as a twofold donor–acceptor bond, as proposed by Lappert,[3a] the Sn$_2$Ni triangle may be described as a cyclic threefold donor–acceptor system: Sn1→Ni1→Sn2→Sn1. Each of the atoms donates to one of the neighboring atoms and accepts from the other.

The ^{119}Sn NMR data are consistent with the solid-state structure persisting in solution. Two singlets with an integration ratio of approximately 1:1 are observed at -19 ppm and 640 ppm, each carrying $^{119/117}$Sn satellites. Both resonances of nickel complex **2** show the same coupling constant of 1720 ± 40 Hz, which is considerably lower than for the uncoordinated starting material **1** (3330 ± 30 Hz), although the structural parameters of the distannene moiety are very similar. This might perhaps be a hint at a weakening of the tin–tin interaction arising from coordination. However, it compares well to the coupling constants of 1784 Hz and 1340 ± 10 Hz of $[Sn_2\{CH(SiMe_3)\}_4]$ observed by solution NMR and ^{119}Sn-CP/MAS NMR (see above). For both resonances of the nickel complex **2**, a shift to higher frequencies is observed compared to the uncoordinated distannene **1**, with the difference in the magnitude of the shift between Sn1 and Sn2 being remarkable. A detailed analysis of high-resolution ^{1}H, ^{13}C{^{1}H}, ^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC, ^{1}H–^{13}C HMBC, and ^{1}H–^{119}Sn HSQC NMR spectra[26] allows the signal at -19 ppm to be assigned to the tin atom corresponding to Sn2 (case **B**) in Figure 2 and the resonance at 640 ppm to Sn1 (case **A**).

Paramagnetic deshielding for tin(II) compounds arises from charge circulation induced by B_0 involving the formally unoccupied Sn 5p$_z$ orbital and mainly the Sn–R bonds rather than the lone pair of the tin atom.[27] Considering this, the experimental data of our nickel complex **2** support the picture of the cyclic threefold donor–acceptor interaction (see above). As the coordination of the nickel has almost no effect on the structural parameters of the Sn–R bonds, the differences of the chemical shift are assumed to arise from differing influences on the Sn 5p$_z$ orbitals. We believe that the 5p$_z$ orbital of Sn1 can be assumed to be mainly affected by the lone pair of Sn2, and the coordination to the nickel has little effect on the chemical shift. In contrast, the Sn 5p$_z$ orbital of Sn2 is more affected by the donation of the nickel atom, causing a rather large shift of the resonance to lower frequencies by somehow reducing the paramagnetic deshielding. DFT calculations confirm the structure of nickel complex **2** and reproduce the trend of the ^{119}Sn NMR chemical shift values.[26]

Experimental Section

Distannene 1: In a glovebox, 9,9-dimethylxanthene (0.44 g, 2.1 mmol) and TMEDA (0.7 mL, 0.9 g, 8 mmol) were dissolved in diethyl ether/hexane (8.5 mL/12.5 mL). An *n*BuLi solution in hexane (1.6 M, 1.3 mL, 2.1 mmol) was added. Subsequent heating of the mixture to 40 °C for 3 h yielded a red solution, which was then precooled to −40 °C. At ambient temperature the solution was slowly added to a vigorously stirred suspension (precooled to −40 °C) of $[\{(2,6\text{-}Mes_2C_6H_3)SnCl\}_2]$ (1.97 g, 4.2 mmol) in diethyl ether/hexane (21 mL/30 mL) and stirred overnight; the color changed to deep blue–green. The solvent was then removed in vacuo and the residue was extracted with a minimal amount of hexane or pentane, and the saturated solution was stored for several days at −40 °C to crystallize. The deep-green product was isolated by cold filtration in 580 mg (26 %) yield. ^{119}Sn NMR ([D$_8$]toluene, 26 °C, 186.50 MHz): $\delta = 862$ ppm (s + d, $^{1}J(^{119}\text{Sn-}^{117}\text{Sn}) = 3330 \pm 30$ Hz). Anal. calcd (%) for $C_{63}H_{62}OSn_2$: C 70.55, H 5.83; found: C 70.73, H 5.56.

Nickel complex 2: Distannene **1** (51 mg, 48 μmol) and [Ni(cod)$_2$] (13.1 mg, 48 μmol) were stirred in hexane (15 mL) overnight, resulting in a color change from dark blue–green to dark green. The solvent was then removed in vacuo and the residue was dried in vacuo. Crystalline material was obtained by redissolving the residue in pentane (5 mL) followed by crystallization at −40 °C for one week. Yield: 15 mg (28 %, pure by elemental analysis). ^{119}Sn NMR (C$_6$D$_6$, 26 °C, 186.50 MHz): $\delta = -19$ (s + d, $^{1}J(^{119}\text{Sn-}^{119/117}\text{Sn}) = 1720 \pm 40$ Hz, Sn2), 640 ppm (s + d, $^{1}J(^{119}\text{Sn-}^{119/117}\text{Sn}) = 1720 \pm 40$ Hz, Sn1). Anal. calcd (%) for $C_{63}H_{62}NiOSn_2$: C 66.89, H 5.52; found: C 67.09, H 5.88.

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[12] Distannene **1** is disordered in the solid state. Geometrical parameters for the minor disorder are given in square brackets. For further details, see the Supporting Information. CCDC 897076 and CCDC 897077 contain 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.

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[22] For Δν1/2, see Experimental Section in the Supporting Information.

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[25] Only polyatomic mixed nickel and tin clusters exhibit longer nickel–tin distances. Based on a survey of the Cambridge Structural Database version 5.33 (August 2012).

[26] See the Supporting Information.

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