Communications

Flexibly Coordinating Tris(arylamido)stannates as Ligands: A [Rh]+/[Sn]− Zwitterion as an Intermediate in the Formation of Rh−Sn Complexes

Michaela Kilian, Hubert Wadepohl, and Lutz H. Gade*

Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

Received March 23, 2007

Summary: Reaction of the lithium stannate MeSi{SiMe₂N(3,5-xyl)}₃SnLi(OEt₂) (1) with ¹/₂ molar equiv of [RhCl(COD)]₂ gave the zwitterionic heterodinuclear complex [MeSi{SiMe₂N(3,5-xyl)}₂Sn{SiMe₂N(η⁶-3,5-xyl)}Rh(COD)] (2), in which one of the peripheral N-bonded 3,5-xylyl groups acts as an η⁶-aryl ligand to which the {Rh(COD)}⁺ cation is bonded. Reaction of the 18-electron complex 2 with nucleophiles leads to an attack at the late transition element, which moves over to the tin atom to form the Rh−Sn-bonded 16-electron complexes [MeSi-{SiMe₂N(3,5-xyl)}₃SnRh(L)(COD)] (L = Ph₃P (3), (PhO)₃P (4), CyNC (5)).

Aryl groups in the periphery of substitutionally inert "anchoring" ligands, such as phosphines, have been shown to act as hemilabile additional coordinating units and may thus react to changes in the coordination sphere of a given metal.[1] This behavior has been most impressively demonstrated by Mirkin and co-workers, who studied the dynamics of such systems[2] as well as the metal-centered redox chemistry.[3]

We have recently employed triamidostannates as monoanionic equivalents of the ER₃ ligands of the group 15 elements and demonstrated their stability in coordination compounds throughout the d block.[4] Built into the [2,2,2]bicyclooctane cage generated by tripodal amido ligands, these ligating molecules possess large cone angles due to the orientation of the N substituents.[5,6] The latter thus induce both steric bulk and the potential of adding further functional groups.
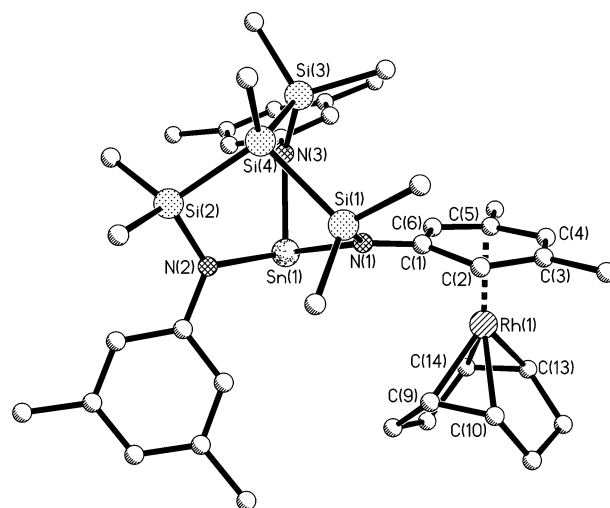
Figure 1. Molecular structure of complex **2**. Principal bond lengths (Å) and angles (deg): N(1)−Sn(1) = 2.263(4), N(2)−Sn(1) = 2.161(5), N(3)−Sn(1) = 2.158(5), C(1)−Rh(1) = 2.460(6), C(2)−Rh(1) = 2.208), C(3)−Rh(1) = 2.297(6), C(4)−Rh(1) = 2.302(6), C(5)−Rh(1) = 2.281(6), C(6)−Rh(1) = 2.382(6), C(1)−N(1) = 1.339(7), C(9)−C(10) = 1.402(9), C(13)−C(14) = 1.407(9), C(9)−Rh(1) = 2.115(6), C(10)−Rh(1) = 2.132(6), C(13)−Rh(1) = 2.151(6), C(14)−Rh(1) = 2.168(6); N(3)−Sn(1)−N(2) = 100.11(18), N(3)−Sn(1)−N(1) = 88.64(17), N(2)−Sn(1)−N(1) = 94.61(17).

By way of introducing additional weakly coordinating donor functions in the periphery of triamidostannates, we have observed the complexation of the alkali-metal counterions;[7] however, no significant interaction with the transition metals has been observed. In this work, we demonstrate how the N-bonded aryl groups in a tripodal tris(arylamido)stannate may provide an alternative binding site which may coordinate to very electron poor transition-metal centers. Since in this capacity the ligands act as formal six-electron donors, this type of ligation

* To whom correspondence should be addressed. Fax: (+49) 6221-545609. E-mail: lutz.gade@uni-hd.de.

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Scheme 1. Synthesis of the Complex Zwitterion 2 and Its Conversion to the Rh−Sn-Bonded Complexes 3−5
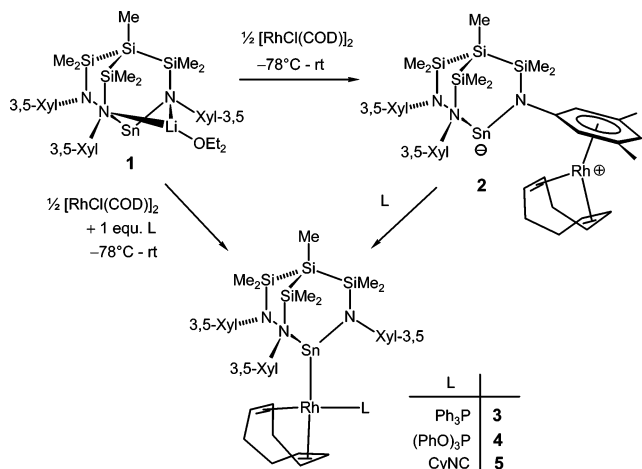
provides an alternative to the otherwise typical Sn−M coordination as a two-electron donor. It may therefore be a precursor state to the latter, which is attained upon attack of an additional ligand at the late-transition-metal center.

Reaction of the lithium stannate MeSi{SiMe₂N(3,5-xyl)}₃-SnLi(OEt₂) (**1**) with ¹/₂ molar equiv of the rhodium dimer [RhCl(COD)]₂ at −78 °C, subsequent warming to ambient temperature, and workup gave the heterodinuclear complex [MeSi{SiMe₂N(3,5-xyl)}₂{SiMe₂N(η⁶-3,5-xyl)}Rh(COD)] (**2**) in high yield. The high-field ^{119}Sn NMR signal at δ −127.8, which displayed no coupling to ^{103}Rh, indicated that a metal−metal bond had not been formed in this reaction. Instead, the proton resonances at δ 5.63 and 4.29 as well as the ^{13}C NMR signals at δ 151.6, 116.3, 95.4, and 92.4, which displayed ^{103}Rh−^{13}C coupling, indicated a π-arene type coordination of the Rh(COD) fragment and, thus, a potentially zwitterionic structure. This was confirmed by a single-crystal X-ray structure analysis of compound **2**, which established an unprecedented structural type in the chemistry of stannates(II). Its molecular
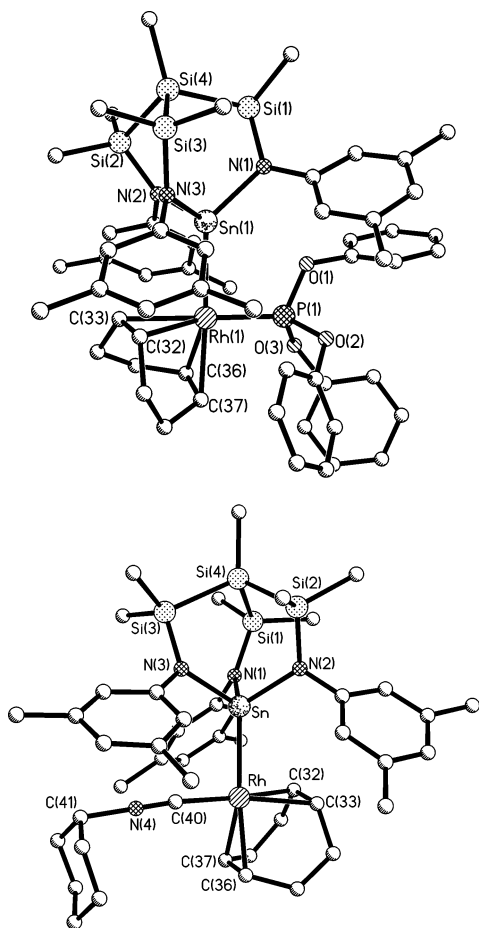
Figure 2. (a, top) Molecular structure of the Rh−Sn complex **4**. Selected bond lengths (Å) and angles (deg): Rh(1)−Sn(1) = 2.6331(4), P(1)−Rh(1) = 2.2049(9), N(1)−Sn(1) = 2.118(3), N(2)−Sn(1) = 2.114(3), N(3)−Sn(1) = 2.109(3), C(32)−C(33) = 1.368(6), C(36)−C(37) = 1.398(5), C(32)−Rh(1) = 2.252(4), C(33)−Rh(1) = 2.299(4), C(36)−Rh(1) = 2.171(3), C(37)−Rh(1) = 2.215(3); P(1)−Rh(1)−Sn(1) = 92.87(2), N(1)−Sn(1)−N(2) = 99.85(11), N(1)−Sn(1)−N(3) = 99.45(11), N(2)−Sn(1)−N(3) = 99.99(11), N(1)−Sn(1)−Rh(1) = 131.65(8), N(2)−Sn(1)−Rh(1) = 101.32(7), N(3)−Sn(1)−Rh(1) = 118.72(7). (b, bottom) Molecular structure of compound **5**. Selected bond lengths (Å) and angles (deg): Rh−Sn = 2.6004(3), C(40)−Rh = 1.922(4), C(40)−N(4) = 1.134(5), C(41)−N(4) = 1.535(7), N(1)−Sn = 2.107(3), N(2)−Sn = 2.092(2), N(3)−Sn = 2.110(2), C(32)−C(33) = 1.372(5), C(36)−C(37) = 1.363(6), C(32)−Rh = 2.229(3), C(33)−Rh = 2.246(3), C(36)−Rh = 2.191(3), C(37)−Rh = 2.194(3); C(40)−Rh−Sn = 89.32(10), N(1)−Sn−N(2) = 99.34(10), N(1)−Sn−N(3) = 98.57(10), N(2)−Sn−N(3) = 101.22(10), N(1)−Sn−Rh = 107.95(7), N(2)−Sn−Rh = 122.60(7), N(3)−Sn−Rh = 122.40(7), N(4)−C(40)−Rh = 172.3(3), C(40)−N(4)−C(41) = 175.1(5).

(8) Complex **2**: monoclinic, space group P2₁/c, a = 14.2713(16) Å, b = 12.3970(15) Å, c = 25.911(3) Å, β = 102.079(3)°, V = 4482.7(9) Å³, Z = 4; 76 870 reflections collected, 8473 independent reflections; heavily disordered solvent of crystallization (toluene) found, the contributions of which were removed from the F_o with the SQUEEZE procedure.^{8a} Final R indices (I > 2σ(I)): R1 = 0.0551, wR2 = 0.1310. Complex **4**: triclinic, space group P1̄, a = 12.3271(10) Å, b = 12.8709(10) Å, c = 20.6506(17) Å, α = 72.1700(10)°, β = 89.6270(10)°, γ = 87.669(2)°, V = 3116.4(4) Å³, Z = 2; 64 764 reflections collected, 15 463 independent reflections; heavily disordered solvent of crystallization (toluene) found, the contributions of which were removed from the F_o with the SQUEEZE procedure.^{8a} Final R indices (I > 2σ(I)): R1 = 0.0420, wR2 = 0.0951. Complex **5**: monoclinic, space group P2₁/n, a = 12.7606(9) Å, b = 13.8360(10) Å, c = 31.050(2) Å, β = 91.8290(10)°, V = 5479.3(7) Å³, Z = 4; 133 095 reflections collected, 17 389 independent reflections; one molecule of toluene solvent refined with planarity restraints. Final R indices (I > 2σ(I)): R1 = 0.0466, wR2 = 0.1089. Data collection was carried out at 100 K (Mo Kα radiation, Bruker AXS Smart 1000 CCD diffractometer). Data were corrected for absorption and other effects (SADABS^{8b}). Structure solution: heavy-atom method combined with structure expansion by direct methods applied to difference structure factors (DIRDIF,^{8c} complexes **2** and **5**) or direct methods (SHELXS,^{8d,e} complex **4**). Refinement: full-matrix least squares on F^2 (SHELXL^{8f}); all non-hydrogen atoms anisotropic, hydrogens at calculated positions. (a) van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194. (b) Sheldrick, G. M. SADABS-2004/1, Bruker AXS, Madison, WI, 2004. (c) Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Gould, R. O.; Israel, R.; Smits, J. M. M. DIRDIF-99; University of Nijmegen, Nijmegen, The Netherlands, 1999. (d) Sheldrick, G. M. SHELXS-86; University of Göttingen, Göttingen, Germany, 1986. (e) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. (f) Sheldrick, G. M. SHELXL-97; University of Göttingen, Göttingen, Germany, 1997.

structure is displayed in Figure 1 along with the principal bond lengths and angles.^{8}

The tri(arylamido)stannate adopts a distorted "lamp shade" arrangement with one of the peripheral N-bonded 3,5-xylyl groups acting as an η⁶-aryl ligand to which the {Rh(COD)}⁺ cation is bonded, thus attaining a valence electron count of 18. The geometry of the arene complex itself resembles those

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previously established for such complexes,[2,9] of which the adducts with the BPh_4^- counterion are perhaps the most closely related examples to complex **2**.[10] As a consequence of this metalation of an aryl substituent, the triamidostannate unit is highly distorted (N(3)−Sn(1)−N(2) = 100.1(2)°, N(3)−Sn(1)−N(1) = 88.7(2)°, N(2)−Sn(1)−N(1) = 94.6(2)°).

The potential combination of the {Rh(COD)}$^+$ unit with the stannate via a Rh−Sn bond would lead to a highly reactive 14-electron complex, and the system thus stabilizes itself by utilizing the arene periphery as a "landing strip" for the cationic rhodium fragment. In this respect, the stannate represents a *flexibly coordinating ligand* with its active, potentially coordinating aryl periphery and complex **2** provides the first such example involving the heavier group 14 elements.

Reaction of the 18-electron complex **2** with nucleophiles leads to an attack at the late transition element, which moves over to the tin atom to form Rh−Sn-bonded 16-electron complexes. In the course of such a transformation, the stannate converts from a 6-electron donor to the usual 2-electron donor ligand. Examples for this behavior were provided by reaction of **2** with triphenylphosphine, triphenyl phosphite, and cyclohexyl isocyanide, giving the respective complexes [MeSi{SiMe$_2$N(3,5-xyl)}$_3$SnRh(L)(COD)] (L = Ph$_3$P (**3**), (PhO)$_3$P (**4**), CyNC (**5**)) (Scheme 1). These compounds could also be directly obtained by reaction of **1** with the chlororhodium complex in the presence of the respective additional ligand. Their analytical and spectroscopic data are consistent with the presence of Rh−Sn bonds and therefore were formulated as square-planar 16-electron complexes. These structural assignments were confirmed by single-crystal X-ray diffraction studies of complexes **4** and **5**. Their molecular structures are represented in parts a and b of Figure 2, respectively, along with selected bond lengths and angles.

Both **4** and **5** adopt square-planar coordination geometries with Rh−Sn bond lengths of 2.6331(4) and 2.6004(3) Å, respectively.[11] The greater Rh−Sn bond length of the former is due to the steric congestion generated by the cis-disposed stannate and triphenyl phosphite. The interligand repulsion in **4** is also evident from the significantly tilted orientation of the stannate (Figure 2a), which bends away from its bulky neighboring ligand (Si(4)−Sn(1)−Rh(1) = 160.80(2)°, compared to 169.24(2)° for the corresponding angle in **5**). In contrast to the structure of the zwitterion **2**, the [2.2.2]bicyclooctane-related triamidostannate cages regain their local threefold symmetry, the N−Sn−N angles being all close to 100°.

In this first report we have demonstrated that the stabilization of an unsaturated transition-metal fragment by an (arylamido)-stannate may occur by way of π coordination of the aryl periphery rather than the group 14 heteroatom. This may play an important role in stoichiometry and catalytic transformations involving complexes bearing such ligands. A closer examination of this aspect is currently in progress.

Supporting Information Available: Text and CIF files giving experimental procedures, characterization data, and crystallographic details for **2**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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