Allyl Tin Complexes

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η^3-Allyl Coordination at Tin(II)—Reactivity towards Alkynes and Benzonitrile**

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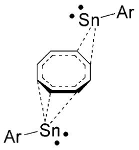
Dedicated to Professor Manfred Scheer on the occasion of his 60th birthday

Abstract: *We herein report the synthesis and characterization of a terphenyl-substituted Sn^{II} allyl compound featuring an η^3 coordination mode in solution and in the solid state. Two examples for the interesting reactivity of the allyl Sn^{II} molecule are presented: Reactions with terminal alkynes result in the formation of tricyclic compounds by C−C bond formation and the dimerization of two Sn moieties whereas the reaction with benzonitrile leads to a sixteen-membered ring system through C−H activation.*

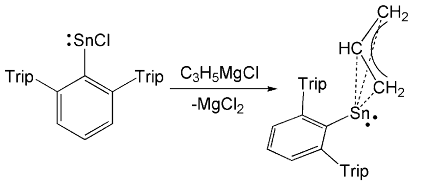
Organotin compounds that feature an allyl group connected to a tin(IV) center have been known for several decades and are well established reagents in organic allylation reactions.[1] In case of tetravalent tin, the allyl substituent binds in the η^1 coordination mode whereas complexes of several other main-group elements feature the allyl ligand in the η^3 coordination mode.[2] Switching the oxidation state of the tin atom from IV to II in allyl tin compounds may result in new coordination modes and reactivity as unoccupied binding sites will then be available at the tin atom.[3] In 2010, Power et al. reported the binding of a tin compound to a hydrocarbon moiety in an η^3 fashion.[4] For the reaction of a distannyne with cyclooctatetraene (COT), they observed the cleavage of the $Sn{\equiv}Sn$ bond and an η^3,η^2 coordination of two aryl tin fragments to the resulting ten-electron π-aromatic $[COT]^{2-}$ in the solid state ($[(ArSn)_2(\mu_2\text{-}\eta^2{:}\eta^3\text{-cot})]$ (**A**); Ar = 2,6-(2,6-$i\text{Pr}_2\text{-}C_6H_3)_2C_6H_3$).[4]



A

We herein present the synthesis of an allyl-substituted tin(II) compound featuring η^3-C_3H_5 coordination at the tin atom, which, to the best of our knowledge, has been unknown to date. Furthermore, we give first insights into the surprising reactivity of the η^3-allyl Sn^{II} compound towards alkynes and benzonitrile.

Isopropyl-substituted *m*-terphenyltinchloride was reacted with an ethereal solution of $(C_3H_5)MgCl$ in a mixture of *n*-hexane and benzene to quantitatively yield allyl Sn^{II} compound **1** (Scheme 1).[5] Pale yellow crystals were obtained by cooling a concentrated *n*-hexane solution of **1** to −40 °C for several days. Allyl Sn^{II} compound **1** is sensitive to air and moisture, but stable under inert conditions both in solution and in the solid state for several days. Allyl complex **1** was fully characterized by NMR spectroscopy, single-crystal structure analysis, and elemental analysis. The crystal structure of **1** with selected interatomic distances and angles is shown in Figure 1.



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Scheme 1. Formation of tin allyl compound **1**. Trip = 2,4,6-triisopropylphenyl.

The minor variations in the distances between Sn1 and the allyl carbon atoms C1–C3 [Sn1–C1 2.418(3), Sn1–C2 2.387(4), Sn1–C3 2.380(4) Å] confirmed the highly symmetric η^3 coordination of the allyl ligand and indicate an interaction of the Sn^{II} center with the four-electron π-system of the allyl anion. The small C4-Sn1-C^{allyl} angles [C1-Sn1-C4 105.5(1)°, C2-Sn1-C4 92.6(1)°, C3-Sn1-C4 105.3(1)°] are consistent with a sterically active free electron pair at the tin center. The Sn1–C4 distance of 2.233(3) Å is in the range of those of known Sn^{II}–Ar compounds.[6] The structural parameters of **1** and **A** are also of similar size.[4] Another negatively charged three-atom ligand system featuring four π-electrons is the amidinate ion, which, in contrast, coordinates at tin(II) centers exclusively in η^2 fashion.[7]

Natural bonding orbital (NBO) analysis and a second-order perturbation theory analysis of **1** support the description of the bonding interaction as a σ-bonded allyl moiety with a donor–acceptor interaction ($42\ \text{kcal mol}^{-1}$) of the π-electrons of the allylic double bond into the empty p orbital at the Sn atom. Furthermore, a donor–acceptor interaction of $46\ \text{kcal mol}^{-1}$ from the Sn−C σ-bond orbital into the antibonding C=C orbital was determined, which is in line with the

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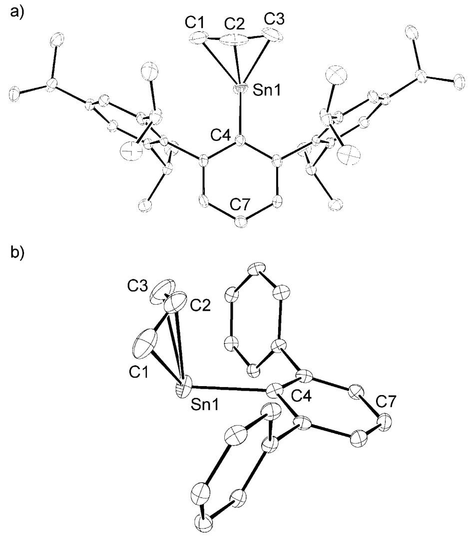


Figure 1. a) Molecular structure of allyl complex **1** in the solid state; ellipsoids set at 50% probability. b) Detailed structure without the isopropyl groups. All hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1–C1 2.418(3), Sn1–C2 2.387(4), Sn1–C3 2.380(4), Sn1–C4 2.233(3); C1-Sn1-C4 105.5(1), C2-Sn1-C4 92.6(1), C3-Sn1-C4 105.3(1), Sn1-C4-C7 164.0(1).

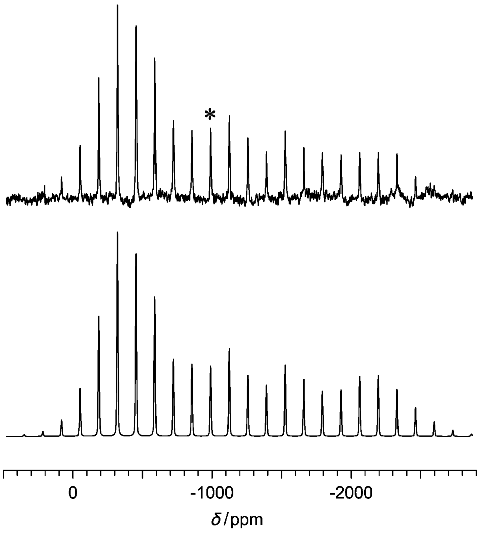
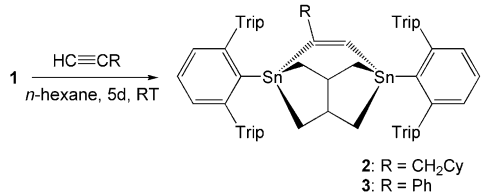


Figure 2. Measured (top) and simulated (bottom) solid-state ^{119}Sn HPDec/MAS NMR spectra of compound **1**. * = isotropic peak.



Scheme 2. Formation of the tricyclic structures **2** and **3**.

resonance stabilization expected for an η^3-coordinated allyl moiety.[8]

^{119}Sn{^{1}H} NMR spectroscopic measurements show one single resonance at −957 ppm at room temperature in C_6D_6. For compound **A**, one single resonance at −85 ppm was reported, which might result from the observed fluxional behavior without defined coordination modes in solution.[4] Consistent with a higher coordination number of four and therefore an increase in ^{119}Sn nuclear shielding, compound **1** closes a gap in the chemical shifts of organotin(II) compounds, which range from > 2000 ppm for double coordination ([Sn(C{SiMe$_3$}$_2$CH$_2$)$_2$]: 2323 ppm)[9] to −2000 ppm for two-fold η^5 coordination ([Sn(η^5-C$_5$H$_5$)$_2$]: −2171.1 ppm).[10] Apart from the characteristic terphenyl signals, **1** shows a doublet at 2.78 ppm and a quintet at 5.39 ppm in its ^{1}H NMR spectrum. The A_4X coupling pattern is consistent with an η^3 ground state (A_2B_2X pattern) in a fluxional situation (A_4X pattern) but would also match a fluxional η^1 coordination.[2] Temperature-dependent ^{1}H NMR measurements in [D$_8$]toluene showed no significant changes in the spectrum up to 100 °C. Towards −80 °C, a broadening of the doublet followed by its complete disappearance into the baseline was observed. The ^{119}Sn NMR signal is shifted upfield from −850 ppm (100 °C) to −1030 ppm (−80 °C), which is consistent with a tighter η^3 coordination at lower temperatures. Solid-state NMR studies revealed an isotropic ^{119}Sn chemical shift of −990 ppm, suggesting that the solution- and solid-state structures are equivalent (Figure 2). The measured magnitude of the large chemical shift anisotropy ($\Delta\delta = 2565$ ppm) is consistent with other values previously reported for Sn^{II} compounds.[11]

We started investigating the reactivity of compound **1** by subjecting it to terminal alkynes (Scheme 2). The reaction progress can easily be monitored by ^{1}H NMR spectroscopy by observing the diminishing intensities of the characteristic allyl quintet and doublet signals. After crystallization, we were able to identify a tricyclic structure as the main product, which resulted from the reaction of **1** with excess alkyne HC≡C−R (R = CH$_2$Cy, Ph; Cy = cyclohexyl). This transformation involves an alkyne-induced dimerization of two tin allyl moieties, the formation of a new C−C bond, and an oxidation of Sn^{II} to Sn^{IV}.

The reaction was performed by dissolving compound **1** in *n*-hexane and adding an excess amount of the respective alkyne, followed by stirring at room temperature for five days. Afterwards, excess alkyne and the solvent were removed in vacuo. The products were highly soluble in apolar solvents. Single crystals were obtained by slow solvent evaporation from a saturated solution of the reaction product **2** in methylcyclohexane. Single crystals of compound **3** (R = Ph) were obtained by cooling/evaporating different combinations of nonpolar solvents; all crystals featured large highly disordered areas causing a lack of structural quality, but revealed the same structural motif.[12] Compounds **2** and **3** were further characterized by elemental analysis and NMR spectroscopy.

The central structural motif is a tricyclic structure, namely tricyclo[3.3.2.0^{3,7}]-1,5-distannadec-9-ene. The saturated carbon analogue was first described in 1979 and as one of the adamantane isomers, it is part of the "adamantaneland".[13] The crystal structure of **2** is shown in Figure 3. A disorder of the HC=C−CH$_2$Cy unit accounts for the slightly

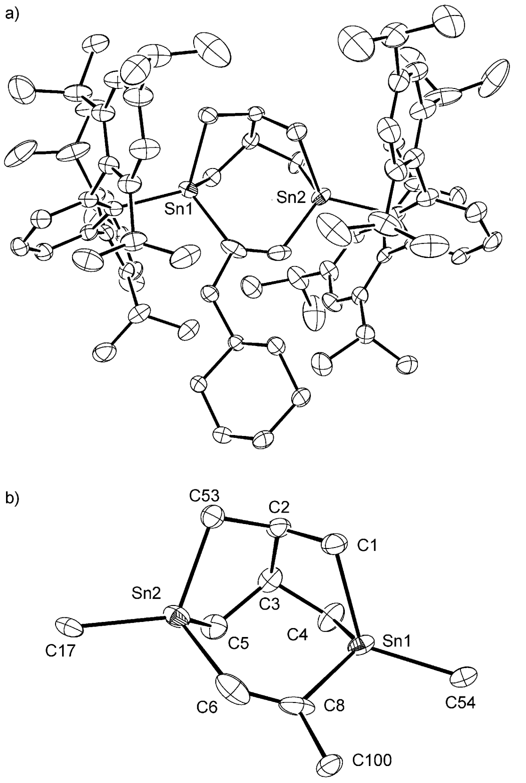


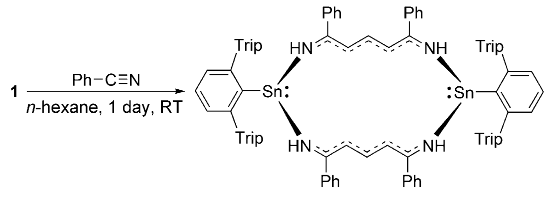
Figure 3. a) Molecular structure of **2** in the solid state; ellipsoids set at 50% probability. b) Detailed structure without solvent, terphenyl substituents, disorder, and the cyclohexyl substituents. All hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1–C1 2.149(2), Sn1–C4 2.153(2), Sn1–C8 2.182(3), Sn1–C54 2.167(2), Sn2–C5 2.148(2), Sn2–C6 2.145(3), Sn2–C17 2.162(2), Sn2–C53 2.152(2), C6–C8 1.323(4), C2–C3 1.602(3); C1-Sn1-C4 82.9(9), C1-Sn1-C8 103.9(1), C4-Sn1-C8 122.2(1), C5-Sn2-C6 104.9(1), C5-Sn2-C53 83.3(1), C6-Sn2-C53 120.1(1).

bigger ellipsoids. Both tin atoms are coordinated in a distorted tetrahedral geometry, which is most likely caused by the steric demands of the substituents and ring strain. The Sn–C distances [2.145(3)–2.182(3) Å] are of typical lengths and can either be compared with those of 1,2-ditin-substituted olefins, which can be obtained from the addition of distannenes to alkynes and feature Sn–C bond lengths of 2.174(6)–2.263(7) Å, or with stanna-cycloalkane structures.[14]

The R substituent in **2** and **3** breaks the symmetry of the molecule, which results in two slightly different ^{119}Sn NMR chemical shifts for the tin atoms (**2**: −52, −34 ppm; **3**: −55, −31 ppm). These values lie in between the shifts previously reported for tetraalkyl Sn^{IV} species (Et_4Sn: 1.4 ppm) and those of tetraaryl/tetravinyl tin species (Ph_4Sn: −128.8 ppm, $(CH_2{=}CH)_4Sn$: −157.4 ppm).[10b] We were able to identify the ^{1}H chemical shifts of the vinyl (C=C*H*) protons for **2** [**3**] at 6.81 ppm [7.77 ppm], which feature multiple tin satellites: $^3J_{^{119}\mathrm{Sn,H}} = 271.2$ Hz, $^3J_{^{117}\mathrm{Sn,H}} = 259.2$ Hz, $^2J_{\mathrm{Sn,H}} = 93.8$ Hz [$^3J_{^{119}\mathrm{Sn,H}} = 247.0$ Hz, $^3J_{^{117}\mathrm{Sn,H}} = 235.6$ Hz, $^2J_{^{119}\mathrm{Sn,H}} = 67.2$ Hz, $^2J_{^{117}\mathrm{Sn,H}} = 65.1$ Hz]. The chemical shifts and coupling constants are consistent with examples reported in the literature.[15] Other characteristic isolated signals of both tricyclic systems are two doublets (2H, $SnCH_2$) at slightly negative shifts of approximately −0.3 ppm. All proton signals of the tricyclic framework have been assigned by ^{1}H–^{1}H COSY NMR studies and are consistent with an AA′BB′MM′NN′XX′ spin system.[16]

Surprisingly, the formation of the tricyclic structures seemed to be a favored reaction pathway. Although the alkynes were used in excess, only half an equivalent was incorporated into the cage compound. Monitoring a reaction mixture in C_6D_6 by NMR analysis over five days revealed a slow conversion (disappearance) of the tin starting material. This contradicts a fast coordination of the alkyne to the allyl compound, and we therefore suggest a reaction pathway that involves the reaction of an allyl exchange dimer or a Sn=Sn dimer existing in low equilibrium concentrations with the acetylene. However, final conclusions concerning the mechanism cannot be made at this point of the investigation.[8]

In the reaction of benzonitrile with allyl tin species **1** at room temperature, we observed the formation of a macrocyclic molecule featuring a sixteen-membered ring. The reaction includes the cleavage of all allyl tin bonds, C–H activation/hydrogen migration, and the dimerization of two stannylene units (Scheme 3). An excess of benzonitrile was added to a solution of compound **1** in *n*-hexane, which resulted in a red solution on stirring at room temperature for one day. Removing all volatile components in vacuo and crystallization from a concentrated *n*-hexane solution yielded macrocycle **4** as red crystals, which were characterized by NMR spectroscopy, elemental analysis, and single-crystal structure analysis.



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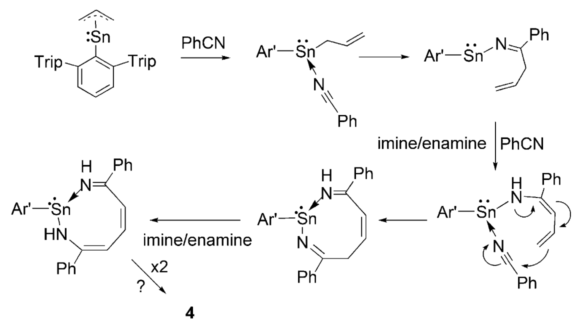
Scheme 3. Reaction of allyl compound **1** with benzonitrile at room temperature.

In contrast to the reaction with alkynes (Scheme 2), the oxidation state of the Sn^{II} atom is conserved when **1** is reacted with benzonitrile. For the double-insertion product of benzonitrile, we suggest the mechanism shown in Scheme 4. However, it remains arguable at which step of the reaction pathway the dimerization occurs. Similar mechanisms have been described for nitrile insertion reactions of the transition-metal compounds [Cp*$_2$Sc–CH$_3$], [Cp*ClCr–CH$_3$], and [Cp*$_2$(CO)$_2$W–((1-ethyl)η^3-1-azaallyl)] to yield metallacycles by insertion of one or two nitriles and subsequent imine/enamine tautomerization (1,3-H migration; Cp* = C_5Me_5).[17] Whereas the tungsten-based complex requires temperatures as high as 80 °C for the nitrile insertion to proceed, the complexes [Cp*$_2$Sc–CH$_3$] and [Cp*ClCr–CH$_3$] and compound **1** show reactivity even at room temperature.

The crystal structure of compound **4**, including the interatomic distances within the ring system and the angles



Scheme 4. Suggested mechanism for the formation of **4**.

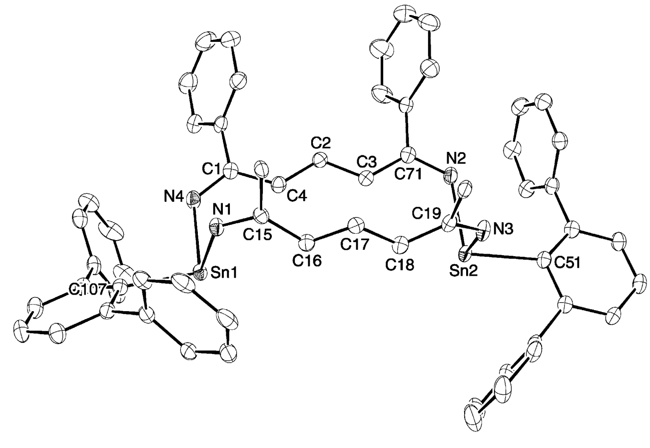


Figure 4. Molecular structure of **4** in the solid state; ellipsoids set at 50% probability. Some parts of the structure were omitted for clarity: isopropyl groups (partially disordered), two phenyl groups, and hydrogen atoms. Selected bond lengths [Å] and angles [°]: Sn1–N1 2.195(2), Sn1–N4 2.208(2), Sn3–N2 2.256(2), Sn3–N3 2.186(2), N1–C15 1.318(2), N2–C71 1.325(3), N3–C19 1.331(3), N4–C1 1.331(3), C15–C16 1.413(3), C16–C17 1.376(3), C17–C18 1.394(3), C18–C19 1.400(3), C1–C4 1.404(3), C4–C2 1.395(3), C2–C3 1.387(3), C3–C71 1.409(3); N1-Sn1-N4 82.6(6), N1-Sn1-C107 92.2(6), N4-Sn1-C107 101.7(7), N2-Sn3-N3 86.3(7), N2-Sn2-C51 102.4(7), N3-Sn2-C51 89.1(7).

at the tin atom, is shown in Figure 4. The C–C bond distances [1.376(3)–1.413(3) Å] within the sixteen-membered ring system are in the range of those reported for aromatic carbon systems and therefore consistent with a delocalized π-electron system as depicted in Scheme 3. Small angles at the tin atoms [82.62(6)–102.41(7)°] reveal a highly pyramidal coordination and are consistent with a sterically demanding free electron pair at the Sn^{II} center. The Sn–N distances lie in the range of values of known amine and amide adducts of Sn^{II}.[18]

The triple-coordinated tin(II) species gives rise to a ^{119}Sn chemical shift of −48 ppm, which could be compared with the signal of $[SnPh_3]^-$ at −98.4 ppm.[19] A broad singlet at 5.80 ppm in the ^1H NMR spectrum was assigned to the NH protons matching the chemical shifts that were reported for the transition-metal complexes mentioned above. The other protons of the sixteen-membered ring system have chemical shifts of 6.46 (CH–$(CH)_2$) and 6.49 ppm (CH–$(CH)_2$), as expected for a delocalized π-system. The ^{15}N NMR chemical shift at 182 ppm ($^1J_{Sn,N} = 165$ Hz) was assigned by two-dimensional ^{15}N–^1H HSQC NMR spectroscopy.

In summary, we have reported a straightforward synthesis for an η^3-allyl tin(II) compound. It features a new coordination mode for allyl substituents in tin chemistry, which in turn results in surprising reactivity. The reactions with alkynes and benzonitrile led to the interesting formation of tricyclic or macrocyclic molecules. When undergoing nitrile insertion, the allyl compound mimics known reaction pathways of transition metals and exhibits competitive reactivity.[20]

Keywords: alkynes · allyl ligands · macrocycles · nitriles · stannylene

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