Tin Ligands

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Nickel-Triad Complexes of a Side-on Coordinating Distannene**

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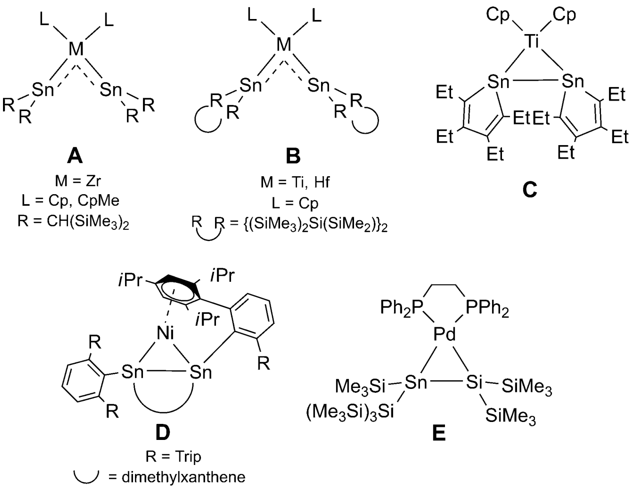
Abstract: *NHC adducts of the stannylene Trip$_2$Sn (Trip = 2,4,6-triisopropylphenyl) were reacted with zero-valent Ni, Pd, and Pt precursor complexes to cleanly yield the respective metal complexes featuring a three-membered ring moiety Sn-Sn-M along with carbene transfer onto the metal and complete substitution of the starting ligands. Thus the easily accessible NHC adducts to stannylenes are shown to be valuable precursors for transition-metal complexes with an unexpected Sn−Sn bond. The complexes have been studied by X-ray diffraction and NMR spectroscopy as well as DFT calculations. The compounds featuring the structural motif of a distannametallacycle comprised of a $[(NHC)_2M^0]$ fragment and Sn$_2$Trip$_4$ represent rare higher congeners of the well-known olefin complexes. DFT calculations indicate the presence of a π-type Sn–Sn interaction in these first examples for acyclic distannenes symmetrically coordinating to a zero-valent transition metal.*

Since Zeise's fundamental discovery of ethylene–platinum complexes, the transition-metal coordination chemistry of olefins and the bonding description within such complexes have been an extremely vivid field of research for almost two centuries.[1] In recent decades, complexes of main-group analogues to olefins have come more and more into focus, and various findings have been made, especially for disilenes.[2] The bonding interaction between two tetrylene units without π-basic substituents that dimerize to form ditetrylenes is more complex than in the parent olefins, and its discussion has influenced the modern understanding of double bonds.[3] Although such stannylenes have long been used as ligands in transition-metal coordination chemistry, only a few bis(stannylene) (Scheme 1, **A**,**B**) complexes have been reported, but there were no examples for side-on coordinating distannenes until very recently (**C**,**D**).[4]



Scheme 1. Some known examples for bis(stannylene) (**A**, **B**) and side-on coordinating distannene complexes (**C**, **D**) as well as one example of a silastannene complex (**E**) for which a cyclic derivative is also known.

A small number of distannenes is known.[3a,b,4h,5] The difficulty of the study of their coordination chemistry as olefin congeners stems from a lack of distannenes that are persistent in solution because stannylenes that are dimeric in the solid state usually tend to dissociate in solution.[3c,f] Marschner's attempts to use a bicyclic distannene led to rearrangement of the backbone and isolation of a bis(stannylene) complex (**B**).[4g] One of the most intriguing properties of complexes such as **A**–**D** is the behavior of two stannylene moieties in the coordination sphere of a metal and the nature of the Sn–Sn interaction, namely the presence of a σ-single bond in distannametallacyclopropanes versus a π-type double bond in side-on coordinating distannenes. In the case of olefins, the situation is described with the Dewar–Chatt–Duncanson model as a continuum in which increasing metallacyclopropane character goes along with increasing π-donation from the metal onto the ligand.[6]

In the case of the coordination chemistry of tin congeners of olefins, the majority of reported studies were conducted on Group 4 ocene complexes including bulky alkyl-, cyclic bis(silyl)-, as well as cyclic olefinic substituted stannylenes with varying coordination behavior. Apart from Saito's recent titanium complex, $[Cp_2M(SnR_2)_2]$ compounds reveal stannylene-like character with a very weak direct Sn−Sn interaction. Recently, side-on complexes of a cyclic silastannene to Group 10 elements have been observed (**E**).[2m] Our group reported the first zero-valent Group 10 complex with a cyclic distannene as a chelating ligand, adding a new unsymmetrical coordination mode, which is maintained in solution, for distannenes (**D**) in which each tin atom reveals an individual electronic interaction to the coordinated metal.[4h] Further bis(stannylene) complexes were reported by Hahn and Růžička.[7] Augmenting the still small number of such structurally characterized complexes, we present the synthesis, structure, and bonding interactions in complexes of the electron-rich $[L_2M^0]$ fragment (M = Ni, Pd, Pt; L = NHC)

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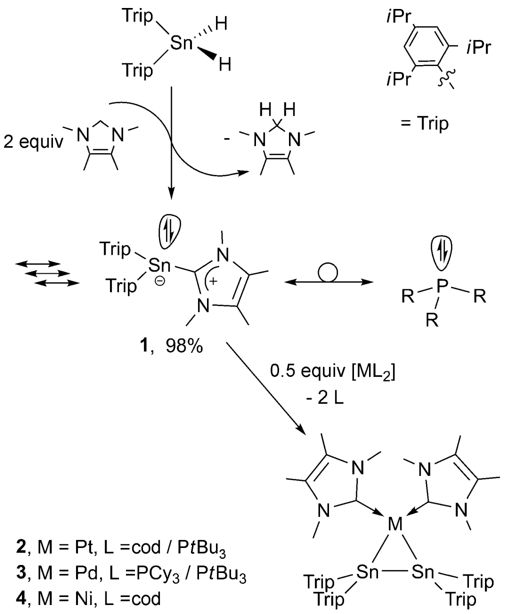
with the sterically encumbered tetraaryl distannene [Sn_2Trip_4] bearing a symmetrical distannametallacyclopropane core.

Recently we reported the facile synthesis of carbene adducts to various stannylenes by the dehydrogenation of tin di- and trihydrides with one equivalent of small N-heterocyclic carbenes (NHC) and subsequent trapping of the intermediately formed stannylene with a second equivalent NHC.[8] This route enables easy and high yielding access to 1,3,4,5-tetramethylimidazol-2-ylidene (^{Me}NHC) adducts of trimeric [$Trip_2Sn$], which has been well-studied in the solid state.[5a,9] The intriguing electronic situation of some mesomeric descriptions of the adduct [$Trip_2Sn^{Me}NHC$] (**1**) as an isoelectronic Group 14 analogue of phosphines (Scheme 2) may allow interesting applications as ligand in coordination chemistry. Therefore two equivalents of the adduct **1** were allowed to react with one equivalent of [Pt(PtBu$_3$)$_2$] in benzene at room temperature and a slow color change from yellow to deep red was observed within four days. ^{31}P NMR spectroscopy revealed quantitative consumption of [Pt(PtBu$_3$)$_2$]. Proton NMR spectroscopy revealed clean formation of one new compound of strongly reduced symmetry compared to the signal pattern of the sole ligand **1**.



Scheme 2. Synthesis of carbene adduct **1** and subsequent reaction with half an equivalent of [ML_2] (M = Ni, L = cod; M = Pd, L = PtBu$_3$, PCy$_3$; M = Pt, L = PtBu$_3$, cod) to form the respective distannametallacyclopropane. cod = 1,5-cyclooctadiene.

The ^{119}Sn resonance of **1** at $\delta = -160.7$ ppm was shifted to higher field by over 500 ppm to a singlet signal at $\delta = -697.8$ ppm. The signal is accompanied by the respective ^{195}Pt satellites with a coupling constant of $J_{\text{Pt-Sn}} \approx 4175$ Hz as well as ^{117}Sn satellites with a coupling constant of $J_{\text{Sn-Sn}} \approx 2125$ Hz. Furthermore, a ^{195}Pt NMR resonance was found at $\delta = -4448.9$ ppm flanked by tin isotope satellites with an integration ratio of twice the natural abundance. This coupling pattern indicated the formation of a moiety encumbering two chemically and magnetically equivalent tin atoms along with a platinum atom.

Removal of volatiles from the resulting mixture of the dark red complex and PtBu$_3$ and dissolving the residue in a minimum amount of n-pentane afforded large deep burgundy crystals after storage of the solution at −40 °C for one week. X-ray analysis of the crystals in the triclinic space group $P\bar{1}$ revealed the structure of the [(^{Me}NHC)$_2$Pt(SnTrip$_2$)$_2$] (**2**) complex to feature a three-membered ring of a bis(NHC)–platinum and two $Trip_2Sn$ fragments with a geometry related to a recent disilene nickel complex (Figure 1).[2n] The asymmetric unit contains two independent molecules of **2** with slight but not significant deviations of bond lengths and geometrical arrangements.

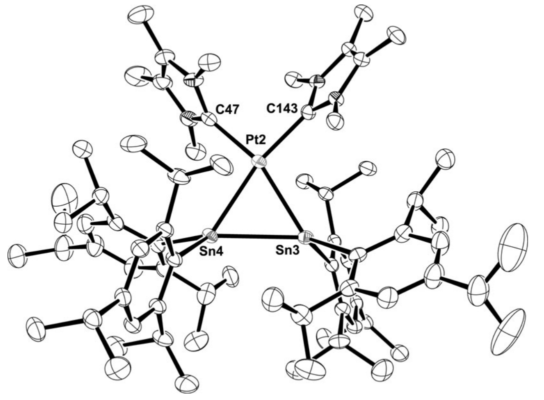


Figure 1. ORTEP plot of one molecule of **2** in the asymmetric unit. Ellipsoids are set at 50% probability; hydrogen atoms and co-crystallized n-pentane are omitted for the sake of clarity. Selected bond lengths [Å] and angles [°] along with the corresponding values for the second molecule [in parentheses]: Sn3–Sn4 2.7704(3) [2.7558(4)], Pt2–Sn3 2.6381(3) [2.6300(3)], Pt2–Sn4 2.6365(3) [2.6436(3)], Pt2–C47 2.031(4) [2.028(4)], Pt2–C143 2.051(3) [2.054(4)]; Sn-Pt-Sn/C-Pt-C: 14.5. The ORTEP plots of molecules **3** and **4** can be found in the Supporting Information.

Analogously to the formation of **2**, we have been able to isolate the corresponding homologous dark red palladium (**3**) and dark yellow nickel (**4**) complexes from the reaction of [Pd(PtBu$_3$)$_2$] or [Pd(PCy$_3$)$_2$] and [Ni(cod)$_2$] with two equivalents of carbene adduct **1** in aromatic solvents at room temperature. Pure **3** and **4** can be obtained similarly to **2**, and their crystal structures reveal comparable geometrical features as found for the platinum homologue (Supporting Information, Figure S1). All of the complexes are extremely sensitive to air and moisture in solution and solid state, as indicated by rapid decolorization on exposure to ambient atmosphere.

The three-membered rings represent essentially isosceles triangles with the Sn−Sn bond shortening negligibly from the platinum complex **2** (2.7703(4) Å) to nickel **4** (2.7471(2) Å). The Sn−Sn bond length is in the range of known stannylene dimers and distannenes (2.575(4)–3.0009(7) Å)[3e,4h,5c,d,10] but is also contained in the range of Sn−Sn single bonds. The present Sn−Sn bond lengths are the shortest distances to date in distannametallacyclopropanes, indicating a strong interac-

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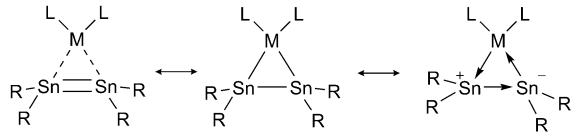
tion.[4h,i] The Sn–M contacts in each triangle deviate slightly with the mean degree of deviation increasing from **2** (0.008 Å) over **3** (0.017 Å) to **4** (0.027 Å).[11] These deviations are arguably small yet consistent. All M–Sn contacts lay within the range of previously reported distances but Pd/Pt-Sn distances are insignificantly shorter than those reported for the silastannene complexes (Pt 2.6613(10) Å, Pd 2.6714(12)/2.6808(6) Å).[2m,12] The ranges of observed carbene–metal bond lengths are unobtrusive compared to metal–carbene distances from recent [$(NHC)_2M(cod)$] (M = Ni, Pt) complexes.[13] The carbene–palladium bonds in **3** are slightly longer than the carbene–platinum bonds in **2**, potentially indicating a stronger share of metal–carbene back-bonding for platinum than for palladium. The coordination geometry at the metal center is essentially planar, with slight twisting of the C-M-C plane out of the ring plane. The orientation of the [R_4Sn_2] fragment toward the transition metal of **2, 3**, and **4** differs from all of the coordinating distannenes reported to date. In general, the bent-back angles found at the tin moieties are relatively small and much smaller than in Saito's complex **C**.[4i] All of the molecules have two different types of arrangements around the tin atoms in terms of the bent-back angle defined as the angle between the centroids of the *ipso*-carbon atoms of the Sn-bound Trip moieties and the Sn–Sn vector and the sum of bond angles around each tin atom within the [Sn_2R_4] fragment. One [R_2Sn] moiety reveals a larger bent-back angle of 31(1)° with a smaller bond-angle sum of 349.4° whilst the respective values at the neighboring tin atom amount to 21(1)° and 354.2°, indicating a more pronounced planarization. Values of around 355° are known for telluradistanniranes as well as azadistanniridines.[14] Consistently, for the crystallographically determined three-membered rings of **2**, **3**, and **4** the more planar Sn atom with the small bent-back angle reveals the longer M–Sn bond.[11] This doubtlessly subtle increase in desymmetrization may be a hint for a change in the bonding interaction from **2** to **4** potentially approaching the coordination mode as observed for the apparent borderline case **D** and an indication for the general relevance of this particular resonance description (Scheme 3).[4h] A more pronounced unsymmetrical free distannene was described earlier.[3e] Nevertheless, compared to **D** complexes **2**–**4** are essentially symmetrical.



Scheme 3. Mesomeric descriptions of the distannametallacycles.

The solution NMR spectra confirm the bonding pattern in the solid state to be maintained in solution, and the structural similarity of **2**, **3**, and **4** found in the solid state was also observed in their ^{1}H NMR spectra. In solution, the slightly different arrangement around each tin is not observed and a C_2 axis of symmetry through M and the Sn–Sn centroid can be considered. For **2**, **3**, and **4**, the accumulation of four Trip-moieties in close proximity causes a loss of free rotation around the Sn–C_{Trip} bond and therefore leading to magnetic inequivalency of all positions of both Trip moieties at the tin atom. Two sets of signals for the carbene methyl groups give rise to a hindered rotation around the Pt–C bond as well. ^{119}Sn NMR spectroscopy on **3** ($\delta = -464.9$ ppm) and **4** ($\delta = -579.6$ ppm) also reflected the shift to higher field, though less pronounced as for the platinum complex. The parent distannene [Sn_2Trip_4] is only known in solution and its tin resonance is found at $\delta = 427.3$ ppm with a coupling constant of $J_{Sn-Sn} = 2930$ Hz.[5a]

Although the geometrical features of the Sn–Sn interaction is essentially identical for **2**, **3**, and **4**, the J_{Sn-Sn} coupling constants differ (Table 1). Whilst Pt complex **2** and **3** reveal comparable constants for nickel complex **4**, an unexpectedly large coupling constant of $J_{Sn-Sn} = 8050$ Hz was found. Such large constants are known for rather different species such as $(R_3Sn)_2Sn$ or strained cyclic distannenes.[5e,15]

Table 1: Overview on NMR spectroscopic characteristics of **2**, **3**, and **4**.

	$\delta(^{119}Sn)$[a]	J_{Sn-Sn}[b]	$\delta(^{13}C)$ C–M[a]
2	−697.8	2125	183.4
3	−464.9	2660	192.5
4	−579.6	8050	193.2

[a] Given in ppm. [b] Given in Hz.

Table 1 summarizes NMR spectroscopic characteristics of **2**, **3**, and **4**. The high-field shift of the ^{119}Sn resonances is in accordance with four-coordinate tin in strained three-membered rings.[2m,5a,14b,16] Disilenes complexes of pronounced π-character reveal low-field-shifted ^{29}Si NMR resonances, whilst those with less pronounced π-character can be found at higher field.[2d,f] Therefore mixed silastannene complex **E** (with high-field ^{29}Si and ^{119}Sn signals) was characterized as a silastannametallacyclopropane complex owing to its high-field ^{29}Si resonance.[2m] Consequently, the ^{119}Sn NMR shift of **2**–**4** accounts for a distannametallacyclopropane character of the complexes. To further evaluate the observed chemical shifts, it is noteworthy that (Ph_3Sn) residues in Pd^{II} or Pt^{II} complexes usually resonate at much lower field (around $\delta = -50$ ppm).[17] In the case of **2** especially, the observation of the platinum–tin coupling constant $J_{Pt-Sn} = 4175$ Hz is of interest because the coupling in respective Ph_3Sn–Pt^{II} complexes is revealed to be between 9500–12500 Hz.[17a–c] The pronounced differences of the ^{119}Sn chemical shifts as well as the metal–tin coupling constants compared to the respective characteristics of M–$SnPh_3$ systems may indicate that the bonding situation within the three-membered ring is not adequately described by a conservative M^{II}–1,2-distannanediide.

To shed further light on the description of the electronic structure of the complexes, DFT calculations were performed on the complexes **2** and **3**. The HOMO and HOMO−1 are shown in Figure 2. The HOMO−1 reflects a π-type bonding interaction from the [L_2M] fragment toward the [Sn_2R_4] fragment, representing the classic π-donation into the olefinic anti-bonding π-orbital, whilst the HOMO indicates a π-type bond between the Sn atoms.

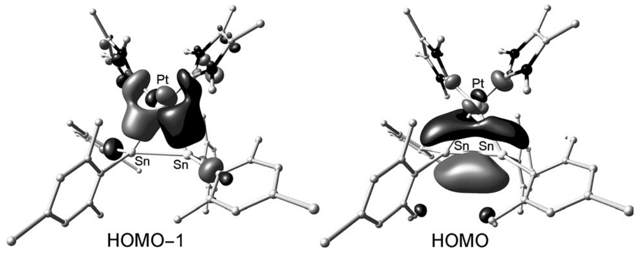


Figure 2. CMOs of **2** (isosurface values at 0.045 value) obtained from calculations at BP86/TZVPP level of theory. The Trip moieties have been replaced by mesityl moieties in this depiction for the sake of clarity.

According to NMR experimental reaction control, complete conversion is achieved for the platinum complex **2**. In case of Ni and Pd clean product formation is observed but the reaction results in a mixture with approximately 90 % of **3** and **4** along with free adduct **1**. This mixture was also observed after dissolution of pure crystals of **3** and **4** within a few minutes. The reaction rates were highly depending on the precursor complexes [ML_2]. Whilst [Pt(cod)$_2$] lead to instant formation of **2**, the reaction proceeded over four days for the respective Pt(P*t*Bu$_3$)$_2$ complex. Compound **3** was formed instantaneously with [Pd(P*t*Bu$_3$)$_2$] as well as [Pd(PCy$_3$)$_2$], whilst **4** was slowly formed from reaction with [Ni(cod)$_2$] after twelve hours.

The mechanism of the reaction remains unclear and may involve stepwise pre-coordination and subsequent carbene transfer from a formally potent Lewis acid [R_2Sn] under formation of a Sn−Sn bond with two equivalents of **1** to form **2**, **3**, and **4**. Our preliminary findings on the reaction behavior of **1** revealed a very strong bonding interaction of the carbene donor toward the stannylene. Thus although it cannot be generally ruled out we do not expect the respective free dissociated species [Trip$_2$Sn] or ^{Me}NHC to be involved in the formation. Carbene transfer from main-group element adducts onto transition metals has recently been established as synthetic method.[2n,18] For the formation of a similar disilene complex with [Ni(cod)$_2$] via a corresponding route, DFT calculations on postulated intermediates have been reported.[2n] Nevertheless following the course of the reaction by means of ^{31}P NMR spectroscopy, only the starting complex or free phosphine were observed, but at no time other species such as [(**1**M(PR$_3$)$_2$] or [(**1**)$_2$M(PR$_3$)].

On storing the solutions of **2**, **3**, or **4** at room temperature over a period of two weeks, no decomposition in the case of **2** was observed. The intensities of the resonances for **3** and **4** slowly decreased, partially accompanied by reformation of **1**. This decomposition can be rationalized by metal extrusion from the complexes; however, mirrors or precipitates of metal have not been observed. In the case of Pd, the ^{1}H NMR spectrum revealed formation of a second set of signals in about 10 % yield, which are assigned to a yet unknown side-product.

In conclusion, the complexes **2**, **3**, and **4** described herein are the first examples for a coordinating ditin homologue of the well-known olefin complexes. A bonding analysis according to the Dewar–Chatt–Duncanson model allows a description as a π-complex with strong back-bonding from the metal onto the [Trip$_4$Sn$_2$] moiety. The perception of the structure as being in between the boundary forms of a pure π-complex and a pure distannametallacyclopropane is in accordance with the geometrical features as well as the NMR spectroscopic characteristics. DFT calculations indicate the presence of a π-type Sn–Sn interaction. Nevertheless, the lack of experimental data for the Sn–Sn interaction of the free distannene [Trip$_4$Sn$_2$] in solid-state and its electronic orbital interactions prevents from thorough comparisons with its coordinated form presented herein. The straightforward preparation of **2**, **3**, and **4** from carbene adducts to stannylenes makes them accessible compounds for subsequent studies and highlights the synthetic value of the NHC-adducts to main-group compounds.

Keywords: coordination chemistry · distannenes · nickel · palladium · platinum

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