Metallostannylenes **Hot Paper**

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The Ruthenostannylene Complex [Cp*(IXy)H$_2$Ru-Sn-Trip]: Providing Access to Unusual Ru-Sn Bonded Stanna-imine, Stannene, and Ketenylstannyl Complexes**

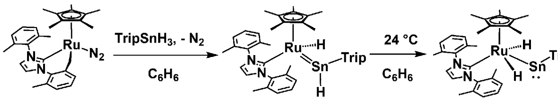
*Hsueh-Ju Liu, Micah S. Ziegler, and T. Don Tilley**

In memory of Gregory L. Hillhouse

Abstract: *Reactivity studies of the thermally stable ruthenostannylene complex [Cp*(IXy)(H)$_2$Ru−Sn−Trip] (**1**; IXy = 1,3-bis(2,6-dimethylphenyl)imidazol-2-ylidene; Cp* = η^5-C$_5$Me$_5$; Trip = 2,4,6-iPr$_3$C$_6$H$_2$) with a variety of organic substrates are described. Complex **1** reacts with benzoin and an α,β-unsaturated ketone to undergo [1+4] cycloaddition reactions and afford [Cp*(IXy)(H)$_2$RuSn(κ^2-O,O-OCPhCPhO)Trip] (**2**) and [Cp*(IXy)(H)$_2$RuSn(κ^2-O,C-OCPhCHCHPh)Trip] (**3**), respectively. The reaction of **1** with ethyl diazoacetate resulted in a tin-substituted ketene complex [Cp*(IXy)(H)$_2$RuSn(OC$_2$H$_5$)(CHCO)Trip] (**4**), which is most likely a decomposition product from the putative ruthenium-substituted stannene complex. The isolation of a ruthenium-substituted stannene [Cp*(IXy)(H)$_2$RuSn(=Flu)-Trip] (**5**) and stanna-imine [Cp*(IXy)(H)$_2$RuSn(κ^2-N,O-NSO$_2$C$_6$H$_4$Me)Trip] (**6**) complexes was achieved by treatment of **1** with 9-diazofluorene and tosyl azide, respectively.*

Since the first molecular stannylene compound, Sn[N(SiMe$_3$)$_2$]$_2$, was discovered in 1974,[1,2] numerous analogues featuring two-coordinate tin species (R−Sn−R′) have been isolated.[3] These stable compounds typically exhibit a bent geometry with a stereochemically active lone pair that occupies an orbital with significant 5s character, and the additional presence of an empty 5p orbital at tin results in both donor and acceptor properties for a stannylene. Thus, these divalent tin species exhibit versatile reactivity and serve as synthetic building blocks for the construction of organotin compounds. For example, tin–heteroatom multiply-bonded compounds such as stanna-imines possessing Sn=N bonds can be prepared by reactions of stannylenes with azides.[4]

Metallostannylenes are metal complexes possessing divalent tin and an M−Sn−R linkage, and they have been known for the past 14 years.[5a] Salt metathesis is the most commonly employed synthetic route to metallostannylenes,[5] which takes advantage of available nucleophilic metal fragments and electrophilic RSnX compounds that are kinetically stabilized by bulky R substituents. Recently, this laboratory has described the generation of metallostannylenes by reactions of primary hydrostannanes (RSnH$_3$) with metal–carbon bonded complexes.[6] Thus, reaction of cyclometalated [Cp*(IXy-H)Ru(N$_2$)] with TripSnH$_3$ at 24 °C leads to clean formation of the first ruthenostannylene, [Cp*(IXy)(H)$_2$Ru−Sn−Trip] (**1**, IXy = 1,3-bis(2,6-dimethylphenyl)imidazol-2-ylidene; "IXy-H" is the deprotonated form of IXy; Cp* = η^5-C$_5$Me$_5$; Trip = 2,4,6-iPr$_3$C$_6$H$_2$) via 1,2-hydrogen migration in an electronically saturated, observable intermediate stannylene complex [Cp*(IXy)(H)Ru=SnHTrip] [Eq. (1)].[6b] The two hydride ligands of **1** appear to stabilize the divalent tin center, by donation of electron density into the formally empty 5p orbital on tin. Theoretical investigations indicate that this unusual α-H migration involves a reversal of the role of the coordinated stannylene ligand, from that of an electron donor to an acceptor in the transition state, thereby lifting the usual requirement for generation of an unsaturated metal center in migration chemistry.[6b]



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Although several examples of the successful isolation of metallostannylenes have been reported, the reaction chemistry of metallostannylenes remains rather unexplored compared to that of organostannylenes, and to date the only reaction reported for a metallostannylene is the trapping of the osmium metallostannylene [Cp*(iPr$_3$P)(H)$_2$Os−Sn−Trip] with trimethylaluminum to afford the corresponding Lewis acid-base adduct.[6a] Herein we report investigations on the reactivity of this novel type of metal complex, which demonstrates transformations at the low-valent tin center of **1** that produce unusual Ru−Sn bonded stanna-imine, stannene, and ketenylstannyl ligands.

It might be expected that as with other divalent Group 14 species, metallostannylenes should react with conjugated molecules, such as dienes, enones, or diketones, to form [1+4] cycloaddition products.[7] However, unlike some stannylenes,[7a,c–f] **1** is stable in the presence of excess 2,3-dimethyl-

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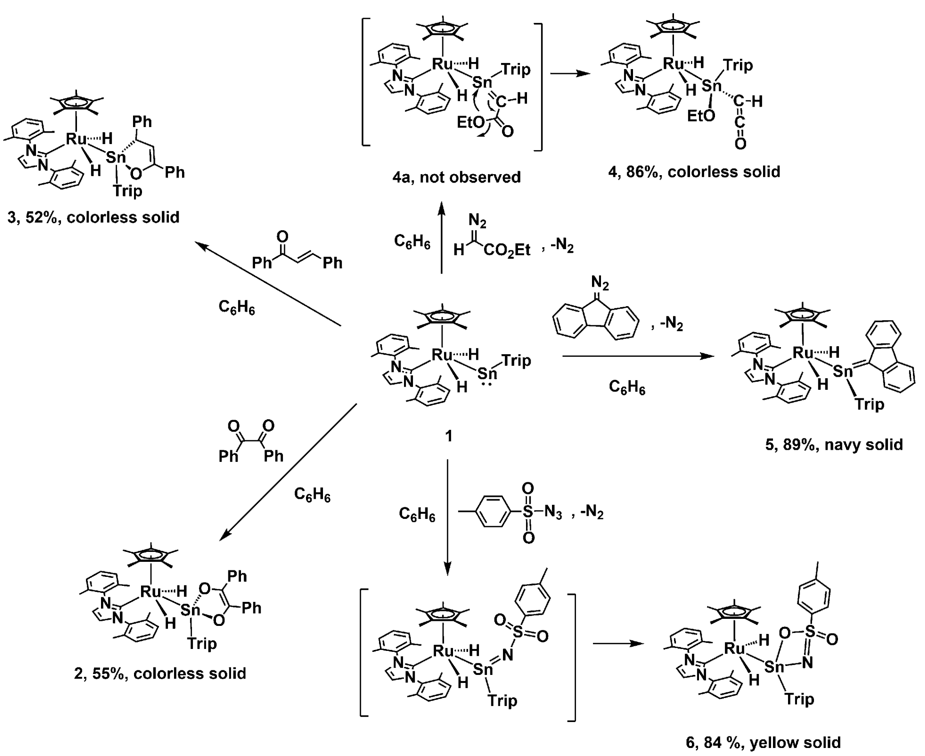


Scheme 1. Reactivity of complex **1** with organic substrates.

1,3-butadiene at 60 °C for 24 h, and no cycloaddition products were detected. Nonetheless, treatment of **1** with one equiv of benzil (dibenzoyl) in benzene at 24 °C led to an immediate color change from purple to pale yellow and formation of complex **2**, which was isolated as an off-white powder in 55 % yield (Scheme 1).

The crystal structure of **2** (Figure 1 a) reveals the presence of a five-membered stannacyclic ring connected to the $\{Cp^*(IXy)(H)_2Ru\}$ fragment, with a Ru–Sn bond length of 2.5478(4) Å. The C–C bond length of 1.364(5) Å in the ring is consistent with double bond character. The ^{1}H NMR spectrum of **2** in $[D_6]$benzene indicates that it has C_s symmetry in solution with chemically equivalent hydride ligands (δ −8.64; $J_{SnH} = 71.0$ Hz).

The hydride ligands were located in the Fourier map, and the relatively long H···Sn distances (2.37(4) and 2.52(4) Å) are consistent with the low J_{SnH} coupling in reflecting a minimal degree of interaction between the hydride and stannyl ligands, as expected for a saturated tin center. For comparison, the osmium stannylene complex $[Cp^*(i\text{Pr}_3\text{P})(H)Os{=}SnHTrip]$, which possesses a direct, unsupported Sn–H bond, exhibits a high $^1J_{SnH}$ value of 775.0 Hz.[6a] In complex **1**, a relatively large J_{SnH} coupling constant of 257.4 Hz indicates the presence of a significant interaction between hydrides and the Sn–Trip moiety, and although the hydride ligands of **1** were not located in the Fourier map, close Ru–H···Sn contacts (2.210 and 2.177 Å) in the DFT-optimized structure of **1** are consistent with the high J_{SnH} value.[6b] The stronger H···Sn interactions in **1** lead to a slight elongation of the Ru–H bonds (1.634 and 1.648 Å) relative to those found in **2** (1.52(4) and 1.47(4) Å).

Analogously, treatment of **1** with an equimolar amount of chalcone (*E*-benzylideneacetophenone) yielded **3** (52 %) (Scheme 1). The solid-state coordination geometry of **3** is similar to that of **2** (Figure 1 b), and the bond lengths and angles of the stannacycles in **2** and **3** are comparable to those of the benzil and ethyl vinyl ketone cycloadducts of a free stannylene, as reported by Eaborn, Smith, and co-workers.[7g] The diastereotopic hydride ligands in **3**, both located in the Fourier map with H···Sn distances of 2.37(4) and 2.46(4), resonate at −8.39 ($J_{SnH} = 91.1$ Hz) and −8.84 ppm ($J_{SnH} = 149.6$ Hz) in the ^{1}H NMR spectrum, reflecting chirality at the tin center.

Despite the reluctance of heavier main group elements to engage in multiple bonding due to poor pπ–pπ overlap,[8] numerous compounds containing double bonds between tin and a first-row main group element, such as stannenes ($R_2Sn{=}CR'_2$)[9] and stanna-imines ($R_2Sn{=}NR'$),[4] have been reported. Stannenes have been obtained by reaction of carbene compounds generated in situ

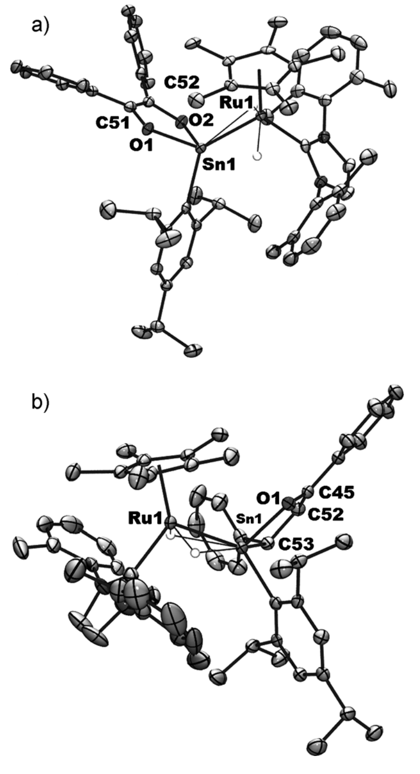


Figure 1. Molecular structures of a) **2** and b) **3**. Ellipsoids are set at 50 % probability; H atoms have been omitted for clarity, except those at Ru1 and Sn1.

with stable stannylenes,[9a,b] or via salt elimination of LiF from R_2SnF–(Flu)Li (Flu = fluorenyl derivatives).[9c–f] In principle, a straightforward and versatile route to stannenes would involve reaction of a stannylene with a diazo compound as a carbene-transfer reagent, but heretofore this reactivity is unreported to the best of our knowledge. In fact, the reaction of **1** with one equiv of ethyl diazoacetate at 24 °C in [D$_6$]benzene resulted in an immediate color change from purple to colorless. The ^{1}H NMR spectrum of the resulting mixture indicated clean formation of a new complex (**4**), which possesses diastereotopic hydrides that appear at $\delta = -8.88$ ($J_{SnH} = 31.8$ Hz) and -9.17 ppm ($J_{SnH} = 61.7$ Hz). Cooling a saturated pentane solution of **4** at −30 °C afforded X-ray-quality colorless crystals in 86 % yield. X-ray crystallography surprisingly reveals that **4** possesses ethoxy and ketenyl (HC=C=O) groups bonded to tin, with bond lengths of 2.009(3) Å (Sn–O), 2.187(5) Å (Sn–C), 1.278(6) Å (C=C), and 1.190(6) Å (C=O), as shown in Figure 2. IR spectroscopy confirms the presence of the ketenyl group in **4** with a ν_{CO} stretch at 2074 cm^{-1}, which is comparable to those of known ketene compounds.[10a] Furthermore, the ^{13}C NMR resonances of the ketenyl group, namely 179.7 (CH=*C*=O) and 60.9 ppm (*C*H=C=O), are similar to those of $Me_3SiC(H)$=C=O.[10] Trimethylstannylketene, $Me_3SnC(H)$=C=O, has been proposed as an intermediate in the thermal decomposition of ethoxyethynyl(trimethyl)tin (Me_3SnC≡COEt) to bis(trimethylstannyl)ketene, $(Me_3Sn)_2C$=C=O, but its thermal instability precludes its isolation.[10b,c] The ^{13}C resonances of the ketenyl group in $(Me_3Sn)_2C$=C=O of 161.7 (C=*C*=O) and −15.4 ppm (*C*=C=O) are much more upfield compared to those of **4**, which is presumably due to the presence of two electron-rich stannyl groups. The formation of **4** likely results from rearrangement of an initially formed, putative stannene intermediate **4a** (Scheme 1). The decomposition of **4a** to **4** is undoubtedly driven by instability of the Sn=C double bond in **4a**, and by formation of strong Sn–C and Sn–O bonds in **4**.

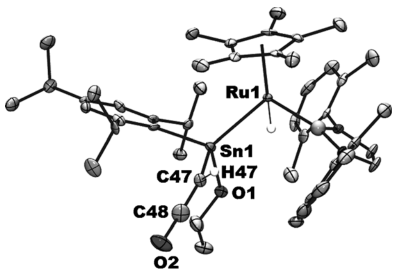


Figure 2. Molecular structure of **4**. Ellipsoids are set at 50% probability; H atoms have been omitted for clarity, except for the ketene-bound H and Ru-bound hydrides, which were located using the Fourier difference map.

To explore the viability of a ruthenium-substituted stannene derivative such as **4a**, an independent route to this type of species was explored. Stannylene **1** was observed to react with the 9-diazofluorene N_2(Flu) (Flu, fluorenyl, $C_{13}H_8$) to give the new complex [Cp*(IXy)(H)$_2$RuSn(=Flu)Trip] (**5**, Scheme 1). This product was obtained as a navy blue solid in 89 % yield, and was structurally characterized by X-ray crystallography (Figure 3) to reveal two independent molecules in an asymmetric unit with average bond distances of 2.5494(9) Å (Ru–Sn) and 2.073(10) Å (Sn–C_{Flu}). The Sn–C_{Flu} bond length of **5** is slightly elongated with respect to those reported for other Sn=C bonds in stannenes (2.016–2.036 Å).[9] Furthermore, a relatively weak Sn–C interaction is consistent with an observed twisting about this bond, defined by a dihedral angle of 21.1(1)° between the fluorenylidene least-squares plane and the RuSnC_{Trip} plane. Nonetheless, both the Sn and C centers in this bond appear to be sp^2-hybridized, as indicated by the sum of bond angles about each atom, of 360.0(9)° and 360.0(5)°, respectively. A single resonance corresponding to two hydride ligands at −7.56 ppm, with a J_{SnH} coupling constant value of 91.4 Hz, implies a relatively weak interaction between the hydrides and the tin center. Furthermore, the eight protons of the fluorenyl group remain inequivalent at 100 °C in [D$_8$]toluene, suggesting a high barrier for rotation about the Sn=C bond. These two observations by ^{1}H NMR spectroscopy reflect double bond character between tin and carbon. It is noteworthy that steric protection of the Sn=C bonds of R_2Sn=Flu derivatives is essential to prevent head-to-tail dimerization[9b] normally found due to the highly polarized Sn–C bond. In this case, the transition-metal fragment appears to provide both electronic and steric stabilization for the stannenyl group. Complex **5** is highly air and moisture sensitive, and upon exposure to air it rapidly decomposes to a colorless solid.

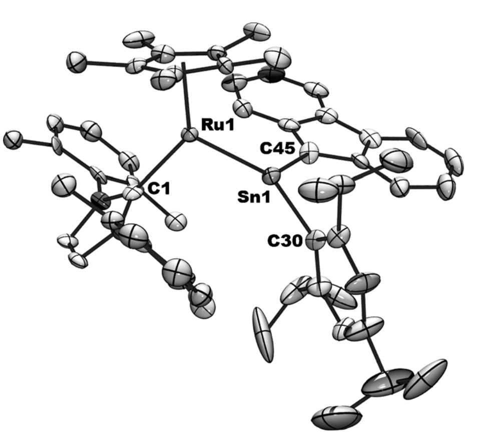
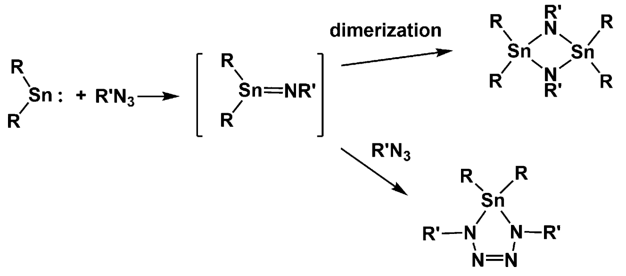


Figure 3. Molecular structure of **5**. Ellipsoids are set at 50% probability; H atoms have been omitted for clarity.

After successful isolation of the stannene complex **5**, it was of interest to investigate the possible formation of other unsaturated Sn species in this system. In this context, several research groups have reported the generation of a stanna-imine by reaction of a stable stannylene with an azide compound, accompanied by dinitrogen elimination. Previous reports indicate that stanna-imines are highly reactive and undergo dimerization,[11a,b] or incorporate a second equivalent of the azide to form a tetraazastannoline SnN_4 ring via [3+2] cycloaddition[11b,c] (Scheme 2). To date, three stanna-imines have been isolated and characterized.[4] Given the large electronegativity difference between tin and nitrogen, the Sn=N bond is significantly polarized toward nitrogen and the



Scheme 2. Decomposition pathways for stanna-imines.

corresponding Sn$^+$–N$^-$ resonance structure is expected to be a major contributor. For a formal Sn=N bond derived from complex **1**, the Sn$^+$–N$^-$ character might be reinforced by an electron-withdrawing group at nitrogen, the electron-rich ruthenium fragment, and the expected donation of hydride ligands to the tin center (see below).

Treatment of **1** with one equiv of TsN$_3$ (Ts = *p*-tolylsulfonyl) in benzene at 24 °C resulted in immediate decoloration of **1** and clean formation of [Cp*(IXy)(H)$_2$RuSn(κ^2-N,O-NSO$_2$C$_6$H$_4$Me)Trip] (**6**) as pale yellow crystals in 84 % yield (Scheme 1). The X-ray crystal structure of complex **6** reveals a κ^2 binding mode for the NSO$_2$C$_6$H$_4$Me group to Sn; thus, little Sn=N double bond character is present. This structure undoubtedly results from favorable tin–oxygen interactions (the Sn–O bond distance is 2.211(2) Å; see Figure 4). The Sn–N bond length of **6**, 2.120(3) Å, is markedly longer than those of typical stanna-imine compounds (ca. 2.01 Å).[4] For comparison, reactions of benzoyl azides with a diamidostannylene did not yield a stanna-imine, or compounds structurally similar to **6**, but instead gave the dimerization products of putative stanna-imines.[11a] Scheme 3 provides selected representations of the bonding for **6** (structures **A**, **B**, and **C**). For structure **C**, the negative charge on nitrogen is stabilized by the Ts group, and the formally cationic, three-coordinate tin center formally possesses an empty 5p orbital available for oxygen coordination. This donation from oxygen to tin is reminiscent of the previously proposed stannene intermediate (**4a**), which decomposes to **4** via a C–O bond cleavage that might be induced by coordination of the ethoxy group to the electron-deficient tin center (Scheme 1).

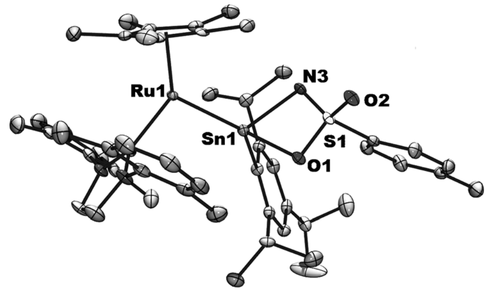
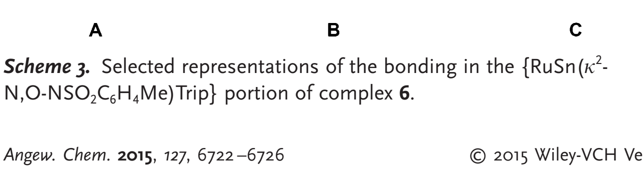


Figure 4. Molecular structure of **6**. Ellipsoids are set at 50% probability; H atoms have been omitted for clarity.



Scheme 3. Selected representations of the bonding in the {RuSn(κ^2-N,O-NSO$_2$C$_6$H$_4$Me)Trip} portion of complex **6**.

In conclusion, [Cp*(IXy)(H)$_2$RuSnTrip] (**1**) is an accessible metallo-tin(II) species that is amenable to reactivity studies. Notably, the transition-metal fragment {Cp*(IXy)(H)$_2$Ru} provides steric and electronic stabilization to the Sn centers of a variety of unsaturated and low-valent Sn-based ligands. This rich and novel chemistry in a ruthenium–tin system, in combination with the simple route utilized to access the metallostannylene from a primary stannane, suggests numerous possibilities for the synthesis of new tin-based compounds.

Experimental Section

Synthetic procedures and crystallographic data for all of the compounds are included in the Supporting Information. CCDC 1052274 (**2**), CCDC 1052275 (**3**), CCDC 1052276 (**4**), CCDC 1052277 (**5**), and CCDC 1052278 (**6**) 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.

Keywords: metallostannylenes · ruthenium · stanna-imines · stannenes · stannylenes

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