Metalations

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Distannylations and Silastannylations of In Situ Generated Allenes**

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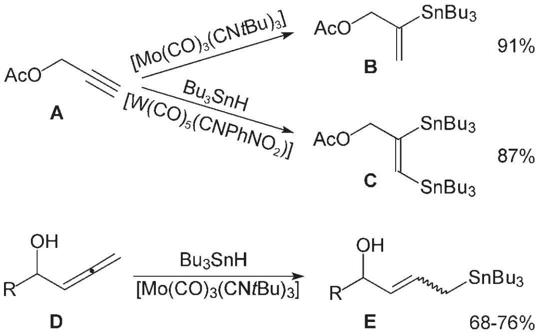
Dedicated to Professor Theophil Eicher on the occasion of his 75th birthday

Owing to their high versatility, organometallic compounds have become extremely valuable building blocks and have found a wide range of applications in organic synthesis, especially in modern cross-coupling chemistry.[1] This development has been possible through the tremendous progress over the past 40 years in the synthesis and applicability of organometallic substrates. Besides the typically used monometalated compounds, also dimetalated derivatives are of enormous interest, especially if different organometallic centers can made to undergo reactions selectively.

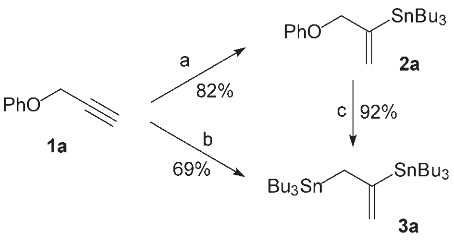
In this context, Mitchell et al. reported on palladium-catalyzed distannylations and silastannylations of alkynes and allenes.[2] The catalytic dimetalation of allenes has the advantage that products are formed that have a vinylic and an allylic metal group as well.[3] Both functionalities can be coupled independently and selectively, which makes the products of the catalytic dimetalation of allenes highly valuable building blocks for organic synthesis.[4–6] Besides diborations,[6] the addition of stannagermanes[7] and silaboranes[5,8] to alkenes and alkynes[9] have been reported as well. Disilylations of allenes are also possible, but in general this reaction requires higher reaction temperatures.[10] In the last few years, Cheng et al. have reported on palladium-catalyzed carbostannylations,[11] carbosilylations,[12] and acyl metalations.[13]

Our group has also been involved for several years in hydro- and distannylations of alkynes[14,15] and allenes,[16] especially in the presence of molybdenum and tungsten catalysts. Depending on the catalyst used, propargyl acetate **A** can selectively be converted either into the vinyl stannane **B**[14b] or the dimetalated allyl acetate **C** (Scheme 1).[15] The molybdenum-catalyzed hydrostannylation of allenyl alcohols **D** provided allyl stannanes **E** in good yields.[16]



Scheme 1. Stannylations of allenes and alkynes.

Herein we present a new protocol towards dimetalated alkenes starting from alkynes or vinyl stannanes. This reaction came into our focus during our investigations of the influence of different catalysts on the regioselectivity of hydrostannylations. While Bu_3SnH addition towards the alkyne **1a** gave rise to the expected vinyl stannane **2a**[17] in the presence of the molybdenum catalyst $[Mo(CO)_3(CNtBu)_3]$ ($MoBI_3$), the palladium-catalyzed reaction surprisingly provided the distannylated product **3a** (Scheme 2). At the beginning it was unclear how this product could be formed, but we speculated that also the palladium-catalyzed reaction provided **2a** as an intermediate, which might undergo elimination to an allene under the reaction conditions. Therefore, we investigated the reaction by NMR, which confirmed that tributylstannylphenolate[18] was formed during the reaction, which is a clear indication for such an elimination process.[19] Because it is well known that Pd complexes can convert Bu_3SnH into $(Bu_3Sn)_2$ by elimination of H_2, a subsequent distannylation of the in situ formed allene might explain the outcome of the reaction. To prove this possibility, we treated the vinyl stannane **2a** with $(Bu_3Sn)_2$ under the same reaction conditions. Indeed, the distannane **3a** was formed in high yield after a shorter reaction time. In contrast, the attempt to obtain **3a** directly from **1a** using $(Bu_3Sn)_2$ was unsuccessful. This is also a good indication that a hydrostannylation is the first step.



Scheme 2. Distannylation of **1a**. a) 3 mol% $MoBI_3$, 2 equiv Bu_3SnH, 5 bar CO, THF, 60 °C, 22 h; b) 2 mol% $[Pd(PPh_3)_4]$, 3.2 equiv Bu_3SnH, THF, 60 °C, 22 h; c) 2 mol% $[Pd(PPh_3)_4]$, 1.05 equiv $(Bu_3Sn)_2$, THF, 60 °C, 6 h.

To figure out if this reaction is a specialty of phenyl ethers, or if it can be applied also to other propargylic substrates, we focused on the stannylated allylic acetate **B**, which should give

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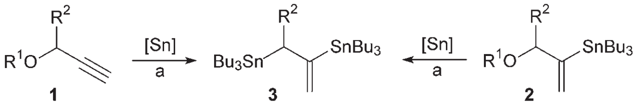
rise to the same product **3a** (Table 1).[20] Indeed, the expected product could be obtained, although the yield was a littler lower in this case (Table 1, entry 1). On the basis of our assumption that the $(Bu_3Sn)_2$ required for the distannylation is formed in situ from Bu_3SnH, we carried out the same reaction also with the tin hydride directly (Table 1, entry 2). The yield obtained under these conditions was even higher than with the distannane. The lower yield obtained with $(Bu_3Sn)_2$ might be caused by the moderate stability of this compound, and therefore, the in situ generation from Bu_3SnH is a significant advantage. Substituents adjacent to the leaving group do not seem to have a negative influence, because with the phenyl-substituted derivative **2b** the same yields were obtained (Table 1, entries 3 and 4). With the phenylated alkyne **1b** we could show that also propargyl acetates can be converted into the distannanes directly with Bu_3SnH (Table 1, entry 5).

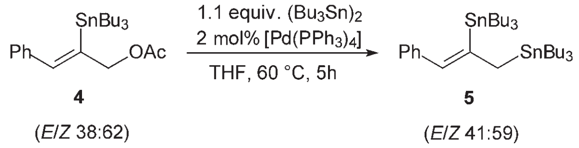
Table 1: Synthesis of distannylated alkenes **3**.



Entry	Substrate	R^1	R^2	[Sn]	Product	Yield[b] [%]
1	**B**	Ac	H	1.05 equiv $(Bu_3Sn)_2$	**3a**	62
2	**B**	Ac	H	2.1 equiv Bu_3SnH	**3a**	74
3	**2b**	Ac	Ph	1.05 equiv $(Bu_3Sn)_2$	**3b**	65
4	**2b**	Ac	Ph	2.1 equiv Bu_3SnH	**3b**	74
5	**1b**	Ac	Ph	3.2 equiv Bu_3SnH	**3b**	41

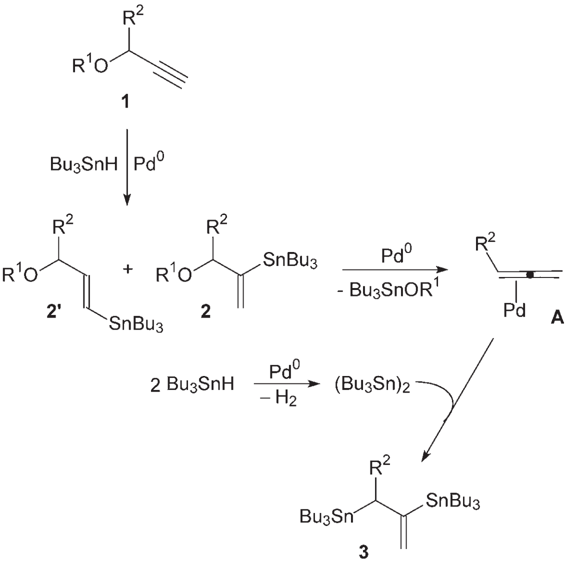
[a] 2% $[Pd(PPh_3)_4]$, THF, 60°C, 2.5–6 h. [b] Compound **3** was obtained together with $(Bu_3Sn)_2$ after flash chromatography. The yields were calculated on the basis of ^{1}H und ^{119}Sn NMR spectroscopy.

The reaction is not restricted to terminal vinyl stannanes, but can also be applied to substituted derivatives, as illustrated with vinyl stannane **4** (Scheme 3). Compound **4** was used as an *E*/*Z* mixture, and the *E*/*Z* ratio did not change during the reaction. Interestingly, the formation of the regioisomeric product **3b** was not observed.



Scheme 3. Regioselective stannylations.

On the basis of these results, we can postulate the mechanism illustrated for alkyne **1** in Scheme 4. The palladium-catalyzed hydrostannylation of propargylic ether **1** gives rise to a mixture of the two regioisomers **2** and **2′**.[21] Only **2** is able to undergo elimination of tributylstannylphenolate, probably promoted by the Pd catalyst.[22] We assume that the elimination proceeds via a π-allyl-Pd intermediate, at least in the case of the corresponding acetates, because with good nucleophiles these compounds undergo allylic alkylations.[23] After elimination, the palladium center probably stays coordinated to the allene (**A**). Otherwise, it would be difficult to explain the good yields obtained, because uncoordinated allene would immediately evaporate from the reaction mixture. Such a palladium complex also explains why the dimetalation occurs exclusively at the double bond which is formed by elimination, and not at the other double bond.[5b] Therefore, the regioisomeric substrates **2b** and **4** provide selectively the isomeric products **3b** and **5**, and the *E*/*Z* ratio remains unchanged during the conversion.



Scheme 4. Postulated mechanism for the Pd-catalyzed distannylation of alkynes **1**.

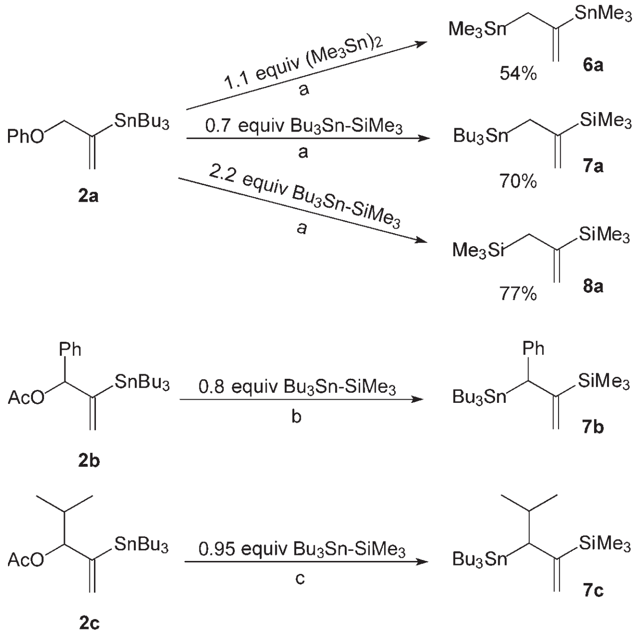
The $(Bu_3Sn)_2$ required for the distannylation is independently formed, also by Pd catalysis, from Bu_3SnH. Oxidative addition of the distannane towards the allene-coordinated Pd center and subsequent insertion/reductive elimination gives rise to the distannylated alkene **3**.

Therefore, in this reaction the Pd catalyst has four functions:

1) hydrostannylation of the alkyne **1**;
2) elimination of tributylstannylphenolate;
3) formation of the distannane from Bu_3SnH;
4) distannylation of the in situ formed allene.

With the assumption that the palladium–allene complex **A** is the key reaction intermediate, stannylated allyl alcohol derivatives **2** should also react with other dimetallic compounds. This option was investigated by using the phenyl ether **2a** (Scheme 5).

Analogously to the synthesis of **2a** (Table 1), 2,3-bis(trimethylstannyl)propene (**6a**) could also be synthesized with $(Me_3Sn)_2$.[24] The application of $Bu_3SnSiMe_3$ led to formation of the silylated products **7a** and **8a**,[25] whereby the formation of **8a** was quite surprising. Interestingly, the outcome depends on the amount of silastannane used. If stoichiometric or substoichiometric amount of this reagent is used, only the expected product **7a** is formed. With two equivalents or more, only the disilylated product **8a** is obtained. With one to two equivalents silastannane and after shorter reaction times, a



Scheme 5. Reactions of vinyl stannanes **2** with dimetallic compounds: a) 2 mol% [Pd(PPh$_3$)$_4$], THF, 60°C, 18 h; b) 2 mol% [Pd(PPh$_3$)$_4$], THF, 60°C, 2 h; c) 2 mol% [Pd(PPh$_3$)$_4$], THF, 60°C, 11 h.

mixture of both products is observed. These observations, in combination with detailed ^{1}H and ^{119}Sn NMR studies, indicate that in both cases the silastannane **7a** is formed first. After longer reaction times and in the presence of an excess of the silyl reagent, **7a** is converted into **8a**. A similar behavior was also observed in reactions of allenyl stannanes, which run via allyl stannane intermediates.[26] This direct pathway to the disilylated compound **8a** offers an interesting alternative to the disilylation of allenes.[27]

This protocol can also be used for substituted substrates, whereby the nature of the substituent apparently does not have a significant influence on the reaction (Scheme 5). Similarly good yields were obtained with both the phenyl-substituted **2b** and isopropyl-substituted **2c**.

In conclusion, we could show that propargylic ethers and esters could be converted directly into distannylated alkenes. Only Bu$_3$SnH is necessary in this Pd-catalyzed reaction. The reaction probably proceeds via a stannylated allyl alcohol derivative, which undergoes elimination and subsequent dimetalation. The two processes can be decoupled, for example, by using a molybdenum catalyst in the hydrostannylation step. This procedure allows the selective reaction of the stannylated intermediates with other dimetallic compounds. Further mechanistic studies as well as synthetic applications are currently under investigation.

Experimental Section

Synthesis of **3a** from **1a**: Phenyl propargyl ether **1a** (132 mg, 1.00 mmol) was dissolved in THF (2 mL) in a pyrex flask with a teflon stopper. A solution of [Pd(PPh$_3$)$_4$][28] (23.1 mg, 20 μmol) in THF (2 mL) was added, followed by Bu$_3$SnH (917 mg, 3.15 mmol). The mixture was heated to 60°C in a heating block. The reaction mixture turned brown from pale yellow, but was yellow again after 3 h. After 22 h the reaction mixture was cooled by liquid N$_2$ and during slow warm-up, the solvent was removed in high vacuum. The crude product was dissolved in hexanes, and the catalyst and all polar side products were removed on a short chromatography column (SiO$_2$, hexanes). The impurities caused by the excess of the (Bu$_3$Sn)$_2$ could not be removed under these conditions. Therefore, the yield was calculated from the NMR spectra. Yield: 428 mg (689 μmol, 69%) **3a** as a colorless liquid.

Synthesis of **3a** from **2a**: The synthesis and the workup were carried out as described before. Vinyl stannane **2a** (212 mg, 500 μmol) was treated with [Pd(PPh$_3$)$_4$] (11.6 mg, 10 μmol) and freshly purified (Bu$_3$Sn)$_2$[28] (609 mg, 1.05 mmol) in THF (2 mL). No color change was observed in this case. The reaction was monitored by TLC and was finished after 5.5 h. Yield: 287 mg (462 μmol, 92%) **3a**. ^{1}H NMR: (400 MHz, CDCl$_3$): $\delta = 0.69$–1.05 (m, 30H), 1.23–1.35 (m, 12H), 1.37–1.52 (m, 12H), 2.02 (d, $J = 1.3$ Hz, $J_{Sn} = 59$ Hz, 2H), 4.81 Hz (d, $J = 2.5$ Hz, $J_{Sn} = 63$, 22 Hz, 1H), 5.44 ppm (dt, $J = 2.5$, 1.3 Hz, $J_{Sn} = 144$, 20 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 9.5$ ($J_{Sn} = 307$ Hz), 9.6 ($J_{Sn} = 307$ Hz), 13.7, 22.4, 27.4 ($J_{Sn} = 55$ Hz), 27.5 ($J_{Sn} = 55$ Hz), 29.2 ($J_{Sn} = 20$ Hz), 120.7, 154.3 ppm; ^{119}Sn NMR (150 MHz, CDCl$_3$): $\delta = -48.4, -19.8$ ppm.

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[20] Unfortunately, propargyl acetate **A** could not be hydrostannylated in the presence of Pd, because the competing formation of allenyl-Pd complexes was faster.

[21] The regioselectivity towards the desired α-stannylated product in general is lower with Pd catalysts in comparison to the molybdenum catalyst $MoBI_3$ (see reference [14], and references therein).

[22] No elimination was observed in the absence of palladium.

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[24] This reaction was not optimized, owing to the high toxicity of the methylstannanes.

[25] Dimetalations with Sn−Si, Sn−B, and Si−B show a high degree of regioselectivity. The following preference for the vinyl position is observed: $B > Si > Sn$. (see references [2a,b,5b,c]). Tanaka et al.[8] und Cheng et al.[5a] reported an inverse regioselectivity in the case of B−Si.

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[27] The direct disilylation requires reaction temperatures of around 120 °C (see reference [10]). The attempt to react **2a** with hexamethyldisilane was unsuccessful.

[28] The reaction is rather sensitive towards impurities in the distannane and the Pd catalyst. Therefore, the distannane was purified directly before use by flash chromatography (hexanes). $[Pd(PPh_3)_4]$ was obtained from Chempur and should be stored under Ar. Even small color changes (from yellow to orange) in $[Pd(PPh_3)_4]$ result in a dramatic drop in yield.