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Improved Protocols for Molybdenum- und Tungsten-Catalyzed Hydrostannations

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Abstract: A series of (isonitrile)tungsten carbonyl complexes of type $W(CO)_m(CNR)_n$ has been synthesized and evaluated as hydrostannation catalysts. The results are compared with those obtained by the previously reported tri(*tert*-butylisonitrile)molybdenum tricarbonyl catalyst, $Mo(CO)_3(CN\text{-}t\text{-}Bu)_3$ (=$MoBI_3$). The yields and selectivities strongly depend on the isonitriles used, and with certain substrates better results are obtained compared to the molybdenum catalyst. No side products are observed in hydrostannations under microwave irradiation or when the reactions are carried out under an atmosphere of carbon monoxide. Based on these findings, a mechanistic rational is given, explaining the different pathways responsible for the formation of hydrostannation or distannation products.

Keywords: hydrostannation; isonitriles; microwave heating; molybdenum; tungsten

Introduction

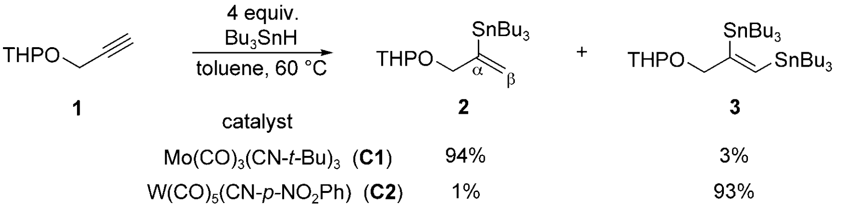
Vinylstannanes are interesting building blocks in organic synthesis, easily available, for example, by hydrostannations of alkynes, either under radical or transition metal-catalyzed conditions.[1] The major drawbacks of these methods result from difficulties in controlling the regioselectivity of the tin hydride addition to unsymmetrical alkynes, although the transition metal-catalyzed version has the advantage of a clean *cis* addition, based on the reaction mechanism.[2] With terminal alkynes, catalytic hydrometallations in general give rise to the terminal (*E*)-vinyl metal compounds, species which can also be generated by stannylcupration.[3] Interestingly, the corresponding (*Z*)-isomers can be obtained in the presence of Lewis acids, as reported by Yamamoto et al.[4] Hale et al. described regioselective radical hydrostannations of propargyl alcohol derivatives, occurring preferentially at the α-position. If internal alkynes are used, also the (*Z*)-isomers are formed preferentially.[5]

A few years ago our group developed a new catalyst for regioselective hydrostannations, based on molybdenum. $Mo(CO)_3(CN\text{-}t\text{-}Bu)_3$ (=$MoBI_3$, **C1**) was found to be an excellent catalyst for highly selective hydrostannations of functionalized alkynes, such as propargylic esters or protected propargyl alcohols (**1**), affording the α-stannylated products (**2**) preferentially.[6] Stannylated allylic esters of this type are excellent building blocks which can be further used, for instance, in Pd-catalyzed allylic alkylations. This approach was used for the synthesis of stannylated amino acids,[7] which are ideal substrates for subsequent Stille couplings.[8]

In general, not only the reactivity but also the regioselectivity towards the α-products increases with the electron-withdrawing properties of the substituents adjacent to the triple bond. For example, propargyl esters are more reactive and more selective than propargylic ethers,[9] sulfones[10] or phosphonates.[11] To increase the performance of our catalyst with these less reactive substrates, we undertook a intense metal and ligand screening, which resulted in the development of a new tungsten-based catalyst with a completely different reaction behaviour. $W(CO)_5(CN\text{-}p\text{-}NO_2Ph)$ (**C2**) gave only traces of hydrostannated product, but an excellent yield of the distannylated allyl compound **3** (Scheme 1) under the same reaction conditions with which **C1** provided the α-stannylated product **2** nearly exclusively.[12] The different reaction behaviour of these two complexes probably can be explained by the different electronic properties of the isonitrile ligands, and this prompted us to investigate these reactions in more detail.

Results and Discussion

Although the $MoBI_3$-catalyzed hydrostannation gives excellent results with electron-poor alkynes, with less



Scheme 1. Hydro- and distannations of propargyl alcohol derivatives.

reactive substrates the reactions are relatively sluggish in some cases, or the reactions stop before complete conversion, even when Bu_3SnH is left over in the reaction mixture. In these slow reactions also another problem becomes visible: the formation of side products such as distannylated alkenes (**3**). Furthermore, protodestannylation can be observed, resulting in an overall reduction of the triple to a double bond. To get rid of these side reactions we tried to optimize our reaction conditions. The reactions can be accelerated dramatically under microwave irradiation,[9] which allows the hydrostannation of thermally labile substrates. Unfortunately, this protocol does not solve the problem of the side reactions. Therefore, we evaluated new catalysts based on tungsten to find better conditions for the hydrostannation and/or the distannation. We chose to synthesize mixed CO/isonitrile complexes to get comparable structures to our previous catalysts **C1** and **C2** (Table 1). We hoped to see an influence of the isonitrile ligand on the selectivity in the addition step. The required isonitriles were easily obtained from the corresponding formamides by dehydration with $POCl_3$.[13] With these isonitriles in hand we performed ligand exchange reactions on $W(CO)_6$ according to a protocol developed by Albers and Coville.[14] $W(CO)_6$ was refluxed with the isonitrile in the presence of catalytic amounts of $CoCl_2$. Depending on the reaction time and the amount of isonitrile used, one to three CO can be replaced by the isoelectronic new ligands. Based on our previous observations made with the molybdenum complexes, we focused preferentially on the $W(CO)_4(CNR)_2$ and the most reactive $W(CO)_3(CNR)_3$ complexes, because the $Mo(CO)_5(CNR)$ complexes showed no significantly higher reactivity compared to $Mo(CO)_6$. Therefore, we used around three equivalents of the isonitrile in the ligand exchange reaction to get the trisisonitrile complexes preferentially (Table 1). Even when the bisisonitrile complexes were obtained under these conditions only as side products, their amount was enough for us to investigate their catalytic properties. The complexes are stable and can be easily separated and purified by flash chromatography.

The known tungsten complex **C4**, the analogue of $MoBI_3$, was prepared according to the literature,[14a] in order to figure out the influence of the central metal atom. In the other new complexes (**C5**–**C10**) the steric and electronic properties of the ligands were varied. The complexes **C9** and **C10** were chosen to evaluate the effect of the strong electron-donating properties of the NMe_2 group in comparison to the strong electron-withdrawing NO_2 group in **C2**. As

4a **4b**

Figure 1. Hydro- and distannations of terminal alkynes.

Table 1. Preparation of mixed tungsten CO/isonitrile complexes.

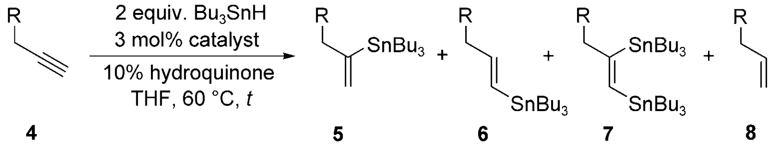
$$W(CO)_6 + \sim 3\ \text{equiv. RNC} \xrightarrow[\text{toluene, 1 – 3 h }\Delta]{\text{8 mol\% CoCl}_2} W(CO)_{6-n}(CNR)_n \qquad n = 2, 3$$

Entry	Isonitrile	Equiv.	Reaction time	Yield [%][a]		Catalyst	Comment[b]
1	*t*-BuNC	3.0	160 min	55	**C3**	$W(CO)_4(CNtBu)_2$[14a]	Together with **C4**
2	*t*-BuNC	3.0	160 min	34	**C4**	$W(CO)_3(CNtBu)_3$[14a]	Together with **C3**
3	*i*-BuNC	3.2	150 min	39	**C5**	$W(CO)_4(CNiBu)_2$	Together with **C6**
4	*i*-BuNC	3.2	150 min	38	**C6**	$W(CO)_3(CNiBu)_3$	Together with **C5**
5	*c*-HexNC	2.9	150 min	26	**C7**	$W(CO)_4(CNc\text{-}Hex)_2$	Together with **C8**
6	*c*-HexNC	2.9	150 min	54	**C8**	$W(CO)_3(CNc\text{-}Hex)_3$	Together with **C7**
7	*p*-Me_2NPhNC	3.3	90 min	21	**C9**	$W(CO)_4(CNPhNMe_2)_2$	Together with **C10**
8	*p*-Me_2NPhNC	3.3	90 min	52	**C10**	$W(CO)_3(CNPhNMe_2)_3$	Together with **C9**

[a] Isolated yields of the separated catalysts.

[b] The corresponding bis- and trisisonitrile complexes were synthesized in one reaction and separated afterwards by flash chromatography.

Table 2. Hydrostannations of propargylic substrates **4**.



4a – 8a R = $4\text{-}NO_2C_6H_4\text{–}O\text{–}$ **4b – 8b** R = $C_6H_5\text{–}SO_2\text{–}$

Entry	Alkyne	Catalyst	Time *t* [h]	Product ratio [%]				
				4	**5**	**6**	**7**	**8**
1	**4a**	**C1**	8	17	71	6	0	6
2	**4a**	**C1**	26	0	80	7	7	6
3	**4a**	**C4**	8	3	72	7	9	9
4	**4a**	**C5**	8	13	49	6	17	15
5	**4a**	**C6**	8	6	59	7	15	13
6	**4a**	**C8**	8	3	82	8	4	3
7	**4a**	**C9**	8	9	84	6	0	1
8	**4a**	**C10**	8	2	91	7	0	0
9	**4b**	**C1**	5	42	38	3	6	11
10	**4b**	**C1**	26	8	44	4	4	40
11	**4b**	**C6**	5	56	35	2	4	3
12	**4b**	**C6**	26	18	63	3	6	10
13	**4b**	**C10**	5	82	7	0	0	10
14	**4b**	**C10**	26	13	35	0	0	52

propargylic substrates we used two different candidates, **4a** and **4b** (Figure 1) which gave only moderate results (yield, selectivity) in our previous investigations of the $MoBI_3$ catalyst, and therefore we saw enough room for improvements.

To be able to compare the results obtained with the different catalysts, the reaction conditions were standardized, and the reactions were run in parallel. In all examples, 1 mmol of substrate was reacted with two equivalents of Bu_3SnH in the presence of 3 mol% catalyst in THF. 10 mol% hydroquinone was added to suppress radical side reactions. The reactions were run under an argon atmosphere and samples were taken *via* syringe after certain times, which were analyzed by NMR.

In principle, four different products can be expected (Table 2): The two regioisomeric hydrostannation products **5** and **6**, the distannylated product **7** and the alkene **8**, resulting from protodestannylation. The side products **7** and **8** are formed preferentially in reactions of unreactive substrates, which require long reaction times. The product distribution was calculated from the ^{1}H, ^{13}C and ^{119}Sn NMR spectra. The most significant results are summarized in Table 2.[15] Only the calculated product ratios are given, not the isolated yields (because samples were taken during the reaction). The reactions with the best catalysts were repeated and the isolated yields of these reactions are summarized in Table 3. The results are compared with those obtained with $MoBI_3$ (**C1**).

Table 3. Isolated yields of hydrostannations.

Entry	Alkyne	Catalyst	Time [h]	Yield [%]	Ratio **5**:**6**
1	**4a**	**C1**	10	68	92:8
2	**4a**	**C10**	10	75	92:8
3	**4b**	**C1**	10	20–40	95:5
4	**4b**	**C6**	24	59	95:5

We started our investigation with the *p*-nitrophenyl ether **4a**, which in general gives very reliable results and acceptable yields and selectivities. With catalyst **C1** ($MoBI_3$) after 8 h still some starting material was left, and the only side product was the alkene **8a** (entry 1). The yield of hydrostannation product (**5a**/**6a**) could be increased slightly by prolonging the reaction time (entry 2), but under these conditions also the formation of distannane **7a** was observed. The corresponding tungsten complex **C4** seems to be slightly more reactive, because the substrate was consumed nearly completely after 8 h (entry 3).

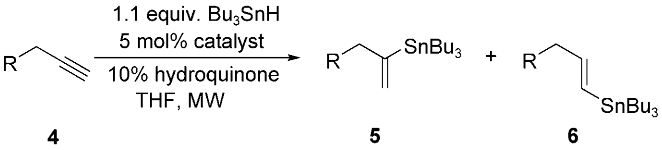
The regioselectivity (ratio **5a**:**6a**) was comparable, but a higher ratio of distannane **7a** was formed. The formation of **7a** was even more tremendous in the reactions catalyzed by the isobutyl isonitrile complexes **C5** and **C6** (entries 4 and 5). The trisisonitrile complex **C6** showed a slightly higher reactivity compared to **C5**, but compared to the other complexes the results were significantly worse: more side products were formed and the regioselectivity was lower. The amount of side products dropped dramatically by switching to the more electron-donating ligands (entries 6–8). Best results were obtained with the *p*-aminophenyl isonitrile complexes, whereby even the bis-isonitrile complex **C9** showed good results. The best catalyst for this reaction was **C10** which gave also a better isolated yield compared to **C1** (Table 3, entries 1 and 2), while the regioselectivity was not affected.

Next we focused on the propargylic sulfone **4b**, which is a relatively critical candidate, because in the $MoBI_3$-catalyzed reaction the yield was not only low, but it also varied strongly from reaction to reaction (Table 3, entry 3).[9] Monitoring the reaction by NMR gave an explanation for this observation. The reaction is relatively slow, but the hydrostannation products are formed with high regioselectivity (Table 2, entry 9). Unfortunately, prolonging the reaction time does not increase the amount of **5b**/**6b**, only the amount of the alkene **8b** (entry 10). Obviously protodestannylation is a significant problem with this substrate. Switching to catalyst **C6**, which was the worst with substrate **4a**, gave a surprising result. Although the reactivity was lower, compared to **C1**, less side products were observed (entry 11). Hereby, the yield could be increased by prolonging the reaction time (entry 12). This allowed us to increase the isolated yield reliably to close to 60% with excellent selectivity (Table 3, entry 4). Surprisingly, **C10**, the best catalyst in the previous studies, failed almost completely with this substrate. Only traces of **5b** were observed after 5 h (Table 2, entry 13), and longer reaction times resulted mainly in the formation of alkene **8b** (entry 14). Similar results were obtained with the catalysts **C8** and **C9**. Definitely, for this kind of substrate, **C6** is the catalyst of choice.

Recently, we observed that the yields of "difficult" hydrostannations could be increased if the reactions are carried out under microwave irradiation.[9] This approach was especially successful with substrates such as **4b**.

Unfortunately, under the microwave conditions the regioselectivity slightly dropped compared to conventional heating. Therefore, we tested out new catalysts also under these conditions, again in comparison to our $MoBI_3$ catalyst (**C1**). With substrate **4a** no side products (**7**/**8**) are formed in any reactions, and so the isolated yields given in Table 4 were generally high. Except for catalyst **C8** (entry 4) all catalysts gave yields comparable to **C1** (80 ± 4%) but better selectivities. The catalyst of choice under these conditions was catalyst **C4** which provided the expected product in nearly quantitative yield (entry 2), even with only 1.1 equivalents of Bu_3SnH (2 equivalents were used in the heating reaction). With substrate **4b** the reaction had to be carried out under milder conditions (to avoid decomposition) and **C1** still seems to be the catalyst of choice in this situation (entry 7). **C6** provided a slightly better regioselectivity, but a significantly lower yield (entry 8). The results with the other catalysts were worse.

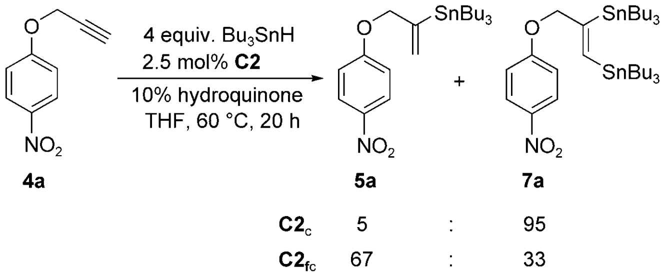
Table 4. Hydrostannations under microwave irradiation.



Entry	Alkyne	Cat.	Reaction Conditions	Yield [%]	Ratio **5**:**6**
1	**4a**	**C1**	150 W, 125 °C, 15 min	81	84:16
2	**4a**	**C4**	150 W, 129 °C, 15 min	95	89:11
3	**4a**	**C6**	150 W, 133 °C, 15 min	84	86:14
4	**4a**	**C8**	150 W, 132 °C, 15 min	61	88:12
5	**4a**	**C9**	150 W, 136 °C, 15 min	78	88:12
6	**4a**	**C10**	150 W, 131 °C, 15 min	81	89:11
7	**4b**	**C1**	100 W, 110 °C, 5 min	72	88:12
8	**4b**	**C6**	100 W, 104 °C, 5 min	47	90:10

During these comparative studies we made an interesting observation. The tungsten catalyst **C2** which was developed as a distannylation catalyst,[12a] gave the expected distannane **7a** preferentially. When we ran out of catalyst we had to synthesize **C2** again, but with this new charge, **7a** was only the side product, while **5a** was the major one (Scheme 2). The only difference between the two catalysts was the purification. While the former charge was used in crystalline form (**C2**$_c$), the new charge was purified by flash chromatography (**C2**$_{fc}$) and used directly without further purification.

In comparison to the other Mo and W complexes, **C2** is a rather sensitive complex, undergoing fast decomposition, for example, during work-up and flash



Scheme 2. Hydro- and distannations of propargyl ether **4a**.

chromatography. Therefore, we were not able to get pure **C2** by chromatography, it was always contaminated by traces of isonitrile (from decomposition). Because this isonitrile is not volatile (in contrast to the others used) these impurities could not be removed under vacuum. Based on these findings, we assume that those traces of isonitrile must be responsible for the different reaction behaviours of our catalyst. Probably the additional isonitrile can coordinate to one of the intermediates in the catalytic cycle changing the properties of our catalyst.

Because distannation was a side reaction in several reactions investigated so far, we decided to reinvestigate our hydrostannations in the presence of additional ligands. The easiest way to do so is to run the reaction under a CO atmosphere (instead of Ar), because CO is isoelectronic to the isonitriles. Therefore, if an *in situ* coordination of this ligand can suppress the distannylation process, one might expect higher yields of the hydrostannation products **5** and **6**. The results obtained under these conditions are summarized in Table 5 (product distribution) and Table 6 (isolated yields). And indeed, while in the hydrostannation of **4a** in the presence of **C1** under Ar the formation of small amounts of **7** and **8** was observed, under a CO atmosphere these side reactions could be suppressed completely (Table 5, entries 1 and 2), and the yield could be increased to 95% under these conditions (Table 6, entries 1 and 2). To prove if this is a general phenomenon, we repeated the reaction using catalyst **C4**, which showed a good reactivity in previous investigations but a significant ratio of side products. Under CO, also here these side reactions could be completely suppressed (Table 5, entries 3 and 4).

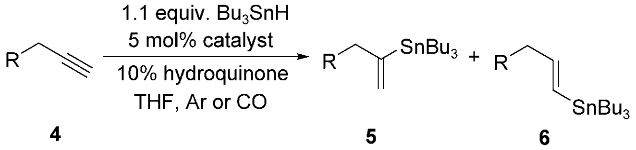
It is worthy of mention that not only the yield increased dramatically, but also the regioselectivity was better under the new reaction conditions (Table 6, entries 3 and 4). That this is a general trend is illustrated with the further examples collected in Table 6. Even complex, highly functionalized substrates such as **4f** can be hydrostannated in excellent yield and a highly regioselective fashion (entry 16).

Based on these observations, we are now able to postulate mechanistic pathways for the hydrostannation/distannation reaction which proceed *via* common intermediates (Scheme 3). The different reaction behaviour of the complex **C2** in contrast to the other catalysts can probably be explained by the different electronic properties of the isonitrile ligands. Replacement of CO ligands, for example, by *tert*-butyl isonitrile as electron-rich ligand results in a reduced metal-CO bond length (1.989–1.994 Å)[16] in comparison to $Mo(CO)_6$ (2.053–2.065 Å).[17] This clearly indicates that *tert*-butyl isonitrile acts preferentially as a σ-donor and less as a π-acceptor and enhanced so the metal-CO bond by increasing of the electron density at the metal.

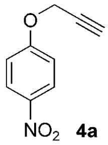
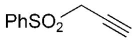
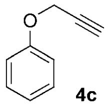
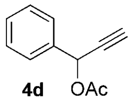
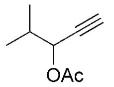
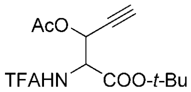
Table 5. Influence of CO on the hydrostannation of alkynes.

Entry	Alkyne	Cat.	Atm.	Product ratio [%]				
				4	**5**	**6**	**7**	**8**
1	**4a**	**C1**	Ar	0	80	8	4	8
2	**4a**	**C1**	CO	0	92	8	0	0
3	**4a**	**C4**	Ar	0	67	7	11	15
4	**4a**	**C4**	CO	2	91	7	0	0

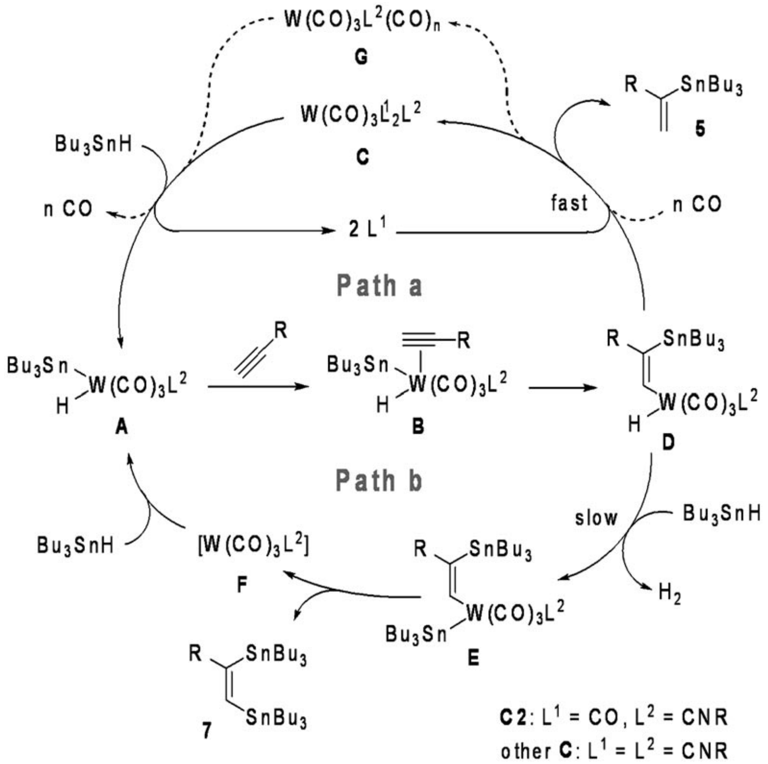
Table 6. Hydrostannations of alkynes under Ar or CO atmosphere (5 bar).



4 **5** **6**

Entry	Alkyne	Cat.	Atm.	Time [h]	Yield [%]	Ratio **5**:**6**
1	 **4a**	**C1**	Ar	20	82	91:9
2		**C1**	CO	20	95	92:8
3		**C4**	Ar	20	65	90:10
4		**C4**	CO	20	89	93:7
5	 **4b**	**C6**	Ar	26	59	95:5
6		**C6**	CO	26	64	95:5
7	 **4c**	**C1**	Ar	5	49	85:15
8		**C1**	CO	5	83	92:8
9		**C6**	Ar	24	46	88:12
10		**C6**	CO	20	83	92:8
11	 **4d**	**C1**	Ar	23	67	85:15
12		**C1**	CO	23	88	87:13
13	 **4e**	**C1**	Ar	23	74	82:18
14		**C1**	CO	23	78	87:13
15	 **4f**	**C1**	Ar	6	72	87:13
16		**C1**	CO	6	90	91:9
17	 **4g**	**C1**	Ar	20	61	–
18		**C1**	CO	20	79	–

Therefore, the isonitrile is the ligand that dissociates (L^1) from the metal as weakest bound ligand opening free coordination sites for the additions of the tin hydride and the alkyne. This would explain the higher reactivity of **C1** and **C4** in comparison to the homoleptic carbonyl complexes $M(CO)_6$ (M = Mo, W). On the other hand, the isonitrile stays in solution, and after the reaction is finished it can recoordinate to the metal, regenerating the catalyst. This is in good



Scheme 3. Mechanistic proposal for the hydrostannation and distannation of alkynes using different types of catalysts.

agreement with the observation, that $MoBI_3$ (**C1**) can be recovered in most cases in high yield without loss of activity. The reaction probably starts with the dissociation of two weak-bonded ligands $\mathbf{L^1}$ from complex **C**. The coordinative unsaturated complex formed can undergo oxidative addition of Bu_3SnH giving rise to complex **A**. Coordination of the alkyne provides complex **B**, and subsequent insertion of the alkyne into the M–Sn bond generates complex **D**, with the sterically more demanding metal-group at the sterically least hindered position. At this point the two competitive pathways start. In case of the trisisonitrile ligands, where the dissociated isonitrile stays in solution, this ligand can recoordinate towards the metal atom, making the reductive elimination of the hydrostannated product **5** easier (path a). In principle, the catalyst **C** is regenerated in this step and can undergo the next catalytic cycle.

Quite different is the situation in the case of the tungsten complex **C2**. IR and Raman spectra show an increase of the C–O bond energy in comparison to $W(CO)_6$, which is equivalent to a reduced metal-CO π-backbonding. The electron-poor isonitrile obviously is tightly bond to the tungsten, and in this case the CO probably is the ligand that dissociates from the metal (L^1). This is also in good agreement with the observation that the electron-poor isonitrile complex **C2** cannot be recovered in contrast to **C1**. In case of catalyst **C2**, where no free ligand is available for coordination, the reductive elimination is slow, and the intermediate complex **D** can undergo a second Bu_3SnH addition under liberation of H_2 (path b).

The complex **E** formed undergoes reductive elimination giving rise to distannane **7** and an unsaturated W fragment **F**, with free coordination sides for oxidative Bu_3SnH addition, closing the catalytic cycle. Distannane complexes similar to **E** were characterized by Schubert et al.[18] Reactions of this type are known from palladium complexes,[19] and these complexes also catalyze the addition of distannanes to alkynes[20] and allenes.[21] Interestingly, in the tungsten-catalyzed version the distannylated products are only formed if Bu_3SnH is used as tin source, but not with distannanes.

In the reactions where the impure catalyst $\mathbf{C2}_{fc}$ was used obviously the traces of isonitrile ligand were enough to skip from pathway b to pathway a. This is also in good agreement with observations we made earlier[22] that, in principle, also $Mo(CO)_6$ can be used as catalyst. Although the yields were low (because of the strong Mo–CO bond) the distannylated product **7** was formed preferentially, while the complexes $Mo(CO)_5(CN\text{-}t\text{-}Bu)$ ($MoBI_1$) and $Mo(CO)_4(CN\text{-}t\text{-}Bu)_2$ ($MoBI_2$) which, in principle, should form the same intermediates **B**–**D**, gave rise to **5** (also in moderate yield).

If the reactions are now run under a CO atmosphere, CO can also act as coordinating ligand (·····) in path a, probably generating complex **G** which also can regenerate **A** on oxidative addition of Bu_3SnH. With the huge excess of the CO ligand, pathway b can be suppressed completely.

Conclusions

In conclusion, we could show that the previously reported Mo catalyst MoBI$_3$ (**C1**) is still one of the best hydrostannation catalysts, giving good yields and regioselectivites with various types of propargylic substrates. In certain cases, the newly developed tungsten catalysts give comparable or even better results, and therefore these complexes should be considered for substrates where MoBI$_3$ gives only unsatisfying results. Detailed mechanistic investigations resulted in an improved protocol for hydrostannations under a CO atmosphere, which allows the suppression of side reactions and better yields and selectivites.

Experimental Section

General Remarks

All air- or moisture-sensitive reactions were carried out in oven-dried glassware (80 °C). Dried solvents were distilled before use: THF was distilled from $LiAlH_4$, CH_2Cl_2 was dried with CaH_2 before distillation. The products were purified by flash chromatography on silica gel columns (Macherey–Nagel 60, 0.063–0.2 mm). Analytical TLC was performed on pre-coated silica gel plates (Macherey–Nagel, Polygram® SIL G/UV$_{254}$). Visualization was accomplished with UV-light, $KMnO_4$ solution or iodine. Melting points were determined with a MEL-TEMP II apparatus and are uncorrected. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded with a Bruker AC-400 [400 MHz (^{1}H), 100 MHz (^{13}C) and 149 MHz (^{119}Sn)] or Bruker DRX-500 [500 MHz (^{1}H), 125 MHz (^{13}C) and 186 MHz (^{119}Sn)] spectrometer in $CDCl_3$. Chemical shifts are reported in ppm (δ) with respect to TMS, and $CHCl_3$ was used as the internal standard. Selected signals for the minor isomers are extracted from the spectra of the isomeric mixture. Mass spectra were recorded with a Finnigan MAT 95 spectrometer using the CI technique. Elemental analyses were performed at the Saarland University.

General Procedure (GP 1) for the Synthesis of Tungsten Complexes

The tungsten complexes **C3–C10** were prepared according to a procedure developed by Albers and Coville and which was used for the synthesis of **C3** and **C4** previously.[14] In general, mixtures of bis- and trisisonitrile complexes were obtained which could be separated by flash chromatography.

$W(CO)_6$ (1.06 g, 3.00 mmol) and $CoCl_2$ (28.6 mg, 0.22 mmol) were dissolved and refluxed in toluene (12 mL). The corresponding isonitrile (~9 mmol) was added, and the reaction was monitored by TLC. After the isonitrile addition the colour of the solution changed from light blue to dark green. When the reaction was finished, the solvent was removed under vacuum. Silica gel (300 vol%) was added to the residue and the mixture was suspended in CH_2Cl_2. The solids were filtered and extracted 5 times with CH_2Cl_2. The combined organic layers were evaporated under vacuum and the crude complexes were purified by flash chromatography.

***cis*-Tetracarbonyl-bis(isovaleroisonitrile)tungsten (C5) and *fac*-tricarbonyl-tris(isovaleroisonitrile)tungsten (C6):** According to the general procedure for complex synthesis (GP 1) **C5** and **C6** were obtained using isovaleroisonitrile (800 mg, 9.60 mmol). After the isonitrile addition, the solution turned dark green at the beginning and pale green during the reaction. After 2.5 h the two complexes were separated by flash chromatography (silica, hexanes/EtOAc 75/25) giving rise to **C5** as a grey solid; yield: 540 mg (1.17 mmol, 39%) and **C6** as a yellow solid; yield: 590 mg (1.14 mmol, 38%). R_f (hexanes/EtOAc 8/2): **C5** 0.23; **C6** 0.18.

C5: mp 50 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.03$ (d, $J = 6.7$ Hz, 12 H), 2.02, (qqd, $J = 6.7$, 6.7, 6.0 Hz, 2 H), 3.42 (d, $J = 6.0$ Hz, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 19.5$, 29.0, 51.4, 197.3, 200.3; IR (cm^{-1}): $\nu = 2967$, 2935, 2876, 2182 (m, NC), 2153 (m, NC), 2012 (m, CO), 1938 (w, CO), 1844 (s, CO), 1517, 1464, 1439, 1390, 1373, 1339, 1296, 1261, 1173 cm^{-1}; HR-MS (CI): *m/z* = 464.0732, calcd. for $C_{14}H_{18}N_2O_4{}^{186}W$ [M]$^+$: 464.0810.

C6: mp 87 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.02$ (d, $J = 6.7$ Hz, 18 H), 1.99, (qqd, $J = 6.7$, 6.6, 6.3 Hz, 3 H), 3.38 (d, $J = 6.3$ Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 19.6$, 29.1, 51.2, 151.3, 203.8; IR (cm^{-1}): $\nu = 2964$, 2931, 2874, 2177 (w, NC), 2134 (s, NC), 1910 (m, CO), 1817 (s, CO), 1515, 1462, 1441, 1389, 1260 cm^{-1}; HR-MS (CI): *m/z* = 519.1616, calcd. for $C_{18}H_{27}N_3O_3{}^{186}W$ [M]$^+$: 519.1596.

***cis*-Tetracarbonyl-bis(cyclohexyl isonitrile)tungsten (C7) and *fac*-Tricarbonyl-tris(cyclohexyl isonitrile)tungsten (C8):**[23] According to the GP 1 **C7** and **C8** were obtained by using cyclohexyl isonitrile (924 mg, 8.79 mmol). After 2.5 h the reaction mixture was purified by flash chromatography (silica, hexanes/EtOAc 85/15) giving rise to **C7** as a white solid; yield: 404 mg (0.785 mmol, 26%) and **C8** as a yellow solid; Yield: 971 mg (1.63 mmol, 54%); R_f (hexanes/EtOAc 8/2): **C7** 0.32; **C8** 0.20.

C7:[23] mp 105 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.30$–1.52 (m, 8 H), 1.69–1.90 (m, 12 H), 3.77 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 22.5$, 25.2, 32.8, 53.5, 203.8.

C8:[23] mp 120 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.30$–1.62 (m, 12 H), 1.69–1.94 (m, 18 H), 3.77 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 22.5$, 25.2, 32.8, 53.5, 204.3; IR: $\nu =$ 2836, 2857, 2162 (w, NC), 2116 (s, NC), 1904 (m, CO), 1820 (s, CO), 1447, 1360, 1347, 1310, 1261, 1244 cm^{-1}; HR-MS (CI): m/z = 597,2071, calcd. for $C_{24}H_{33}N_3O_3{}^{186}W$ [M]$^+$: 597.2066; elemental analysis: calcd. (%) for $C_{24}H_{33}N_3O_3W$ (595.38): C 48.42, H 5.59, N 7.06; found: C 48.52, H 5.34, N 6.84.

***cis*-Tetracarbonyl-bis(4-dimethylaminophenyl isonitrile)-tungsten (C9) and *fac*-Tricarbonyl-tris(4-dimethylamino-phenyl isonitrile)tungsten (C10):** According to GP1 $W(CO)_6$ (524 mg, 1.49 mmol), $CoCl_2$ (14.3 mg, 110 μmol) and *p*-dimethylaminophenyl isonitrile[13] were refluxed in toluene for

1.5 h. Flash chromatography (silica, 1) hexanes/CH_2Cl_2 1/1; 2) CH_2Cl_2) provided **C9** as a pale yellow solid; yield: 184 mg (313 μmol, 21%) and **C10** as an achre solid; yield: 549 mg (775 μmol, 52%); R_f (hexanes/EtOAc 50/50 to 0/100): **C9** 0.37; **C10** 0.18.

C9: mp 141 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.98$ (s, 12 H), 6.61 (d, $J = 9.1$ Hz, 4 H), 7.20 (d, $J = 9.1$ Hz, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 40.4$, 112.0, 127.3, 197.3, 200.7, 111.5, 149.8, 152.8; IR: $\nu = 2896$, 2813, 2142 (w, NC), 2107 (m, NC), 2003 (m, CO), 1866 (s, CO), 1598, 1513, 1441, 1358, 1224, 1166, 809 cm^{-1}; HR-MS (CI): m/z = 590.1258, calcd. for $C_{22}H_{20}N_4O_4{}^{186}W$ [M]$^+$: 590.1028; elemental analysis: calcd (%) for $C_{22}H_{20}N_4O_4W$ (588.26): C 44.92, H 3.43, N 9.52; found: C 45.48, H 4.00, N 9.18.

C10: mp 173 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.96$ (s, 18 H), 6.57 (d, $J = 9.1$ Hz, 6 H), 7.19 (d, $J = 9.1$ Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 40.3$, 111.9, 117.3, 127.2, 149.5, 156.9, 204.0; IR: $\nu = 2891$, 2801, 2134 (w, NC), 2075 (s, NC), 1930 (w, CO), 1922 (m, CO), 1904 (m, CO), 1843 (s, CO), 1599, 1511, 1442, 1357, 1223, 1165 cm^{-1}.

General Procedure (GP 2) for Hydrostannations under "Standard Conditions"

The acetylenic substrate (1.00 mmol) was dissolved in absolute THF (2 mL) under argon in a Schlenk tube. A solution of the corresponding catalyst (30 μmol, 3 mol%) and freshly sublimed hydroquinone (11.0 mg, 100 μmol, 10 mol%) in THF (2 mL) was added, followed by the tin hydride (300 mg, 1.05 mmol). The Schlenk tube was heated in a block heater to 60 °C. After 2 h further Bu_3SnH (300 mg, 1.05 mmol) was added. The reaction was monitored by TLC. After the reaction was complete, the solvent was removed under vacuum and the crude product was purified by flash chromatography.

General Procedure (GP 3) for Hydrostannations under Microwave Irradiation

In a pyrex reaction vessel the corresponding catalyst (50.0 μmol, 5 mol%) and freshly sublimed hydroquinone (11.0 mg, 100 μmol, 10 mol%) was dissolved in THF (2 mL). The alkyne (1.00 mmol) and Bu_3SnH (310 mg, 1.10 mmol) were added, the pyrex vessel was sealed with a teflon septum, and the mixture was irradiated in a microwave oven (100 W or 250 W) for 5–20 min. The work-up was carried out as described in GP 2.

General Procedure (GP 4) for Hydrostannations under a CO Atmosphere

The reactions were carried out in pyrex tubes with a special constructed PTFE stopper, which allowed the addition or removal of substrates *via* syringe. A solution of the alkyne (1.00 mmol) in THF (2 mL) was added *via* syringe to a solution of the catalyst (30.0 mmol, 3 mol%) and hydroquinone (11.0 mg, 100 μmol, 10 mol%) followed by Bu_3SnH (570 mg, 2.0 mmol). The vessel was purged twice with CO, before the CO pressure was increased to 5 bar and the mixture was warmed up to 60 °C in a block heater. The work-up was carried out as described for GP 3.

The hydrostannations and the products obtained from alkynes **4a–c** were described previously.

Hydrostannation of 1-phenylpropargyl acetate (4d): According to GP 4 alkyne **4d** (432 mg, 2.48 mmol) was reacted with Bu_3SnH (1.46 g, 5.00 mmol) in the presence of **C1** (22.8 mg, 53 μmol) and hydroquinone (30.4 mg, 280 μmol) in THF (2 mL). Flash chromatography (hexanes/Et_2O 95/5 to 85/15) gave rise to **5d/6d** as an isomeric mixture (ratio **5d/6d** 87/13) as a colorless liquid; yield: 1.02 g (2.18 mmol, 88%); R_f (hexanes/EtOAc 95/5): **5d** 0.37; **6d** 0.33.

5d: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.74$ (dt, $J_{Sn} = 51.7$ Hz, $J = 8.2$ Hz, 6 H), 0.83 (t, $J = 7.3$ Hz, 9 H), 1.23 (tq, $J = 7.3$, 7.3 Hz, 6 H), 1.28–1.40 (m, 6 H), 2.09 (s, 3 H), 5.35 (ddd, $J_{Sn} = 59.0$ Hz, $J = 1.8$, 1.8 Hz, 1 H), 5.96 (ddd, $J_{Sn} = 122.6$ Hz, $J = 1.8$, 1.8 Hz, 1 H), 6.36 (ddd, $J_{Sn} = 31.5$ Hz, $J = 1.8$, 1.8 Hz, 1 H), 7.23–7.38 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 9.9$ ($J_{Sn} = 334.0$ Hz), 13.6, 21.3, 27.3 ($J_{Sn} = 59.5$ Hz), 28.9 ($J_{Sn} = 20.2$ Hz), 81.6, 125.4 ($J_{Sn} = 19.2$ Hz), 127.3, 127.9, 128.3, 139.5, 153.2, 169.8; ^{119}Sn NMR (149.2 MHz, $CDCl_3$): $\delta = -41.3$.

6d (selected signals): ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.10$ (s, 1 H), 6.07 (ddd, $J_{Sn} = 21.1$ Hz, $J = 19.6$, 4.7 Hz, 1 H), 6.21 (ddd, $J_{Sn} = 67.2$ Hz, $J = 19.6$, 1.3 Hz, 1 H), 6.22 (dd, $J = 4.7$, 1.3 Hz, 1 H), 7.23–7.38 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 9.5$ ($J_{Sn} = 358.9$ Hz), 13.7, 21.3, 27.2, 29.0, 78.3, 127.3, 128.0, 128.4, 131.2, 139.3, 145.0, 171.6; ^{119}Sn NMR (149.2 MHz, $CDCl_3$): $\delta = -46.3$; HR-MS (CI): *m/z* = 409.1152, calcd. for $C_{19}H_{29}O_2{}^{120}Sn$ [M−Bu]$^+$: 409.1190; elemental analysis: calcd. (%) for $C_{23}H_{38}O_2Sn$ (465.26): C 59.37, H 8.23; found: C 59.36, H 8.04.

Hydrostannation of 1-isopropylpropargyl acetate (4e): According to GP 4 alkyne **4e** (1.42 mg, 1.00 mmol) and Bu_3SnH (582 mg, 20.0 mmol) were reacted in the presence of **C1** (13.1 mg, 30.6 μmol) and hydroquinone (10.1 mg, 92.0 μmol). After 23 h and flash chromatography (hexanes/Et_2O 95/5) a mixture of **5e** and **6e** (ratio 87:13) was obtained as a colorless liquid; yield: 340 mg (0.79 mmol, 78%); R_f (hexanes/EtOAc 95/5): **5e** 0.38; **6e** 0.38.

5e: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.82$–1.00 (m, 21 H), 1.30 (tq, $J = 7.3$, 7.3 Hz, 6 H), 1.42–1.52 (m, 6 H), 1.71 (qqd, $J = 7.7$, 7.7, 7.5 Hz, 1 H), 2.03 (s, 3 H), 5.06 (dddd, $J_{Sn} = 50.7$ Hz, $J = 7.5$, 1.1, 1.0 Hz, 1 H), 5.28 (ddd, $J_{Sn} = 62.2$ Hz, $J = 2.2$, 1.0 Hz, 1 H), 5.78 (ddd, $J_{Sn} = 128.2$ Hz, $J = 2.2$, 1.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 10.1$ ($J_{Sn} = 331.6$ Hz), 13.6, 17.9, 19.2, 21.2, 27.4 ($J_{Sn} = 58.0$ Hz), 29.0 ($J_{Sn} = 19.8$ Hz), 32.0, 86.4 ($J_{Sn} = 33.0$ Hz), 127.1 ($J_{Sn} = 19.1$ Hz), 153.0, 170.2; ^{119}Sn NMR (149.2 MHz, $CDCl_3$): $\delta = -44.5$.

6e (selected signals): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.71$ (qqd, $J = 6.5$, 6.5, 6.5 Hz, 1 H), 2.05 (s, 3 H), 4.97–5.02 (m, 1 H), 5.82 (ddd, $J_{Sn} = 25.6$ Hz, $J = 19.2$, 6.2 Hz, 1 H), 5.78 (ddd, $J_{Sn} = 70.8$ Hz, $J = 19.2$, 1.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 9.5$, 13.7, 18.0, 18.1, 21.2, 27.2, 29.1, 31.8, 81.7, 131.6, 144.2, 170.3; ^{119}Sn NMR (149.2 MHz, $CDCl_3$): $\delta = -47.8$; HR-MS (CI); m/z = 373.1361, calcd. for $C_{16}H_{31}O_2{}^{118}Sn$ [M−Bu]$^+$: 373.1340; elemental analysis: calcd. (%) for $C_{20}H_{40}O_2Sn$ (431.24): C 55.70, H 9.35; found: C 55.70, H 9.19.

Hydrostannation of propargylic amino acid derivative 4f: According to GP 4, **4 f** (81.1 mg, 250 μmol)[24] was subjected to hydrostannation using Bu_3SnH (146 mg, 500 μmol), **C1** (4.4 mg, 10.3 μmol) and hydroquinone (4.70 mg, 42.7 μmol) in THF (3 mL). After 6 h reaction time and work-up (silica, hexanes/Et_2O 9/1 to 8/2) **5f** and **6f** were obtained as a colourless liquid; yield: 139 mg (226 μmol, 90%) (ratio **5f/6f**: 91/9); R_f (hexanes/EtOAc 8/2): **5f** 0.46; **6f** 0.46.

5f (major diastereomer): ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.87 (t, J = 7.3 Hz, 9H), 0.96 (dt, J_{Sn} = 50.7 Hz, J = 8.2 Hz, 6H), 1.30 (tq, J = 7.3, 7.3 Hz, 6H), 1.42–1.54 (m, 6H), 1.45 (s, 1H), 2.06 (s, 3H), 4.73 (dd, J = 8.2, 4.6 Hz, 1H), 5.40 (ddd, J_{Sn} = 56.7 Hz, J = 1.6, 1.5 Hz, 1H), 5.63 (dddd, J_{Sn} = 34.1 Hz, J = 4.6, 1.5, 1.5 Hz, 1H), 5.87 (ddd, J_{Sn} = 116.5 Hz, J = 1.6, 1.5 Hz, 1H), 6.99 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 10.2 (J_{Sn} = 317.7 Hz), 13.6, 20.9, 27.3 (J_{Sn} = 60.9 Hz), 28.0, 28.9, 55.5, 79.6, 84.0, 115.6 (q, J_F = 288.3), 128.1, 149.7, 156.9 (q, J_F = 38.2), 166.6, 169.8; ^{119}Sn NMR (149.2 MHz, CDCl$_3$): δ = −38.7.

5f (minor diastereomer): ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.88 (t, J = 7.3 Hz, 9H), 0.98 (dt, J_{Sn} = 50.7 Hz, J = 8.3 Hz, 6H), 1.31 (tq, J = 7.4, 7.4 Hz, 6H), 1.42–1.54 (m, 6H), 1.44 (s, 1H), 2.07 (s, 3H), 4.73 (dd, J = 9.2, 3.1 Hz, 1H), 5.03 (ddd, J_{Sn} = 56.7 HzJ = 1.6, 1.5 Hz, 1H), 5.79 (dd, J = 1.6, 1.5 Hz, 1H), 5.93 (dddd, J_{Sn} = 19.8 Hz, J = 3.1, 1.5, 1.5 Hz, 1H), 6.67 (d, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 10.0, 13.6, 20.6, 27.3 (J_{Sn} = 60.9 Hz), 27.8, 28.8, 55.4, 77.7, 83.8, 126.1, 148.7, 166.8, 168.8; ^{119}Sn NMR (149.2 MHz, CDCl$_3$): δ = −41.4.

6f (major diastereomer, selected signals): ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.84 (dd, J = 8.3, 3.5 Hz, 1H), 5.56 (ddd, J = 6.2, 3.5, 1.3 Hz, 1H), 6.37 (ddd, J_{Sn} = 62.2 Hz, J = 19.1, 1.3 Hz, 1H), 6.92 (d, J = 8.3 Hz, 1H).

6f (minor diastereomer, selected signals): ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.79 (dd, J = 9.2, 2.6 Hz, 1H), $^4J_{1,3}$ = 1.3 Hz, 1H), 6.23 (dd, J = 20.3, 2.6 Hz, 1H), 6.75 (d, J = 9.2 Hz, 1H); HR-MS (CI): m/z = 558.1489, calcd. for $C_{21}H_{35}F_3NO_5{}^{120}Sn$ [M−Bu]$^+$: 558.1489; elemental analysis: calcd (%) for $C_{25}H_{44}F_3NO_5Sn$ (614.33): C 48.88, H 7.22, N 2.28; found: C 48.66, H 6.97, N 2.61.

Hydrostannation of diethyl 1,4-butynediol dicarbonate (4g): According to GP 4 **4g** (932 mg, 4.05 mmol) was hydrostannated using Bu$_3$SnH (2.33 g, 8.00 mmol), **C1** (54.1 mg, 126 μmol) and hydroquinone (194 mg, 110 μmol) in THF (4 mL). After 20 h the crude product was purified by flash chromatography (hexanes/Et$_2$O 9/:1 to 85/15) to give **5g** as a colourless liquid; yield: 1.67 g (3.20 μmol, 79%); R_f (hexanes/EtOAc 8/2): **5g** 0.46. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.86 (t, J = 7.3 Hz, 9H), 0.91 (dt, J_{Sn} = 50.2 Hz, J = 8.2 Hz, 6H), 1.22–1.33 (m, 12H), 1.40–1.50 (m, 6H), 4.16 (q, J = 7.3 Hz, 2H), 4.18 (q, J = 7.3 Hz, 2H), 4.67 (ddt, J_{Sn} = 9.4 Hz, J = 6.0, 1.0 Hz, 2H), 4.86 (ddt, J_{Sn} = 32.9 Hz, J = 2.1, 1.0 Hz, 2H), 5.74 (dtt, $^2J_{3,Sn}$ = 60.5 Hz, J = 6.0, 2.1 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 10.0 (J_{Sn} = 338.2 Hz), 13.6, 14.2, 14.3, 27.3 (J_{Sn} = 58.0 Hz), 28.9 (J_{Sn} = 19.8 Hz), 63.9, 64.1, 64.3, 69.0 (J_{Sn} = 16.8 Hz), 133.7 (J_{Sn} = 20.5 Hz), 145.9, 154.9, 155.0; ^{119}Sn NMR (149.2 MHz, CDCl$_3$): δ = −33.2; HR-MS (CI); m/z = 465.1206, calcd. for $C_{18}H_{33}O_6{}^{120}Sn$ [M]$^+$: 465.1299.

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[24] Compound **4f** was obtained as a diastereomeric mixture (62:38) by an aldol reaction of TFA-Gly-O-*t*-Bu and *C*-silylated propynal. Subsequent desilylation and *O*-acetylation provided **4f** in overall 55% yield.