Reaction Mechanisms

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Ruthenium-Catalyzed *trans*-Selective Hydrostannation of Alkynes**

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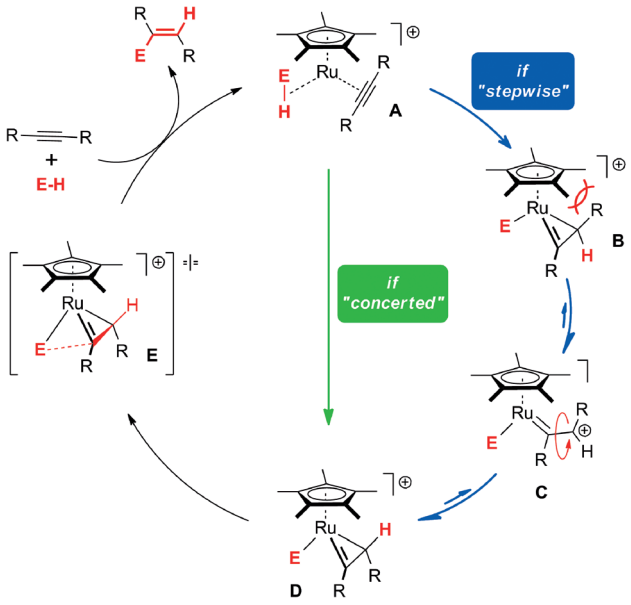
Dedicated to Professor Walter Thiel on the occasion of his 65th birthday

Abstract: *In contrast to all other transition-metal-catalyzed hydrostannation reactions documented in the literature, the addition of Bu_3SnH across various types of alkynes proceeds with excellent trans selectivity, provided the reaction is catalyzed by [Cp*Ru]-based complexes. This method is distinguished by a broad substrate scope and a remarkable compatibility with functional groups, including various substituents that would neither survive under the conditions of established Lewis acid mediated trans hydrostannations nor withstand free-radical reactions. In case of unsymmetrical alkynes, a cooperative effect between the proper catalyst and protic functionality in the substrate allows outstanding levels of regioselectivity to be secured as well.*

We have recently disclosed preliminary results on ruthenium-catalyzed hydrogenation as well as hydroboration reactions of internal alkynes, reactions which are strictly *trans* selective and hence violate the stereochemical principles which have governed these transformations since their inception.[1,2] Although our understanding for the origin of the high *trans* selectivity is provisional, both transformations are thought to be different incarnations of a common mechanism, which supposedly also underlies the *trans*-hydrosilylation chemistry pioneered by Trost and co-workers shortly after the turn of the millennium.[3–5] Details aside, these processes are believed to involve loaded complexes of type **A** which carry the reagent E–H [E = H, B(pin), SiR_3] in σ-bound form (Scheme 1).[6–8] This assumption is based on calculations for the hydrosilylation case[9] and on control experiments with a pertinent σ-H_2 complex for the *trans* hydrogenation.[1] Hydride delivery to the bound alkyne may or may not occur directly, without formation of discrete metal hydride intermediates.[10] The resulting metallacyclopropene intermediates (η^2-vinyl complexes) are fluxional by reversible hapticity change (**B**⇌**C**⇌**D**),[11] which allows the larger substituent, R, to get out of the way of the bulky Cp* ligand which blocks one face of the coordination sphere about the central metal. In accord with this interpretation, the extended



Scheme 1. Mechanistic hypothesis explaining the *trans* addition of reagents of the type E–H [E = H, B(pin), SiR_3] across acetylene derivatives in the presence of (cationic) [Cp*Ru]-based catalysts. A priori, one may conceive that the conversion of the loaded complex **A** into **D** is either stepwise or concerted. Cp* = η^5-C_5Me_5, pin = 4,4,5,5-tetramethyl[1,3,2]dioxaborolanyl (pinacolyl).

umbrella of the Cp* ring is necessary for high *trans* selectivity, independent of whether E = H, SiR_3, or B(pin).[1–4,12,13] Alternatively, one may conceive a concerted pathway, in which hydride delivery is geared to a rotary motion which leads to intermediates of type **D** without intervention of open cationic species.[9] In any case, a final reductive elimination via **E** explains the formation of the observed *trans* adducts.

This rationale insinuates that other reagents, E–H (or even E–E), might also be amenable to similar *trans*-addition processes. Stannanes are obvious candidates,[14] not least for their known ability to form σ-complexes with different electron-deficient metal fragments.[15] The available data indicate that the Sn–H bond of a σ-bound stannane is significantly more elongated than that of an analogous σ-bound silane. This higher degree of activation might either translate into particularly good *trans*-donor qualities or prime the complexes to decomposition with release of H_2 upon contact with excess R_3SnH.[15a] Anyway, it was not clear whether the conceived *trans* hydrostannation could prevail over this potentially facile but unproductive side track.

Building upon on our previous experiences,[1,2,4] a few test reactions sufficed to answer this question. Using the cyclo-

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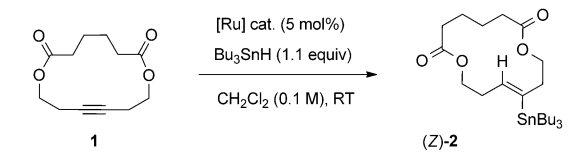
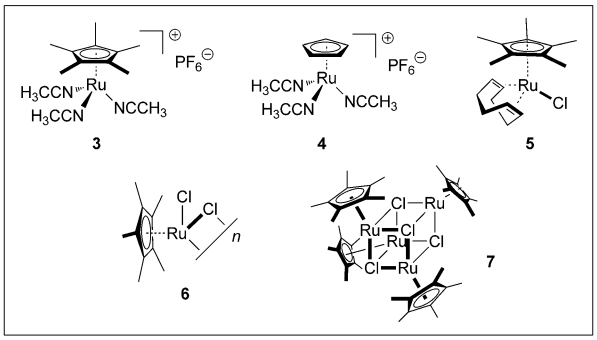
Table 1: Optimization of the *trans*-hydrostannation reaction.[a]





Entry	Catalyst	Solvent	Yield [%][b]	Z/E[c]
1	**3**	CH_2Cl_2	97 (94)[d]	85:15
2	**4**	CH_2Cl_2	83	63:37
3	**5**	CH_2Cl_2	34	84:16
4	**6**	CH_2Cl_2	85	89:11
5	**3**	$ClCH_2CH_2Cl$	97	84:16
6	**3**	acetone	41[e]	83:17
7	**3**	MeCN[f]	66[f]	82:18
8	**3**	diglyme	81	83:17
9	**3**	CH_2Cl_2[g]	94[g]	85:15[g]
10	**3**	CH_2Cl_2[h]	78[h]	86:14[h]

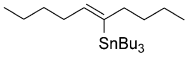
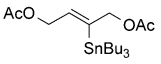
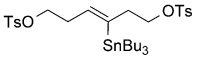
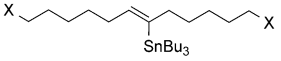
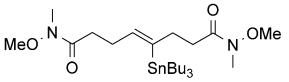
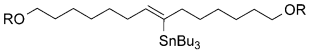
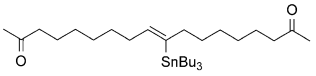
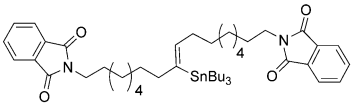
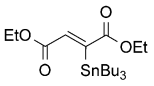
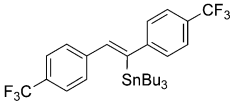
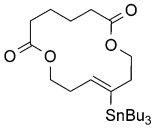
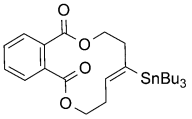
[a] Bu_3SnH was added dropwise over 5 min to a 0.1 M solution of the substrate and the catalyst (5 mol%) in the indicated solvent under Ar atmosphere; the reaction was worked up after 15 min. [b] Yield of isolated product. [c] Determined by ^1H NMR spectroscopy. [d] In 0.5 M solution. [e] Conversion (^1H NMR). [f] The stannane is hardly soluble in this medium. [g] The reaction was performed in the dark. [h] In the presence of TEMPO (1 equiv). TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy, free radical.

alkyne **1**[16,17] as our model substrate and commercial [Cp*Ru(MeCN)$_3$]PF_6 (**3**) as the catalyst, the product (*Z*)-**2** was obtained with appreciable selectivity in fair to excellent yields (Table 1).[18] Like in our previous studies,[1,2] **3** outperformed its less bulky sibling [CpRu(MeCN)$_3$]PF_6 (**4**), thus confirming a large steric component in the stereodetermining step. As expected for a cationic catalyst, noncoordinating solvents gave the best results. Typical experiments were carried out in CH_2Cl_2 (0.1–0.5 M) by slowly adding commercial Bu_3SnH[19] over the course of 5–10 minutes to avoid excessive distannane formation, which wins out if the stannane is added at once. For less reactive substrates it is advisable to adjust the addition time.[20] Most reactions were exceptionally fast and definitely more rapid than the analogous *trans* hydroboration of the same substrate with pin-BH.[2] Control experiments showed that the *trans* hydrostannation proceeds with uncompromised rate and selectivity in the dark (entry 9) as well as in the presence of one equivalent of TEMPO (entry 10), which strongly advocates a nonradical pathway.

Next, a selection of symmetrical alkynes was subjected to *trans*-hydrostannation under the standard reaction conditions (Table 2). In many cases, the isomer ratio reached the detection limit ($\geq$99:1, ^1H NMR). Somewhat ironically though, **1**, serving as the model compound in the initial screening exercise, gave the lowest Z/E ratio of all substrates investigated (see Table 2, entry 13). Using simple 5-decyne, we probed the robustness of the method, which basically furnished identical results on both a 80 mg and 1.4 g scale (Table 2, entry 1).

In close analogy to the *trans* hydroboration,[2] the reaction tolerates a variety of functional groups and is applicable to substrates containing electron-deficient arene rings.[21] Most

Table 2: *trans*-Selective hydrostannation of symmetrical internal alkynes.[a]

Entry	Major Product	Z/E[b]	Yield [%][c]
1		99:1	96 (94)[d]
2		99:1	80
3		99:1	98
4		97:3	80 (X = Br)
5		98:2	56 (X = N_3)
6		99:1	88
7		99:1	76 (R = H)
8		99:1	89 (R = TBS)
9		99:1	94
10		99:1	98
11		94:6 (99:1)[e]	69[e]
12		98:2	98
13		85:15	97
14		95:5	97

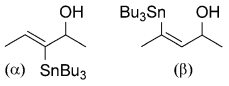
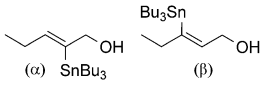
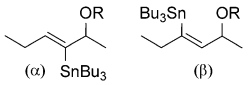
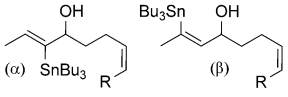
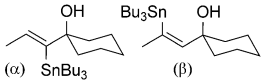
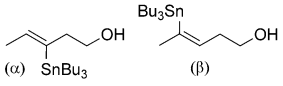
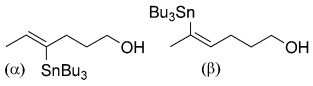
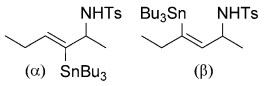
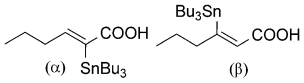
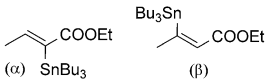
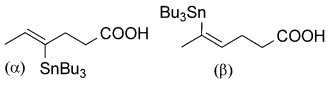
[a] Unless state otherwise, all reactions were performed on 0.1–0.2 mmol scale by adding the commercial Bu_3SnH (1.1 equiv) over the course of ca. 5 min to a solution of the substrate and complex **3** (5 mol%) in CH_2Cl_2 (0.2 M) at RT under Ar. [b] Ratio in the crude reaction mixture, as determined by ^1H NMR spectroscopy. [c] Isolated material. [d] 3.5 mmol Scale using only 1.05 equiv of the stannane. [e] After flash chromatography. TBS = *tert*-butyldimethylsilyl, Ts = *p*-toluenesulfonyl.

noticeable is the compatibility with primary bromides (Table 2, entry 4) as well as with azides (entry 5), which would not survive if free tin radicals were involved at any stage. Moreover, several other polar or reducible sites remain intact (ester, ketone, phthalimide, Weinreb amide, primary tosylate, silyl ether, unprotected alcohols, and acids). This remarkable chemoselectivity profile distinguishes the current method from an otherwise also highly *trans*-selective hydrostannation using strong Lewis acids such as $ZrCl_4$ in substoichiometric or stoichiometric amounts.[22] Such harsh promoters, however, do not tolerate most functionality, and even benzyl ethers are incompatible.[22]

In an attempt to further extend the scope, we initially encountered the usual regioselectivity issues which tend to trouble hydrometalations of unsymmetrical alkynes. The reaction of pent-3-yne-2-ol under the standard reaction conditions gave a disappointing 74:26 mixture of the proximally and distally stannylated products (Table 3, entry 1), both of which derive from a *trans*-addition process.[23] Gratifyingly though, replacement of the cationic complex **3** by other commercial Cp*-containing precatalysts led to much more rewarding outcomes (entries 2–4). Specifically, the use of either [Cp*Ru(cod)Cl] (**5**), the oligomeric Ru^{III} species $[\{Cp^*RuCl_2\}_n]$ (**6**), or the tetrameric cluster $[\{Cp^*RuCl\}_4]$ (**7**)[24] resulted in an almost exclusive formation of a single isomer.

As manifested in Table 3 (entries 2–11), this pattern is independent of whether the propargylic alcohol site is primary, secondary, or tertiary. Increasing the steric demand does not override this pronounced bias, as is often the case in hydrostannations catalyzed by other transition metals.[25] Comparison of entries 7 and 8 confirms that the largely improved regioselectivity is intimately related with the presence of an unprotected hydroxy group and not merely caused by dipolar interactions in the transition state. Even if the OH group was shifted to the (bis)homopropargylic position, appreciable regioselectivity is retained (entries 12 and 13). Likewise, a propargylic sulfonamide also showed high preference for proximate stannylation when reacted in the presence of the complex **7** (entry 14). In contrast, the hydrostannation of an α-methyl branched alkyne led to product mixtures, irrespective of the chosen precatalyst.[26] Therefore we conclude that a massive cooperative effect between the protic functionality and the catalyst must be operational. The fate of **7** in the presence of Bu_3SnH and a protic substrate and hence the nature of the active species responsible for this striking regioselectivity are presently under investigation.[27–29]

Table 3: *trans*-Hydrostannation of unsymmetrical alkynes (for the full Table, see the Supporting Information).[a]

Entry	Products	Cat.[b]	α/β[c]	*Z*/*E*[c]	Yield [%]
1		**3**	74:26	99:1 (α)	91
2		**5**	97:3	99:1 (α)	73
3		**6**	97:3	99:1 (α)	88[d]
4		**7**	98:2	99:1 (α)	81
5		**3**	60:40	99:1 (α)	quant.[e]
6		**7**	95:5	99:1 (α)	83[f]
7		**7**	98:2	99:1 (α)	84 (R = H)[g]
8		**7**	75:25	94:6 (α)	86 (R = Ac)
9		**7**	97:3	99:1 (α)	77 (R = H)
10		**7**	98:2	99:1 (α)	72 (R = Bu)
11		**7**	99:1	99:1 (α)	97
12		**7**	81:19	95:5 (α)	81
13		**7**	83:17	99:1 (α)	86
14		**7**	99:1	99:1 (α)	90
15		**3**	50:50	91:9 (β)	77
16		**7**	90:10	96:4 (α)	87[d,h]
17		**3**	40:60	99:1 (β)	90
18		**7**[i]	6:94	95:5 (β)	71[i,j]
19		**7**	93:7	99:1 (α)	87[h,k]

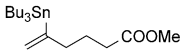
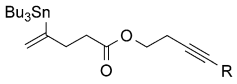
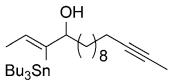
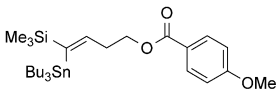
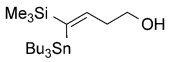
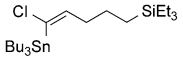
[a] Unless stated otherwise, all reactions were performed on 0.1–0.2 mmol scale by adding Bu_3SnH (1.1 equiv) over ca. 5 min to a solution of the substrate and the respective catalyst in CH_2Cl_2 (0.2 M) under Ar. [b] Using either 5 mol% of **3** or **5**, or 1.25 mol% of **7**. [c] Ratio is that of the crude reaction mixture, as determined by ^1H NMR spectroscopy. [d] ≥1 mmol Scale. [e] Conversion (^1H NMR). [f] 2.1 mmol Scale. [g] Small amounts of the corresponding ketone were also found. [h] Using 1.0 equiv of Bu_3SnH. [i] The stannane was added over 1.5 h. [j] The yield refers to the pure *Z*-configured β-stannylated isomer obtained by flash chromatography. [k] 0.6 mmol Scale.

An equally pronounced effect was recorded for acetylene carboxylate derivatives. Hydrostannations in the presence of **3**, albeit highly *trans* selective, were regio-indiscriminative (Table 3, entries 15 and 17). In contrast, the use of **7** forced the acid to react with high preference at the proximal α-position (entry 16), most likely by a steering mechanism which echoes the results of the propargylic alcohol series. If this cooperativity with the protic functionality is lacking, the outcome is different. Thus, acetylenic esters exhibit the opposite preference for stannylation at the distal β-site

(entry 18). This dichotomy is obviously useful in preparative terms and nicely distinguishes the current method from other transition-metal-catalyzed hydrostannations, which tend to be α-selective even in the acetylenic ester series.[14,30]

The new *trans* hydrostannation was also successfully applied to terminal acetylenes,[31,32] to alkynes capped by a Me_3Si-group, as well as to a terminally chlorinated substrate, none of which is suited for *trans* hydrogenation or *trans* hydroboration at the present stage of development (Table 4).[1,2] The evidently broader substrate scope suggests

Table 4: *trans*-Hydrostannation of terminal, silylated, or chlorinated alkynes or diynes.[a]

Entry	Major Product	Isomer ratio[b]	Z/E[b]	Yield [%]
1		97:3	–	73
2		76:24[c]	–	89 (R = Me)
3		93:7[c]	–	96 (R = $SiMe_3$)
4		n.d.	99:1	55[d]
5		98:2	99:1	98
6		96:4	99:1	82
7		99:1	99:1	94

[a] In case of terminal alkynes, the reactions (0.1–0.2 mmol scale) were performed by adding a solution of the substrate and Bu_3SnH (1.1 equiv) in CH_2Cl_2 to a solution of the catalyst (5 mol%) in the same solvent over ca. 12 min under Ar; all other reactions were performed by adding Bu_3SnH (1.0–1.1 equiv) over ca. 5 min to a solution of the substrate and complex **3** (5 mol%) in CH_2Cl_2 (0.2 M). [b] Ratio in the crude reaction mixture as determined by ^1H NMR spectroscopy. [c] Refers to the ratio of stannylation of the two different alkynes present in the substrate. [d] Using complex **7** (1.25 mol%). n.d. = not determined.

that Sn–H activation by a cationic ruthenium species is particularly favorable. Preliminary data even indicate a useful differential in reactivity, since terminal acetylenes could be addressed with decent selectivity in the presence of internal or silylated triple bonds (entries 2 and 3). Likewise, it is possible to discriminate between two internal acetylenes, provided one of them is propargylic (entry 4).

In summary, we present an exceptionally productive *trans* hydrostannation which nicely complements or exceeds the established methodologies, be they metal-catalyzed or free-radical-based. It is distinguished by a unique and rewarding chemo-, regio-, and stereoselectivity profile. Despite some toxicity concerns, alkenyltin reagents remain indispensable for synthesis because of their reliability and versatility.[33] Actually, a number of advanced applications are documented in the literature where tin reagents fared significantly better than other nucleophiles.[34] From a heuristic perspective, the present study adds another important entry to a growing list of *trans*-addition reactions which seemingly violate very basic concepts of metal catalysis. As such, it invigorates our efforts to further generalize and better understand this intriguing and enabling reactivity pattern.[35]

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