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Communication

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Catalytic Dehydrogenative Stannylation of C(sp)–H Bonds Involving Cooperative Sn–H Bond Activation of Hydrostannanes

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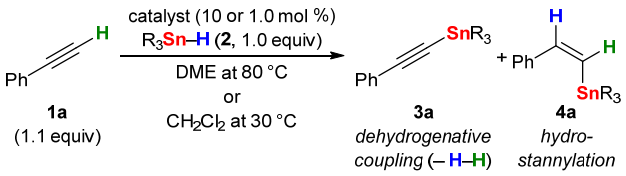
Supporting Information Placeholder

ABSTRACT: The catalytic generation of a stannylium-ion-like tin electrophile by heterolytic cleavage of the Sn–H bond in hydrostannes at the Ru–S bond of Ohki–Tatsumi complexes is reported. Reacting these activated hydrostannanes with terminal acetylenes does not lead to hydrostannylation of the C–C triple bond but to dehydrogenative stannylation of the alkyne terminus. The scope of this rare direct C(sp)–H bond stannylation with hydrostannanes is broad, and a mechanism involving a β-tin-stabilized vinyl cation having a bridged structure is presented.

One way to achieve cross-coupling at an sp-hybridized carbon atom[1] is by the Stille reaction.[2] The necessary coupling partner is an alkynyl-substituted tin compound, and these are commonly prepared by the reaction of an (earth) alkali metal acetylide with a tin electrophile such as R_3SnCl and R_3SnBr (R = alkyl and aryl).[3] Alternatively, tin amides[4] and alkoxides[5] engage in direct bond formation with terminal acetylenes. Recently, the limited scope of these methods was greatly expanded by Baba and co-workers who discovered that $ZnBr_2$ catalyzes the stannylation of terminal alkynes with nBu$_3$SnOMe.[6] We are aware of an unexpected finding by Mitchell where the use of Me_3SnH instead of nBu$_3$SnH in the planned rhodium-catalyzed hydrostannylation of the terminal triple bond of propargyl ethers resulted in unexpected dehydrogenative C(sp)–Sn coupling.[7] Aside from this isolated report, the formation of vinyl stannanes is the usual outcome of reactions of alkynes and hydrostannanes.[8]

Inspired by the recent work of Stoltz and Grubbs,[9] we tested alkali metal hydroxides and *tert*-butoxides as catalysts in the C(sp)–H bond stannylation of alkynes **1** with hydrostannanes **2** but that merely led to decomposition of **2** (Table 1, entries 1–3); the same setup had allowed for efficient C(sp)–H bond silylation. We then turned toward Ohki–Tatsumi complexes [**5**]$^+$[A]$^-$ as catalysts (Figure 1).[10] The Ru–S bond in [**5**]$^+$[A]$^-$ mediates the cooperative activation of main-group metal hydrides,[11] and we have been able to develop several dehydrogenative couplings based on this activation mode, particularly with hydrosilanes.[12] To our delight, any of our typical catalysts [**5**]$^+$[BAr$^F_4$]$^-$ promoted the C(sp)–Sn coupling (**1a** → **3aa**; Table 1, entries 4–7). The yield was highest with [**5b**]$^+$[BAr$^F_4$]$^-$ (entry 5), and hydrostannylation became a minor pathway with [**5d**]$^+$[BAr$^F_4$]$^-$ (**1a** → **4aa**; entry 7). [**5b**]$^+$[B(C$_6$F$_5$)$_4$]$^-$[13] with a different counteranion performed equally well (entry 8). Changing the hydrostannane from nBu$_3$SnH (**2a**) to Et$_3$SnH (**2b**) or Ph$_3$SnH (**2c**) afforded lower yield and diminished selectivity (entry 9) or resulted in hydrostannane degradation (entry 10). When using hydrostannanes **2a** and **2b**, the corresponding distannanes did form in trace amounts but cleavage of the Sn–Sn bond by [**5**]$^+$[A]$^-$ did not occur as verified by independent experiments.—We note that **2** was used as the limiting reagent for practical reasons; full consumption of the hydrostannane **2** avoided its removal.

Table 1. Optimization of the Dehydrogenative C(sp)–Sn Coupling[a]



entry	catalyst (mol %)	stannane (R in **2**)	t (h)	**3a**:**4a** (%)[b]	conv. (%)[b,c]
1	NaOH (10)	nBu (**2a**)	72	—	>99[d]
2	KOtBu (10)	nBu (**2a**)	72	—	>99[d]
3	NaOtBu (10)	nBu (**2a**)	72	—	>99[d]
4	[**5a**]$^+$[BAr$^F_4$]$^-$ (1.0)	nBu (**2a**)	18	>99:1	32
5	[**5b**]$^+$[BAr$^F_4$]$^-$ (1.0)	nBu (**2a**)	18	>99:1	>99 (90)
6	[**5c**]$^+$[BAr$^F_4$]$^-$ (1.0)	nBu (**2a**)	18	>99:1	80
7	[**5d**]$^+$[BAr$^F_4$]$^-$ (1.0)	nBu (**2a**)	18	96:4	32
8	[**5b**]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (1.0)	nBu (**2a**)	18	>99:1	>99
9	[**5b**]$^+$[BAr$^F_4$]$^-$ (1.0)	Et (**2b**)	24	93:7	>99 (66)
10	[**5b**]$^+$[BAr$^F_4$]$^-$ (1.0)	Ph (**2c**)	24	—	90[d]

[a]All reactions were performed according to the reported procedure (entries 1–3; Ref. 9) and General Procedure 1 (entries 4–11; see the Supporting Information for details). [b]Ratios and conversions were determined by GLC analysis using tetracosane as an internal standard. [c]Isolated yield after filtration over Al_2O_3. [d]Decomposition of the hydrostannane was observed.

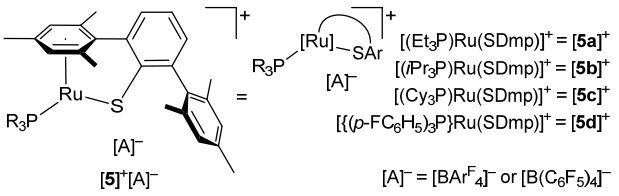
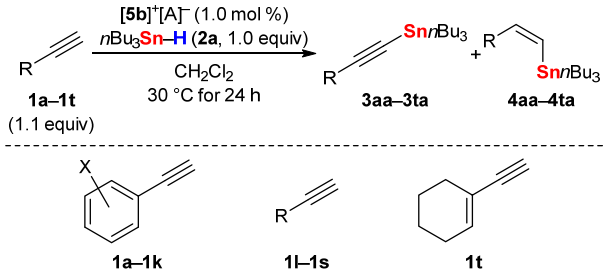


Figure 1. Coordinatively unsaturated Ru–S complexes for cooperative activation of main-group metal hydrides. Ar^F = 3,5-bis(trifluoromethyl)phenyl.

With proper catalysts [**5b**]$^+$[A]$^-$ identified (Table 1, entries 5 and 8), we assessed the functional-group tolerance of the method (Table 2). High yields and selectivities were obtained for essentially any of the phenyl acetylene derivatives used (**1a–1k** → **3aa–3ka**; entries 1–11). The general trend was that reactions were slower with electron-withdrawing and vice versa with electron-donating substituents in the *para* position, providing early indication of a cationic intermediate (for an intermolecular competition experiment, see the Supporting Information). However, the counteranion [A]$^-$ of the catalyst had an influence on the selectivity. This generally dropped to approx. 90:10 with [**5b**]$^+$[BAr^F_4]$^-$ but the high selectivity previously seen in the model reaction was restored with [**5b**]$^+$[$B(C_6F_5)_4$]$^-$. Alkyl- and likewise silyl-substituted alkynes **1l–1s** converted into alkynyl stannanes **3la–3sa** exclusively (entries 12–19). An enyne reacted also in good yield (**1t** → **3ta**; entry 20).—For comparison only, the hydrostannylation of an internal alkyne was tested; at 80 °C, 1-phenylprop-1-yne afforded the vinyl stannane as a 3:1 mixture of regioisomers (see the Supporting Information for details).

Table 2. Scope of the Dehydrogenative C(sp)–Sn Coupling[a]

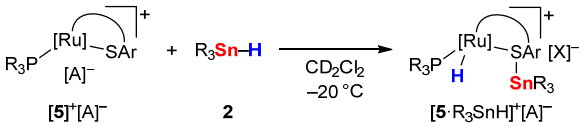


entry	alkyne **1**	counter-anion [A]$^-$	**3**:**4** (%)[b]	yield of **3** (%)[c]
1	**1a** (X = H)	[BAr^F_4]$^-$	>99:1	90[d] (**3aa**)
2	**1b** (X = 4-F)	[$B(C_6F_5)_4$]$^-$	>99:1	90 (**3ba**)
3[e]	**1c** (X = 4-CF_3)	[$B(C_6F_5)_4$]$^-$	99:1	82 (**3ca**)
4	**1d** (X = 4-CO_2Me)	[BAr^F_4]$^-$	>95:5[f]	75 (**3da**)
5	**1e** (X = 4-Cl)	[$B(C_6F_5)_4$]$^-$	96:4	86 (**3ea**)
6	**1f** (X = 4-Br)	[$B(C_6F_5)_4$]$^-$	>95:5[f]	83 (**3fa**)
7[e]	**1g** (X = 4-OMe)	[$B(C_6F_5)_4$]$^-$	>95:5[f]	85 (**3ga**)
8	**1h** (X = 4-Ph)	[$B(C_6F_5)_4$]$^-$	97:3	90 (**3ha**)
9	**1i** (X = 4-Me)	[BAr^F_4]$^-$	97:3	86 (**3ia**)
10	**1j** (X = 3-Me)	[BAr^F_4]$^-$	>99:1	86 (**3ja**)
11	**1k** (X = 2-Me)	[BAr^F_4]$^-$	>99:1	94 (**3ka**)
12	**1l** (R = Bn)	[BAr^F_4]$^-$	>95:5[f]	88 (**3la**)
13	**1m** (R = *c*Pent)	[BAr^F_4]$^-$	>99:1	90 (**3ma**)
14	**1n** (R = Cy)	[BAr^F_4]$^-$	>99:1	89 (**3na**)
15	**1o** (R = *n*Bu)	[BAr^F_4]$^-$	>99:1	92 (**3oa**)
16	**1p** (R = $(CH_2)_3Cl$)	[BAr^F_4]$^-$	>99:1	88 (**3pa**)
17[e]	**1q** (R = $(CH_2)_2Br$)	[BAr^F_4]$^-$	99:1	66 (**3qa**)
18[e]	**1r** (R = $SiMe_3$)	[$B(C_6F_5)_4$]$^-$	>99:1	87 (**3ra**)
19	**1s** (R = Si*i*Pr_3)	[BAr^F_4]$^-$	>99:1	45 (**3sa**)
20	**1t**	[BAr^F_4]$^-$	>99:1	84 (**3ta**)

[a]All reactions were performed according to General Procedure 1 (see the Supporting Information for details). [b]Unless otherwise noted, ratios were determined by GLC analysis using tetracosane as an internal standard. [c]Reactions were run until complete consumption of nBu$_3$SnH; isolated yields after filtration over Al_2O_3. [d]91% isolated yield were obtained on a 1.0 mmol scale. [e]Reaction was quenched after 48 h. [f]Ratio was determined by ^{1}H NMR analysis (no baseline separation in the GLC analysis).

To understand the reaction mechanism, we began with an investigation of the Sn–H bond activation. We had shown before that the Ru–S bond in cationic Ohki–Tatsumi complexes [**5**]$^+$[A]$^-$ splits dihydrogen[10] as well as main-group metal hydrides with Si–H,[11,12] B–H,[14] and Al–H[13] bonds into the corresponding neutral ruthenium(II) hydride and the sulfur-stabilized main-group electrophile. Hence, combining complexes [**5**]$^+$[A]$^-$ and hydrostannanes **2** in CD_2Cl_2 at −78 °C instantly delivered the hydrostannane adducts [**5**·R_3SnH]$^+$[A]$^-$. These fleeting intermediates were fully characterized by NMR spectroscopy at −20 °C or −60 °C (Table 3).[15] The observed hydride shifts at δ(^{1}H) ~ −8.5 ppm and $^2J_{H,P}$ coupling constants of ~48 Hz were similar to those found for hydrosilane adducts.[10b] The $\Delta\delta$ value in the ^{119}Sn NMR spectrum for the adduct formation of nBu$_3$SnH (**2a**) is approx. 246 ppm, arising from −86.6 ppm for **2a** to approx. +155 ppm for [**5**·nBu$_3$SnH]$^+$[A]$^-$ (entry 1 vs entries 3–6). Et_3SnH (**2b**) exhibited the same trend (entry 7), and Ph_3SnH (**2c**) again led to decomposition (entry 8). Those downfield shifts are strong evidence for the formation of stannylium-like electrophiles.[16] For comparison, the resonance signal of neutral DmpSSnnBu$_3$ (Dmp = 2,6-dimesitylphenyl) is at δ(^{119}Sn) +79.6 ppm (entry 2), and other known heteroatom-stabilized stannylium ions are in the same range, e.g., δ(^{119}Sn) +165 ppm for [nBu$_3$Sn(OEt$_2$)]$^+$[BAr^F_4]$^-$ (entry 9).[16a] The chemical shifts of benzene-coordinated [nBu$_3$Sn(C_6H_6)]$^+$ [$B(C_6F_5)_4$]$^-$ and *free* [nBu$_3$Sn]$^+$[BAr^F_4]$^-$ have been detected at δ(^{119}Sn) +263 ppm[16b] and +356 ppm,[16a] respectively (entries 10 and 11).

Table 3. Sn–H Bond Activation at the Ru–S Bond: $^2J_{H,P}$ Coupling Constants as well as ^{1}H and ^{119}Sn NMR Shifts of the Hydrostannane Adducts[a]



entry	adduct	$^2J_{H,P}$ [Hz]	^{1}H NMR [ppm]	^{119}Sn NMR [ppm]
1	nBu$_3$SnH (**2a**)	—	+4.7	−86.6
2	DmpSSnnBu$_3$	—	—	+79.6

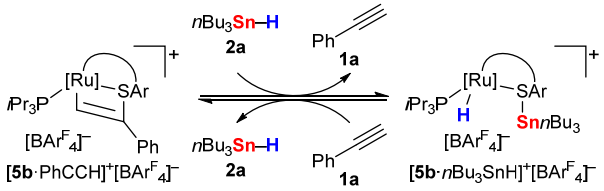
3[b]	[**5a**·nBu$_3$SnH]$^+$[BAr$^F_4$]$^-$	49.7	–8.6	+158.1
4	[**5b**·nBu$_3$SnH]$^+$[BAr$^F_4$]$^-$	47.7	–8.4	+156.5
5	[**5c**·nBu$_3$SnH]$^+$[BAr$^F_4$]$^-$	48.7	–8.6	+151.1
6[b]	[**5d**·nBu$_3$SnH]$^+$[BAr$^F_4$]$^-$	49.5	–8.3	+154.5
7	[**5b**·Et$_3$SnH]$^+$[BAr$^F_4$]$^-$	47.0	–8.4	+150.2
8[c]	[**5b**·Ph$_3$SnH]$^+$[BAr$^F_4$]$^-$	—	—	—
9[16a]	[nBu$_3$Sn(OEt$_2$)]$^+$[BAr$^F_4$]$^-$	—	—	+165
10[16b]	[nBu$_3$Sn(C$_6$H$_6$)]$^+$[B(C$_6$F$_5$)$_4$]$^-$	—	—	+263
11[16a]	[nBu$_3$Sn]$^+$[BAr$^F_4$]$^-$	—	—	+360

[a]Experiments were performed in a J. Young NMR tube using complexes [**5**]$^+$[A]$^-$ (1.0 equiv) and hydrostannane **2** (1.2 equiv).[b]NMR characterization performed at –60 °C [c]Decomposition was observed.

As for the hydrosilane activation,[10b] [**5b**]$^+$[BAr$^F_4$]$^-$ promoted ^{1}H/^{2}H scrambling between nBu$_3$SnD (**2a**-d_1) and Et$_3$SnH (**2b**). In our hands, no deuterium exchange occurred in the absence of the catalyst at 30 °C[17] (see the Supporting Information for details).

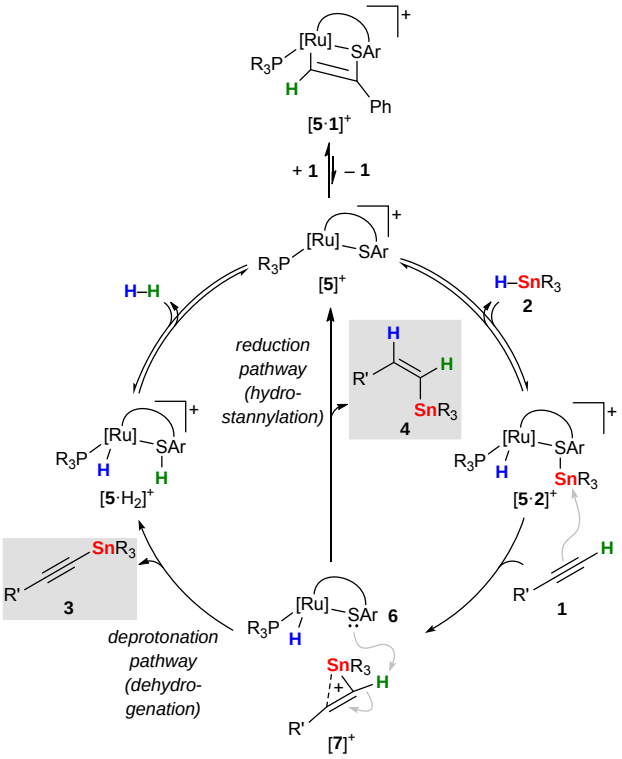
That proven Sn–H bond activation competes, however, with the addition of the Ru–S bond across the C–C triple bond of the substrate. Ohki and Tatsumi had described the adduct formation of [**5**]$^+$[BAr$^F_4$]$^-$ and an aryl- as well as an alkyl-substituted acetylene before;[10a] the molecular structure of the resulting Markovnikov adduct [**5**·PhCCH]$^+$[BAr$^F_4$]$^-$ with Ph$_3$P as ligand was crystallographically secured. The interconversion of [**5b**·PhCCH]$^+$[BAr$^F_4$]$^-$ and [**5b**·nBu$_3$SnH]$^+$[BAr$^F_4$] by dissociative processes was then demonstrated by us (Scheme 1). Both setups, that is premixing [**5b**]$^+$[BAr$^F_4$]$^-$ with either phenyl acetylene (**1a**) or nBu$_3$SnH (**2a**) prior to the addition of the other reactant, led to the formation of the alkynyl stannane **3aa** (see the Supporting Information for details). This is further evidence of the reversibility of both the addition across the C–C triple bond and the Sn–H bond. We also found that the reaction is faster starting from [**5b**·nBu$_3$SnH]$^+$[BAr$^F_4$]$^-$, indicating that the generation of [**5b**·**1a**]$^+$[BAr$^F_4$]$^-$ is favored over [**5b**·**2a**]$^+$[BAr$^F_4$]$^-$.

Scheme 1. Competitive Activation of the Hydrostannane and the Terminal Alkyne



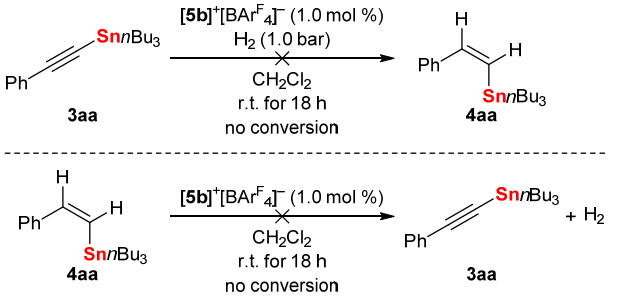
Based on the above and our earlier[12] observations, we delineate the following catalytic cycle (Scheme 2). Alkyne adduct [**5**·**1**]$^+$[BAr$^F_4$]$^-$ is an off-cycle intermediate, reversibly converting into the stannane adduct [**5**·**2**]$^+$[BAr$^F_4$]$^-$ through catalyst [**5**]$^+$[BAr$^F_4$]$^-$ (cf. Scheme 1). The stannylium-ion-like electrophile [**5**·**2**]$^+$[BAr$^F_4$]$^-$ is then nucleophilically attacked by the C–C triple bond of **1** to yield a β-tin-stabilized[18] vinyl cation[19] along with the ruthenium(II) hydride **6**. According to Wrackmeyer's work,[20] that vinyl cation is best represented as the bridged structure [**7**]$^+$[BAr$^F_4$]$^-$. These neutral complexes **6** are rather poor hydride donors,[21] and the sulfur atom in **6** serves as an internal Brønsted base instead.[12] Hence, **6** abstracts the proton α to the tin atom in [**7**]$^+$[BAr$^F_4$]$^-$ to reestablish the C–C triple bond ([**7**]$^+$[BAr$^F_4$]$^-$ → **3**, *deprotonation pathway*). The resulting dihydrogen adduct [**5**·H$_2$]$^+$[BAr$^F_4$]$^-$ of catalyst [**5**]$^+$[BAr$^F_4$]$^-$ eventually releases H$_2$ gas, thereby completing the dehydrogenation.[10] The vinyl stannane **4** is, if at all, seen in minor quantities and likely stemming from the competing but disfavored hydride transfer ([**7**]$^+$[BAr$^F_4$]$^-$ → **4**, *reduction pathway*). To exclude the possibility of dehydrogenation followed by hydrogenation (**1** → **3** → **4**)[22] or hydrostannylation followed by dehydrogenation (**1** → **4** → **3**), we performed two control experiments (Scheme 3). Catalyst [**5b**]$^+$[BAr$^F_4$]$^-$ was neither able to reduce the alkynyl stannane (**3aa** → **4aa**; top) nor to dehydrogenate the vinyl stannane (**4aa** → **3aa**; bottom).

Scheme 2. Catalytic Cycle for the Dehydrogenative Stannylation of Alkynes[a]



[a]The BAr$^F_4$$^-$ counteranion was omitted for the sake of clarity.

Scheme 3. Attempted Hydrogenation of an Alkynyl Stannane and Dehydrogenation of a Vinyl Stannane



To summarize, we reported here the catalytic activation of the Sn–H bond in hydrostannanes (tin hydrides) by heterolytic cleavage at the Ru–S bond of cationic ruthenium(II)

complexes. This cooperative bond activation[11] leads to a stannylium-ion-like tin electrophile together with the corresponding neutral ruthenium hydride. With this catalyst–hydrostannane adduct terminal acetylenes are converted into alkynyl stannanes; hardly any or no vinyl stannane is detected. This outcome, that is the preference of dehydrogenation over reduction, has been rationalized by the intermediacy of a tin-bridged vinyl cation which is deprotonated by the sulfur atom in the ruthenium(II) hydride rather than reduced by the ruthenium(II) hydride. The mild method is of broad scope and a rare example of a direct C(sp)–H stannylation with hydrostannanes.

ASSOCIATED CONTENT

Supporting Information

Experimental details, characterization as well as ^{1}H, ^{13}C, ^{11}B, ^{19}F, ^{31}P, and ^{119}Sn NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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REFERENCES

(1) Schaub, T. A.; Kivala, M. In *Metal-Catalyzed Cross-Coupling Reactions and More*; de Meijere, A., Bräse, S., Oestreich, M., Eds.; Wiley-VCH: Weinheim, Germany, 2014, pp 665–762.

(2) *The Stille Reaction*; Farina, V., Krishnamurthy, V., Scott, W. J.; Wiley: New York, 2004.

(3) Hartmann, H.; Honig, H. *Angew. Chem.* **1957**, *69*, 614 (R_3SnCl and R_3SnBr with R = alkyl and aryl).

(4) Jones, K.; Lappert, M. F. *J. Organomet. Chem.* **1965**, *3*, 295–307.

(5) (a) Neumann, W. P.; Kleiner, F. G. *Tetrahedron Lett.* **1964**, *5*, 3779–3782. (b) Kleiner, F. G.; Neumann, W. P. *Liebigs Ann. Chem.* **1968**, *716*, 19–28.

(6) Kiyokawa, K.; Tachikake, N.; Yasuda, M.; Baba, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 10393–10396.

(7) Mitchell, T. N.; Moschref, S.-N. *Synlett* **1999**, 1259–1260.

(8) (a) Yoshida, H. *Synthesis* **2016**, *48*, 2540–2552. (b) Trost, B. M.; Ball, Z. T. *Synthesis* **2005**, 853–887.

(9) Toutov, A. A.; Betz, K. N.; Schuhman, D. P.; Liu, W.-B.; Fedorov, A.; Stoltz, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2017**, *139*, 1668–1674.

(10) (a) Ohki, Y.; Takikawa, Y.; Sadohara, H.; Kesenheimer, C.; Engendahl, B.; Kapatina, E.; Tatsumi, K. *Chem. - Asian J.* **2008**, *3*, 1625–1635. (b) Lefranc, A.; Qu, Z.-W.; Grimme, S.; Oestreich, M. *Chem. - Eur. J.* **2016**, *22*, 10009–10016.

(11) (a) Omann, L.; Königs, C. D. F.; Klare, H. F. T.; Oestreich, M. *Acc. Chem. Res.* **2017**, *50*, 1258–1269. (b) Stahl, T.; Hrobárik, P.; Königs, C. D. F.; Ohki, Y.; Tatsumi, K.; Kemper, S.; Kaupp, M.; Klare, H. F. T.; Oestreich, M. *Chem. Sci.* **2015**, *6*, 4324–4334.

(12) (a) Klare, H. F. T.; Oestreich, M.; Ito, J.-i.; Nishiyama, H.; Ohki, Y.; Tatsumi, K. *J. Am. Chem. Soc.* **2011**, *133*, 3312–3315. (b) Königs, C. D. F.; Klare, H. F. T.; Ohki, Y.; Tatsumi, K.; Oestreich, M. *Org. Lett.* **2012**, *14*, 2842–2845. (c) Königs, C. D. F.; Müller, M. F.; Aiguabella, N.; Klare, H. F. T.; Oestreich, M. *Chem. Commun.* **2013**, *49*, 1506–1508. (d) Hermeke, J.; Klare, H. F. T.; Oestreich, M. *Chem. - Eur. J.* **2014**, *20*, 9250–9254. (e) Omann, L.; Oestreich, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 10276–10279.

(13) Forster, F.; Metsänen, T. T.; Irran, E.; Hrobárik, P.; Oestreich, M. *J. Am. Chem. Soc.* **2017**, *139*, 16334–16342.

(14) Stahl, T.; Müther, K.; Ohki, Y.; Tatsumi, K.; Oestreich, M. *J. Am. Chem. Soc.* **2013**, *135*, 10978–10981.

(15) Depending on the phosphine ligand, hydrostannane adducts $[\mathbf{5}{\cdot}R_3SnH]^+[A]^-$ decompose at room temperature within a few hours. Sufficient chemical stability is secured at –20 °C or –60 °C, and NMR spectra are meaningful at this temperature.

(16) (a) Kira, M.; Oyamada, T.; Sakurai, H. *J. Organomet. Chem.* **1994**, *471*, C4–C5. (b) Lambert, J. B.; Zhao, Y.; Wu, H.; Tse, W. C.; Kuhlmann, B. *J. Am. Chem. Soc.* **1999**, *121*, 5001–5008. (c) Zharov, I.; King, B. T.; Havlas, Z.; Pardi, A.; Michl, J. *J. Am. Chem. Soc.* **2000**, *122*, 10253–10254. (d) Lambert, J. B.; Lin, L.; Keinan, S.; Müller, T. *J. Am. Chem. Soc.* **2003**, *125*, 6022–6023. (e) Wright II, J. H.; Mueck, G. W.; Tham, F. S.; Reed, C. A. *Organometallics* **2010**, *29*, 4066–4070.

(17) Neumann and Sommer had reported rapid scrambling without a catalyst at 40 °C: Neumann, W. P.; Sommer, R. *Angew. Chem., Int. Ed.* **1963**, *2*, 547.

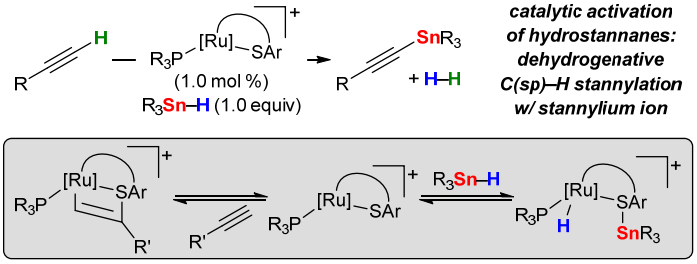
(18) For the β-effect of the stannyl group in the stabilization of vinyl cations, see: Dallaire, C.; Brook, M. A. *Organometallics* **1990**, *9*, 2873–2874.

(19) For a recent review of vinyl cations, see: Vasilyev, A. V. *Russ. Chem. Rev.* **2013,** *82*, 187–204 and cited references.

(20) Wrackmeyer, B.; Kundler, S.; Boese, R. *Chem. Ber.* **1993**, *126*, 1361–1370.

(21) Stahl, T.; Klare, H. F. T.; Oestreich, M. *J. Am. Chem. Soc.* **2013**, *135*, 1248–1251.

(22) Bähr, S.; Oestreich, M. *Organometallics* **2017**, *36*, 935–943.


R
H
[Ru]
SAr
R3P
(1.0 mol %)
R3Sn–H (1.0 equiv)
SnR3
+ H–H
catalytic activation of hydrostannanes: dehydrogenative C(sp)–H stannylation w/ stannylium ion
R'
R3Sn–H