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Regioselective Formation of (*E*)-β-Vinylstannanes by a Topologically-Controlled Molybdenum-Based Alkyne Hydrostannation Catalyst

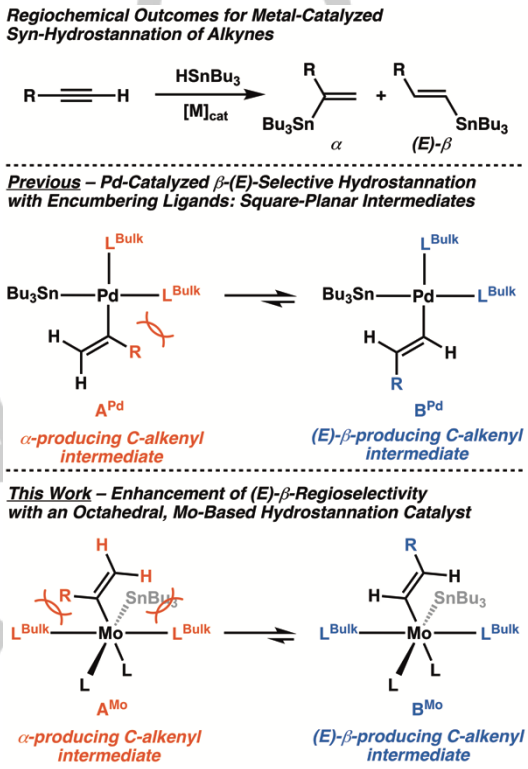
Kyle A. Mandla, Curtis E. Moore, Arnold L. Rheingold and Joshua S. Figueroa*

Dedication ((optional))

Abstract: Regioselective formation of (*E*)-β-vinylstannanes has been a long-standing challenge in transition-metal-catalyzed alkyne hydrostannation. Here we report a well-defined molybdenum-based system featuring two encumbering *m*-terphenyl isocyanides that reliably and efficiently delivers high regioselectivity for (*E*)-β–vinylstannanes from a range of terminal and internal alkynes. The system is particularly effective for aryl alkynes and can discriminate between alkyl chains of low steric encumbrance in unsymmetrically-substituted dialkyl alkynes. Catalytic hydrostannation in this system is also characterized by an electronic effect that degrades regioselectivity when electron-withdrawing groups are present on the alkyne substrate.

Vinylstannanes are well recognized as versatile synthetic precursors for C-C bond formation reactions.[1-2] Accordingly, transition-metal-catalyzed alkyne hydrostannation has been extensively investigated as an efficient, atom-economical route to vinylstannanes.[3-4] However, despite substantial progress in the development of alkyne hydrostannation catalysts, precise control over hydrometallation regioselectivity continues to be an important challenge. Several catalysts have now been reported that reliably provide α-vinnylstannane products via catalyst-controlled hydrometallation (Scheme 1, top).[3-11] In contrast, catalysts that deliver (*E*)-β-vinylstannanes by regioselective *syn* Sn-H addition have been particularly difficult to develop for alkyne substrates that lack steric or electronic directing groups (Scheme 1, top).[4,12-16] Indeed, the only systems known to provide reasonable regioselectivity for (*E*)-β-vinylstannanes are highly-encumbered palladium/phosphine catalysts that operate through a formal Pd(0)/Pd(II) couple.[3,4,12,14,15] However, the regioselectivity of these systems is not general over a wide scope of substituted alkynes,[4,15] and the systems lack the predictability associated with the most highly-regioselective catalysts for the production of α-vinylstannanes.

A commonality among the Pd catalysts that show selectivity for (*E*)-β-vinylstannanes is the formation of a square-planar, *cis*-Pd(*C*-alkenyl)(SnR_3)L_2 intermediate during the hydrometallation process (Scheme 1 middle). The square-planar coordination geometry of this intermediate positions ancillary ligands both *cis* and *trans* to the key *C*-alkenyl fragment that is generated upon initial hydride transfer to the alkyne substrate. When these catalyst systems are sufficiently encumbered, it has been argued that regioselectivity for (*E*)-β-vinylstannanes originates from steric pressure between the *cis*-ancillary ligand and the α-vinylstannane-producing *C*-alkenyl unit (Intermediate **A^{Pd}**, Scheme 1).[15] These unfavorable interactions encourage the formation of the (*E*)-β-vinylstannane-producing *C*-alkenyl intermediate, where steric interference from the *cis*-ancillary ligand is minimized (**B^{Pd}**, Scheme 1). Based on this postulate, we reasoned that a modified catalyst architecture, where *two* encumbering ligands are positioned *cis* to the *C*-alkenyl unit, could further destabilized the formation of α-vinylstannane-producing intermediates and lead to increased regioselectivity for the formation of (*E*)-β-vinylstannanes via *syn*-hydrometallation.



Scheme 1. (top) Generalized reaction scheme for the production of vinylstannane regio-isomers from metal-catalyzed syn-hydrostannation of terminal alkynes. (middle) The key square-planar, *C*-alkenyl intermediates proposed to be responsible for regioselectivity in Pd-catalyzed alkyne hydrostannation. (bottom) Coneptual framework for enhancement of (*E*)-β-regioselectivity by application of additional steric pressures in a six-coordinate Mo-based alkyne-hydrostannation catalyst system. L^{Bulk} = encumbering ligand.

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Accordingly, we sought to develop an encumbered alkyne-hydrostannation system where an overall octahedral metal coordination geometry was conserved throughout the hydrometallation process. Such a modification would allow two additional axial ligands to exert mutually-*cis* steric pressures on a *C*-alkenyl unit in a manner not achivable for systems that generate square-planar intermediates (Scheme 1, bottom).[3,4,12,14,15]

Previously, we reported the six-coordinate complex, $MoI_2(CO)_2(CNAr^{Dipp2})_2$ (**1**; Ar^{Dipp2} = 2,6-(2,6-(*i*-Pr)$_2$C$_6$H$_3$)$_2$C$_6$H$_3$; Figure 1),[17] which features two sterically encumbering *m*-terphenyl isocyanide ligands in a *trans* orientation.[18-20] Notably, diiodide **1** is related to the six-coordinate, *cis*-Mo(*C*-alkenyl)(SnR$_3$)L$_4$ intermediates proposed by Kazmaier for alkyne hydrostannation by the zero-valent, tris-isocyanide tricarbonyl catalyst precursor, Mo(CN-*t*-Bu)$_3$(CO)$_3$).[6,21-25] Indeed, Mo(CN-*t*-Bu)$_3$(CO)$_3$ possesses relatively unencumbered ligands and, correspondingly, its use as an alkyne hydrostannation pre-catalyst results in excellent regioselectivity for α-vinylstannanes.[6,21-25] Here we show that the more sterically encumbered complex **1** also serves as a highly-efficient alkyne-hydrostannation catalyst precursor. However, due to its increased steric profile, **1** affords regioselective formation of (*E*)-β-vinylstannanes for a wide scope of terminal and unsymmetrically-substituted internal alkynes without the need for sterically-biased substrates. Pre-catalyst **1** can be activated readily under mild conditions to a well-defined and stabilized 14e$^-$ zero-valent active species, in which the rigid and encumbering *trans* topology of the *m*-terphenyl isocyanide ligands is maintained. In addition, we show that this ligand orientation is responsible for the system's high regioselectivity for (*E*)-β-vinylstannanes, which can be further modulated by substrate-dependent electronic perturbation of key intermediates during hydrometallation.

In an initial screen of **1** for catalytic hydrostannation, diphenyl acetylene was chosen as a test substrate. Using 2 mol% **1** and 1.05 equiv of HSnBu$_3$, the *syn*-hydrostannation product (*E*)-tributyl(1,2-diphenylvinyl)stannane was produced in 98% isolated yield after 20 min of reaction at room temperature in C$_6$D$_6$ solution (Figure 1, top). Notably, the efficiency of this reaction at room temperature indicates that diiodide **1** is rapidly converted to a catalytically-active species. Indeed, treatment of diiodide **1** with 2.0 equiv of HSnBu$_3$ in the absence of alkyne substrate leads rapidly to the Mo(0) tetracarbonyl complex $Mo(CO)_4(CNAr^{Dipp2})_2$ (**2**)[18] through an apparent reduction/ligand redistribution process, along with H$_2$ and ISnBu$_3$, as assayed by ^{1}H NMR spectroscopy and GCMS. Hydride-for-halide exchange has been observed previously in reactions between HSnBu$_3$ and metal-halide complexes and likely proceeds by a radical-chain mechanism.[26-27] Accordingly, for this system, we propose that a double H/I exchange process produces an intermediate Mo(0) ML$_4$ species that is active for alkyne hydrostannation, but redistributes when substrate is not present (Figure 1).

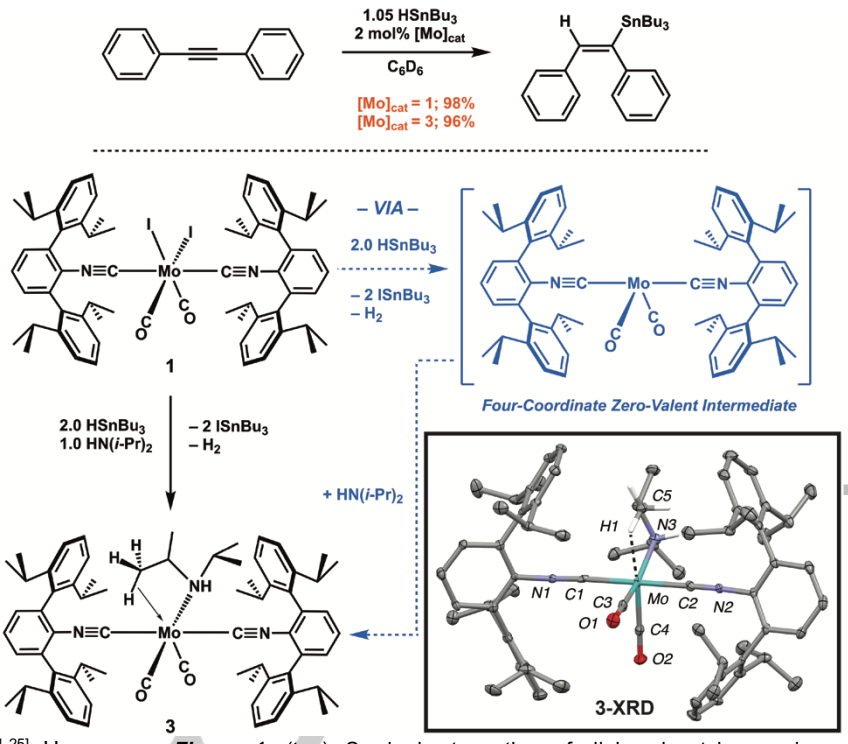

Figure 1. (top) *Syn*-hydrostannation of diphenylacetylene using molybdenum pre-catalysts **1** and **3**. (bottom) Synthesis, proposed formation and molecular structure of the zero-valent amine/*C,H*-agostic complex **3** from divalent diiodide **1**. Selected bond distances (Å) and angles (°) for **3**: Mo-H1 = 2.126(5), Mo-C5 = 2.806(2), Mo-N3 = 2.327(3), Mo-H1-C5 = 125.11(30).[36]

Most notably, when diiodide **1** is treated with stoichiometric HSnBu$_3$ in the presence of diisopropylamine (HN(*i*-Pr)$_2$), the Mo(0) amine/C-H-agostic complex **3** can be isolated in *ca.* 80% yield (Figure 1). Structural characterization of complex **3** reveals a *trans*-orientation of $CNAr^{Dipp2}$ ligands similar to that found in diiodide **1** and an HN(*i*-Pr)$_2$ ligand bound through an unusual κ^1-*N*/η^2-*H,C* chelate (Figure 1). The isolation of complex **3** strongly suggests that the four-coordinate, zero-valent species $[Mo(CO)_2(CNAr^{Mes2})_2]$, which is analogous to the intermediate proposed for hydrostannation by Mo(CN-*t*-Bu)$_3$(CO)$_3$,[21] is likely produced in this reaction sequence and is sufficiently reactive to be trapped with a weakly-coordinating substrate such as HN(*i*-Pr)$_2$. Consistent with this notion, **3** is also highly active for diphenylacetylene hydrostannation, producing the corresponding vinylstannane in 96% isolated yield under the same reaction conditions as those employed for diiodide **1** (Figure 1, top).

Whereas complex **3** yields an active system for catalysis, the operational simplicity of *in situ* activation of diiodide **1** with only a slight excess HSnBu$_3$ rendered it our preferred precursor for additional hydrostannation studies. Accordingly, at 2.0 mol% loading, complex **1** is effective for the hydrostannation of a range of terminal and internal alkynes to (*E*)-β-vinylstannanes with exceptional regioselectivity. In addition, catalytic hydrostannation mediated by **1** proceeds efficiently at room temperature using only 1.05 equiv of HSnBu$_3$ per alkyne substrate and without need for additives or radical scavengers (Table 1).[6,24] For example, under these conditions, **1** converts phenylacetylene to the corresponding (*E*)-β-vinylstannane with 13:87 α:(*E*)-β regioselectivity after 20 min in C$_6$D$_6$ solution (entry 1). The (*Z*)-β-

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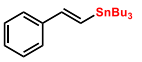
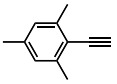
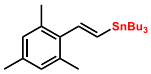
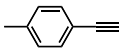
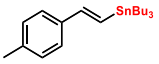
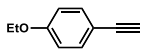
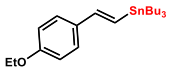
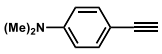
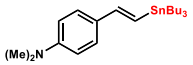
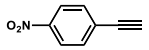
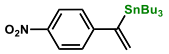
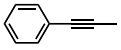
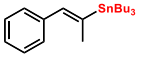
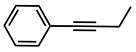
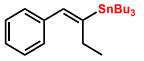
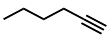
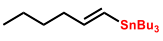
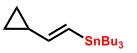
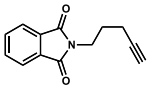
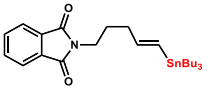
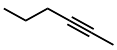
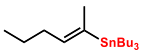
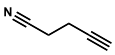
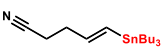
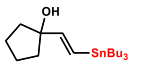
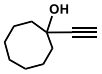
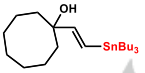
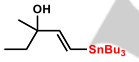
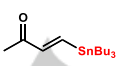
Table 1. Hydrostannation of Aryl and Alkyl Alkynes using $MoI_2(CO)_2(CNAr^{Dipp2})_2$ (**1**).[a]

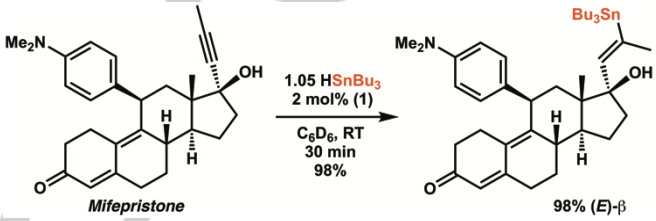
Entry	R_1—≡—R_2	Major Product	Select.[b] (% (*E*)-β)	Yield[c] (%)
1			87	95
2			98	97
3			91	92
4			98	94
5			99	93
6			45	86
7			92	94
8			80	96
9			91	94
10			91	93
11			92	94
12			89	94
13			61	84
14			90	92
15			97	97
16			83	92
17			78	95

[a] Reaction conditions: 2.0 mol % **1**; 1.05 equiv $HSnBu_3$; C_6D_6; room temperature; 30 min. [b] Selectivity determined by ^1H NMR analysis of the reaction mixture. [c] Isolated as a mixture of α and β-(*E*) isomers. All runs showed complete conversion to vinylstannanes in crude reaction mixtures.

vinylstannane isomer, which is known to form in some metal-catalyzed hydrostannation processes,[4] is not produced in this reaction. Notably, this level of α:(*E*)-β regioselectivity for phenylacetylene hydrostannation is markedly superior to that of the well-utilized catalyst precursor $PdCl_2(PPh_3)_2$ (*i.e.* α:(*E*)-β = 46:54).[4-5] Complex **1** also out-performs the more encumbered catalyst system $Pd_2(dba)_3$/$[HPCy_3]BF_4$/$NEt(i\text{-}Pr)_2$, which has previously yielded the greatest level of α:(*E*)-β regioselectivity for phenylacetylene hydrostannation (*i.e.* α:(*E*)-β = 19:81).[15]

Other terminal aryl alkynes can also be converted with high regioselectivity. As shown in Table 1, complex **1** transforms sterically demanding (entry 2) and electron-rich (entries 3-5) terminal aryl alkynes to (*E*)-β-vinylstannanes with regioselectivities greater than 98%. Similarly, unsymmetrically-substituted aryl-alkyl internal alkynes can be converted to vinylstannanes with a high degree of preferential placement of the [$SnBu_3$] unit proximal to the alkyl group (i.e. formal α-H addition; entries 7 and 8).[28] These results indicate that the catalytic intermediates generated by complex **1** likely impose strong steric control over alkyne orientation during hydrostannation. However, it is critical to note that the presence of strongly electron-withdrawing substituents, such as in the case of *p*-nitrophenyl acetylene, significantly degrades the regioselectivity displayed by the system (entry 6). In fact, for this substrate, the α-vinylstannane is marginally favored.

Scheme 2. Hydrostannation of mifepristone using pre-catalyst **1**.



Remarkably, aliphatic alkynes also undergo hydrostannation to (*E*)-β-vinylstannanes with high regioselectivity using complex **1** (entries 9-13). Of these latter examples, the conversion of 2-hexyne to the corresponding (*E*)-β-vinylstannane with 9:91 α:(*E*)-β regioselectivity is particularly noteworthy (entry 12), as this result indicates that the molecular topology accessible from **1** can finely discriminate between methyl and propyl groups on opposing ends of an unsymmetrically-substituted dialkyl alkyne. However, when electron-withdrawing substituents are present, as in the case of 4-cyano-1-butyne (entry 13), the regioselectivity of the hydrostannation process is again diminished. This observation illustrates that the electronic properties of the alkyne substrate can alter the regioselectivity governed by the inherent topological features of the catalyst system. It is also important to note that sterically-biased propargyl alcohols can be converted to β-(*E*)-vinylstannanes with high regioselectivity (entries 14-16), as has been reported previously for other hydrostannation catalysts.[4] Accordingly, the scope of regioselective alkyne hydrostannation to (*E*)-β-vinylstannanes using complex **1** is expanded, rather than compromised, relative to other catalyst systems. To this end, it is noteworthy that **1** produces the (*E*)-β-vinylstannane isomer of mifepristone (Scheme 2) with 2:98 α:(*E*)-β regioselectivity and in 98% yield, thereby demonstrating that a fair degree of molecular complexity can be accommodated by the system without loss of selectivity or activity. Catalysis can be scaled without significant loss of selectivity or activity as well. This was demonstrated by the hydrostannation of 1.0 g of the internal alkyne 1-phenyl-1-propyne, which proceeds in 90% yield and 91% regioselectivity for the (*E*)-β-vinylstannane isomer at room temperature in 2 hours. Nevertheless, use of 3-butyne-2-one results in a non-negligible degradation of regioselectivity (entry 17), further illustrating that electron-withdrawing groups predictably alter the regiochemical outcome of hydrostannation in this system.[29]

A preliminary assessment of the hydrostannation mechanism by both experimental and computational studies

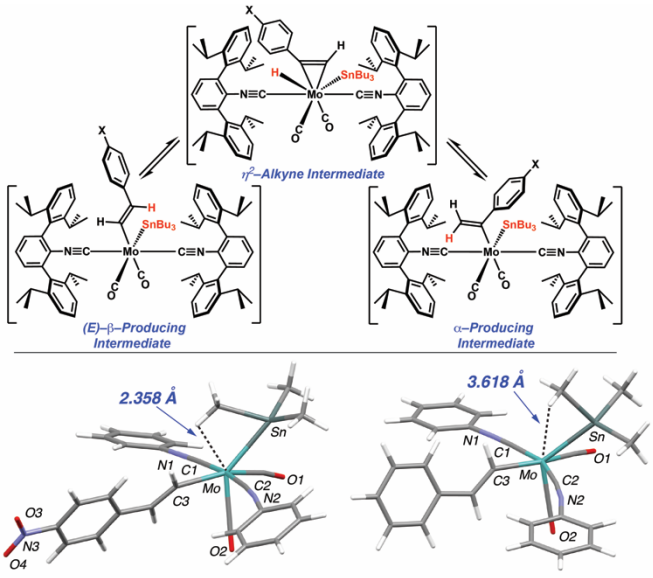


Figure 2. (top) Proposed interconversion of Mo-based (*E*)-β- and α-producing *C*-alkenyl intermediates via reversible β-H elimination/migratory insertion. (bottom) DFT-calculated structures for (*E*)-β-producing, aryl-substituted Mo-based *C*-alkenyl intermediates for X = NO_2 (left) and H (right), with closest Mo···H contacts between the $SnMe_3$ group indicated.

suggests that the encumbering steric profile of the $CNAr^{Dipp2}$ ligands is primarily responsible for the regiochemical preference of hydrostannation in post-insertion steps. However, the electronic properties of the alkyne substrates also exert an important influence over the properties of certain intermediates along the hydrostannation pathway. Hydrostannation of phenylpropyne using complex **1** and a 1:1 mixture of $HSnBu_3$/$DSnBu_3$ (3:1 $[Sn]_{tot}$:[alkyne]) resulted in an intermolecular-competition H/D isotope effect of 1.11(7), thereby indicating that neither Sn-H bond cleavage nor C-H bond formation, through either migratory-insertion or reductive elimination, are the rate limiting aspects of catalysis in this system.[30-31] Importantly, a plot of log(α:(*E*)-β) vinylstannane isomeric ratio vs Hammett σ^+-parameter (Figure S4.4) for the *p*-substituted terminal aryl alkynes listed in Table 1 reveals a distinct positive correlation between selectivity for the (*E*)-β-vinylstannane isomer and electron-releasing capacity of the *para* substituent. We believe these observations reflect that the electronic properties of the alkyne substrate affect the stability of post-insertion intermediates, which are ulitimately responsible for dictating the regiochemical outcome of the hydrostannation processs prior to rate-limiting Sn-C bond reductive elimination.

It has been well established that Chalk-Harrod-type hydrometallation processes are governed by interconversion of *C*-alkenyl metal intermediates via reversible hydride migratory insertion/β-H elimination (Figure 2).[32-34] In addition, in our studies on Group 6 metal complexes featuring two $CNAr^{Dipp2}$ ligands, we have previously shown that the steric encumbrance of these isocyanides enforce a mutually-*trans* orientation through multiple redox transformations of the metal center.[18-19] We believe that to relieve steric pressures, this constrained, *trans*-isocyanide environment around the metal center shifts the equilibrium between the two *C*-alkenyl insertion products to the configuration favoring production of the (*E*)-β-vinylstannane isomer (Figure 2). This argument is analogous to that made for regioselective (*E*)-β-vinylstannane formation using Pd and encumbering phosphine ligands,[15] with the added feature that two *cis*-oriented ligands provide steric pressures in this six-coordinate Mo system.

Notably, DFT calculations on the truncated, *C*-alkenyl intermediates, $[Mo(\kappa^1\text{–}C\text{–}(C(H)=C(H)C_6H_4\text{-}p\text{-}X))(SnMe_3)(CNPh)_2(CO)_2]$, which would give rise to (*E*)-β-vinylstannanes after C-Sn bond reductive elimination, optimize to stable minima and have unremarkable structural features for X = H, Me, OMe and NMe_2 (Figure 2 and S5.1). However, for X = NO_2, the calculations reveal a pronounced *H,C*-agostic interaction between the Mo center and a methyl group of trimethylstannyl unit (Figure 2). This result indicates that the Lewis acidity of the Mo center is augmented when electron-withdrawing substituents are present on the (*E*)-β-producing *C*-alkenyl intermediate. Inclusion of the full $SnBu_3$ ligand in the calculations also results in a stable minimum featuring an agostic interaction between an α-methylene group and the Mo center (Figure S5.2). We therefore tentatively propose that this increase in metal Lewis acidity may produce a favorable pathway for β-hydride elimination/alkyne-reinsertion to the α-vinylstannane-producing *C*-alkenyl intermediate,[35] despite the steric preference of the catalyst. Lending credence to this notion is finding that hydrostannation of *p*-nitrophenylacetylene with $Mo(CN\text{-}t\text{-}Bu)_3(CO)_3$ produces the α-vinylstannane with >98% regioselectivity (see the ESI), thereby indicating that in the absence of encumbering ligands, the electronic profile of the alkyne dominates the regiochemical outcome. While we are further evaluating the validity of this mechanistic proposal, the combined observations suggest that regioselective production of (*E*)-β-vinylstannanes by complex **1** is sterically driven, but can be predictably modulated by the electronic properties of the alkyne substrate or a reduction in the steric profile of the Mo catalyst. Nevertheless, we anticipate that this catalytic alkyne-hydrostannation system may be particularly useful in applications when (*E*)-β-vinylstannanes are desired and strongly electron-withdrawing substituents are not in close proximity to either end of the alkyne substrate.

Acknowledgements

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Keywords: Catalysis • Hydrostannaton • Alkynes • Molybdenum • Isocyanides

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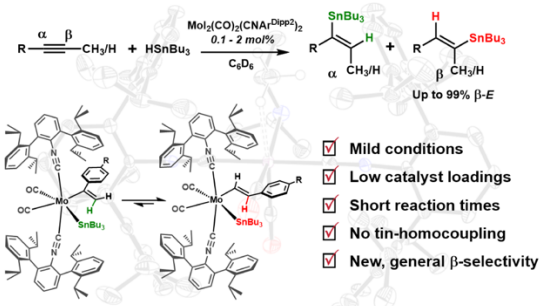
Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Opposite side of the issue: Alkyne hydrostannation catalysts are traditionally effective at providing 1,1-vinylstannanes (α-products), with the selective delivery of *E*-1,2- vinylstannanes ((*E*)-β-products) being much more challenging. Reported here is a highly regioselective Mo/isocyanide-based catalyst that overcomes this difficulty.



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Regioselective Formation of (E)-β-Vinylstannanes by a Topologically-Controlled Molybdenum-Based Alkyne Hydrostannation Catalyst