Hydrosilylation

Regiodivergent and Stereoselective Hydrosilylation of 1,3-Disubstituted Allenes**

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Abstract: Methods for the highly stereoselective and regiodivergent hydrosilylation of 1,3-disubstituted allenes have been developed. The synthesis of E allylsilanes is accomplished with palladium NHC catalysts, and trisubstituted Z alkenylsilanes are accessed with nickel NHC catalysts. Unsymmetrically substituted allenes are well tolerated with nickel catalysis and afford Z alkenylsilanes. Evidence for a plausible mechanism was obtained through an isotopic double-labeling crossover study.

Alkenyl- and allylsilanes are both useful structural classes for a broad array of synthetic transformations.[1] For example, alkenylsilanes are versatile nucleophiles in Hiyama–Denmark cross-couplings,[2] and allylsilanes are attractive intermediates for cycloaddition reactions[3] and allylation processes.[4] The benefits of silane reagents over alternative metalated species are their low toxicity, ease of isolation and storage, and stability through multistep synthetic sequences without observed degradation.[1] Numerous successful approaches to alkenyl- and allylsilanes by catalytic hydrosilylation methods involving alkyne or 1,3-diene substrates have permitted access to these product classes with a variety of metal catalysts.[5] However, even the best methods often lack high levels of regio- and stereoselectivity for substrates without inherent steric or electronic biases. Allenes represent a reagent class that potentially offers access to both alkenyl and allylsilanes by regiodivergent hydrosilylation reactions, but the presence of two orthogonal and often comparably reactive π-systems presents a considerable challenge in terms of regiocontrol.[6,7] For these reasons, allene hydrosilylations have received little attention,[8] with the Lewis acid catalyzed hydrosilylation of 1,3-disubstituted allenes towards trisubstituted *E*-configured trialkyl alkenylsilanes (Figure 1) being a rare example that exhibits regiocontrol and stereoselectivity.[8a]

As part of a general program to develop and understand regiodivergent catalytic processes,[9] previous studies from our laboratory described the regiodivergent hydrosilylation of
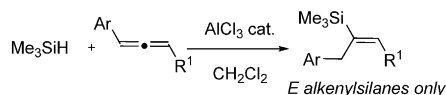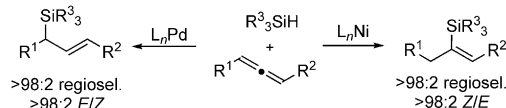

Figure 1. Regio- and stereoselective allene hydrosilylation.

terminal allenes in processes that exploit the electronic and steric bias of monosubstituted allenes and that utilize metal identity and ligand structure as key control elements.[10] In contrast to our earlier studies, 1,3-disubstituted allenes present a more substantial challenge in terms of regiocontrol given the steric and electronic similarity of the two contiguous π-systems.[6g,11] Compared with functionalizations of monosubstituted allenes, hydrosilylations involving 1,3-disubstituted allenes present considerably more potential value given the greater range of structural diversity and stereochemical complexity that can be installed in the product structures. Herein, we describe highly regioselective hydrosilylations of 1,3-disubstituted allenes that complement the stereochemical outcome of previously reported Lewis acid catalyzed processes.

We initially employed a strategy for catalyst generation that requires an N-heterocyclic carbene (NHC) hydrochloride salt with KO*t*Bu as the base and either [Pd$_2$dba$_3$] or [Ni(cod)$_2$] precatalysts (Table 1). In reactions of symmetrically *n*-hexyl-disubstituted allene **1**, the bulky ligand IPr*^{*OMe} (**6**) was found to be ineffective for promoting the Pd-catalyzed hydrosilylation as only starting material was recovered (Table 1, entry 1). As the steric demands placed on the system by ligand **6** likely prevented reactivity, the smaller NHC ligand IMes (**4**) was instead employed with Pd and favored the formation of *E* allylsilane **2a** with excellent regioselectivity (> 98:2 allyl/alkenyl) but only moderate d.r. (75:25 *E/Z*) in 80% yield (entry 2). However, changing the NHC ligand to IPr (**5**) resulted in the formation of *E* allylsilane **2a** with excellent regio- and stereoselectivity (> 98:2 **2a**/ **3a**, > 98:2 *E/Z*) in 75% yield (entry 3).

After identifying conditions that favored the formation of *E* allylsilanes with Pd^0, we examined how stereodefined alkenylsilanes could be accessed with nickel catalysis (Table 1, entries 4 and 5). Using the same catalyst-generation strategy, it was found that reactions with Ni and the large ligand IPr (**5**) primarily afforded *Z* alkenylsilane **3a** with moderate regioselectivity (60:40 vinyl/allyl) and in 84% yield,

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Table 1: Initial screen of allene hydrosilylations with a nickel or palladium catalyst.

Entry	Precatalyst[a]	L·HX[b]	Yield [%]	2a/3a[c]	2a (E/Z)	3a (Z/E)
1	[Pd$_2$dba$_3$]	6	n.r.	–	–	–
2	[Pd$_2$dba$_3$]	4	80	>98:2	75:25	n.d.
3	[Pd$_2$dba$_3$]	5	75	>98:2	>98:2	n.d.
4	[Ni(cod)$_2$]	5	84	40:60	75:25	>98:2
5	[Ni(cod)$_2$]	6	89	<2:98	n.d.	>98:2

[a] For reactions with the Ni catalyst: [Ni(cod)$_2$] (10 mol%), **5** or **6** (10 mol%). For reactions with the Pd catalyst: [Pd$_2$dba$_3$] (2.5 mol%), L·HX (5.0 mol%). [b] Ligands **4** and **5** were used as the HCl salt with KO*t*Bu. Ligand **6** was used as the neutral ligand without base. [c] Regioselectivity determined by ^{1}H NMR spectroscopy and GC analysis of the crude reaction mixture. dba = (E,E)-dibenzylideneacetone, cod = cycloocta-1,5-diene, n.d. = not determined, n.r. = no reaction.

L·HX =

IMes (**4**)   IPr (**5**)   IPr*^{OMe} (**6**)   R =
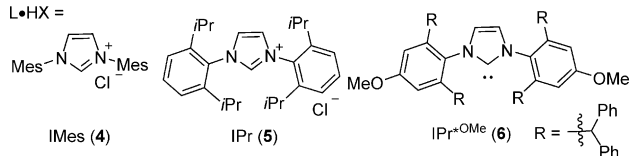
but as a mixture of the diastereomeric allylsilanes (75:25 E/Z; entry 4). However, increasing the steric bulk of the NHC ligand through the use of IPr*^{OMe} (**6**) provided an efficient solution for Z alkenylsilane generation, as **3a** was exclusively formed with exceptional regio- and stereoselectivity (>98:2 **3a/2a** and d.r.) in an excellent yield of 89% (entry 5).

Further exploration of these complementary methods involved the evaluation of symmetrically substituted 1,3-disubstituted allenes with Me$_2$PhSiH and BnMe$_2$SiH for both the Pd^0-based (conditions A) and Ni^0-based (conditions B) procedures (Table 2). Reactions with *n*-aliphatic substrates using conditions A afforded allylsilanes functionalized with BnMe$_2$SiH (**2a**) or Me$_2$PhSiH (**2b**) in excellent yields and stereoselectivities (entries 1 and 2). Products with a more hindered aliphatic substituent (**2c**) or silyl-ether-containing moieties (**2d**) were also afforded using the palladium-based procedure with high stereo- and regioselectivities (entries 3 and 4). The Ni^0 method afforded Z alkenylsilanes with *n*-aliphatic substituents (**3a** and **3b**) with both BnMe$_2$SiH and Me$_2$PhSiH (entries 5 and 6, respectively). Substrates with more hindered aliphatic substituents and a silyl-ether-containing allene could be coupled with Me$_2$PhSiH in high yields and selectivities (**3c** and **3d**, respectively; entries 7 and 8).

Cyclic allenes were also viable substrates in the nickel- and palladium-based procedures to afford cyclic Z alkenylsilanes or E allylsilanes (Scheme 1). For example, 15-membered cyclic allene **7** was converted into Z alkenylsilane **8** using nickel catalysis in excellent yield and stereoselectivity (>98:2). The reaction with the same substrate using the Pd^0 method afforded E allylsilane **9** in moderate yield (66%) and exceptional regio- and stereoselectivity (>98:2).

The evaluation of the reaction scope continued with the study of unsymmetrically 1,3-disubstituted allenes. The Pd-

Table 2: Metal-divergent hydrosilylations of symmetric allenes.

Entry	R^1	Cond.[a]	Silane	Product	Yield [%]	2/3[b]	d.r. (E/Z)
1	*n*Hex	A	BnMe$_2$SiH	**2a**	75	>98:2	>98:2
2	*n*Hex	A	Me$_2$PhSiH	**2b**	84	>98:2	>98:2
3	Cy	A	Me$_2$PhSiH	**2c**	58	>98:2	>98:2
4	TBSO	A	Me$_2$PhSiH	**2d**	64	>98:2	>98:2
5	*n*Hex	B	BnMe$_2$SiH	**3a**	89	<2:98	<2:98
6	*n*Hex	B	Me$_2$PhSiH	**3b**	85	<2:98	<2:98
7	Cy	B	Me$_2$PhSiH	**3c**	65	<2:98	4:96
8	TBSO	B	Me$_2$BnSiH	**3d**	75	<2:98	15:85

[a] Conditions A: [Pd$_2$dba$_3$] (2.5 mol%), KO*t*Bu (5.0 mol%), L·HX (5.0 mol%). Conditions B: [Ni(cod)$_2$] (10 mol%), **6** (10 mol%). Ligand **6** was used without base. [b] Regioselectivity determined by ^{1}H NMR spectroscopy and GC analysis of the crude reaction mixture.
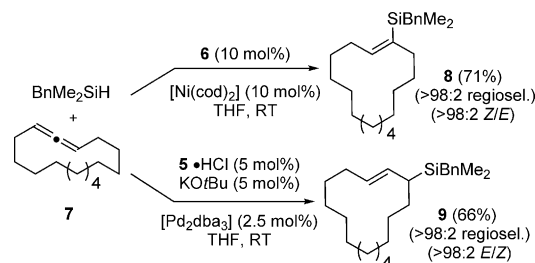
Scheme 1. Regiodivergent hydrosilylation of a cyclic allene.
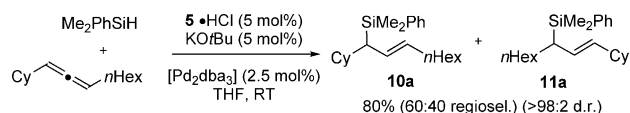
Scheme 2. Palladium-catalyzed hydrosilylation of an unsymmetric allene.

catalyzed hydrosilylation resulted in low regioselectivity favoring silyl addition to the more hindered carbon atom (Scheme 2). A mixture of the regioisomers **10a** and **11a** (60:40) was afforded when Me$_2$PhSiH was employed as the silylating reagent (Scheme 2).

In contrast, the nickel-based coupling of unsymmetric 1,3-disubstituted allenes with silanes afforded Z alkenylsilanes with excellent selectivities when the allene substituents were sufficiently different in size (Table 3). For example, an allene with isobutyl and *n*-hexyl substituents afforded an equal mixture of the corresponding Z alkenylsilanes in a moderate 49% yield (**12a** and **13a**; entry 1). However, by increasing the size of one of the substituents to isopropyl while maintaining a less hindered *n*-hexyl group, Z-alkenylsilane **12b** could be obtained with exceptional regio- and stereoselectivity (>98:2) in 64% yield (entry 2). This effect was further explored with sterically differentiated allenes functionalized with one cyclohexyl and one *n*-hexyl substituent (**12c** and

Table 3: Hydrosilylations of unsymmetrically substituted allenes.

Entry	R[1]	R[2]	Silane	Prod.	Yield [%]	Vinyl/allyl[a]	12/13	Z/E
1	iBu	nHex	BnMe$_2$SiH	12a	49	91:9	50:50	>98:2
2	iPr	nHex	BnMe$_2$SiH	12b	64	98:2	98:2	>98:2
3	Cy	nHex	Me$_2$PhSiH	12c	51	>98:2	>98:2	>98:2
4	Cy	nHex	BnMe$_2$SiH	12d	70	>98:2	>98:2	>98:2
5	tBu	nHex	BnMe$_2$SiH	12e	52	>98:2	>98:2	>98:2
6	Cy	Ph	BnMe$_2$SiH	12f	66	>98:2	>98:2	95:5
7	Cy	BnO	BnMe$_2$SiH	12g	72	>98:2	>98:2	90:10

[a] Regioselectivity determined by ^{1}H NMR spectroscopy and/or GC analysis of the crude reaction mixture.

12d) and both Me$_2$PhSiH and BnMe$_2$SiH and for allenes with one *tert*-butyl and one *n*-hexyl substituent (**12e**). All reactions favored the formation of the *Z* alkenylsilanes where the hydride has been added to the terminal carbon atom of the allene closest to the larger substituent. Further elaboration of the less hindered substituent while maintaining one substituent with greater steric encumbrance is also possible as allenes with aromatic (**12f**) or benzyl ether (**12g**) moieties resulted in highly regio- and stereoselective outcomes favoring the *Z* alkenylsilane isomers.

To probe the mechanism of the addition process, a series of double-labeling studies were performed with cyclohexylallene and the Ni or Pd catalyst (Scheme 3) utilizing mixtures of Et$_3$SiD and *n*Pr$_3$SiH.[12] Additions to a monosubstituted allene were studied to simplify the analysis, as this substrate permitted the highest regioselectivities using commercially available deuterated silane reagents. For both the nickel- and palladium-catalyzed reactions, only traces of the crossover products were observed, indicating that a single molecule of R$_3$SiH delivers the SiR$_3$ and H to a single product molecule, thus ruling out the involvement of metal hydrides that lack the silyl group or metal silyl species that lack the hydride. This
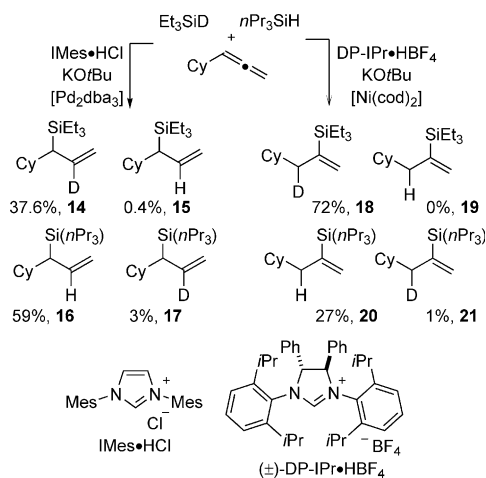
Scheme 3. Double-labeling studies of the metal-dependent hydrosilylation pathways.

outcome stands in contrast to a recent study by Schmidt and Tafazolian who observed the crossover products when cationic catalysts were used, thus indicating that the mechanism of allene hydrosilylation is highly catalyst-dependent.[8c] Based on this outcome, a likely mechanism involves coordination of the nickel or palladium catalyst to the sterically least encumbered face of the allene to form complex **22** or **23** (Figure 2). Notably, only the nickel-catalyzed hydro-
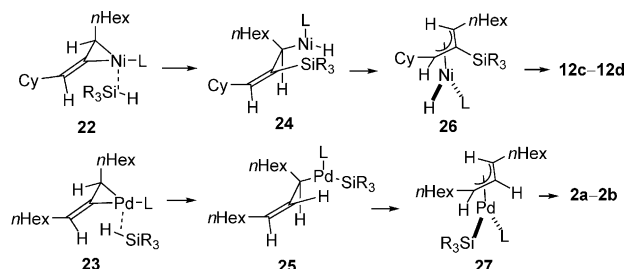
Figure 2. Proposed origin of the metal-directed regiodivergence.

silylation effectively differentiates the π-systems of unsymmetric allenes (compare Scheme 2 and Table 3). Subsequent Si−H cleavage and insertion across the least hindered π-bond affords **24** with Ni or **25** with Pd. Evidence for this step can be found in recent computational studies that have indicated that Si−H cleavage and migratory insertion take place in one step.[13] Bond rotation of the σ-allyl species occurs to form π-allyl intermediate **26** (with Ni) or **27** (with Pd), thus minimizing allylic 1,3-strain. Reductive elimination occurs directly from these intermediates as governed by the geometry of the trigonal π-complex, with a high kinetic barrier for exchange as has been observed in diborations[6a] and silaborations[6e] of allenes. The selectivity in additions to unsymmetric allenes with the nickel-catalyzed procedure is likely a result of site-selective coordination to the sterically least encumbered π-bond followed by migratory insertion. Analogous mechanistic proposals have been made by Jamison and Ng in the development of regioselective reductive couplings of 1,3-disubstituted allenes and aldehydes, which afforded allylic alcohol derivatives with *Z* configuration.[14]

The ability to transform unsymmetrically substituted allenes into regio- and stereodefined *Z* alkenylsilanes can be paired with a variety of synthetic operations (Scheme 4). For example, alkenylsilane intermediate **12d**, afforded by regio- and stereoselective allene hydrosilylation, can afford **28** in 86% yield; this transformation represents a new strategy for the site-selective installation of an *E* alkene. Treatment of **12d**
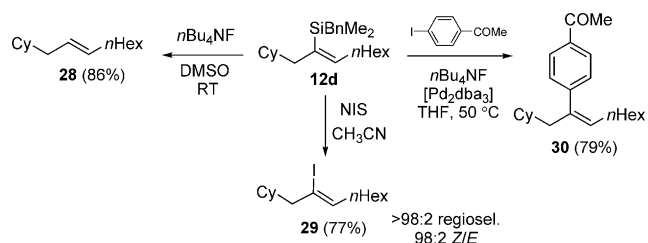
Scheme 4. Synthetic manipulations of a trisubstituted *Z* alkenylsilane.

with NIS enabled the formation of stereodefined iodide **29** in 77 % yield. Furthermore, the Pd-catalyzed cross-coupling reaction of **12 d** with 4′-iodoacetophenone furnished trisubstituted *Z*-arylalkene **30** in an excellent 79 % yield.

In summary, the hydrosilylation of 1,3-disubstituted allenes is an effective method for the synthesis of *E* allylsilanes and *Z* alkenylsilanes. The metal identity (Pd vs. Ni) can be exploited not only to direct the regiochemical outcome, but also to control the olefin geometry. Mechanistic investigations suggest that both pathways involve mechanisms where the Si−H unit is installed into a single molecule of product. Future work will explore the expansion of these findings to other regiodivergent transformations.

[1] a) M. A. Brook in *Silicon in Organic, Organometallic, and Polymer Chemistry*, Wiley, Chichester, **2000**; b) I. Fleming, A. Barbero, D. Walter, *Chem. Rev.* **1997**, *97*, 2063–2192; c) I. Ojima, Y. Z. Li, J. W. Zhu in *Chemistry of Organic Silicon Compounds* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, UK, **1998**; d) D. S. W. Lim, E. A. Anderson, *Synthesis* **2012**, 983–1010.

[2] a) Y. Nakao, T. Hiyama, *Chem. Soc. Rev.* **2011**, *40*, 4893–4901; b) W.-T. T. Chang, R. C. Smith, C. S. Regens, A. D. Bailey, N. S. Werner, S. E. Denmark, *Org. React.* **2011**, *75*, 213–745.

[3] a) S. R. Angle, N. A. El-Said, *J. Am. Chem. Soc.* **2002**, *124*, 3608–3613; b) W. R. Judd, S. Ban, J. Aubé, *J. Am. Chem. Soc.* **2006**, *128*, 13736–13741.

[4] a) A. Hosomi, M. Endo, H. Sakurai, *Chem. Lett.* **1976**, 941–942; b) C. E. Masse, J. S. Panek, *Chem. Rev.* **1995**, *95*, 1293–1316.

[5] For alkyne hydrosilylation procedures, see: a) D. A. Rooke, E. M. Ferreira, *Angew. Chem. Int. Ed.* **2012**, *51*, 3225–3230; *Angew. Chem.* **2012**, *124*, 3279–3284; b) B. M. Trost, Z. T. Ball, *J. Am. Chem. Soc.* **2001**, *123*, 12726–12727; c) Z. T. Ball, B. M. Trost, *J. Am. Chem. Soc.* **2005**, *127*, 17644–17655; d) G. Berthon-Gelloz, J. Schumers, G. De Bo, I. E. Markó, *J. Org. Chem.* **2008**, *73*, 4190–4197; e) G. De Bo, G. Berthon-Gelloz, B. Tinant, I. E. Markó, *Organometallics* **2006**, *25*, 1881–1890; f) S. E. Denmark, Z. Wang, *Org. Lett.* **2001**, *3*, 1073–1076; g) Y. Kawasaki, Y. Ishikawa, K. Igawa, K. Tomooka, *J. Am. Chem. Soc.* **2011**, *133*, 20712–20715; h) M. R. Chaulagain, G. M. Mahandru, J. Montgomery, *Tetrahedron* **2006**, *62*, 7560–7566; i) M. F. Lappert, T. A. Nile, S. Takahashi, *J. Organomet. Chem.* **1974**, *72*, 425–439; j) S. E. Denmark, W. Pan, *Org. Lett.* **2003**, *5*, 1119–1122; for 1,3-diene hydrosilylation procedures, see: k) I. Ojima, M. Kumagai, *J. Organomet. Chem.* **1978**, *157*, 359–379; l) J. Y. Wu, B. N. Stanzl, T. Ritter, *J. Am. Chem. Soc.* **2010**, *132*, 13214–13216; m) S. Onozawa, T. Sakakura, M. Tanaka, *Tetrahedron Lett.* **1994**, *35*, 8177–8180; n) J. Tsuji, M. Hara, K. Ohno, *Tetrahedron* **1974**, *30*, 2143–2146; for *trans* hydrometalation reactions of alkynes, see: o) K. Radkowski, B. Sundararaju, A. Fürstner, *Angew. Chem. Int. Ed.* **2013**, *52*, 355–360; *Angew. Chem.* **2013**, *125*, 373–378; p) B. Sundararaju, A. Fürstner, *Angew. Chem. Int. Ed.* **2013**, *52*, 14050–14052; *Angew. Chem.* **2013**, *125*, 14300–14304; q) S. M. Rummelt, A. Fürstner, *Angew. Chem. Int. Ed.* **2014**, *53*, 3626–3630; *Angew. Chem.* **2014**, *126*, 3700–3704.

[6] For allene diboration reactions, see: a) H. E. Burks, S. Liu, J. P. Morken, *J. Am. Chem. Soc.* **2007**, *129*, 8766–8773; b) N. F. Pelz,

J. P. Morken, *Org. Lett.* **2006**, *8*, 4557–4559; c) N. F. Pelz, A. R. Woodward, H. E. Burks, J. D. Sieber, J. P. Morken, *J. Am. Chem. Soc.* **2004**, *126*, 16328–16329; d) F.-Y. Yang, C.-H. Cheng, *J. Am. Chem. Soc.* **2001**, *123*, 761–762; for allene silaboration reactions, see: e) Y. Abe, K. Kuramoto, M. Ehara, H. Nakasuji, M. Suginome, M. Murakami, I. Masahiro, Y. Ito, *Organometallics* **2008**, *27*, 1736–1742; f) T. Ohmura, H. Taniguchi, M. Suginome, *J. Am. Chem. Soc.* **2006**, *128*, 13682–13683; for allene silylcupration reactions, see: g) Y. Tani, T. Fujihara, J. Terao, Y. Tsuji, *J. Am. Chem. Soc.* **2014**, *136*, 17706–17709; h) I. Fleming, F. J. Pulido, *J. Chem. Soc. Chem. Commun.* **1986**, 1010–1011; i) I. Fleming, M. Rowley, P. Cuadrado, A. M. Gonzàlez-Nogal, F. J. Pulido, *Tetrahedron* **1989**, *45*, 413–424; j) F. J. Blanco, P. Cuadrado, A. M. Gonzàlez, F. J. Pulido, I. Fleming, *Tetrahedron Lett.* **1994**, *35*, 8881–8882.

[7] For non-hydrosilylation-based methods to access allylsilanes, see: a) R. Moser, T. Nishikata, B. H. Lipshutz, *Org. Lett.* **2010**, *12*, 28–31; b) C. K. Hazra, M. Oestreich, *Org. Lett.* **2012**, *14*, 4010–4013; c) J. R. McAtee, G. P. A. Yap, D. A. Watson, *J. Am. Chem. Soc.* **2014**, *136*, 10166–10172; for other non-hydrosilylation-based methods to access alkenylsilanes, see: d) B. M. Trost, M. U. Frederiksen, J. P. N. Papillon, P. E. Harrington, S. Shin, B. T. Shireman, *J. Am. Chem. Soc.* **2005**, *127*, 3666–3667; e) S. E. Denmark, S. Fujimori, *J. Am. Chem. Soc.* **2005**, *127*, 8971–8973; f) G. W. O'Neil, A. J. Phillips, *Tetrahedron Lett.* **2004**, *45*, 4253–4256; g) T. P. Heffron, G. L. Simpson, E. Merino, T. F. Jamison, *J. Org. Chem.* **2010**, *75*, 2681–2701; h) J. R. McAtee, S. E. Martin, A. R. Cinderella, W. B. Reid, K. A. Johnson, D. A. Watson, *Tetrahedron* **2014**, *70*, 4250–4256; i) S. E. S. Martin, D. A. Watson, *J. Am. Chem. Soc.* **2013**, *135*, 13330–13333; j) J. R. McAtee, S. E. S. Martin, D. T. Ahneman, K. A. Johnson, D. A. Watson, *Angew. Chem. Int. Ed.* **2012**, *51*, 3663–3667; *Angew. Chem.* **2012**, *124*, 3723–3727; k) D. A. Rooke, E. M. Ferreira, *J. Am. Chem. Soc.* **2010**, *132*, 11926–11928.

[8] a) T. Sudo, N. Asao, V. Gevorgyan, T. Yamamoto, *J. Org. Chem.* **1999**, *64*, 2494–2499; b) G. Huang, M. Isobe, *Tetrahedron* **2001**, *57*, 10241–10246; c) H. Tafazolian, J. A. R. Schmidt, *Chem. Commun.* **2015**, *51*, 5943–5946.

[9] a) H. A. Malik, G. J. Sormunen, J. Montgomery, *J. Am. Chem. Soc.* **2010**, *132*, 6304–6305; b) P. Liu, J. Montgomery, K. N. Houk, *J. Am. Chem. Soc.* **2011**, *133*, 6956–6959; c) E. P. Jackson, J. Montgomery, *J. Am. Chem. Soc.* **2015**, *137*, 958–963.

[10] a) Z. D. Miller, W. Li, T. R. Belderrain, J. Montgomery, *J. Am. Chem. Soc.* **2013**, *135*, 15282–15285; b) Z. D. Miller, J. Montgomery, *Org. Lett.* **2014**, *16*, 5486–5489.

[11] For other regiodivergent additions to terminal allenes, see: a) K. Xu, N. Thieme, B. Breit, *Angew. Chem. Int. Ed.* **2014**, *53*, 7268–7271; *Angew. Chem.* **2014**, *126*, 7396–7399; b) K. Xu, N. Thieme, B. Breit, *Angew. Chem. Int. Ed.* **2014**, *53*, 2162–2165; *Angew. Chem.* **2014**, *126*, 2194–2197; c) B. Alcaide, P. Almendros, T. Martínez del Campo, *Angew. Chem. Int. Ed.* **2007**, *46*, 6684–6687; *Angew. Chem.* **2007**, *119*, 6804–6807; d) J. L. Arbour, H. S. Rzepa, A. J. P. White, K. K. Hii, *Chem. Commun.* **2009**, 7125–7127.

[12] For a recent example of double-labeling isotopic studies, see: M. T. Haynes, P. Liu, R. D. Baxter, A. J. Nett, K. N. Houk, J. Montgomery, *J. Am. Chem. Soc.* **2014**, *136*, 17495–17504.

[13] H. Xie, L. Zhao, L. Yang, Q. Lei, W. Fang, C. Xiong, *J. Org. Chem.* **2014**, *79*, 4517–4527.

[14] a) S.-S. Ng, T. F. Jamison, *J. Am. Chem. Soc.* **2005**, *127*, 7320–7321; b) S.-S. Ng, T. F. Jamison, *Tetrahedron* **2006**, *62*, 11405–11417.