

Hydrosilylation of Alkynes

Deutsche Ausgabe: DOI: 10.1002/ange.201605501
Internationale Ausgabe: DOI: 10.1002/anie.201605501

Highly Chemo-, Regio-, and Stereoselective Cobalt-Catalyzed Markovnikov Hydrosilylation of Alkynes

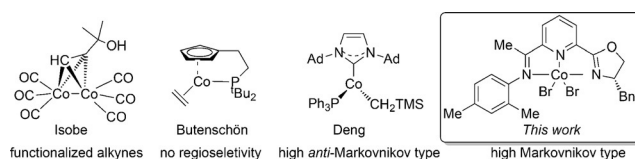
Jun Guo and Zhan Lu*

Abstract: A highly chemo-, regio- and stereoselective cobalt-catalyzed Markovnikov hydrosilylation of alkynes was developed. Various functionalized groups, such as halides, free alcohols, free aniline, ketones, esters, amides, and nitriles are tolerated, which may lead to further applications and late-stage derivatizations. To date, this is the most efficient cobalt catalytic system ($\text{TOF} = 65\,520\text{ h}^{-1}$; $\text{TOF} = \text{turnover frequency}$) for hydrosilylation of alkynes. The Hiyama–Denmark cross-coupling reactions of vinylsilanes with aryl iodides underwent smoothly to afford 1,1-diarylethenes. A unique regioselectivity-controllable hydrosilylation/hydroboration reaction of alkynes was also described.

The development of efficient, selective, economic, and environmentally benign catalysts^[1] for valuable chemicals is highly desirable and particularly beneficial for exploring new transformations. Vinylsilanes are highly attractive intermediates because of versatile applications in organic synthesis and materials science.^[2] Hydrosilylation of alkynes with silanes is one of the most straightforward and atom-economical strategies.^[3] However, only a few examples using noble transition-metal catalysts, such as ruthenium,^[4] have been used for general Markovnikov-type hydrosilylation of alkynes. Because of good tolerance to various functional groups, as well as the lower costs and toxicity of cobalt catalysts, rapid progress has been made in cobalt-catalyzed reactions during the last two decades.^[5] Recently, the research groups of Chirik,^[6] Hanson,^[7] Holland,^[8] Deng,^[9] and Huang^[10] and our group^[11] reported low-valent cobalt complexes that efficiently catalyze hydrogenation, hydrosilylation, hydroboration, and isomerization of unsaturated carbon–carbon double bonds. However, the cobalt-catalyzed hydrosilylation of terminal alkynes is still challenging.^[12]

Isobe and co-workers reported that a cobalt carbonyl complex promoted the hydrosilylation reaction of functionalized terminal alkynes with silanes to afford vinylsilanes, however, with 1.2/1 to 6.7/1 regioselectivities.^[13] Butenschön and co-workers found that the cyclopentadienylcobalt complex with a pendant phosphane donor catalyzed the hydrosilylation of internal alkynes with high *syn*-selectivity, however, no regioselectivity was observed in the hydrosilylation

of terminal alkynes.^[14] Deng and co-workers demonstrated that a three-coordinate carbene–phosphane cobalt complex showed highly catalytic β -selectivity in the hydrosilylation of terminal alkynes.^[15] The use of cobalt complexes for promoting the efficient, general and highly α -regioselective hydrosilylation of alkynes has not been described previously. Here, we developed a highly chemo-, regio-, and stereoselective cobalt-catalyzed hydrosilylation of terminal and internal alkynes to α -vinyl silanes (Scheme 1).



Scheme 1. Cobalt complexes for catalytic hydrosilylation of terminal alkynes

A simple phenylacetylene was chosen as a model substrate and reacted with Ph_2SiH_2 . The bench-stable oxazoline iminopyridine (OIP) cobalt complex **L1**· CoCl_2 was selected as a precatalyst in which the OIP ligand could be easily synthesized from substituted 2-bromopyridines and oxazolines.^[16] The reaction was carried out in the presence of 2 mol % cobalt precatalyst **L1a**· CoCl_2 and 6 mol % NaBHET_3 as a reductant in a solution of tetrahydrofuran (THF) at room temperature to afford a mixture of branched- and linear-selective products in 18% yield with a ratio of 67:33 (see entry 1 in Table 1). A significant increase in the yield as well as in the regioselectivity was observed when a smaller benzyl group was used on the oxazoline, which gave rise to vinylsilane in 83% yield with 87/13 regioselective ratio (*rr*; entries 1–3). When the substituent was further reduced in size to a methyl group, the yield and regioselectivity slightly decreased (entry 4). We were pleased to find that the regioselectivities were improved to 94:6 using less steric bulky 2,6-dimethyl or 2,4-dimethyl aniline-derived ligands (entries 5 and 6). Using bromide or iodide as an anion instead of chloride, a regioselectivity of up to 97:3 was observed (entries 7 and 8). A variety of reductants, as well as various solvents and silanes have also been investigated, but no further improvement was observed (see the Supporting Information). Control experiments were conducted and showed cobalt complexes with well-defined ligands, such as pyridine bisoxazoline (Pybox), bisiminopyridine (BIP), and iminopyridine (IP), that promoted the reactions, however, with slightly lower regioselectivities (entries 9–11).

[*] J. Guo, Prof. Z. Lu
Department of Chemistry, Zhejiang University
Hangzhou, Zhejiang 310058 (China)
E-mail: luzhan@zju.edu.cn
Homepage: <http://mypage.zju.edu.cn/lu>

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under <http://dx.doi.org/10.1002/anie.201605501>.

Table 1: Optimizations.^[a]

L1a• CoCl₂, X=Cl, R¹=tBu, R²=R³=iPr, R⁴=H
L1b• CoCl₂, X=Cl, R¹=iPr, R²=R³=iPr, R⁴=H
L1c• CoCl₂, X=Cl, R¹=Bn, R²=R³=iPr, R⁴=H
L1d• CoCl₂, X=Cl, R¹=Me, R²=R³=iPr, R⁴=H
L1e• CoCl₂, X=Cl, R¹=Bn, R²=R³=Me, R⁴=H
L1f• CoCl₂, X=Cl, R¹=Bn, R²=R⁴=Me, R³=H
L1f• CoBr₂, X=Br, R¹=Bn, R²=R⁴=Me, R³=H
L1f• Co₂, X=I, R¹=Bn, R²=R⁴=Me, R³=H

L2•CoBr₂ **L3**•CoBr₂ **L4**•CoBr₂

Ph—C≡C—H (1a) + Ph₂SiH₂ (2) $\xrightarrow[\text{THF (0.5 M), r.t., 5 min}]{\text{[Co] (2 mol%), NaBHET}_3 \text{ (6 mol%)}}$ Ph—C(SiHPh₂)=CH₂ (3a) + Ph—C(SiHPh₂)=CH—Ph (4a)

Entry	[Co]	Yield ^[b] [%] (b/l)
1	L1a •CoCl ₂	18 (67/33)
2	L1b •CoCl ₂	38 (71/29)
3	L1c •CoCl ₂	83 (87/13)
4	L1d •CoCl ₂	77 (85/15)
5	L1e •CoCl ₂	77 (93/7)
6	L1f •CoCl ₂	88 (94/6)
7	L1f •CoBr ₂	90 (97/3)
8	L1f •Co ₂	88 (96/4)
9	L2 •CoBr ₂	79 (86/14)
10	L3 •CoBr ₂	61 (69/31)
11	L4 •CoBr ₂	87 (78/22)

[a] Phenylacetylene (1 mmol), Ph₂SiH₂ (1 mmol), cobalt complex (2 mol%), NaBHET₃ (6 mol %) in THF (2 mL). [b] Yield and regioselective ratio were determined by ¹H NMR using TMSPh as an internal standard.

The scope of this catalytic system turned out to be broad (Table 2). Under the optimal conditions using **L1f**•CoBr₂ complex,^[17] a variety of alkynes bearing electron-donating or electron-withdrawing substituents on the phenyl ring

Table 2: Scope for hydrosilylation of terminal alkynes.^[a]

R—C≡C—H (1) + Ph₂SiH₂ (2) $\xrightarrow[\text{THF (0.5 M), r.t., 5 min}]{\text{L1f} \cdot \text{CoBr}_2 \text{ (2 mol%), NaBHET}_3 \text{ (6 mol%)}}$ R—C(SiHPh₂)=CH₂ (3) + R—C(SiHPh₂)=CH—Ph (4)

3a, 86%, 97/3 **3b**, 96%, 93/7 **3c**, 85%, 89/11 **3d**, 83%, 93/7
3e, 95%, 97/3 **3f**^[b], 79%, 95/5 **3g**, 89%, 93/7 **3h**, 96%, 93/7
3i^[b], 65%, 93/7 **3j**^[b], 85%, 93/7 **3k**^[b], 30%, 93/7 **3l**^[b], 92%, 92/8
3m^[b], 69%, 94/6 **3n**^[b], 65%, 88/12 **3o**, 80%, 95/5 **3p**, 88%, 97/3
3q^[b], 85%, 98/2 **3r**^[b], 62%, 93/7 **3s**, 83%, 69/31 **3t**, 87%, 80/20

[a] **1** (1 mmol), Ph₂SiH₂ (1 mmol), **L1f**•CoBr₂ (2 mol%), NaBHET₃ (6 mol %) in THF (2 mL), isolated yield and ratio of b/l. [b] Reacted for 30 minutes.

underwent the reactions with Ph₂SiH₂ to afford the corresponding hydrosilylation products (**3a–n**) in high yields and excellent regioselectivities. For more broadly synthetic interests, various functionalized groups, such as halides, free alcohols, free aniline, ketones, esters, amides, and nitriles were tolerated. The reaction of **1k** containing an aldehyde moiety were carried out to afford **3k** in a slightly lower yield with 93/7 *rr*. 2-Naphthyl (**1o**), 1-naphthyl (**1p**), 2-thienyl (**1q**), 3-pyridyl (**1r**) alkynes could be delivered to α-silyl alkenes in 80–89% yields with 93/7 to 98/2 *rr*. The reaction of alkyl-substituted terminal alkynes^[18] and silylalkynes^[19] underwent smoothly with a slightly lower regioselectivity. A variety of gram-scale reactions using 0.4 mol % of **L1f**•CoBr₂ were carried out and the crude products were purified by recrystallization to afford the corresponding vinyl silylanes in 80–89% yields at gram scale (Table 3).

Table 3: Gram-scale reactions.^[a]

Ar—C≡C—H (1, 5 mmol) + Ph₂SiH₂ $\xrightarrow[\text{THF (2.5 M), r.t., 20 min}]{\text{L1f} \cdot \text{CoBr}_2 \text{ (0.4 mol%), NaBHET}_3 \text{ (1.5 mol%)}}$ Ar—C(SiHPh₂)=CH₂ (3)

3a, 1.2358 g, 83% **3b**, 1.3414 g, 89% **3c**, 1.3763 g, 87% **3h**^[b], 1.4638 g, 80%
3g^[b], 1.4502 g, 80% **3o**^[b], 1.4289 g, 86% **3p**^[b], 1.3448 g, 80% **3q**^[b], 1.2660 g, 87%

[a] **1** (5 mmol), Ph₂SiH₂ (5 mmol), **L1f**•CoBr₂ (0.4 mol%), NaBHET₃ (1.5 mol %) in THF (2 mL), isolated yield of **3**. [b] 1.0 mol % of **L1f**•CoBr₂ was used.

Internal alkynes could also be hydrosilylated under this cobalt-catalyzed conditions (Table 4). The hydrosilylations of symmetric dialkyl alkynes (**5a,b**), as well as diaryl alkyne (**5c**), provided only *syn*-addition products with high stereoselectivity. The unsymmetric internal alkynes, such as aryl alkyl alkynes (**5d–h**), were suitable for this method to produce 1-aryl-1-silyl-2-alkyl alkenes in 79–90% yield and 85:15 to 91:9 *rr*. The aryl heteroaryl alkyne (**5i**) and alkyl alkyl

Table 4: Hydrosilylation of internal alkynes.^[a]

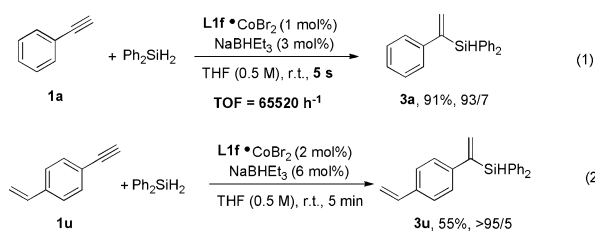
R¹—C≡C—R² (5) + Ph₂SiH₂ $\xrightarrow[\text{THF (0.5 M), r.t., 5 min}]{\text{L1f} \cdot \text{CoBr}_2 \text{ (2 mol%), NaBHET}_3 \text{ (6 mol%)}}$ Ph₂Si—C(R¹)=C(R²)—H (6) + Ph₂Si—C(R¹)=C(R²)—Ph (7)

6a, 84% **6b**, 97% **6c**, 33% **6d**, 90%, 85:15
6e, 88%, 89/11 **6f**, 79%, 90/10 **6g**, 90%, 90/10 **6h**, 91%, 91/9
6i, 68%, 90/10 **6j**, 89%, >99/1

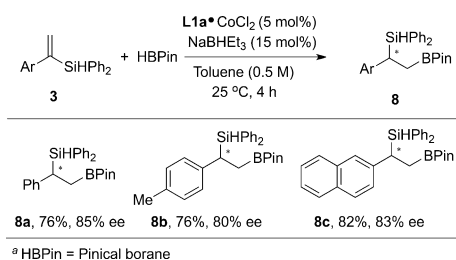
[a] **5** (1 mmol), Ph₂SiH₂ (1 mmol), **L1f**•CoBr₂ (2 mol%), NaBHET₃ (6 mol %) in THF (2 mL), isolated yield and ratio of **6/7**.

alkyne (**5j**) could be converted to hydrosilylation products **6i** and **6j** in 68 % yield with 90/10 *rr* and 89 % yield with > 99/1 *rr*, respectively.

The reaction could complete even in 5 s using 1 mol % of catalyst to afford silylation products in 91 % yield with 93/7 *rr* [Eq. (1)] in which the turnover frequency was up to 65 520 h⁻¹. To date, this is the most efficient cobalt catalytic system for hydrosilylation of alkynes. 4'-Vinylphenylacetylene **1u** could be converted to the alkyne hydrosilylation product **3u** in 55 % yield with > 95/5 *rr* without any alkene hydrosilylation product [Eq. (2)] which suggested that the catalytic system could differentiate between terminal alkyne and terminal alkene which used to be active in cobalt-catalyzed hydrosilylation reactions.^[11,20] Based on the above experimental results and those in previously reported literatures, a Chalk–Harrod mechanism^[20b] for hydrosilylation of alkenes was proposed, however, we did not have any evidence and further mechanistic studies should be carried out [Eqs. (1) and 2].

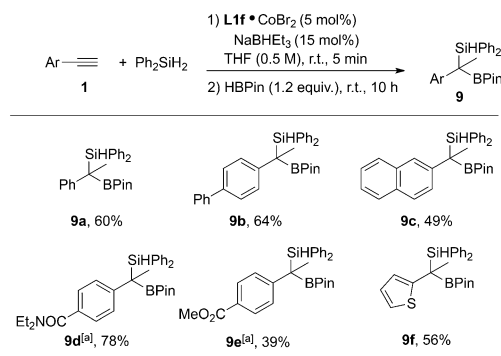


Hydroboration of alkenes is one of the most useful methods to access alkylboronic acid derivatives which are widely used in modern organic synthesis.^[21] Only few examples on hydroboration of vinylsilanes were reported,^[22] however, enantioselective reactions have not been previously described thus far. To explore the broader utility of α -silyl alkenes, the cobalt-catalyzed asymmetric *anti*-Markovnikov hydroboration^[10a,11a] of α -silyl alkenes with pinacol borane (HBPin) using **L1a**–CoCl₂ as a precatalyst and NaBHET₃ as a reductant in a solution of toluene underwent smoothly to exclusively afford **8** in 76–82 % yields and 80–85 % *ee* (Scheme 2).



Scheme 2. Asymmetric *anti*-Markovnikov hydroboration of α -silyl alkenes.

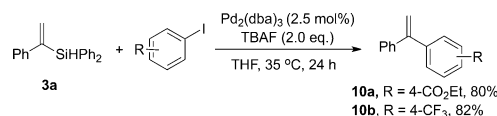
To our surprise, the combination of hydrosilylation and hydroboration reactions of alkynes in THF in one pot did provide double-Markovnikov hydrosilylation/hydroboration^[23] products **9** in 39–78 % yields which were difficult to



Scheme 3. Double-Markovnikov hydrosilylation/hydroboration of alkynes. [a] 2 mol % of the catalyst were used.

obtain^[24] (Scheme 3). The solvent effect might be the major effect for the switch in regioselectivity (see the Supporting Information). Various functional groups, such as esters, amides, naphthyl and thienyl, were tolerated. Although poor enantioselectivities (around 10 % *ee*) were observed, the same cobalt complex promoted two different reactions in one pot.

The Hiyama–Denmark coupling reactions^[25] of **3a** with aryl iodides (see Scheme 4) was carried out smoothly to afford the 1,1-diarylethene **10a** and **10b** in 80 % and 82 % yield, respectively.



Scheme 4. Hiyama–Denmark coupling reactions of **3a**.

In summary, we developed a highly chemo-, regio-, and stereoselective cobalt-catalyzed hydrosilylation of alkynes with silanes to produce α -vinylsilanes. Various functionalized groups, such as halides, free alcohols, free aniline, ketones, esters, amides, and nitriles, are tolerated to increase the possibility for further applications and late-stage derivatizations. To date, this is the most efficient cobalt catalytic system (TOF = 65 520 h⁻¹; TOF = turnover frequency) for the hydrosilylation of alkynes. The direct asymmetric hydroboration of α -vinylsilanes exclusively afforded *anti*-Markovnikov products. The one-pot reaction combined with hydrosilylation and hydroboration provided double-Markovnikov addition products. It is the first time that regioselectivity-controllable hydrosilylation/hydroboration of alkynes were observed. The Hiyama–Denmark cross-coupling reaction of vinylsilanes with aryl iodides underwent smoothly to afford 1,1-diarylethenes. Mechanistic studies will be conducted in our laboratory.

Acknowledgements

Financial support was provided by the National 973 Program (2015CB856600), NSFC (grant number 21472162), and the “Thousand Youth Talents Plan”.

Keywords: alkynes · cobalt catalysis · homogeneous catalysis · hydroboration · hydrosilylation

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 10835–10838
Angew. Chem. **2016**, *128*, 10993–10996

- [1] *Catalysis without Precious Metals* (Ed.: R. M. Bullock), Wiley-VCH, Weinheim, **2010**.
- [2] a) T. H. Chan, I. Fleming, *Synthesis* **1979**, 761; b) T. A. Blumenkopf, L. E. Overman, *Chem. Rev.* **1986**, *86*, 857; c) E. Langkopf, D. Schinzer, *Chem. Rev.* **1995**, *95*, 1375; d) I. Fleming, A. Barbero, D. Walter, *Chem. Rev.* **1997**, *97*, 2063.
- [3] a) T. Hiyama, T. Kusumoto in *Comprehensive Organic Synthesis*, Vol. 8 (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, p. 763; b) H. Brunner, *Angew. Chem. Int. Ed.* **2004**, *43*, 2749; *Angew. Chem.* **2004**, *116*, 2805; c) *Hydrosilylation: A Comprehensive Review on Recent Advances* (Ed.: B. Marciniec), Springer, Amsterdam, **2009**.
- [4] a) B. M. Trost, Z. T. Ball, *J. Am. Chem. Soc.* **2001**, *123*, 12726; b) B. M. Trost, Z. T. Ball, *J. Am. Chem. Soc.* **2005**, *127*, 17644; c) Y. Na, S. Chang, *Org. Lett.* **2000**, *2*, 1887; d) Y. Kawanami, Y. Sonoda, T. Mori, K. Yamamoto, *Org. Lett.* **2002**, *4*, 2825; e) C. Menozzi, P. I. Dalko, J. Cossy, *J. Org. Chem.* **2005**, *70*, 10717; f) H. F. Sore, D. T. Blackwell, S. J. F. MacDonald, D. R. Spring, *Org. Lett.* **2010**, *12*, 2806.
- [5] For selected reviews on cobalt chemistry: a) F. Hebrard, P. Kalck, *Chem. Rev.* **2009**, *109*, 4272; b) K. Gao, N. Yoshikai, *Acc. Chem. Res.* **2014**, *47*, 1208; c) H. Pellissier, H. Clavier, *Chem. Rev.* **2014**, *114*, 2775; d) P. Gandeepan, C. Cheng, *Acc. Chem. Res.* **2015**, *48*, 1194; e) N. Kaeffer, M. Chavarot-Kerlidou, V. Artero, *Acc. Chem. Res.* **2015**, *48*, 1286; f) P. J. Chirik, *Acc. Chem. Res.* **2015**, *48*, 1687; g) Y. Li, S. Yu, W. Shen, J. Gao, *Acc. Chem. Res.* **2015**, *48*, 2587.
- [6] a) S. Monfette, Z. R. Turner, S. P. Semproni, P. J. Chirik, *J. Am. Chem. Soc.* **2012**, *134*, 4561; b) M. R. Friedfeld, M. Shevlin, J. M. Hoyt, S. W. Krska, M. T. Tudge, P. J. Chirik, *Science* **2013**, *342*, 1076; c) J. V. Obligation, P. J. Chirik, *J. Am. Chem. Soc.* **2013**, *135*, 19107; d) M. R. Friedfeld, G. W. Margulieux, B. A. Schaefer, P. J. Chirik, *J. Am. Chem. Soc.* **2014**, *136*, 13178; e) C. C. H. Atienza, T. Diao, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, J. L. Boyer, A. K. Roy, P. J. Chirik, *J. Am. Chem. Soc.* **2014**, *136*, 12108; f) J. V. Obligation, J. M. Neely, A. N. Yazdani, I. Pappas, P. J. Chirik, *J. Am. Chem. Soc.* **2015**, *137*, 5855; g) M. R. Friedfeld, M. Shevlin, G. W. Margulieux, L.-C. Campeau, P. J. Chirik, *J. Am. Chem. Soc.* **2016**, *138*, 3314.
- [7] a) G. Zhang, B. L. Scott, S. K. Hanson, *Angew. Chem. Int. Ed.* **2012**, *51*, 12102; *Angew. Chem.* **2012**, *124*, 12268; b) G. Zhang, K. V. Vasudevan, B. L. Scott, S. K. Hanson, *J. Am. Chem. Soc.* **2013**, *135*, 8668.
- [8] a) C. Chen, T. R. Dugan, W. W. Brennessel, D. J. Weix, P. L. Holland, *J. Am. Chem. Soc.* **2014**, *136*, 945; b) C. Chen, M. B. Hecht, A. Kavara, W. W. Brennessel, B. Q. Mercado, D. J. Weix, P. L. Holland, *J. Am. Chem. Soc.* **2015**, *137*, 13244.
- [9] Z. Mo, Y. Liu, L. Deng, *Angew. Chem. Int. Ed.* **2013**, *52*, 10845; *Angew. Chem.* **2013**, *125*, 11045.
- [10] a) L. Zhang, Z. Zuo, X. Wan, Z. Huang, *J. Am. Chem. Soc.* **2014**, *136*, 15501; b) X. Du, Y. Zhang, D. Peng, Z. Huang, *Angew. Chem. Int. Ed.* **2016**, *55*, 6671; *Angew. Chem.* **2016**, *128*, 6783.
- [11] a) J. Chen, T. Xi, X. Ren, J. Guo, B. Cheng, Z. Lu, *Org. Chem. Front.* **2014**, *1*, 1306; b) J. Chen, C. Chen, C. Ji, Z. Lu, *Org. Lett.* **2016**, *18*, 1594.
- [12] J. Sun, L. Deng, *ACS Catal.* **2016**, *6*, 290.
- [13] a) M. Isobe, R. Nishizawa, T. Nishikawa, K. Yoza, *Tetrahedron Lett.* **1999**, *40*, 6927; b) S. Tojo, M. Isobe, *Tetrahedron Lett.* **2005**, *46*, 381; c) K.-H. Huang, M. Isobe, *Eur. J. Org. Chem.* **2014**, 4733; d) T. Konno, K. Taku, S. Yamada, K. Moriyasu, T. Ishihara, *Org. Biomol. Chem.* **2009**, *7*, 1167.
- [14] L. Yong, K. Kirleis, H. Butenschön, *Adv. Synth. Catal.* **2006**, *348*, 833.
- [15] Z. Mo, J. Xiao, Y. Gao, L. Deng, *J. Am. Chem. Soc.* **2014**, *136*, 17414.
- [16] a) J. Chen, T. Xi, Z. Lu, *Org. Lett.* **2014**, *16*, 6452; b) T. Xi, Y. Mei, Z. Lu, *Org. Lett.* **2015**, *17*, 5939.
- [17] CCDC 1435433 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [18] For a selected example on highly selective hydrosilylation of alkyl alkynes, see: P. Wang, X.-L. Yeo, T.-P. Loh, *J. Am. Chem. Soc.* **2011**, *133*, 1254.
- [19] For a selected example on highly selective hydrosilylation of silyl alkynes, see: S. Ding, L.-J. Song, L. W. Chung, X. Zhang, J. Sun, Y.-D. Wu, *J. Am. Chem. Soc.* **2013**, *135*, 13835.
- [20] For selected examples on cobalt-catalyzed hydrosilylation of alkenes, see: a) J. F. Harrod, A. J. Chalk, *J. Am. Chem. Soc.* **1965**, *87*, 1133; b) A. J. Chalk, J. F. Harrod, *J. Am. Chem. Soc.* **1967**, *89*, 1640; c) A. J. Chalk, *J. Organomet. Chem.* **1970**, *21*, 207; d) F. Seitz, M. S. Wrighton, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 289; *Angew. Chem.* **1988**, *100*, 281; e) M. Brookhart, B. E. Grant, *J. Am. Chem. Soc.* **1993**, *115*, 2151.
- [21] For some selected reviews, see: a) H. C. Brown, *Organic Synthesis via Boranes*, Wiley, New York, **1975**; b) H. C. Brown, B. Singaram, *Pure Appl. Chem.* **1987**, *59*, 879; c) R. Jana, T. P. Pathak, M. S. Sigman, *Chem. Rev.* **2011**, *111*, 1417; d) H. K. Scott, V. K. Aggarwal, *Chem. Eur. J.* **2011**, *17*, 13124; For some selected examples, see: e) J. L. Stymiest, V. Bagutski, R. M. French, V. K. Aggarwal, *Nature* **2008**, *456*, 778; f) V. Bagutski, R. M. French, V. K. Aggarwal, *Angew. Chem. Int. Ed.* **2010**, *49*, 5142; *Angew. Chem.* **2010**, *122*, 5268; g) A. Bonet, M. Oda-chowski, D. Leonori, S. Essafi, V. K. Aggarwal, *Nat. Chem.* **2014**, *6*, 584.
- [22] D. J. Parks, W. E. Piers, *Tetrahedron* **1998**, *54*, 15469.
- [23] For a review on catalytic regioselective functionalization of alkenes, see: M. Beller, J. Seayad, A. Tillack, H. Jiao, *Angew. Chem. Int. Ed.* **2004**, *43*, 3368; *Angew. Chem.* **2004**, *116*, 3448.
- [24] V. K. Aggarwal, M. Binanzer, M. C. D. Ceglie, M. Gallanti, B. W. Glasspoole, S. J. F. Kendrick, R. P. Sonawane, A. Vázquez-Romero, M. P. Webster, *Org. Lett.* **2011**, *13*, 1490.
- [25] a) Y. Hatanaka, S. Fukushima, T. Hiyama, *Heterocycles* **1990**, *30*, 303; b) S. E. Denmark, Z. Wang, *J. Organomet. Chem.* **2001**, *624*, 372; c) S. E. Denmark, J. H.-C. Liu, *J. Am. Chem. Soc.* **2007**, *129*, 3737.

Received: June 6, 2016

Published online: July 21, 2016