

RESEARCH ARTICLE

View Article Online

View Journal | View Issue



Cite this: *Org. Chem. Front.*, 2017, 4, 1517

Received 30th March 2017,
Accepted 23rd April 2017

DOI: 10.1039/c7qo00250e

rs.c.li/frontiers-organic

Pincer cobalt complex-catalyzed Z-selective hydrosilylation of terminal alkynes†

Xiaoyong Du, Wenjun Hou, Yanlu Zhang and Zheng Huang*

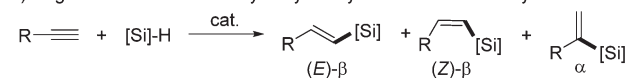
A phosphine-iminopyridine ($P^C NN$) cobalt-catalyzed Z-selective hydrosilylation of terminal alkynes with Ph_2SiH_2 has been developed for the synthesis of (Z)- β -vinylsilanes with high regio- and stereoselectivity and wide functional group tolerance. Furthermore, the Co-catalyzed hydrosilylations of unsymmetrical arylalkyl disubstituted internal alkynes afford *syn*-addition products with unique regioselectivity: the silyl group is added to the alkyl-substituted carbon, instead of the aryl-substituted carbon. The (Z)- β -vinylsilane products are further applied to Pd-catalyzed Hiyama–Denmark cross-couplings for stereoselective synthesis of (Z)-disubstituted alkenes.

Introduction

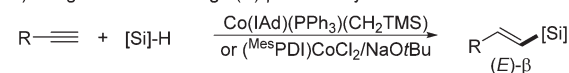
Transition metal-catalyzed hydrosilylation of alkynes with hydrosilanes is one of the most atom-economical approaches to access vinylsilanes,¹ which are valuable intermediates in organic synthesis.² The hydrosilylation of a terminal alkyne can generate three possible products, (E)- β -, (Z)- β -, and α -vinylsilanes (Scheme 1a), and thus controlling the regio- and stereoselectivity is a key issue during the H–Si addition process. The selective synthesis of (Z)- β -vinylsilanes is considered to be more challenging than the formation of the thermodynamically more stable (E)- β -isomers. Indeed, many transition metal-catalyzed hydrosilylation reactions selectively form (E)- β -vinylsilanes.³ Nevertheless, a number of catalysts using noble-metals, such as Rh,⁴ Ir,^{4g,5} and Ru,⁶ have been developed for the (Z)- β -selective hydrosilylation of terminal alkynes.

Over the past decade, the low abundance, high cost, and the environmental concerns associated with the noble metals have spurred extensive studies toward developing earth-abundant base-metal alternatives.⁷ So far, Fe,⁸ Co,⁹ and Ni¹⁰ complexes have been proven effective for alkyne hydrosilylation, but only bis(imino)pyridine iron complexes gave high (Z)- β -selectivity in the hydrosilylations of two terminal alkyne substrates.^{8c,d} Very recently, several groups reported that cobalt complexes could catalyze the hydrosilylation of terminal alkynes with high α - or (E)- β -selectivity. In 2014, Deng developed a carbene-ligated Co(I) complex and applied it to the

a) Regio- and stereoselectivity in hydrosilylation of terminal alkyne



b) Deng and Thomas: high (E)- β -selectivity



inal alkenes.¹⁷ Moreover, the (P^CNN)Co catalyst effects the hydrosilylation of internal alkynes, and intriguingly, the reactions of arylalkyl disubstituted alkynes produce vinylsilanes containing the silyl unit at the alkyl-substituted olefinic carbon, rather than the aryl-substituted one. The (Z)-β-vinylsilane products can undergo Pd-catalyzed Hiyama-Denmark cross-couplings to form (Z)-disubstituted alkenes.

Results and discussion

We commenced our studies by examining the P^CNN ligand-supported Fe and Co catalysts for the hydrosilylation of a simple aliphatic alkyne, 1-hexyne (**3a**), with Ph₂SiH₂ as the silicon source. The results are summarized in Table 1. Using NaHBet₃H (2 mol%) as the activator, both *t*Bu- and *i*Pr-substituted Fe complexes, ((^{*t*Bu}P^CNN^{*i*Pr}))FeCl₂ (**1a**, 1 mol%) and ((^{*i*Pr}P^CNN^{*i*Pr}))FeCl₂ (**1b**, 1 mol%), were inactive for the hydrosilylation (entries 1 and 2). However, 1-hexyne (1.2 equiv.) reacted with Ph₂SiH₂ to give (Z)-β-vinylsilane **4a** and (E)-β-vinylsilane **5a** when the Co analogues were employed. Using the most sterically hindered complex **2a** (1 mol%) bearing a *t*Bu-substituted phosphino group and *i*Pr substituents at the 2,6-positions of the *N*-aryl ring, the hydrosilylation in THF at 25 °C gave 13% **4a** and 18% **5a** after 24 h (entry 3). Reducing the steric hindrance of the P^CNN ligands resulted in a significant improvement of the activity and selectivity for the desired

(Z)-β-product. The reactions using complexes ((^{*i*Pr}P^CNN^{*i*Pr}))CoCl₂ **2b** and ((^{*i*Pr}P^CNN^{Me}))CoCl₂ **2c** containing *i*Pr-substituted phosphino groups formed **4a** in 85% and 83% yield; α-vinylsilane was not observed in both cases (entries 4 and 5).

Further optimizations were conducted to improve the selectivity for *cis*-vinylsilane. The best Z-selectivity was obtained when the reaction occurred under solvent-free conditions using a 1.5 : 1 ratio of **3a** : Ph₂SiH₂ in the presence of 1 mol% of **2b** and 2 mol% of NaHBet₃H; the run at 25 °C for 24 h produced (Z)-vinylsilane **4a** in 95% yield with the Z/E stereoselectivity of 95 : 1 (entry 6). A control experiment without the precatalyst **2b**, but with NaHBet₃H, gave no hydrosilylation product (entry 7), and another control without NaHBet₃ indicated that the addition of the activator was necessary for the catalysis (entry 8). Finally, we explored the catalytic performance of this Co catalyst for hydrosilylations with primary and tertiary hydrosilanes. Tertiary silanes (EtO)₃SiH, MD'M (1,1,1,3,5,5,5-heptamethyltrisiloxane), Et₃SiH and PhMe₂SiH were unreactive under the reaction conditions (entries 9–12). Although the reaction with PhSiH₃ gave the *anti*-Markovnikov products in high yield (95% totally), the stereoselectivity was low (Z/E = ~1 : 1) (entry 13).

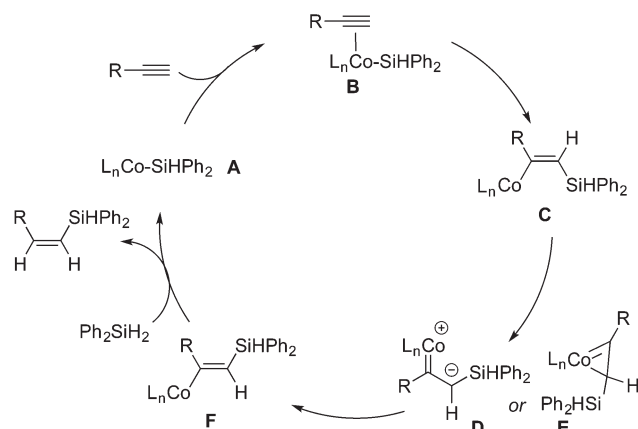
To evaluate the scope of the Co-catalyzed alkyne hydrosilylation, the reactions with a variety of functionalized terminal alkynes and a number of internal alkynes were carried out using **2b** as the precatalyst. The results are summarized in Table 2. All reactions with Ph₂SiH₂ proceeded to completion within 24 h at room temperature under solvent-free conditions. For terminal alkyne substrates, most reactions were highly selective for the formation of the (Z)-β-vinylsilane products (Z/E > 95 : 5). Linear terminal alkynes gave the corresponding products **4a–d** in moderate-to-high isolated yield with excellent selectivity. 3-Cyclohexyl-1-propyne **3e** and 3-cyclopentyl-1-propyne **3f** underwent hydrosilylations in useful yields and high selectivities. The catalyst is compatible with terminal alkynes bearing various functional groups, including chloride (**4g**), nitrile (**4h**), tertiary amine (**4i**, **4j**), amide (**4k**) and even ester (**4o**). Aliphatic alkynes containing protecting groups, such as silyl ether (**4l**, **4m**) and tosylate (**4n**, 88%), afforded the desired (Z)-β-vinylsilanes in high yields and high selectivities. Aryl terminal alkynes are un

Table 2 Cobalt-catalyzed hydrosilylation of various terminal and internal alkynes with Ph_2SiH_2 ^a

$\begin{array}{c} \text{R}-\text{C}\equiv\text{C}-\text{H} \\ \text{or} \\ \text{R}-\text{C}\equiv\text{C}-\text{R}' \end{array}$		$\xrightarrow[\text{neat, rt, 24 h}]{\begin{array}{c} 1 \text{ mol\% } \mathbf{2b} \\ 2 \text{ mol\% } \text{NaBEt}_3\text{H} \\ 100 \text{ mol\% } \text{Ph}_2\text{SiH}_2 \end{array}}$	$\begin{array}{c} \text{R}-\text{CH}=\text{CH}-\text{SiHPh}_2 \\ \text{or} \\ \text{R}-\text{CH}=\text{CH}-\text{SiHPh}_2 \end{array}$
3a-w			4a-w
	4a , 88%, 99:1		4b , 88%, 98:2
	4c , 91%, 99:1		4d , 61%, 93:7
	4e , 83%, 91:9		4f , 58%, 90:10
	4g , 83%, 98:2		4h , 68%, 84:16 ^b
	4i , 92%, 98:2		4j , 88%, 98:2
	4k , 85%, 97:3		4l , 90%, 98:2
	4m , 93%, 98:2		4n , 88%, 99:1
	4o , 80%, 98:2 ^c		4p , 84%, 99:1
	4q , 71%, 99:1		4r , 82%, 99:1 ^d
	4s , 80%, 90:10 ^d		4t , 94%, 91:9 ^d
	4u , 93%, 88:12 ^d		4v , 91%, 91:9 ^d

^a Reaction conditions: Ph_2SiH_2 (0.6 mmol) and alkyne (0.9 mmol) at 25 °C. Yield of isolated products. *Z/E* ratios of isolated products were determined by ^1H NMR spectroscopy. ^b With 1.2 mmol **3h**. A 84:16 *Z/E* ratio was determined by ^1H NMR spectroscopy. ^c With 2 mol% **2b** and 4 mol% NaBEt_3H . ^d Regioselectivities determined by ^1H NMR spectroscopy.

Noteworthy, the processes exhibited good regioselectivities, furnishing tri-substituted olefins with the Ph_2HSi unit



Scheme 2 Proposed mechanism involving the Ojima–Crabtree type rearrangement for Co-catalyzed (Z)-selective hydrosilylation of terminal alkynes.

gave the corresponding products **7k** and **7l** in 66 and 64% isolated yields, respectively. Functional Z-vinylsilanes such as **4g** and **4o** reacted with 4-iodo-1,1'-biphenyl under standard conditions and gave the corresponding Z-alkenes **7m** and **7n** in excellent yields and selectivities.

A mechanism accounting for the formation of (Z)- β -vinylsilane is presented in Scheme 2. On the basis of the precedents of Co-catalyzed hydrosilylation processes,^{11,16,17,21} we propose that the catalytic cycle involves a low-valent Co(I) silyl intermediate. The insertion of the coordinated terminal alkyne into the Co–Si bond forms a vinyl Co intermediate, (Z)- β -vinyl-l-alken-2-yl-cobalt (**C**). Due to the significant steric repulsion between the bulky silyl group and the metal moiety, complex **C** undergoes isomerization to form a sterically less demanding complex **F**, (E)- β -vinyl-l-alken-2-yl-cobalt, through the Ojima–Crabtree type rearrangement.^{4h,5g} **E** then reacts with Ph_2SiH_2 to form (Z)-vinylsilane and regenerate the Co(I) silyl species **A**.

Conclusions

In conclusion, we have developed a highly efficient cobalt-catalyzed regio- and stereoselective hydrosilylation of terminal alkynes with Ph_2SiH_2 to generate (Z)- β -vinylsilanes with high functional group tolerance. The silyl groups introduced into the vinylsilane products offer flexible synthetic manipulations as demonstrated by the Hiyama–Denmark cross-couplings with aryl halides, allowing a convenient, stereoselective synthesis of *Cis*-disubstituted alkenes.

Acknowledgements

We gratefully acknowledge the financial support from the National Natural Science Foundation of China (No. 21272255, 21121062).

Notes and references

- (a) H. Brunner, *Angew. Chem., Int. Ed.*, 2004, **43**, 2749; (b) B. M. Trost and Z. T. Ball, *Synthesis*, 2005, 853; (c) S. J. Clarson, *Silicon*, 2009, **1**, 57; (d) D. S. W. Lim and E. A. Anderson, *Synthesis*, 2012, 983.
- (a) T. H. Chan and I. Fleming, *Synthesis*, 1979, 761; (b) T. A. Blumenkopf and L. E. Overman, *Chem. Rev.*, 1986, **86**, 857; (c) E. Langkopf and D. Schinzer, *Chem. Rev.*, 1995, **95**, 1375; (d) I. Fleming, A. Barbero and D. Walter, *Chem. Rev.*, 1997, **97**, 2063.
- (a) H. Aneetha, W. Wu and J. G. Verkade, *Organometallics*, 2005, **24**, 2590; (b) G. De Bo, G. Berthon-Gelloz, B. Tinant and I. E. Markó, *Organometallics*, 2006, **25**, 1881; (c) Y. Nakao, H. Imanaka, J. Chen, A. Yada and T. Hiyama, *J. Organomet. Chem.*, 2007, **692**, 585; (d) G. Berthon-Gelloz, J.-M. Schumers, G. De Bo and I. E. Markó, *J. Org. Chem.*, 2008, **73**, 4190; (e) A. Hamze, O. Provot, J.-D. Brion and M. Alami, *J. Organomet. Chem.*, 2008, **693**, 2789; (f

- L. A. Oro, *Organometallics*, 2016, **35**, 2410; (g) R. S. Tanke and R. H. Crabtree, *J. Am. Chem. Soc.*, 1990, **112**, 7984.
- 6 (a) M. A. Esteruelas, J. Herrero and L. A. Oro, *Organometallics*, 1993, **12**, 2377; (b) H. Katayama, K. Taniguchi, M. Kobayashi, T. Sagawa, T. Minami and F. Ozawa, *J. Organomet. Chem.*, 2002, **645**, 192; (c) C. S. Arico and L. R. Cox, *Org. Biomol. Chem.*, 2004, **2**, 2558; (d) S. V. Maifeld, M. N. Tran and D. Lee, *Tetrahedron Lett.*, 2005, **46**, 105; (e) C. Menozzi, P. I. Dalko and J. Cossy, *J. Org. Chem.*, 2005, **70**, 10717; (f) M. Nagao, K. Asano, K. Umeda, H. Katayama and F. Ozawa, *J. Org. Chem.*, 2005, **70**, 10511; (g) R. Gao, D. R. Pahls, T. R. Cundari and C. S. Yi, *Organometallics*, 2014, **33**, 6937; (h) C. Conifer, C. Gunanathan, T. Rinesch, M. Hölscher and W. Leitner, *Eur. J. Inorg. Chem.*, 2015, 333; (i) Y. Na and S. Chang, *Org. Lett.*, 2000, **2**, 1887.
- 7 (a) K. Junge, K. Schroder and M. Beller, *Chem. Commun.*, 2011, **47**, 4849; (b) B. D. Sherry and A. Fürstner, *Acc. Chem. Res.*, 2008, **41**, 1500; (c) I. Bauer and H.-J. Knölker, *Chem. Rev.*, 2015, **115**, 3170; (d) M. D. Greenhalgh, A. S. Jones and S. P. Thomas, *ChemCatChem*, 2015, **7**, 190; (e) J. Sun and L. Deng, *ACS Catal.*, 2016, **6**, 290; (f) X. Du and Z. Huang, *ACS Catal.*, 2017, 1227.
- 8 (a) S. C. Bart, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.*, 2004, **126**, 13794; (b) C. Belger and B. Plietker, *Chem. Commun.*, 2012, **48**, 5419; (c) M. D. Greenhalgh, D. J. Frank and S. P. Thomas, *Adv. Synth. Catal.*, 2014, **356**, 584; (d) A. J. Challinor, M. Calin, G. S. Nichol, N. B. Carter and S. P. Thomas, *Adv. Synth. Catal.*, 2016, **358**, 2404.
- 9 (a) M. Isobe, R. Nishizawa, T. Nishikawa and K. Yoza, *Tetrahedron Lett.*, 1999, **40**, 6927; (b) L. Yong, K. Kirleis and H. Butenschön, *Adv. Synth. Catal.*, 2006, **348**, 833; (c) T. Konno, K.-i. Taku, S. Yamada, K. Moriyasu and T. Ishihara, *Org. Biomol. Chem.*, 2009, **7**, 1167; (d) K.-H. Huang and M. Isobe, *Eur. J. Org. Chem.*, 2014, 4733; (e) A. Rivera-Hernández, B. J. Fallon, S. Ventre, C. Simon, M.-H. Tremblay, G. Gontard, E. Derat, M. Amatore, C. Aubert and M. Petit, *Org. Lett.*, 2016, **18**, 4242.
- 10 (a) T. Bartik, G. Nagy, P. Kvintovics and B. Happ, *J. Organomet. Chem.*, 1993, **453**, 29; (b) A. Tillack, S. Pulst, W. Baumann, H. Baudisch, K. Kortus and U. Rosenthal, *J. Organomet. Chem.*, 1997, **532**, 117; (c) M. R. Chaulagain, G. M. Mahandru and J. Montgomery, *Tetrahedron*, 2006, **62**, 7560; (d) J. Berding, J. A. van Paridon, V. H. S. van Rixel and E. Bouwman, *Eur. J. Inorg. Chem.*, 2011, 2450.
- 11 Z. Mo, J. Xiao, Y. Gao and L. Deng, *J. Am. Chem. Soc.*, 2014, **136**, 17414.
- 12 J. H. Docherty, J. Peng, A. P. Dominey and S. P. Thomas, *Nat. Chem.*, 2017, DOI: 10.1038/nchem.2697.
- 13 (a) J. Guo and Z. Lu, *Angew. Chem., Int. Ed.*, 2016, **55**, 10835; (b) J. Guo, X. Shen and Z. Lu, *Angew. Chem., Int. Ed.*, 2017, **56**, 615.
- 14 Z. Zuo, J. Yang and Z. Huang, *Angew. Chem., Int. Ed.*, 2016, **55**, 10839.
- 15 Note that (Z)- β -selective hydroboration of terminal alkynes has been previously reported by Chirik *et al.* See: J. V. Obligation, J. M. Neely, A.