ORGANIC
LETTERS

2008
Vol. 10, No. 12
2505−2508

Silaborations of 1,3-Enynes − Substrate Controlled Allene/1,3-Diene Selectivity

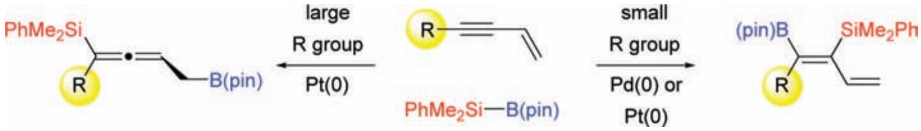
Christian Lüken and Christina Moberg*

*KTH School of Chemical Science and Engineering, Organic Chemistry,
SE 100 44 Stockholm, Sweden*

kimo@kth.se

Received April 4, 2008

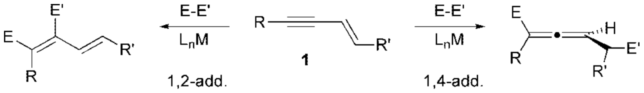
ABSTRACT



Silaboration of 1,3-enynes catalyzed by group 10 metal complexes affords 1,3-dienes with vinylborane and vinylsilane functions or 1,2-dienes with allylborane and vinylsilane functions. The type of product formed is determined by the size of the alkyne substituent.

Silaborations of unsaturated organic substrates catalyzed by group 10 metal complexes constitute synthetically versatile processes providing adducts containing both boron and silicon functionalities, which subsequently can be used for further transformations.[1,2] Among the reactions studied, those involving alkynes have been most thoroughly explored, but additions to 1,2- and 1,3-dienes also proceed readily to afford 1,2- and 1,4-adducts, respectively. Enantioselective reactions with both types of substrates have been achieved by employing chiral metal catalysts,[3,4] although additions to 1,4-disubstituted 1,3-dienes are limited to cyclic compounds, acyclic substrates resulting mainly in disproportionation affording equimolar amounts of allylsilanes and dienylboranes.[5] We became interested in extending the reactions to 1,3-enynes. Although 1,6- and 1,7-enynes have been subjected to silaborations[6] and other interelement additions[7] to afford products either from addition to the triple bond or from carbocyclization, we are aware of only one single example of a reaction of a conjugated enyne, 1-ethynylcyclohexene, which resulted in pure 1,2-addition to the triple bond.[8] Besides 1,2-addition, 1,4-addition to 1,3-enynes, leading to allenic derivatives, may be envisaged (Scheme 1). Both types of processes have large synthetic potential leading either to 1,2-functionalized dienes (1,2-addition) or adducts containing both allylic and vinylic reactive groups (1,4-addition).

Scheme 1. 1,2- and 1,4-Addition to 1,3-Enynes



To explore these possibilities, we subjected a number of 1,3-enynes (**1**) to metal-catalyzed silaborations using 2-(dimethylphenylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**).[9] The enynes were prepared by Pd-catalyzed coupling of the appropriate vinyl and alkyne derivatives. First (5*E*)-

---

(1) (a) Ito, Y. *J. Organomet. Chem.* **1999**, *576*, 300. (b) Suginome, M.; Ito, Y. *J. Organomet. Chem.* **2003**, *680*, 43.

(2) General reviews on E−E′ additions: (a) Suginome, M.; Ito, Y. *Chem. Rev.* **2000**, *100*, 3221. (b) Beletskaya, I.; Moberg, C. *Chem. Rev.* **1999**, *99*, 3435. (c) Beletskaya, I.; Moberg, C. *Chem. Rev.* **2006**, *106*, 2320.

(3) 1,2-Dienes: (a) Suginome, M.; Ohmura, T.; Miyake, Y.; Mitani, S.; Ito, Y.; Murakami, M. *J. Am. Chem. Soc.* **2003**, *125*, 11174. (b) Ohmura, T.; Suginome, M. *Org. Lett.* **2006**, *8*, 2503. (c) Ohmura, T.; Taniguchi, H.; Suginome, M. *J. Am. Chem. Soc.* **2006**, *128*, 13682.

(4) 1,3-Dienes: Gerdin, M.; Moberg, C. *Adv. Synth. Catal.* **2005**, *347*, 749.

(5) Gerdin, M.; Moberg, C. *Org. Lett.* **2006**, *8*, 2929.

(6) Onozawa, S.; Hatanaka, Y.; Tanaka, M. *Chem. Commun.* **1997**, 1229.

(7) (a) Mori, M.; Hirose, T.; Wakamatsu, H.; Imakuni, N.; Sato, Y. *Organometallics* **2001**, *20*, 1907. (b) Lautens, M.; Mancuso, J. *Synlett* **2002**, 394. (c) Kuniyasu, H.; Ogawa, A.; Miyazaki, S.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1991**, *113*, 9796.

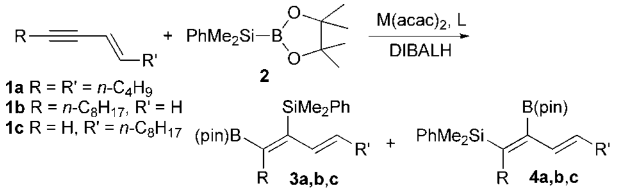
(8) Suginome, M.; Nakamura, H.; Ito, Y. *Chem. Commun.* **1996**, 2777.

(9) Suginome, M.; Matsuda, T.; Ito, Y. *Organometallics* **2000**, *19*, 4647.

10.1021/ol800768x CCC: $40.75

dodec-5-en-7-yne[10] (**1a**) was reacted with **2** under different conditions. Use of catalysts prepared from Pd(acac)$_2$, DIBALH, and ligand (PEt$_3$, P(OEt)$_3$, PPhMe$_2$, or PPh$_3$) resulted in pure 1,2-addition to the triple bond to yield a single regioisomer, determined to be **3a** by NOESY experiments. Best results, full conversion of starting material and 72% isolated yield of **3a**, were achieved with PEt$_3$ as ligand at 80 °C (Table 1, entry 1). Lower temperatures resulted in incomplete conversion of starting material. The remaining phosphines gave lower conversions but equally high regioselectivity (entries 2−4). In contrast, with catalysts prepared from Ni(acac)$_2$ or Pt(acac)$_2$ and PEt$_3$, mixtures of **3a** and the regioisomer **4a** were obtained, in the former case with slight preference for **4a** (entries 5 and 6). The structure of **4a** was also confirmed by a NOESY experiment.

Table 1. Silaboration of Enynes **1a**−**c**[a]



entry	enyne	M	L	% conversion (% yield, NMR[b])	**3**:**4**
1	**1a**	Pd[c]	PEt$_3$	100/72[d]	>98:2
2	**1a**	Pd	P(OEt)$_3$	76	>98:2
3	**1a**	Pd	PPhMe$_2$	16	>98:2
4	**1a**	Pd	PPh$_3$	19	>98:2
5	**1a**	Ni	PEt$_3$	100	43:57
6	**1a**	Pt[c]	PEt$_3$	100	76:24
7	**1b**	Pd	PEt$_3$	100	60:40
8	**1b**	Pd	P(OEt)$_3$	100	80:20
9	**1b**	Pd	PPhMe$_2$	100[f]	64:36
10	**1b**	Ni	PEt$_3$	100[f]	60:40
11	**1b**	Pt[e]	PEt$_3$	100 (100)[f]	28:72
12	**1b**	Pt[e]	PPh$_3$	100 (93)[f]	28:72
13	**1c**	Pd	PEt$_3$	100 (90)	>98:2
14	**1c**	Pd	P(OEt)$_3$	100	>98:2
15	**1c**	Pd	PPhMe$_2$	100 (88)	>98:2
16	**1c**	Pt	PEt$_3$	100	>98:2

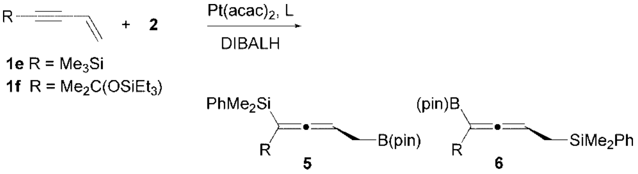
[a] 10 mol % catalyst, M:L = 1:2, DIBALH, toluene, 80 °C, 44 h. [b] Determined by integration of the olefinic signals with 1-methoxynaphthalene as internal standard. [c] Reaction complete after 24 h. [d] Isolated yield. [e] 5 mol % catalyst. [f] 20 h.

Next enynes **1b**[11] and **1c**[12] with terminal alkene and alkyne functions, respectively, were subjected to the same conditions as **1a**. In all cases pure addition to the alkyne function took place. With **1b** the additions exhibited poor regioselectivity, resulting in mixtures of regioisomers **3b** and **4b**, even with catalysts containing Pd (entries 7−12). From **1c** a single isomer, **3c** according to NOESY, was obtained in high yield with catalysts containing Pd and Pt (entries 13−16), whereas use of the Ni catalyst resulted in a mixture of several products.

The results demonstrate that, with the appropriate choice of catalyst, highly regioselective 1,2-additions can be achieved with 1,4- and 4-substituted enynes whereas those lacking substituents in the 4-position provide mixtures of regioisomers with all types of catalytic systems studied.

Since addition to the triple bond resulted in pure 1,2-addition, we reasoned that initial borylmetalation of the olefinic bond might provide a more successful route to 1,4-adducts. Although the alkyne function usually exhibits higher reactivity than the olefinic bond, we speculated that a bulky substituent at the triple bond might decrease its reactivity and favor initial addition to the olefinic bond. Allenic products from 1,4-addition were indeed observed by Hayashi and co-workers in palladium-catalyzed hydrosilylations of 1,3-enynes with bulky alkyne substituents.[13] We therefore turned our attention to enynes **1e**,[14] **1f**, and **1g**.[13a] We were pleased to find that, in addition to analogues of the previously observed dienes **3** and **4**, allene derivatives **5** were observed under certain conditions (Tables 2 and 3). Although no product was obtained from reaction of **1e** in the presence of a catalyst prepared from Pt(acac)$_2$, DIBALH, and P(OEt)$_3$ (Table 2, entry 1) the use of PPh$_3$, PPhMe$_2$, or PCy$_3$ as ligand yielded mixtures of 1,2- and 1,4-adducts, with the latter as the major products (entries 2−4). The allenic product formed preferentially was shown by NOESY to be the regioisomer **5e**. A triplet at δ 4.48 in the ^{1}H NMR spectrum, a signal at 212.9 in the ^{13}C NMR spectrum, and an IR band at 1921

Table 2. Silaboration of Enynes **1e** and **1f** Employing Pt(acac)$_2$/L/DIBALH[a]



entry	enyne	L	*T* (°C)	% yield**5**[b]	% yield **6**[b]	1,4:1,2 add.
1	**1e**	P(OEt)$_3$	80			
2	**1e**	PPhMe$_2$	100	18	4	90:10
3	**1e**	PPh$_3$	100	13	25	70:30
4	**1e**	PCy$_3$	100	37		70:30
5	**1e**	POCy$_3$	100	73		>98:2
6	**1e**		100	75		>98:2
7	**1f**	PCy$_3$	100	26		55:45
8	**1f**	POCy$_3$	100	47		>98:2
9	**1f**		100	46	15	>98:2

[a] 5 mol % Pt(acac)$_2$, M:L = 1:2, DIBALH, toluene, 20 h. [b] By NMR with 1-methoxynaphthalene as internal standard.

---

(10) (a) Yang, C.; Nolan, S. P. *J. Org. Chem.* **2002**, *67*, 591. (b) Zweifel, G.; Lynd, R. A.; Murray, R. E. *Synthesis* **1977**, 52.

(11) Kasatkin, A.; Whitby, R. J. *J. Am. Chem. Soc.* **1999**, *121*, 7039.

(12) Negishi, E.; Kotora, M.; Caiding, X. *J. Org, Chem.* **1997**, *62*, 8957.

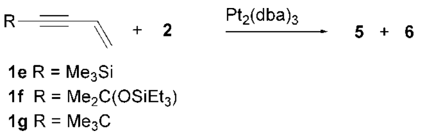
(13) (a) Han, J. W.; Tokunaga, N.; Hayashi, T. *J. Am. Chem. Soc.* **2001**, *123*, 12915. (b) Ogasawara, M.; Ito, A.; Yoshida, K.; Hayashi, T. *Organometallics* **2006**, *25*, 2715.

(14) Waser, J.; González-Gómez, J. C.; Nambu, H.; Huber, P.; Carreira, E. M. *Org. Lett.* **2005**, *7*, 4249.

cm^{-1}, characteristic for allenes, support the suggested structure. The structure of the second allenic regioisomer, **6e**, was also supported by NOESY. Performing the reaction with $POCy_3$ or without addition of ligand resulted in clean formation of **5e** without any detectable amounts of 1,2-adducts (entries 5 and 6). Similar results were obtained for **1f** (entries 7−9), although "ligandless" conditions for this substrate gave a mixture of the two regioisomers. Pt/$POCy_3$ yielded only **5f**, however.

Exclusive formation of allene **5e** from **1e** was also achieved with $Pt_2(dba)_3$ (93% isolated yield, Table 3, entry 1). The second regioisomer was observed along with 1,2-addition products in reactions with **1f** and **1g** (entries 2−7), however. For these substrates the best results were obtained at 60 °C, a higher reaction temperature resulting in lower yield and regioselectivity. Although 1,4-addition products were obtained smoothly from 1-substituted enynes, we have so far not been able to isolate any allenic products from 1,4-disubstituted enynes.

Table 3. Silaboration of Enynes **1e**−**g** Employing $Pt_2(dba)_3$[a]

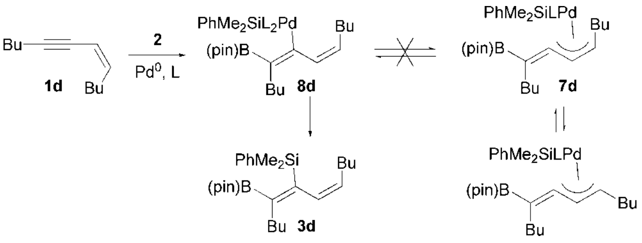


entry	enyne	*T* (°C)	% isolated yield **5** + **5′** (by NMR)	**5**: **6**	1,4:1,2 add.
1	**1e**	80	93	>98:2	>98:2
2	**1f**	60	91	10:1	90:10
3	**1f**	80	(71)	2:1	90:10
4	**1f**	100	(42)	1:2	65:35
5	**1g**	60	78	20:1	>98:2
6	**1g**	80	(81)	10:1	>98:2
7	**1g**	100	(67)	10:1	>98:2

[a] 2.5 mol % $Pt_2(dba)_3$, toluene, 21 h.

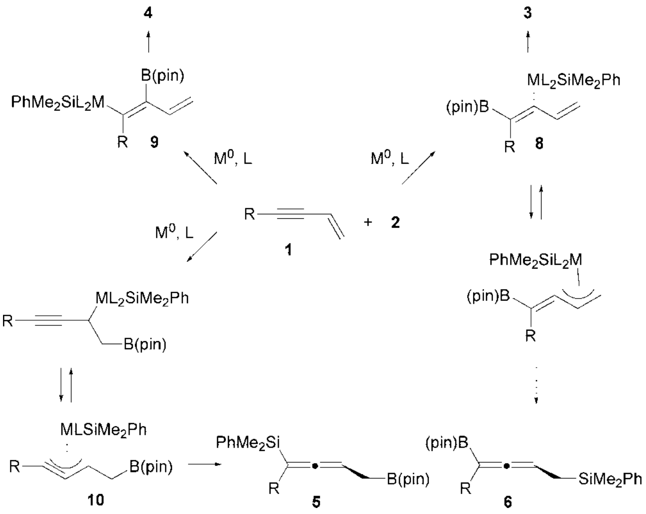
The reactions are assumed to take place via oxidative addition of silylborane **2** to M(0) followed by borylmetalation, which usually is favored over silylmetalation,[15] of the triple bond. Final reductive elimination is expected to afford the observed 1,2-addition products. For 1,4-addition to result from initial addition to the triple bond, it is assumed that formation of an η^3-allyl metal complex is required. To test whether an allyl complex was involved, (5*Z*)-dodec-5-en-7-yne (**1d**), prepared by reduction of dodeca-5,7-diyne,[16] was used in the catalytic reaction. The presence of only the cis-product **3d** from reactions employing either $Pd(acac)_2$ or $Pt(acac)_2$ and PEt_3 (full conversion after 24 h at 80 °C) is a strong indication against the intermediacy of an η^3-allyl complex (**7d**), since isomerization to the *syn*-allyl complex, assumed to be more stable than the initially formed *anti*-complex, and subsequent formation of **3a** would then have been expected (Scheme 2). Reductive elimination from the intermediate **8d** to form the observed product therefore most likely is more rapid than formation of an allyl complex, at least in reactions with 1,4-disubstituted enynes.

Scheme 2. Possible Mechanism for Silaboration of **1d**



If it is assumed that insertion of the unsaturated moiety proceeds into the metal−boron bond rather than into the metal−silicon bond, addition of "B-M-Si" to the alkyne function can give rise to regioisomers **8** and **9**, which after reductive elimination provide **3** and **4**, respectively (Scheme 3). The formation of allenic product **6** can also be explained by the intermediacy of adduct **8**, provided that, contrary to what was observed for **1a** and **1d**, initial addition to the triple bond leads to an η^3-allyl complex; the different structures of **1a**/**1d** and **1e**−**g** may provide a rationale for the different reactivities. In contrast, isomer **5** cannot be obtained from **9**, but requires either insertion of the alkyne into the metal−silicon bond, which is commonly not observed, or initial addition to the olefinic bond. We prefer the latter explanation since **5** was obtained only from substrates with triple bonds carrying sterically crowded substituents. A feasible route to allenes **5** thus proceeds via η^3-propargyl metal complex **10**, which is expected to undergo reductive elimination to form the observed compounds **5**.

Scheme 3. Reaction Pathways of Enynes **1e**−**g**



---

(15) Sagawa, T.; Asano, Y.; Ozawa, F. *Organometallics* **2002**, *21*, 5879.
(16) Delas, C.; Urabe, H.; Sato, F. *Chem. Commun.* **2002**, 272.

In conclusion, we have found conditions for silaborations of 1,3-enynes which, depending on the structure of the substrate, lead either to stereo- and regiochemically well-defined functionalized 1,3-dienes or to allenes containing silyl and boron functional groups. The 1,4-addition is limited to substrates containing bulky substituents in the 1-position and no substituent in the 4-position. Preliminary results show that analogous products can be obtained from diboration of enynes **1**. Our present efforts are devoted to attempts to achieve nonracemic adducts by using catalysts containing chiral ligands.

Acknowledgment. This work was supported by the Carl Trygger Foundation for Research. We would like to thank Dr. Krister Zetterberg, KTH School of Chemical Science and Engineering, for valuable discussions.

Supporting Information Available: Experimental procedures for starting materials and for silaborations and ^{1}H and ^{13}C NMR spectra of products from silaboration. This material is available free of charge via the Internet at http://pubs.acs.org.

OL800768X