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Trans- and *Cis*-Selective Lewis Acid Catalyzed Hydrogermylation of Alkynes

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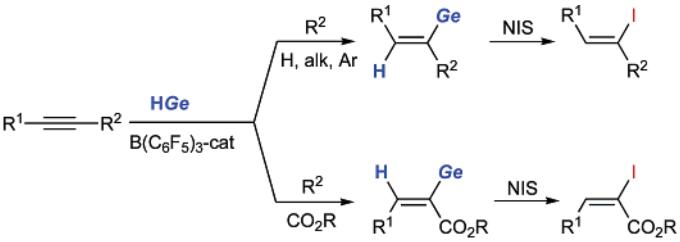
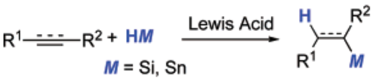
ABSTRACT



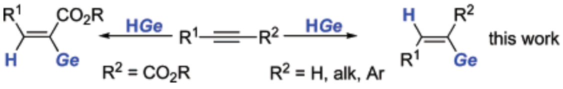
The first examples of Lewis acid catalyzed hydrogermylation of alkynes have been demonstrated. It was found that this method has much higher functional group compatibility compared to the known Lewis acid catalyzed hydrosilylation and hydrostannation reactions. Remarkably, the stereochemical outcome of this hydrogermylation reaction depends on the nature of the alkyne used: proceeding via a *trans*-addition pathway with simple alkynes and *cis*-addition with propiolates. Mechanistic studies strongly support the proposed rationale on the origins of *cis*-selectivity in the hydrogermylation of activated alkynes.

Hydrometalation of alkynes is a simple and efficient approach to vinylmetals, useful synthetic intermediates in organic chemistry.[1] Normally, transition-metal-catalyzed hydrometalation serves as a mild protocol toward *cis*-addition products.[2,3] Alternatively, *trans*-addition products can be obtained via Lewis acid catalyzed hydrometalations of C−C multiple bonds (eq 1).[4,5] Unfortunately, these methods exhibit low functional group tolerance,[6,7] thus justifying development of milder *trans*-selective general hydrometalation.[8] Herein, we report the first Lewis acid catalyzed hydrogermylation reaction,[9] which not only exhibits higher functional group tolerance in comparison to the previously reported Lewis acid catalyzed hydrometalation reactions but also exhibits perfect *trans*-addition for simple alkynes and *cis*-addition for propiolates (eq 2).



Oertle 1985
Yamamoto 1996
Jung 1999
Gevorgyan 2002

(1)



this work

(2)

During our continuing studies on $B(C_6F_5)_3$-catalyzed reductions with hydrosilanes,[10] we found this system to be

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[1] Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375.

[2] (a) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1989; p 1479. (b) Marciniec, B. *Comprehensive Handbook on Hydrosilylation*; Pergamon Press: Oxford, 1992. (c) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds. Pergamon Press: Oxford, 1991; Vol. 8, p 763.

[3] An isolated case of transition-metal-catalyzed *trans*-addition has recently been disclosed. See: (a) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2001**, *123*, 12726. (b) Trost, B. M.; Ball, Z. T.; Jöge, T. *J. Am. Chem. Soc.* **2002**, *124*, 7922.

[4] For Si, see: (a) Oertle, K.; Wetter, H. *Tetrahedron Lett.* **1985**, *26*, 5511. (b) Asao, N.; Sudo, T.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 7654. (c) Sudo, T.; Asao, N.; Gevorgyan, V.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 2494. (d) Song, Y.-S.; Yoo, B. R.; Lee, G.-H.; Jung, I. N. *Organometallics* **1999**, *18*, 3109. (e) Rubin, M.; Schwier, T.; Gevorgyan, V. *J. Org. Chem.* **2002**, *67*, 1936.

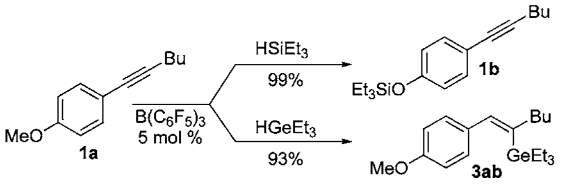
[5] For Sn, see: Asao, N.; Liu, J.-X.; Sudoh, T.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 4568.

[6] The harsh conditions employed limited the functional group compatibility to bulky TBS- or TIPS-protected alcohols; see refs 4 and 5.

[7] $(Me_3Si)_3SiH$ was used in the radical and Lewis acid catalyzed hydrosilylation of of terminal propiolates, though the stereochemistry of addition is not established. See: Liu, Y.; Yamazaki, S.; Yamabe, S. *J. Org. Chem.* **2005**, *70*, 556.

10.1021/ol0521026 CCC: $30.25

highly efficient for the cleavage of alkyl−aryl ethers[10b] and for the hydrosilylation of olefins.[4e] While investigating the functional group compatibility of these reactions, we discovered that treatment of ambident substrate **1a** with 1 equiv of triethylsilane resulted in quantitative formation of the cleavage product **1b** with no traces of hydrosilylation products detected (eq 3). It was hypothesized that the chemoselectivity of the reaction can be affected by switching silicon to a metal of lower oxophilicity. To this end, we examined the reactivity of **1a** with triethylgermane. *To our great delight, this reaction resulted in clean hydrogermylation without disturbing the methoxy moiety, even with excess germane (eq 3)!*



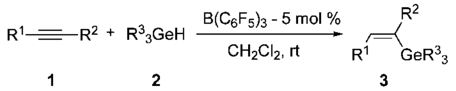
1a **1b** **3ab**

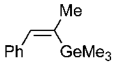
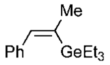
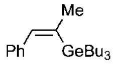
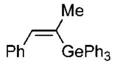
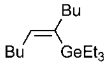
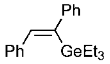
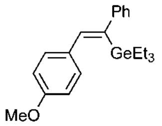
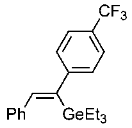
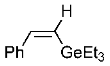
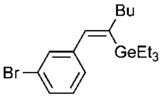
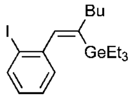
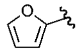
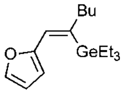
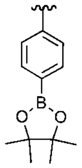
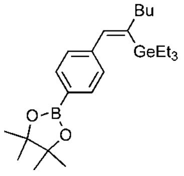
(3)

Encouraged by this result, we tested hydrogermylation of different alkynes under these reaction conditions (Table 1). It was found that, regardless of the hydrogermane used, the reaction with **1c** proceeded with perfect regio- and stereoselectivity, providing the corresponding (*Z*)-vinylgermanes in virtually quantitative yield (entries 1−4). Hydrogermylation of symmetrically substituted alkynes **1d** and **1e** proceeded uneventfully to give the corresponding products in excellent yields (entries 5 and 6). Reaction with unsymmetrical tolanes **1f** and **1g** provided the stilbene derivatives with high regioselectivity and high yields (entries 7 and 8). Likewise, terminal alkyne **1h** gave (*Z*)-vinylgermane **3hb** in 96% yield (entry 9). Aryl alkynes possesing halogen at the aromatic ring reacted uneventfully to produce the corresponding vinylgermanes in quantitative yield (entries 10 and 11). Furyl-containing alkyne **1k** reacted smoothly to give the (*Z*)-vinylgermane **3kb** in 89% yield (entry 12). Remarkably, the pinacolborane moiety did not interfere with the hydrogermylation reaction: the corresponding vinylgermane was obtained quantitatively (entry 13).

It deserves mention that this hydrometalation methodology exhibits wider functional group tolerance compared to that displayed in previously known Lewis acid catalyzed methodologies. Indeed, anisole derivative **1f** and furyl derivative **1k** would not be tolerated in any previous Lewis acid catalyzed hydrometalation reactions,[4] whereas employment of aryl-containing metal hydride **2d** (entry 4) would lead to a decrease in yields.[11] Furthermore, it should be emphasized that this method offers wider functional group tolerance vs radical hydrogermylation,[8] which would not tolerate aryl halides **1i** and **1j**.[12]

Table 1. *Trans*-Hydrogermylation of Simple Alkynes



#	R^1	R^2		R^3	Product **3**		% yield[a]
1	Ph	Me	(**c**)	Me (**a**)		**3ca**	>99%
2	"	"		Et (**b**)		**3cb**	99%
3	"	"		Bu (**c**)		**3cc**	>99%
4	"	"		Ph (**d**)		**3cd**	>99%
5	Bu	Bu	(**d**)	Et (**b**)		**3db**	95%
6	Ph	Ph	(**e**)	Et (**b**)		**3eb**	99%
7	Ph	p-OMe-Ph	(**f**)	Et (**b**)		**3fb**	93%
8	p-CF3-Ph	Ph	(**g**)	Et (**b**)		**3gb**	>99%
9	Ph	H	(**h**)	Et (**b**)		**3hb**	96%
10	m-Br-Ph	Bu	(**i**)	Et (**b**)		**3ib**	>99%
11	o-I-Ph	Bu	(**j**)	Et (**b**)		**3jb**	>99%
12		Bu	(**k**)	Et (**b**)		**3kb**	89%
13		Bu	(**l**)	Et (**b**)		**3lb**	>99%

[a] Isolated yields.

We propose the following mechanism to account for the *trans*-selective hydrogermylation of simple alkynes (Scheme 1). Equilibration between germane **2** and $B(C_6F_5)_3$ produces ate-complex **a**, analogous to that formed from hydrosilane

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[8] For *trans*-selective radical hydrogermylation of alkyl-substituted alkynes with triphenylgermane, see: Ichinose, Y.; Nozaki, K.; Wakamatsu, K.; Oshima, K. *Tetrahedron Lett.* **1987**, *28*, 3709.

[9] $EtAlCl_2$ was used in the functionalization of Ge(100) surfaces, though the stereoselectivity of this transformation was not investigated. See: Choi, K.; Buriak, J. M. *Langmuir* **2000**, *16*, 7737.

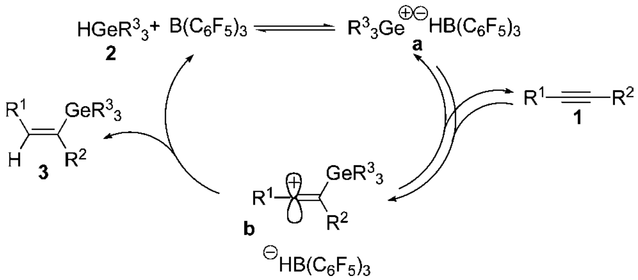
[10] (a) Gevorgyan, V.; Liu, J.-X.; Rubin, M.; Benson, S.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 8919. (b) Gevorgyan, V.; Rubin, M.; Benson, S.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 6179. (c) Gevorgyan, V.; Rubin, M.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **2001**, *66*, 1672.

[11] It was observed that employment of arylsilanes led to decreased reaction yields in the hydrosilylation of alkynes (see ref 4b) and Friedel−Crafts alkylations of the aryl groups at silicon in the hydrosilylation of olefins (see ref 4d).

[12] Nakamura, T.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 747.

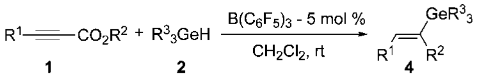
and $B(C_6F_5)_3$, proposed by Piers.[13] Direct reversible addition of coordinated germylium[14] to alkyne produces vinyl cation **b**. The regiochemistry of this step is governed by the stability of the forming cation, which is in perfect agreement with the observed regiochemistry of the products. Vinyl cation **b** is quenched by bulky hydride, $^{-}HB(C_6F_5)_3$, from the least hindered site to give *trans*-addition product **3** and regenerate the catalyst.[15]

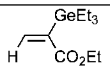
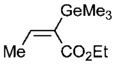
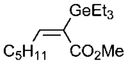
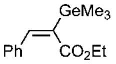
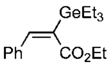
Scheme 1. Mechanism for *Trans*-Hydrogermylation



Investigating the scope of hydrogermylation, we found that the *ester* group can be *perfectly tolerated in this reaction!* Thus, hydrogermylation of **2** with propiolates proceeded with very good yields (Table 2). Remarkably, in striking contrast to all known Lewis acid catalyzed hydrometalations, this reaction proceeded *with cis-selectivity!* A variety of terminal (entry 1), alkyl- (entries 2–3), and aryl-substituted propiolates (entries 4–5) reacted to give vinyl germanes **4** in high yields.

Table 2. *Cis*-Hydrogermylation of Differently Substituted Propiolates

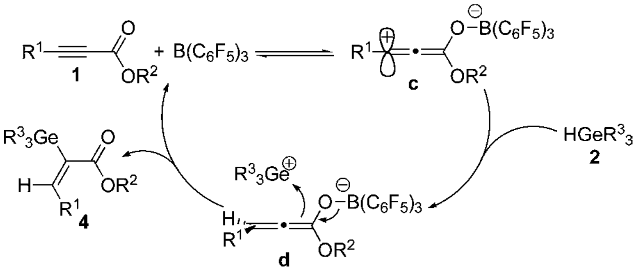


#	R^1	R^2		R^3	Product **4**		% yield[a]
1	H	Et	(**m**)	Et (**b**)		**4mb**	89%
2	Me	Et	(**n**)	Me (**a**)		**4na**	>99%
3	n-C_5H_{11}	Me	(**o**)	Et (**b**)		**4ob**	>99%
4	Ph	Et	(**p**)	Me (**a**)		**4pa**	85%
5	"	"		Et (**b**)		**4pb**	>99%

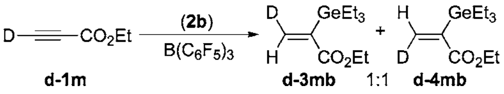
[a] Isolated yields.

It is believed that hydrogermylation of propiolates follows a different mechanistic path than that for nonactivated alkynes (Scheme 2). Reversible coordination of propiolate to $B(C_6F_5)_3$ produces zwitterionic complex **c**, which abstracts hydride from germane **2**[16] to produce allenolate **d**. Trapping of the latter with germylium-type species occurs from the less hindered face, *cis* to H, thus leading to *cis* hydrogermylation products **4**.[17]

Scheme 2. Mechanism for *Cis*-Hydrogermylation

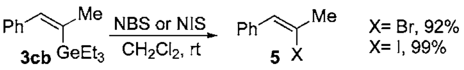


To gain additional support for this mechanism, we tested the hydrogermylation of deuterium analogue d-**1i** (eq 4). If the above idea on the origins of *cis*-selectivity is correct, trapping allenolate **d** generated from d-**1i** (R^1 = D) with germylium species should have no facial preference, thereby generating an equimolar mixture of *cis*- and *trans*-addition products d-**3ib** and d-**4ib**. Indeed, the experiment resulted in a 1:1 mixture of d-**3ib** and d-**4ib**, thus confirming the proposed rationale.

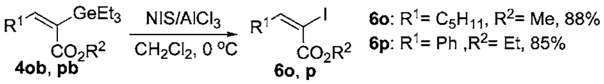


(4)

To test the synthetic utility of hydrogermylation, we pursued transformation of the obtained vinylgermanes into synthetically useful vinylhalides. As expected, halodegermylation of **3cb** proceeded efficiently, producing vinyl halides **5** in excellent yields (eq 5).[18] Iododegermylation of **4** under slightly modified conditions proceeded smoothly, affording vinyl iodides **6** in good yields (eq 6). Importantly, all halodegermylation reactions proceeded with perfect retention of the double-bond geometry.[19]



(5)



(6)

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[13] Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090.

[14] For a stoichiometric reaction between solvated germylium cation and alkene, see: Lambert, J. B.; Zhao, Y.; Wu, H. *J. Org. Chem.* **1999**, *64*, 2729.

[15] This mechanism is analogous to that proposed by Yamamoto for Zr-catalyzed hydrostannation of alkynes (see ref 5) and by us for the hydrosilylation of alkenes (see ref 4e).

[16] It was shown that hydrogermanes are excellent hydride donors for carbocations. See: Mayr, H.; Basso, N. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1046.

[17] An analogous mechanism was proposed for the $AlCl_3$-catalyzed hydrosilylation of terminal propiolates. See ref 6.

In summary, we have demonstrated the first examples of Lewis acid catalyzed hydrogermylation of alkynes. The hydrogermylation reaction exhibits excellent chemoselectivity compared to the analogous hydrosilylation reaction owing to the lower oxophilicity of germanium relative to silicon. Depending on the nature of alkyne, the reaction proceeds with high *trans*- or *cis*-selectivity. It was also shown that halodegermylation of obtained vinylgermanes proceeded smoothly to afford the corresponding (*Z*)- and (*E*)-vinyl halides in high chemical yield, with complete preservation of the double-bond geometry. This methodology allowed for efficient synthesis of bifunctional vinylgermanes **3ib**, **3jb**, and **3lb** which can serve as either electrophilic components in transition-metal-catalyzed cross-coupling reactions at the aryl halide moiety (**3ib** and **3jb**) or as the nucleophilic component in the Suzuki cross-coupling reaction (**3lb**) followed by transformation to the respective vinyl halides via halodegermylation.

Acknowledgment. The support of the Petroleum Research Fund (AC1-40691), administered by the American Chemical Society, and of the National Science Foundation (CHE 0354613) is gratefully acknowledged.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

OL0521026

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(18) For halodegermylation reactions, see: Oda, H.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 3221.

(19) GC/MS analysis of the reaction mixtures showed formation of a single product **6**. Chromatographic isolation of which results in formation of a trace amount (<5%) of *Z*-vinyl iodide.