ORGANIC LETTERS

2010
Vol. 12, No. 5
1056−1058

Ruthenium-Catalyzed *trans*-Hydrogermylation of Alkynes: Formation of 2,5-Disubstituted Germoles through Double *trans*-Hydrogermylation of 1,3-Diynes

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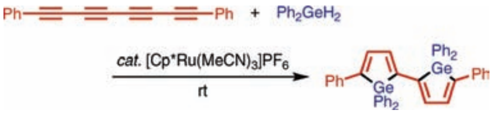
Received January 8, 2010

ABSTRACT



Reaction of triethylgermane and alkynes in the presence of a ruthenium catalyst occurred in a trans fashion. The ruthenium-catalyzed *trans*-hydrogermylation of 1,3-diynes with dihydrogermanes afforded 2,5-disubstituted germoles in good yield through a two fold addition process. The hydrogermylation reaction was successfully applied to synthesis of 2,2′-bigermole.

The synthetic chemistry of organogermanium compounds[1] falls behind that of organosilicon compounds. Nonetheless, the hydrogermylation reaction of unsaturated carbon−carbon bonds provides one of the most reliable processes for making carbon−germanium bonds.[2,3] Transition-metal-catalyzed hydrogermylation of alkynes generally occurs in a cis fashion.[2c,f,h] Trost et al. reported in 2001 that the cationic ruthenium complex [Cp*Ru(MeCN)$_3$]PF$_6$ (**1**) catalyzed a hydrosilylation reaction of alkynes in a trans fashion.[4] Their study prompted us to develop a new synthetic method of siloles (silacyclopentadienes)[5] by applying the complex **1** to the double *trans*-hydrosilylation of 1,3-diynes.[6] We next examined the use of the ruthenium complex **1** as the catalyst for hydrogermylation of alkynes. Herein is described our study on the ruthenium-catalyzed *trans*-selective hydrogermylation reaction of alkynes and its extension to the synthesis of germoles (germacyclopentadienes).[7] The hydrogermylation reaction proceeds so efficiently that even quadruple hydrogermylation of 1,3,5,7-tetrayne is achieved to provide a straightforward access to a 2,2′-bigermole skeleton.

First, hydrogermylation of oct-4-yne (**2**) was examined using triethylgermane (Et$_3$GeH, **3a**) and triphenylgermane (Ph$_3$GeH, **3b**). When **2** was reacted with **3a** (1.1 equiv) in the presence of **1** (10 mol %) in 1,2-dichloroethane at room temperature, a hydrogermylation reaction successfully occurred in a trans fashion to afford (*Z*)-4-(triethylgermyl)oct-4-ene (**4a**) in 77% isolated yield (Scheme 1). The reaction was so stereoselective that the corresponding (*E*)-isomer was not observed in the ^{1}H NMR spectrum of the unpurified reaction mixture. In contrast, the hydrogermylation reaction of **2** with **3b** resulted in the formation of an almost equimolar mixture of the geometric isomers **4b** (45%), although the reason for this divergence in selectivity was unclear.

We next examined hydrogermylation of phenyl-substituted alkynes **5a** and **5b** with **3a** (1.1 equiv). In the reaction of

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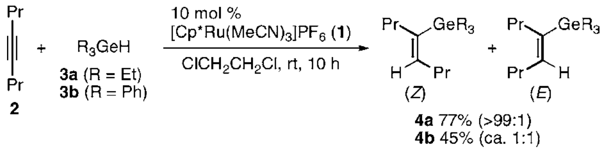
(1) (a) Lesbre, M.; Mazerolles, P.; Satge, J. *The Organic Compounds of Germanium*; Wiley: New York, 1971. (b) *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Rappoport, Z., Ed.; Wiley: Chichester, 2002; Vol. 2.

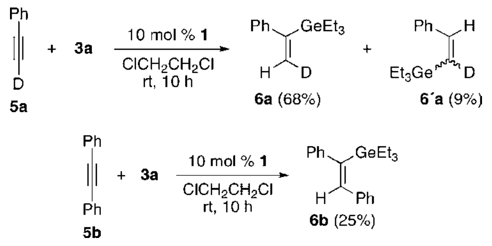
10.1021/ol1000445

Scheme 1. Ruthenium-Catalyzed *trans*-Hydrogermylation of Oct-4-yne (**2**)



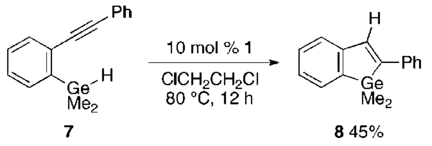
phenylacetylene-*d* (**5a**), *trans*-hydrogermylation gave rise to the branched alkenylgermane **6a** (68%) along with the regioisomers **6′a** (9%) (Scheme 2).[8] The reaction of diphenylacetylene (**5b**) afforded the *trans*-adduct **6b** stereoselectively, albeit in a lower yield.

Scheme 2. Hydrogermylation of **5a** and **5b**



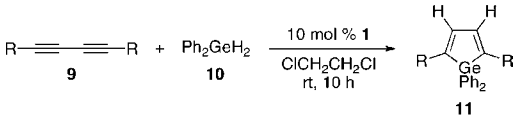
The intramolecular variant of the *trans*-hydrogermylation reaction using **7** required heating at 80 °C, and 1-germaindene **8** was produced in 45% isolated yield (Scheme 3).

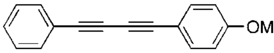
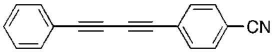
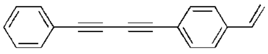
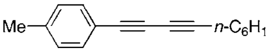
Scheme 3. Intramolecular Hydrogermylation of **7**



Next, we applied the complex **1** to the reaction of 1,3-diynes **9** with dihydrogermanes[9] to compare the catalytic activity of **1** to the double hydrosilylation reaction of dihydrosilanes. Double *trans*-hydrogermylation using diphenylgermane (Ph_2GeH_2, **10**) occurred with significantly increased efficiency to produce 2,5-disubstituted germoles (Table 1). For example, the reaction of 1,4-diphenylbuta-1,3-diyne (**9a**) with **10** (3 equiv) in the presence of 10 mol % of **1** furnished 1,1,2,5-tetraphenylgermole (**11a**) in 93% yield (entry 1), whereas the yield of the corresponding silole was only 29% with the use of 20 mol % of **1**.[6] The germole **11a** was produced without significant decrease of the yield even when 1.2 equiv of **10** was employed. Di(2-naphthyl)butadiyne **9b** was also converted to germole **11b** in a reasonable yield (entry 2), whereas the reaction of sterically more demanding di(1-naphthyl)butadiyne was unsuccessful. Methoxy-substituted diphenylbutadiyne **9c** was a good substrate to afford **11c** in 87% yield (entry 3). The presence of halogen, boron, and silicon functional groups on the phenyl rings was tolerated (entries 4−7). However, a lower yield was observed with the 1,3-diyne **9h** carrying strongly electron-withdrawing nitro groups on the two phenyl rings (entry 8). The 1,3-diynes **9i** and **9j** with the 1- and 4-positions substituted by heteroaromatic groups furnished 2,5-di(heteroaryl)germoles **11i** and **11j**, respectively (entries 9 and 10). Di(cyclohexen-1-yl)butadiyne **9k** reacted with **10** to afford 2,5-dicyclohexenylgermole **11k** in 70% yield (entry 11).

Table 1. Ruthenium-Catalyzed Double *trans*-Hydrogermylation of 1,3-Diynes **9** with Diphenylgermane (**10**)



entry	**9** (R)	**11**	%yield[b]
1	**9a** (Ph)	**11a**	93 (90[c])
2	**9b** (2-naphthyl)	**11b**	66
3	**9c** (4-MeOC_6H_4)	**11c**	87
4	**9d** (4-FC_6H_4)	**11d**	80
5	**9e** (3-BrC_6H_4)	**11e**	93
6	**9f** (3-(pin)BC_6H_4[d])	**11f**	91
7	**9g** (4-$Me_3SiC_6H_4$)	**11g**	75
8	**9h** (4-$O_2NC_6H_4$)	**11h**	40
9	**9i** (3-thienyl)	**11i**	94
10	**9j** (5-pyrimidyl)	**11j**	69
11	**9k** (cyclohexen-1-yl)	**11k**	70
12	 OMe (**9l**)	**11l**	95
13	 CN (**9m**)	**11m**	71
14	 (**9n**)	**11n**	87
15	 Me ... n-C_6H_{13} (**9o**)	**11o**	44

[a] The reaction was carried out with 1,3-diyne **9** and **10** (3.0 equiv) in 1,2-dichloroethane at rt in the presence of **1** (10 mol %). [b] Isolated yield by preparative TLC. [c] Result with 1.2 equiv of **10**. [d] pin = pinacolato (−$OCMe_2CMe_2O$−).

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(2) (a) Fischer, A. K.; West, R. C.; Rochow, E. G. *J. Am. Chem. Soc.* **1954**, *76*, 5878. (b) Kolesnikov, S. P.; Nefedov, O. M. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 352. (c) Corriu, R. J. P.; Moreau, J. J. E. *J. Chem. Soc., D* **1971**, 812. (d) Nozaki, K.; Ichinose, Y.; Wakamatsu, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2268. (e) Wada, F.; Abe, S.; Yonemaru, N.; Kikukawa, K.; Matsuda, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1701. (f) Esteruelas, M. A.; Martín, M.; Oro, L. A. *Organometallics* **1999**, *18*, 2267. (g) Widenhoefer, R. A.; Vadehra, A.; Cheruvu, P. K. *Organometallics* **1999**, *18*, 4614. (h) Kinoshita, H.; Nakamura, T.; Kakiya, H.; Shinokubo, H.; Matsubara, S.; Oshima, K. *Org. Lett.* **2001**, *3*, 2521. (i) Faller, J. W.; Roman, G. K. *Organometallics* **2003**, *22*, 199. (j) Schwier, T.; Gevorgyan, V. *Org. Lett.* **2005**, *7*, 5191. (k) Miura, K.; Ootsuka, K.; Hosomi, A. *J. Organomet. Chem.* **2007**, *692*, 514. (l) Marciniec, B.; Ławicka, H. *Appl. Organomet. Chem.* **2008**, *22*, 510, and references therein.

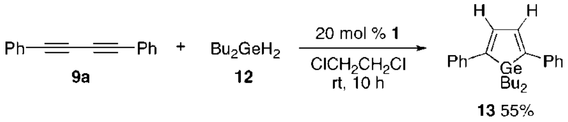
(3) For a recent review on hydrometalation, see: Trost, B. M.; Ball, Z. T. *Synthesis* **2005**, 853.

(4) (a) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2001**, *123*, 12726. (b) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2003**, *125*, 30. (c) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2005**, *127*, 17644, and references therein.

Unsymmetrically substituted 1,4-diaryl-1,3-diynes (**9l** and **9m**) also underwent the hydrogermylation (entries 12 and 13). It is of note that 1,3-diyne **9n** containing a styrene moiety reacted with **10** with the vinyl group remaining intact, affording germole **11n** in 87% yield (entry 14). Unsymmetrical 1,3-diyne **9o** having one alkyl group and one aryl group gave the corresponding germole in moderate yield (entry 15). Double hydrogermylation failed to occur with hexa-2,4-diyne (R = Me) and 1,4-bis(trimethylsilyl)buta-1,3-diyne (R = $SiMe_3$), as is the case of the double hydrosilylation reaction.[6]

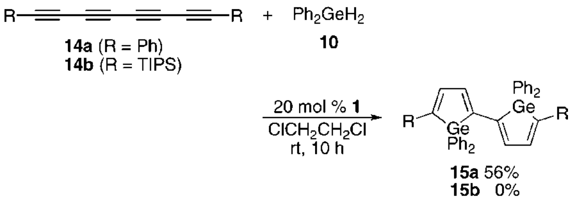
When dibutylgermane (Bu_2GeH_2, **12**) was employed instead of diphenylgermane (**10**), double hydrogermylation also proceeded to produce germole **13**, albeit with lower efficiency (Scheme 4).

Scheme 4. Hydrogermylation of **9a** with Bu_2GeH_2 (**12**)



As a further application of the highly efficient double hydrogermylation reaction, quadruple hydrogermylation of tetraynes was examined. When 1,8-diphenylocta-1,3,5,7-tetrayne (**14a**) was reacted with 6 equiv of **10** at room temperature, the conjugated 1,3-diyne and 5,7-diyne moieties of **14a** both underwent the double *trans*-hydrogermylation to give 2,2′-bigermole **15a** in 56% yield (Scheme 5). For comparison, the tetrayne **14b** end-capped with triisopropylsilyl (TIPS) groups was subjected to analogous reaction conditions. However, **14b** failed to react with **10** and remained intact even after 10 h. Although there is enough space around the inner 3,5-diyne moiety for **10** to approach, the 3,5-diyne moiety flanked by two carbon−carbon triple bonds likely lacks reactivity to undergo the double hydrogermylation.

Scheme 5. Hydrogermylation of Tetraynes **14a** and **14b**



Like siloles, germoles have an energetically low-lying LUMO which is associated with the $\sigma^*-\pi^*$ orbital interaction.[7c] The UV−vis absorption spectrum of **11a** in $CHCl_3$ shows a maximum at 378 nm, and the fluorescence spectrum in hexane exhibited a maximum at 454 nm. The maxima are both shorter than those of 1,1,2,5-tetraphenylsilole by 4 and 13 nm, respectively. Moreover, the germole **11a** has higher fluorescence quantum efficiency (0.81) than the corresponding silole (0.64). Other germoles **11** also exhibited blue-green fluorescence with varying quantum efficiencies (0.03−0.64).

In summary, the hydrogermylation of alkynes proceeds stereoselectively in a trans fashion in the presence of a cationic ruthenium catalyst. The ruthenium-catalyzed double *trans*-hydrogermylation of 1,3-diynes provides a facile synthetic route to 2,5-disubstituted germoles. Exploration of the electronic properties of germole derivatives is in progress.

Acknowledgment. We thank the Japan Society for the Promotion of Science for the fellowship support to S.K.

Supporting Information Available: Experimental procedures and NMR spectral data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) For reviews, see: (a) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215. (b) Yamaguchi, S.; Tamao, K. *J. Chem. Soc., Dalton Trans.* **1998**, 3693. (c) Hissler, M.; Dyer, P. W.; Réau, R. *Coord. Chem. Rev.* **2003**, *244*, 1. (d) Zhan, X.; Barlow, S.; Marder, S. R. *Chem. Commun.* **2009**, 1948.

(6) Matsuda, T.; Kadowaki, S.; Murakami, M. *Chem. Commun.* **2007**, 2627.

(7) For the synthesis of germoles, see: (a) Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 1883. (b) Freeman, W. P.; Tilley, T. D.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 10457. (c) Yamaguchi, S.; Itami, Y.; Tamao, K. *Organometallics* **1998**, *17*, 4910. (d) Sohn, H.; Sailor, M. J.; Magde, D.; Trogler, W. C. *J. Am. Chem. Soc.* **2003**, *125*, 3821, and references therein.

(8) The trans stereochemistry of **6a** was assumed from Trost's study (ref 4b).

(9) Palladium-catalyzed hydrogermylative polymerization of diynes with Ph_2GeH_2 has been reported: Yamashita, H.; Channasanon, S.; Uchimaru, Y. *Chem. Lett.* **2006**, *35*, 398.