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Palladium- and Platinum-Catalyzed Silaboration of Methylenecyclopropanes through Selective Proximal or Distal C−C Bond Cleavage

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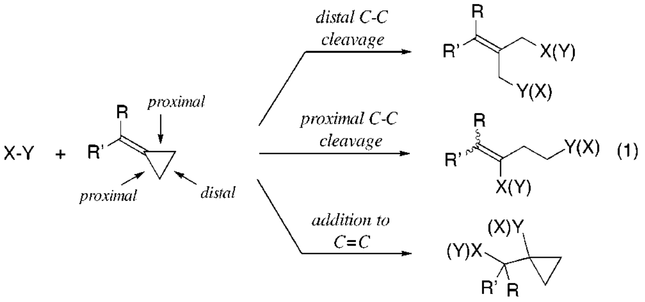
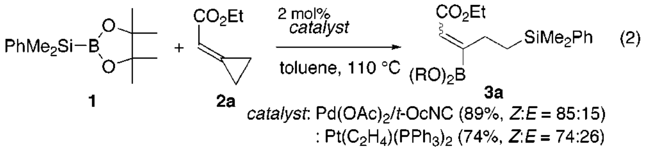
Methylenecyclopropanes (MCPs) are highly strained but readily accessible molecules that have served as useful building blocks in organic synthesis.[1] Especially, increasing attention has been paid to the transition-metal catalyzed reactions of MCPs, which have been employed for construction of complex organic molecules.[2] The use of the transition-metal catalysts for the activation of MCPs may involve σ-bond metathesis reactions with concomitant C−X and C−Y bond formations in the presence of appropriate reactants X−Y such as $R_3Si{-}CN$,[3] $R_3Si{-}H$,[4] $R_3Sn{-}H$,[5] RO−H,[6] $R_2N{-}H$,[7] and $R_2B{-}BR_2$.[8,9]

An attractive but often troublesome feature of MCPs is their multiform reactivities that may lead to formation of a variety of products (eq 1). Besides the three σ-bonds (two proximal and one distal bonds) in the cyclopropane ring to be cleaved, the C=C bond may undergo the addition reaction with X−Y in the presence of the transition-metal catalysts.[3,5,8] Furthermore, for the reactions with unsymmetrical X−Y reagents, the regiochemistry, with which X and Y are introduced to the inequivalent carbon atoms, may make the reaction complicated. Although some σ-bond metathesis reactions of MCPs were found to proceed in a selective fashion to afford one of those possible products, selective synthesis of different products from common reactants by choice of catalyst has never been reported.[2,10] Such synthetic transformations may be highly important from the viewpoint of transition-metal catalysis as well as organic synthesis.



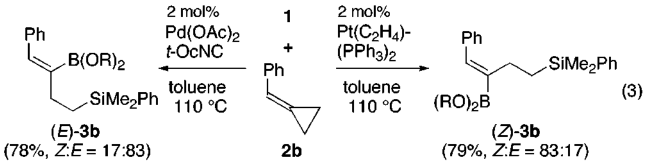
We have developed transition-metal catalyzed reactions of silylboranes with unsaturated organic compounds for selective introduction of silicon- and boron-functionalities to the carbon−carbon multiple bonds, leading to the regio- and stereoselective synthesis of new silylated organoboron compounds.[11,12] Herein, we disclose palladium- and platinum-catalyzed reactions of MCPs with silylborane **1**, in which appropriate choice of metals and ligands selectively promoted the cleavage of the proximal or the distal C−C bond of MCPs, giving the corresponding silaboration products regio- and stereoselectively.

We initially examined the reaction of ethyl cyclopropylideneacetate (**2a**) with **1** in the presence of a palladium/*t*-OcNC catalyst (*t*-OcNC: 1,1,3,3-tetramethylbutyl isocyanide), which was reported as an effective catalyst for silaborations of carbon−carbon multiple bonds with **1**.[12b,c] The reaction was completed within 4 h at 110 °C in toluene to afford α,β-unsaturated ester **3a** in 89% yield as a 85:15 mixture of *Z* and *E* isomers (eq 2). The product possessed a vinylic boryl group as well as a homoallylic silyl group in the molecule, indicating the proximal C−C/Si−B metathesis proceeded regioselectively. The exclusive proximal C−C bond cleavage with an introduction of the boryl group to the sp^2 carbon was also achieved with $Pt(CH_2{=}CH_2)(PPh_3)_2$.

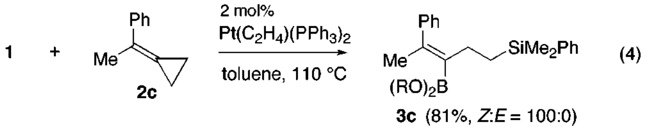


catalyst: $Pd(OAc)_2$/*t*-OcNC (89%, *Z*:*E* = 85:15)
: $Pt(C_2H_4)(PPh_3)_2$ (74%, *Z*:*E* = 74:26)

Of interest is that the stereoselective silaborative cleavage at the proximal C−C bond of **2b** either *cis* or *trans* to the phenyl group depended upon the catalyst employed. While the platinum catalyst gave (*Z*)-**3b** selectively via a cleavage of the proximal C−C bond *trans* to the phenyl group, the palladium catalyst afforded the corresponding *E* product predominantly via the proximal *cis*-C−C bond cleavage (eq 3).



Higher selectivity for the Pt-catalyzed cleavage at the less sterically hindered proximal C−C bond was observed in the reaction of **2c**, giving alkenylborane (*Z*)-**3c** in high yield as a sole product (eq 4). With this substrate, however, use of the palladium-isonitrile catalyst resulted in low conversion with formation of a complex mixture of products.



Similarly, **2d** reacted with **1** in the presence of the platinum catalyst, resulting in the selective formation of alkenylborane **3d** via the proximal C−C bond cleavage (eq 5; Table 1, entry 1). Although the palladium-isonitrile catalyst failed to achieve high

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[1] Synthesis of MCPs: Brandi, A.; Goti, A. *Chem. Rev.* **1998**, *98*, 589.

[2] Reviews: (a) Binger, P.; Büch, H. M. *Top. Curr. Chem.* **1987**, *135*, 77. (b) Ohta, T.; Takaya, H. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, 1991; Vol. 5, p 1185.

[3] Chatani, N.; Takeyasu, T.; Hanafusa, T. *Tetrahedron Lett.* **1988**, *29*, 3979.

[4] Bessmertnykh, A. G.; Blinov, K. A.; Grishin, Yu. K.; Donskaya, N. A.; Tveritinova, E. V.; Yur'eva, N. M.; Beletskaya, I. P. *J. Org. Chem.* **1997**, *62*, 6069.

[5] Lautens, M.; Meyer, C.; Lorenz, A. *J. Am. Chem. Soc.* **1996**, *118*, 10676.

[6] Camacho, D. H.; Nakamura, I.; Saito, S.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 3365.

[7] Nakamura, I.; Itagaki, H.; Yamamoto, Y. *J. Org. Chem.* **1998**, *63*, 6458.

[8] Ishiyama, T.; Momota, S.; Miyaura, N. *Synlett* **1999**, 1790.

[9] For the related σ-bond metathesis reactions of MCPs with malonates and derivatives, see: Tsukada, N.; Shibuya, A.; Nakamura, I.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 8123.

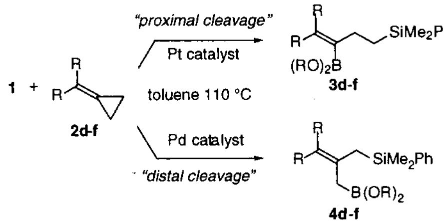
[10] Such examples have been known for the cycloaddition reactions: (a) Bapuji, S. A.; Motherwell, W. B.; Shipman, M. *Tetrahedron Lett.* **1989**, *30*, 7107. Compare the following reports: (b) Noyori, R.; Kumagai, Y.; Umeda, I.; Takaya, H. *J. Am. Chem. Soc.* **1972**, *94*, 4018. (c) Binger, P.; Schuchardt, U. *Angew. Chem.* **1977**, *89*, 254.

[11] Suginome, M.; Ito, Y. *Chem. Rev.* **2000**, *100*, 3221.

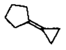
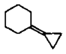
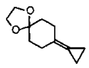
[12] For recent examples, see: (a) Suginome, M.; Matsuda, T.; Yoshimoto, T.; Ito, Y. *Org. Lett.* **1999**, *1*, 1567. (b) Suginome, M.; Ohmori, Y.; Ito, Y. *Synlett* **1999**, 1567. (c) Suginome, M.; Matsuda, T.; Nakamura, H.; Ito, Y. *Tetrahedron* **1999**, *55*, 8787.

10.1021/ja002885k CCC: $19.00

Table 1. Reactions of Cycloalkylidenecyclopropanes **2d**−**f** with Silylborane **1** in the Presence of Palladium and Platinum Catalysts[a]



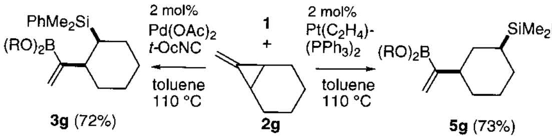
(5)

entry	2	catalyst	%yield of 3^b (proximal)	%yield of 4^b (distal)
1	 (**2d**)	$Pt(C_2H_4)(PPh_3)_2$	75 (**3d**)	–
2	**2d**	$Pd(dba)_2/P(OEt)_3$	–	73 (**4d**)
3	 (**2e**)	$Pt(C_2H_4)(PPh_3)_2$	49 (**3e**)	19 (**4e**)
4	**2e**	$Pt(dba)_2/PMePh_2$	71 (**3e**)	–
5	**2e**	$Pd(dba)_2/P(OEt)_3$	–	72 (**4e**)
6	 (**2f**)	$Pt(dba)_2/PMePh_2$	62 (**3f**)	–
7	**2f**	$Pd(dba)_2/P(OEt)_3$	–	70 (**4f**)

[a] A mixture of **1**, **2** (1.2−2.0 equiv), and the catalyst [metal/P = 1/2, 2 mol % (entries 1−3) or 5 mol % (entries 4−7) of the metals] was heated in toluene at 110 °C. [b] Isolated yield.

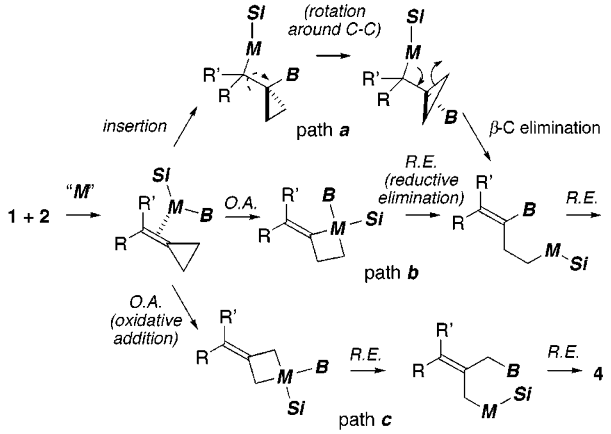
conversion, we found that a catalyst prepared from $Pd(dba)_2$ (dba: dibenzylideneacetone) with $P(OEt)_3$ (2 equiv to Pd) promoted the reaction of **2d** with **1** effectively (entry 2). To our surprise, however, the silaboration product **4d** was derived regioselectively from the distal C−C bond cleavage. The exclusive distal cleavage was also observed in the reactions of related cycloalkylidenecyclopropanes **2e** and **2f** in the presence of the palladium-phosphite catalyst system (entries 5 and 7). It should be noted that a reaction of **2e** with **1** in the presence of $Pt(C_2H_4)(PPh_3)_2$ resulted in the formation of a mixture of proximal and distal bond cleavage products with the former predominating (entry 3). It was found that $Pt(dba)_2/PMePh_2$ catalyzed selectively the proximal C−C cleavage, giving **3e** in good yield (entry 4).[13] The catalyst system was successfully applied to the selective synthesis of **3f** without formation of **4f** (entry 6).

Finally, we refer to the reaction of **2g**, which has substituents on the cyclopropane ring (eq 6). The palladium-isonitrile catalyst induced the silaborative proximal C−C bond cleavage effectively to give 1-organosilyl-2-(α-borylvinyl)cyclohexane **3g** as a single *cis* isomer. In contrast, a platinum catalyst provided *cis*-1,3-disubstituted cyclohexane **5g** stereoselectively in good yield, which may also be derived via the proximal C−C bond cleavage.



(6)

Scheme 1. Possible Mechanisms (Paths ***a***−***c***) for the Reactions of MCPs (**2**) with **1**[a]



[a] ***Si***, ***B***, and ***M*** stand for $SiMe_2Ph$, $B(OR)_2$, and ML*n*, where M = Pd or Pt.

For the closely related reactions of MCPs with hydrosilanes (Rh cat.),[4] tributylstannane (Pd cat.),[5] and diboron (Pt cat.), which proceed through the proximal bond cleavage,[8] a mechanism involving migratory insertion of the C=C bond of MCP and subsequent β-carbon elimination (e.g., path ***a*** in Scheme 1) has been proposed for the formation of intermediary homoallylic transition-metal complexes. The unexpected formation of **5g** may arise from β-hydride elimination from the corresponding homoallylic platinum intermediate and subsequent re-addition of the H−Pt with the opposite direction.[14] Concerning the mechanism involving path ***a***, the *E*/*Z* selectivity in the reactions of unsymmetrically substituted MCPs such as **2b** and **2c** is determined by the direction of σ-bond rotation prior to the β-C elimination step. The rotation should occur so as to avoid steric repulsion, favoring the formation of *Z* isomers regardless of the nature of the metal. However, this mechanism can hardly explain the observed higher *Z*-selectivity for the Pt-catalyzed reaction of **2c** than that for **2b**, since **2c** has less pronounced difference in steric bulkiness between R and R′ than **2b**. We may suggest another mechanistic possibility, which involves oxidative addition of the proximal C−C bond to the transition-metal (path ***b***). The selectivity of the C−C bond cleavage can be affected by the electronic nature of R and R′. The mechanism may be operative predominantly, when the migratory insertion step for path ***a*** is unfavorable due to the substituent(s) at the C=C bond as well as the nature of the metals and ligands. The direct oxidative addition mechanism may also be involved in the distal bond cleavage (path ***c***).[15]

The present reactions of MCPs with **1** may be utilizable for preparation of a variety of synthetically useful silyl-substituted alkenylboranes and allylboranes, which are otherwise inaccessible.

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Supporting Information Available: Experimental procedures including those of transformation for characterization and spectral data for the new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] Use of $Pt(dba)_2$ with no additional ligands resulted in the formation of a complex mixture. See ref 8.

[14] Suginome, M.; Nakamura, H.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2516.

[15] For theoretical studies on transition-metal catalyzed reactions of MCPs with unsaturated organic molecules, see: Suzuki, T.; Fujimoto, H. *Inorg. Chem.* **2000**, *39*, 1113 and references therein.