Boron Catalysis Hot Paper

International Edition: DOI: 10.1002/anie.201700864
German Edition: DOI: 10.1002/ange.201700864

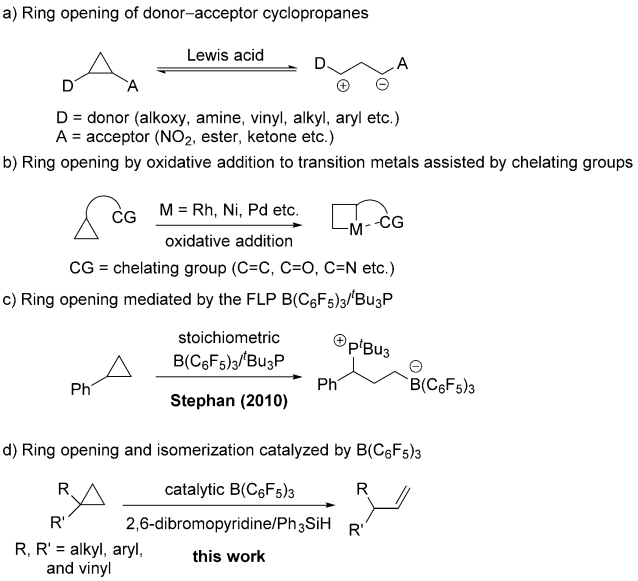
$B(C_6F_5)_3$-Catalyzed Ring Opening and Isomerization of Unactivated Cyclopropanes

*Zi-Yu Zhang[+], Zhi-Yun Liu[+], Rui-Ting Guo, Yu-Quan Zhao, Xiang Li, and Xiao-Chen Wang**

Abstract: *Catalytic amounts of $B(C_6F_5)_3$ promote the ring opening and subsequent isomerization of a series of unactivated cyclopropanes to afford terminal olefins in good yields when a hydrosilane and 2,6-dibromopyridine are employed as additives.*

Cyclopropanes are versatile structural motifs in organic synthesis. Their high ring strain (ca. 115 kJ mol^{-1})[1] is often harnessed to cleave a C–C bond for further functionalizations on the disconnected carbon atoms. Common strategies to selectively open the cyclopropane ring include 1) the Lewis acid catalyzed activation of donor–acceptor (D-A) cyclopropanes[2–4] and 2) transition-metal-mediated processes that often proceed by oxidative addition.[5–7] The former approach requires the presence of electron-donating and -accepting groups to create sufficient electronic bias across the C–C bond (Scheme 1 a).[2–4] The latter approach usually utilizes a chelating group to capture transition metals to facilitate the process and/or direct transition metals towards the target C–C bond (Scheme 1 b).[5–7] However, C–C bond cleavage in simple alkyl- and aryl-substituted cyclopropanes has rarely been studied because their bonds are much less polarized, and they do not have a preinstalled functional group to interact with either Lewis acids or transition metals.[8]

Recently, a seminal study reported by Stephan and coworkers revealed that simple aryl cyclopropanes can be activated with stoichiometric amounts of the frustrated Lewis pair (FLP) $B(C_6F_5)_3$/^{t}Bu$_3$P,[9] and phenylcyclopropane was heterolytically cleaved to afford the zwitterionic phosphonium borate as the final product (Scheme 1 c). The reaction possibly occurred by initial Lewis acid activation of the cyclopropane, prompting cooperative Lewis base attack.[9] Inspired by this work, we sought to develop a catalytic process that utilizes the reactivity of $B(C_6F_5)_3$ towards these unactivated cyclopropanes. Herein, we report that in the presence of a hydrosilane and 2,6-dibromopyridine, $B(C_6F_5)_3$ effectively promotes the C–C bond cleavage of alkyl-, aryl-, and vinyl-substituted cyclopropanes. A subsequent 1,2-hydride migration followed by dissociation of the Lewis acid provides terminal olefins in good yields in a catalytic process (Scheme 1 d).



Scheme 1. Cyclopropane ring-opening reactions.

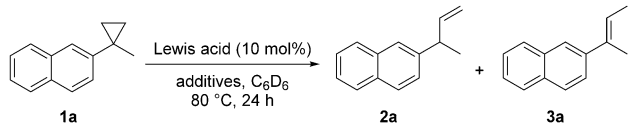
We began our investigations with cyclopropane **1a** as the model substrate to test various reaction conditions (Table 1). Treatment of **1a** with 10 mol% $B(C_6F_5)_3$ in C_6D_6 at 80 °C for 24 h gave the ring-opening/isomerization products **2a** and **3a** in 15 and 5% yield, respectively (entry 1). Interestingly, we found that the addition of a hydrosilane significantly increased the reaction yield. Et_3SiH, Ph_3SiH, and $(EtO)_3SiH$ (20 mol%) were all effective, affording olefin **2a** as the only ring-opened product in 66, 70, and 69% yield, respectively (entries 2–4). We then investigated whether Lewis bases could further improve the reactivity. In the presence of Ph_3SiH, applying ^{t}Bu$_3$P, which was used by Stephan and coworkers to activate aryl cyclopropanes,[9] resulted in full recovery of the starting material (entry 5). A similar inhibitory effect was observed with Ph_3P (entry 6). With pyridine Lewis bases,[10] although 2,6-lutidine and 2,6-di-*tert*-butylpyridine were not effective (entries 7 and 8), 2,6-dibromopyridine improved the yield to 86% (entry 9; for a detailed screening of the reaction conditions, see the Supporting Information). Notably, even in the absence of Ph_3SiH, 2,6-dibromopyridine was found to promote the reaction, albeit in a lower yield (entry 10). Under the same conditions, commonly used Lewis acids, including $BF_3{\cdot}OEt_2$, $TiCl_4$, $Sc(OTf)_3$, $Zn(OTf)_2$, and $Cu(OTf)_2$, were found to be inactive (entries 11–15).

[*] Z.-Y. Zhang,[+] Z.-Y. Liu,[+] R.-T. Guo, Y.-Q. Zhao, X. Li, Prof. Dr. X.-C. Wang
State Key Laboratory and Institute of Elemento-Organic Chemistry
Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University
94 Weijin Road, Tianjin 300071 (China)
E-mail: xcwang@nankai.edu.cn
Homepage: http://www.wangnankai.com/

[+] These authors contributed equally to this work.

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: http://dx.doi.org/10.1002/anie.201700864.

Table 1: Optimization of the ring-opening and isomerization reaction of cyclopropane **1a**.[a]

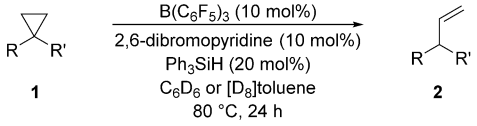


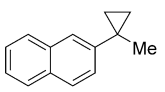
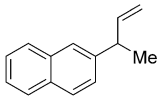
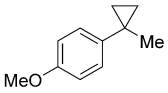
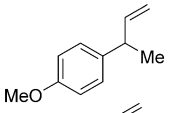
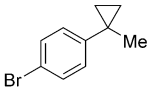
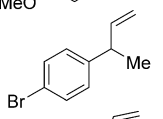
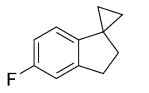
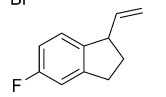
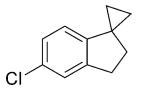
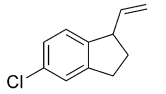
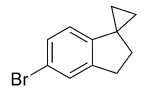
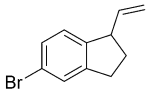
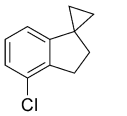
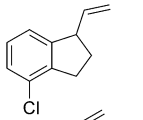
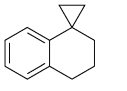
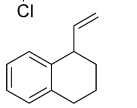
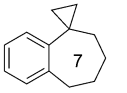
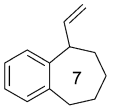
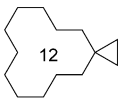
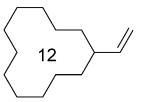
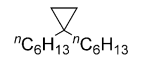
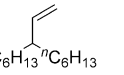
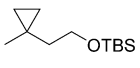
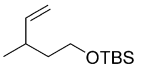
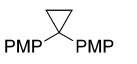
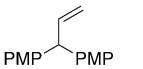
Entry	Lewis acid	Additive (mol%)	**2a** [%][b]
1	$B(C_6F_5)_3$	–	15 (5)[c]
2	$B(C_6F_5)_3$	Et_3SiH (20)	66
3	$B(C_6F_5)_3$	Ph_3SiH (20)	70
4	$B(C_6F_5)_3$	$(EtO)_3SiH$ (20)	69
5	$B(C_6F_5)_3$	Ph_3SiH (20)/$^tBu_3P$ (10)	n.d.
6	$B(C_6F_5)_3$	Ph_3SiH (20)/Ph_3P (10)	n.d.
7	$B(C_6F_5)_3$	Ph_3SiH (20)/2,6-lutidine (10)	18
8	$B(C_6F_5)_3$	Ph_3SiH (20)/2,6-di-*tert*-butylpyridine (10)	52
9	$B(C_6F_5)_3$	Ph_3SiH (20)/2,6-dibromopyridine (10)	86
10	$B(C_6F_5)_3$	2,6-dibromopyridine (10)	60
11	$BF_3{\cdot}OEt_2$	Ph_3SiH (20)/2,6-dibromopyridine (10)	n.d.
12	$TiCl_4$	Ph_3SiH (20)/2,6-dibromopyridine (10)	n.d.
13	$Sc(OTf)_3$	Ph_3SiH (20)/2,6-dibromopyridine (10)	n.d.
14	$Zn(OTf)_2$	Ph_3SiH (20)/2,6-dibromopyridine (10)	n.d.
15	$Cu(OTf)_2$	Ph_3SiH (20)/2,6-dibromopyridine (10)	n.d.

[a] Unless otherwise specified, all reactions were performed in 0.5 mL C_6D_6 with 0.1 mmol **1a** under N_2 atmosphere. [b] Determined by NMR analysis with CH_2Br_2 as the internal standard. [c] Yield of **3a**; **3a** was not formed in all other entries. n.d. = not detected.

With optimized reaction conditions in hand, we investigated the generality of this reaction with a series of cyclopropanes (Table 2). The reaction worked well with 1-methyl-1-(*p*-methoxyphenyl)cyclopropane, providing the desired product in 81% yield (entry 2), whereas electron-deficient 1-methyl-1-(*p*-bromophenyl)cyclopropane only underwent moderate conversion into the product, which was isolated in 50% yield (entry 3). The reaction was found to be particularly efficient for spiro cyclopropanes with an indane or tetralin scaffold, and high conversions were achieved even with substrates bearing electron-withdrawing substituents such as F, Cl, or Br (entries 4–8). The significantly decreased yield of isolated product **2d** compared to the NMR yield was due to product evaporation during workup because of its low boiling point. The enhanced reactivity of these substrates was attributed to the ring strain of the spiro-bicyclic backbone, which facilitates the cleavage of the cyclopropane ring. However, for the spiro cyclopropane linked to a benzocycloheptene ring (**1i**), the reactivity dropped significantly, presumably owing to the decreased ring strain (entry 9). We also subjected 1,1-dialkylcyclopropanes to these reaction conditions. The olefins **2j**, **2k**, and **2l** were obtained in good yields after the ring-opening/isomerization reaction (entries 10–12). For 1,1-diarylcyclopropanes, however, only cyclopropane **1m**, which bears two electron-rich aryl rings, worked well, delivering olefin **2m** in 94% yield (entry 13). Notably, other olefin isomers were either not formed or formed only in trace amounts (< 5%, GC-MS) during our studies with these 1,1-disubstituted cyclopropanes. Unfortunately, monoalkyl-, monoaryl-, and 1,2-disubstituted cyclopropanes were unreactive under the current reaction conditions (see the Supporting Information for details).

Table 2: Scope of 1,1-disubstituted cyclopropanes.[a]

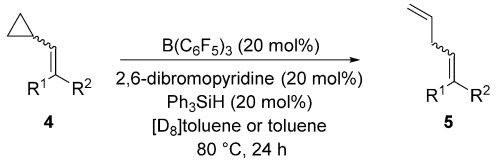


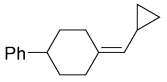
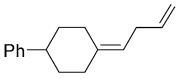
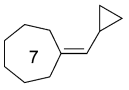
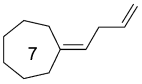
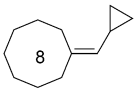
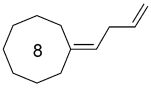
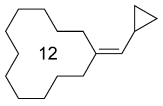
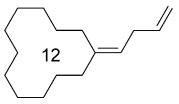
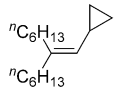
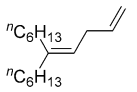
Entry	Substrate		Product		Yield [%][b]
1		**1a**		**2a**	82
2[c]		**1b**		**2b**	81
3[d]		**1c**		**2c**	50
4		**1d**		**2d**	73 (81)
5		**1e**		**2e**	81
6		**1f**		**2f**	82
7		**1g**		**2g**	88
8		**1h**		**2h**	86
9[d]		**1i**		**2i**	57
10		**1j**		**2j**	82
11[d]		**1k**		**2k**	82
12[d]		**1l**		**2l**	72
13[c,d]		**1m**		**2m**	94

[a] Unless otherwise specified, all reactions were performed in 0.5 mL solvent (C_6D_6 for entry 1 and $[D_8]$toluene for all other entries) with **1** (0.1 mmol) under N_2 atmosphere. Products **2a**–**2i** and **2l** are all racemic. [b] Yields of isolated products are given. Yields determined by NMR analysis with an internal standard are given in parentheses. [c] $(EtO)_3SiH$ (0.2 equiv) was used instead of Ph_3SiH to avoid demethylation/silylation of the methoxy group. [d] With $B(C_6F_5)_3$ (20 mol%) and 2,6-dibromopyridine (20 mol%). PMP = *para*-methoxyphenyl, TBS = *tert*-butyldimethylsilyl.

The scope of the reaction was successfully extended to vinyl-substituted cyclopropanes, which produced non-conjugated 1,4-dienes after the ring-opening/isomerization reaction (Table 3). The reaction worked well with a number of styryl cyclopropanes bearing different substituents (**4a**–**4g**), affording the desired 1,4-dienes in moderate to good yields

Table 3: Scope of vinyl cyclopropanes.[a]

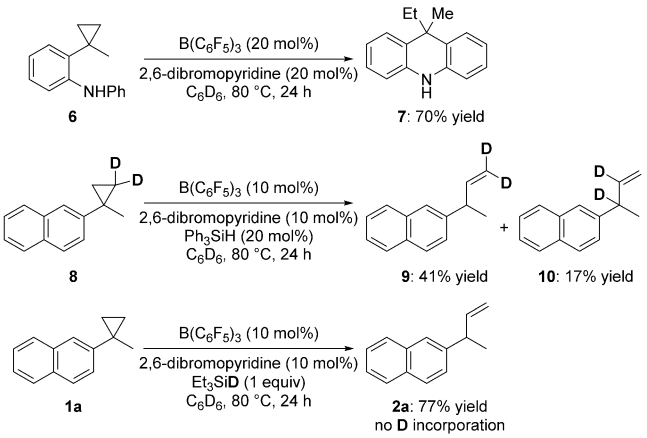


Entry	Substrate (*E*/*Z*)	Product (*E*/*Z*)	Yield [%][b]
1	**4a**: R^1 = Ph, R^2 = Me (1:6.2)	**5a** (1:5.5)	74 (90)
2	**4b**: R^1 = *p*-FC_6H_4, R^2 = Me (1:3.7)	**5b** (1:3.7)	74 (86)
3	**4c**: R^1 = *p*-BrC_6H_4, R^2 = Me (1:2.7)	**5c** (1:3)	72
4	**4d**: R^1 = *p*-IC_6H_4, R^2 = Me (1:2.7)	**5d** (1:3.8)	66
5	**4e**: R^1 = *o*-$CH_3C_6H_4$, R^2 = Me (1:2.8)	**5e** (1:3.2)	70 (83)
6	**4f**: R^1 = Ph, R^2 = ^{i}Pr (1:4.7)	**5f** (1:4)	60
7	**4g**: R^1 = Ph, R^2 = Ph	**5g**	57
8		**4h** 	**5h** 69
9[c]		**4i** 	**5i** 71 (91)
10[c]		**4j** 	**5j** 80
11[c]		**4k** 	**5k** 78
12		**4l** 	**5l** 62

[a] Unless otherwise specified, all reactions were performed in 0.5 mL solvent ([D_8]toluene for entries 1, 2, 5, 6, 7, 9, and 10 and toluene for all other entries) with **4** (0.1 mmol) under N_2 atmosphere. [b] Yields of isolated products are given. Yields determined by NMR analysis with an internal standard are given in parentheses. [c] With $B(C_6F_5)_3$ (10 mol%) and 2,6-dibromopyridine (10 mol%).

(entries 1–7). Again, the significantly decreased yields of isolated products compared to the NMR yields were due to product evaporation during workup. The reaction also proceeded with vinyl cyclopropanes bearing aliphatic substituents (**4h**–**4l**), providing the dienes in yields of 62 to 80% (entries 8–12).

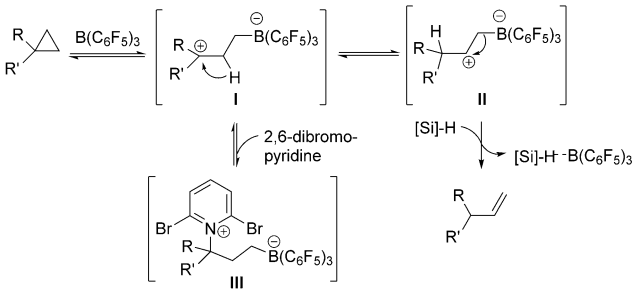
To study the mechanism, we performed several experiments (Scheme 2). When cyclopropane **6** was reacted with catalytic amounts of $B(C_6F_5)_3$ in the presence of 2,6-dibromopyridine, 9,10-dihydroacridine **7** was obtained in 70% yield, suggesting the generation of a $B(C_6F_5)_3$-ligated carbocation intermediate that was trapped through an intramolecular Friedel–Crafts reaction. Then, [D_2]-labeled cyclopropane **8** was subjected to the standard reaction conditions. Two isotopomers (compounds **9** and **10**) were formed depending on which C–C bond was cleaved. The formation of olefin **10** clearly shows that a 1,2-hydride migration occurs after C–C bond cleavage. To investigate the role of the hydrosilane additive, one equivalent of Et_3SiD was used in the reaction of **1a**, but no deuterium incorporation was detected in **2a**. We also monitored the reaction of **1a** by NMR spectroscopy, but failed to observe any silicon-containing intermediates. These experimental results indicate that the hydrosilane additive, albeit crucial for the reactivity, is not directly reacting with the cyclopropane. Whereas hydrosilanes have been shown to act as water scavengers during catalysis with $B(C_6F_5)_3$,[11] the absence of $Ph_3SiOSiPh_3$ in the reaction mixture ruled out this possibility. At the end of the reaction, Ph_3SiH and 2,6-dibromopyridine were mostly recovered. According to studies performed by the groups of Piers,[12] Oestreich,[13] and Sakata,[14] hydrosilanes can coordinate to perfluoroaryl boranes through the interaction of the Si–H bond with the boron atom to form an acid–base adduct. Moreover, this adduct formation was recently confirmed by single-crystal X-ray analysis by Piers, Tuononen, and co-workers.[15] Therefore, we speculate that the hydrosilane might function as a borane-specific Lewis base in our reaction, facilitating the dissociation of $B(C_6F_5)_3$ from the reactive intermediate by competitive coordination and thereby improving catalyst turnover.



Scheme 2. Mechanistic studies.

A possible reaction mechanism is depicted in Scheme 3. Cyclopropane ring opening with $B(C_6F_5)_3$ gives zwitterionic borate **I**, which subsequently undergoes 1,2-hydride migration to afford intermediate **II**. Afterwards, dissociation of $B(C_6F_5)_3$ from **II** assisted by hydrosilane coordination gives the olefin product. During this process, the stabilization of **I** through a reversible FLP-type interaction[9] (**I** to **III**) might account for the yield enhancement upon addition of 2,6-dibromopyridine.

In summary, we have developed a catalytic cyclopropane ring-opening reaction that provides olefins by $B(C_6F_5)_3$-mediated C–C bond cleavage. This reaction is compatible with a broad range of unactivated cyclopropanes that are difficult to activate by other Lewis acids or transition metals.



Scheme 3. Possible reaction mechanism.

We anticipate that our findings will enable the development of other catalytic processes initiated by Lewis acid activation of unactivated cyclopropanes. Further studies exploring such processes, including asymmetric variants, are underway in our laboratory.

Acknowledgements

Financial support was provided by the National Natural Science Foundation of China (21602114), the 1000-Talent Youth Program, and Nankai University. We thank Prof. Michael P. Doyle at UTSA for helpful discussions.

Conflict of interest

The authors declare no conflict of interest.

Keywords: boron · carbocations · C–C activation · isomerization · strained molecules

[1] A. de Meijere, *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 809 – 826; *Angew. Chem.* **1979**, *91*, 867 – 884.

[2] For reviews on D-A cyclopropanes, see: a) H.-U. Reissig, R. Zimmer, *Chem. Rev.* **2003**, *103*, 1151 – 1196; b) M. Yu, B. L. Pagenkopf, *Tetrahedron* **2005**, *61*, 321 – 347; c) C. A. Carson, M. A. Kerr, *Chem. Soc. Rev.* **2009**, *38*, 3051 – 3060; d) F. De Simone, J. Waser, *Synthesis* **2009**, 3353 – 3374; e) M. A. Cavitt, L. H. Phun, S. France, *Chem. Soc. Rev.* **2014**, *43*, 804 – 818; f) T. F. Schneider, J. Kaschel, D. B. Werz, *Angew. Chem. Int. Ed.* **2014**, *53*, 5504 – 5523; *Angew. Chem.* **2014**, *126*, 5608 – 5628; g) H. K. Grover, M. R. Emmett, M. A. Kerr, *Org. Biomol. Chem.* **2015**, *13*, 655 – 671.

[3] For selected recent reports on transformations of D-A cyclopropanes, see: a) W. J. Humenny, P. Kyriacou, K. Sapeta, A. Karadeolian, M. A. Kerr, *Angew. Chem. Int. Ed.* **2012**, *51*, 11088 – 11091; *Angew. Chem.* **2012**, *124*, 11250 – 11253; b) F. de Nanteuil, J. Waser, *Angew. Chem. Int. Ed.* **2011**, *50*, 12075 – 12079; *Angew. Chem.* **2011**, *123*, 12281 – 12285; c) S. Racine, F. de Nanteuil, E. Serrano, J. Waser, *Angew. Chem. Int. Ed.* **2014**, *53*, 8484 – 8487; *Angew. Chem.* **2014**, *126*, 8624 – 8627; d) J. Kaschel, T. F. Schneider, D. Kratzert, D. Stalke, D. B. Werz, *Angew. Chem. Int. Ed.* **2012**, *51*, 11153 – 11156; *Angew. Chem.* **2012**, *124*, 11315 – 11318; e) L. K. B. Garve, M. Pawliczek, J. Wallbaum, P. G. Jones, D. B. Werz, *Chem. Eur. J.* **2016**, *22*, 521 – 525; f) W. Zhu, J. Fang, Y. Liu, J. Ren, Z. Wang, *Angew. Chem. Int. Ed.* **2013**, *52*, 2032 – 2037; *Angew. Chem.* **2013**, *125*, 2086 – 2091; g) S. Chakrabarty, I. Chatterjee, B. Wibbeling, C. G. Daniliuc, A. Studer, *Angew. Chem. Int. Ed.* **2014**, *53*, 5964 – 5968; *Angew. Chem.* **2014**, *126*, 6074 – 6078.

[4] For selected recent reports on enantioselective transformations of D-A cyclopropanes, see: a) H. Xu, J.-P. Qu, S. Liao, H. Xiong, Y. Tang, *Angew. Chem. Int. Ed.* **2013**, *52*, 4004 – 4007; *Angew. Chem.* **2013**, *125*, 4096 – 4099; b) Q.-K. Kang, L. Wang, Q.-J. Liu, J.-F. Li, Y. Tang, *J. Am. Chem. Soc.* **2015**, *137*, 14594 – 14597; c) Y. Xia, X. Liu, H. Zheng, L. Lin, X. Feng, *Angew. Chem. Int. Ed.* **2015**, *54*, 227 – 230; *Angew. Chem.* **2015**, *127*, 229 – 232; d) Y. Xia, L. Lin, F. Chang, Y. Liao, X. Liu, X. Feng, *Angew. Chem. Int. Ed.* **2016**, *55*, 12228 – 12232; *Angew. Chem.* **2016**, *128*, 12416 – 12420; e) F. de Nanteuil, E. Serrano, D. Perrotta, J. Waser, *J. Am. Chem. Soc.* **2014**, *136*, 6239 – 6242.

[5] For reviews on cyclopropane ring-opening reactions mediated by transition metals, see: a) P. A. Wender, G. G. Gamber, T. J. Williams in *Modern Rhodium-Catalyzed Organic Reactions* (Ed.: P. A. Evans), Wiley-VCH, Weinheim, **2005**, pp. 263 – 299; b) M. Rubin, M. Rubina, V. Gevorgyan, *Chem. Rev.* **2007**, *107*, 3117 – 3179; c) L. Jiao, Z.-X. Yu, *J. Org. Chem.* **2013**, *78*, 6842 – 6848; d) L. Souillart, N. Cramer, *Chem. Rev.* **2015**, *115*, 9410 – 9464; e) M. H. Shaw, J. F. Bower, *Chem. Commun.* **2016**, *52*, 10817 – 10829.

[6] For selected recent reports on transition-metal-catalyzed ring-opening reactions of vinylcyclopropanes (VCPs) and alkylidene cyclopropanes (ACPs), see: a) P. A. Wender, A. B. Lesser, L. E. Sirois, *Angew. Chem. Int. Ed.* **2012**, *51*, 2736 – 2740; *Angew. Chem.* **2012**, *124*, 2790 – 2794; b) P. A. Wender, D. N. Fournogerakis, M. S. Jeffreys, R. V. Quiroz, F. Inagaki, M. Pfaffenbach, *Nat. Chem.* **2014**, *6*, 448 – 452; c) X. Hong, M. C. Stevens, P. Liu, P. A. Wender, K. N. Houk, *J. Am. Chem. Soc.* **2014**, *136*, 17273 – 17283; d) B. M. Trost, P. J. Morris, S. J. Sprague, *J. Am. Chem. Soc.* **2012**, *134*, 17823 – 17831; e) X. Hong, B. M. Trost, K. N. Houk, *J. Am. Chem. Soc.* **2013**, *135*, 6588 – 6600; f) M. Lin, G.-Y. Kang, Y.-A. Guo, Z.-X. Yu, *J. Am. Chem. Soc.* **2012**, *134*, 398 – 405; g) Y. Feng, Z.-X. Yu, *J. Org. Chem.* **2015**, *80*, 1952 – 1956; h) A. P. Dieskau, M. S. Holzwarth, B. Plietker, *J. Am. Chem. Soc.* **2012**, *134*, 5048 – 5051; i) P. A. Inglesby, J. Bacsa, D. E. Negru, P. A. Evans, *Angew. Chem. Int. Ed.* **2014**, *53*, 3952 – 3956; *Angew. Chem.* **2014**, *126*, 4033 – 4037; j) P. A. Evans, D. E. Negru, D. Shang, *Angew. Chem. Int. Ed.* **2015**, *54*, 4768 – 4772; *Angew. Chem.* **2015**, *127*, 4850 – 4854.

[7] For selected recent reports on transition-metal-catalyzed cyclopropane ring-opening reactions assisted by carbonyl groups, see: a) M. H. Shaw, E. Y. Melikhova, D. P. Kloer, W. G. Whittingham, J. F. Bower, *J. Am. Chem. Soc.* **2013**, *135*, 4992 – 4995; b) M. H. Shaw, N. G. McCreanor, W. G. Whittingham, J. F. Bower, *J. Am. Chem. Soc.* **2015**, *137*, 463 – 468; c) M. H. Shaw, R. A. Croft, W. G. Whittingham, J. F. Bower, *J. Am. Chem. Soc.* **2015**, *137*, 8054 – 8057; d) N. G. McCreanor, S. Stanton, J. F. Bower, *J. Am. Chem. Soc.* **2016**, *138*, 11465 – 11468.

[8] For a rare example of a ring-opening and isomerization reaction of alkyl cyclopropanes catalyzed by rhodium, see: S. C. Bart, P. J. Chirik, *J. Am. Chem. Soc.* **2003**, *125*, 886 – 887. In this process, the distal C–C bond was cleaved when no chelating group was present, and the initially formed terminal olefins easily underwent double-bond migration along the alkyl chain to give a mixture of olefin isomers.

[9] J. G. M. Morton, M. A. Dureen, D. W. Stephan, *Chem. Commun.* **2010**, *46*, 8947 – 8949.

[10] For studies of the interactions between $B(C_6F_5)_3$ and pyridines, see: a) S. J. Geier, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 3476 – 3477; b) S. J. Geier, A. L. Gille, T. M. Gilbert, D. W. Stephan, *Inorg. Chem.* **2009**, *48*, 10466 – 10474.

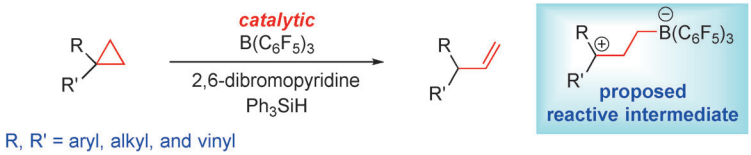
[11] We found that treatment of H_2O (1 equiv) with Ph_3SiH (2 equiv) in the presence of catalytic $B(C_6F_5)_3$ in toluene gave immediate H_2 extrusion and produced $Ph_3SiOSiPh_3$. Indeed, we have utilized this reactivity to remove the coordinated H_2O from the purchased $B(C_6F_5)_3$ to secure the high performance of $B(C_6F_5)_3$. See the Supporting Information for details.
[12] For a pioneering report on $B(C_6F_5)_3$-catalyzed hydrosilylation, see: a) D. J. Parks, W. E. Piers, *J. Am. Chem. Soc.* **1996**, *118*, 9440 – 9441; for detailed mechanistic studies, see: b) D. J. Parks, J. M. Blackwell, W. E. Piers, *J. Org. Chem.* **2000**, *65*, 3090 – 3098.
[13] For confirmation of the S_N2 mechanism in the $B(C_6F_5)_3$-catalyzed hydrosilylation of carbonyl compounds, see: S. Rendler, M. Oestreich, *Angew. Chem. Int. Ed.* **2008**, *47*, 5997 – 6000; *Angew. Chem.* **2008**, *120*, 6086 – 6089; for a related study on $B(C_6F_5)_3$-catalyzed imine hydrosilylation, see: M. Mewald, M. Oestreich, *Chem. Eur. J.* **2012**, *18*, 14079 – 14084.
[14] For a quantum-chemical study, see: K. Sakata, H. Fujimoto, *J. Org. Chem.* **2013**, *78*, 12505.
[15] A. Y. Houghton, J. Hurmalainen, A. Mansikkamäki, W. E. Piers, H. M. Tuononen, *Nat. Chem.* **2014**, *6*, 983 – 988.

Manuscript received: January 24, 2017
Final Article published: ■■ ■■, ■■■■

Communications

Boron Catalysis

Z.-Y. Zhang, Z.-Y. Liu, R.-T. Guo, Y.-Q. Zhao, X. Li, X.-C. Wang* _____ ■■■■–■■■■



R, R' = aryl, alkyl, and vinyl

$B(C_6F_5)_3$-Catalyzed Ring Opening and Isomerization of Unactivated Cyclopropanes

Opening inert cyclopropanes: $B(C_6F_5)_3$-catalyzed ring-opening and isomerization reactions of aryl-, alkyl-, and vinyl-substituted cyclopropanes are described. These reactions generate terminal olefins after a sequential process of C–C bond cleavage, 1,2-hydride migration, and $B(C_6F_5)_3$ dissociation. The addition of 2,6-dibromopyridine and Ph_3SiH is crucial for the reactivity.