CHEMISTRY
A EUROPEAN JOURNAL

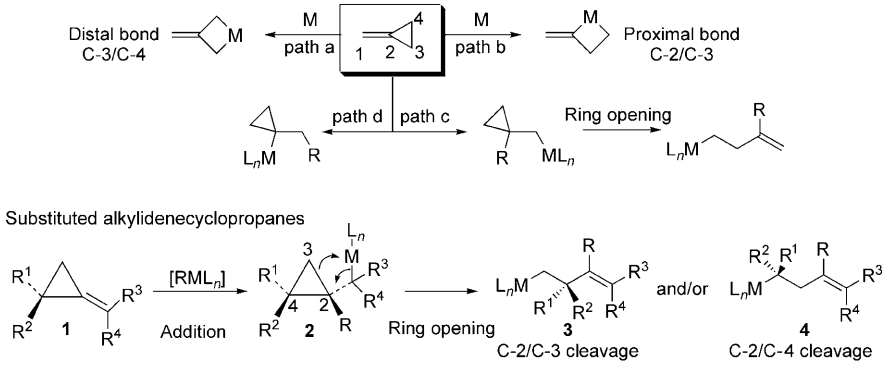
DOI: 10.1002/chem.200902656

Metal-Catalyzed Ring-Opening of Alkylidenecyclopropanes: New Access to Building Blocks with an Acyclic Quaternary Stereogenic Center

Samah Simaan,[a] Alexander F. G. Goldberg,[a] Stephane Rosset,[b] and Ilan Marek*[a]

Dedicated to Professor Alexandre Alexakis on the occasion of his 60th birthday

A very stimulating and dynamic area in organic synthesis nowadays is the asymmetric construction of molecules with quaternary carbon stereocenters, that is, carbon centers with four different non-hydrogen substituents,[1] and the top-of-the-art still remains the asymmetric construction of such stereocenters in acyclic systems.[2] Over the last few years, we[3] and others[4] have been involved in the development of such synthetic strategies. We recently questioned whether it might be possible to develop a simple metal-catalyzed ring-opening reaction of substituted alkylidenecyclopropanes (ACPs) into linear products with complete preservation of the stereochemical integrity of pre-existing stereogenic centers.



Scheme 1. General features of the reaction of ACP.

The reaction of ACPs in the presence of transition-metal catalysts M is known and has been summarized into the following patterns (Scheme 1): insertion of M into the distal bond C-3/C-4 (path a); insertion of M into the proximal bond C-2/C-3 (path b); and addition of organometallic derivative RML_n across the exomethylene double bond leading to two possible products (paths c and d). In the former case (path c), the addition product may be eventually followed by a further ring opening of the cyclopropyl unit (path c).[5] Therefore, the attractive but often troublesome feature of ACPs is their multiform reactivities that may lead to the formation of a variety of products. Among all the reported transformations,[5] the metal-catalyzed hydroboration of ACPs has surprisingly never received attention.[6] In this context, a particularly interesting reaction would be the regioselective anti-Markovnikov addition of pinacol borane[7] to the *exo*-alkylidene moiety of **1**, followed by a regioselective ring-opening reaction of the intermediate **2**. If the ring cleavage occurs through the C-2/C-3 bond, a primary acyclic organometallic species **3** would be obtained potentially with full preservation of the stereochemical information (Scheme 1). On the other hand, if the ring opening occurs through the cleavage of the C-2/C-4 bond, the less stable trisubstituted organometallic species **4** would result. Based on the stability of primary versus tertiary organometallic species (**3** versus **4**, respectively), we anticipated that only the regioisomer **3** would be obtained in such a process. The pur-

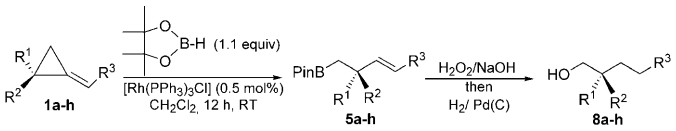
[a] Dr. S. Simaan, A. F. G. Goldberg, Prof. Dr. I. Marek
Contribution from the Mallat Family Laboratory of Organic Chemistry
Schulich Faculty of Chemistry and
the Lise Meitner-Minerva Center for Computational Quantum Chemistry
Technion-Israel Institute of Technology
Technion City, Haifa 32000 (Israel)
Fax: (+972) 48293709
E-mail: chilanm@tx.technion.ac.il

[b] S. Rosset
Departement de Chimie Organique, Universite de Geneve
30 Quai Ernest Ansermet, 1211 Geneve 4 (Switzerland)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200901488.

pose of our initial investigation was to develop this concept and to delineate the reactivity of **1** towards the metal-catalyzed hydroboration reaction. As a test reaction, we subjected methylene- and alkylidenecyclopropanes to pinacol borane (HBPin, 1.1 equiv) in the presence of the Wilkinson catalyst (0.5 mol%) in CH_2Cl_2 at room temperature as shown in Table 1.[8] We chose to use pinacolborane (HBPin)

Table 1. Rh-catalyzed hydroboration of MCPs and ACPs.



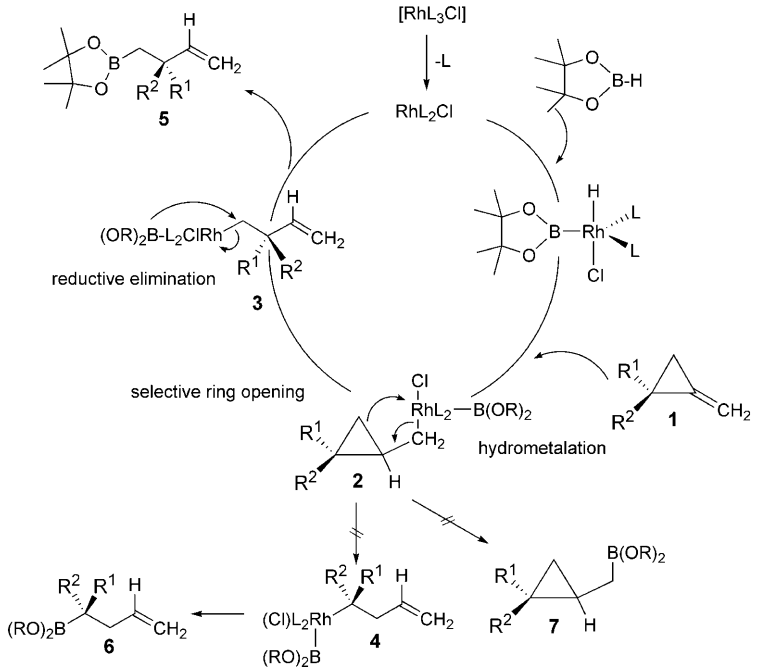
Entry	R^1	R^2	R^3	Yield **5** [%][a]	Yield **8** [%][b]
1 (**1a**)	Bu	Hex	H	90 (**5a**)	81 (**8a**)[c]
2 (**1b**)	Me	Ph	H	89 (**5b**)	81 (**8b**)[c]
3 (**1c**)	Bu	Et	Me[d]	81 (**5c**)	87 (**8c**)
4 (**1d**)	Me	Et	$(CH_2)_2Ph$[d]	83 (**5d**)	83 (**8d**)
5 (**1e**)	Me	Ph	$(CH_2)_2Ph$[e]	83 (**5e**)	81 (**8e**)
6 (**1f**)	Me	Et	Ph[d]	80 (**5f**)	87 (**8f**)
7 (**1g**)	Me	Bu	Ph[d]	84 (**5g**)	81 (**8g**)
8 (**1h**)	Me	Hex	Ph[d]	90 (**5h**)	85 (**8h**)

[a] Boronate esters **5** are unstable by column chromatography and yields were determined by ^1H NMR spectroscopy. [b] Isolated yields after purification by column chromatography. [c] Yields determined based on the non-reduced double bond. [d] Mixture of geometrical isomers was obtained *E*/*Z* 2:1. [e] Mixture of geometrical isomers was obtained *E*/*Z* 4:1.

because the reductive elimination to form the carbon–boron bond is slower than other boronate esters (i.e., catechol borane), a feature attributed to pinacolborane's lower Lewis acidity.[9] Our choice of a less reactive substrate would ideally stack the deck in favor of ring-opening as opposed to direct addition. Remarkably, the reaction proceeds smoothly and when methylenecyclopropane (MCP) **1a** was subjected to our experimental conditions, a single boronate ester **5a** was observed (Table 1, entry 1). The formation of the isomer **5a** could be rationalized through the following mechanism (Scheme 2).[10] Oxidative addition of the catalyst into the H–B bond of HBPin gives the corresponding metal hydride species that add to the double bond of MCP **1** through a hydrometalation reaction to form the alkyl metal **2**.[11]

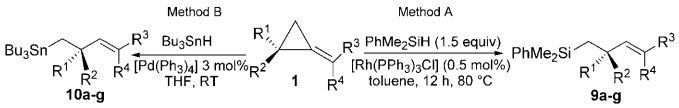
The ring-opening process is indeed faster than reductive elimination, since no cyclopropylborane **7** was detected in the crude reaction mixture. Moreover, the ring opening is selective, since we could not detect the formation of **6**, which would have resulted from the most substituted carbon–carbon bond ring-cleavage (through reductive elimination of **4**). Only the non-substituted proximal bond undergoes the ring cleavage to give the corresponding acyclic alkyl–rhodium intermediate **3**, which leads to **5** after reductive elimination (Scheme 2).[12] Therefore, the Rh-catalyzed hydroboration of methylenecyclopropane derivatives is a remarkable combination of several consecutive chemical steps that proceeds to cleanly lead to the unique formation of **5**.

Whatever the methylenecyclopropane derivatives used (Table 1, entries 1 and 2) a single isomer **5** was always obtained, even when a potentially tertiary benzylic organometallic species could be formed (Table 1, entry 2). When alkylidenecyclopropane derivatives were engaged in the same reaction (R^3 = alkyl or aryl), the chemical outcome is similar and excellent isolated yields of the single ring-opened products **5** were obtained (no traces of **6**, Table 1, entries 3–8). Following oxidation with hydrogen peroxide and reduction of the double bond,[13] the resulting saturated alcohols **8c–h** were isolated by column chromatography in excellent yields. Following our initial success with pinacol borane, we further decided to investigate the rhodium- and palladium-catalyzed addition of silanes[14] and stannanes,[15] respectively, of alkylidenecyclopropane derivatives and confirm that a selective ring-opening should also be observed as described in Table 2.[16] We were pleased to see that the Rh^I-catalyzed hydrosilylation of alkylidenecyclopropanes (method A)[14] also proceeds with selective cleavage of the less substituted carbon–carbon bond of the cyclopropane ring according to our mechanistic hypothesis described in Scheme 2. Only homoallylsilanes **9** were produced in good to excellent isolated yields (see Table 2, method A, entries 1–7). Moreover, the reaction is stereoselective as the *E*/*Z* ratios of homoallylsil-



Scheme 2. Mechanistic hypothesis.

Table 2. Rh-catalyzed hydrosilylation and Pd-catalyzed hydrostannations of ACPs.



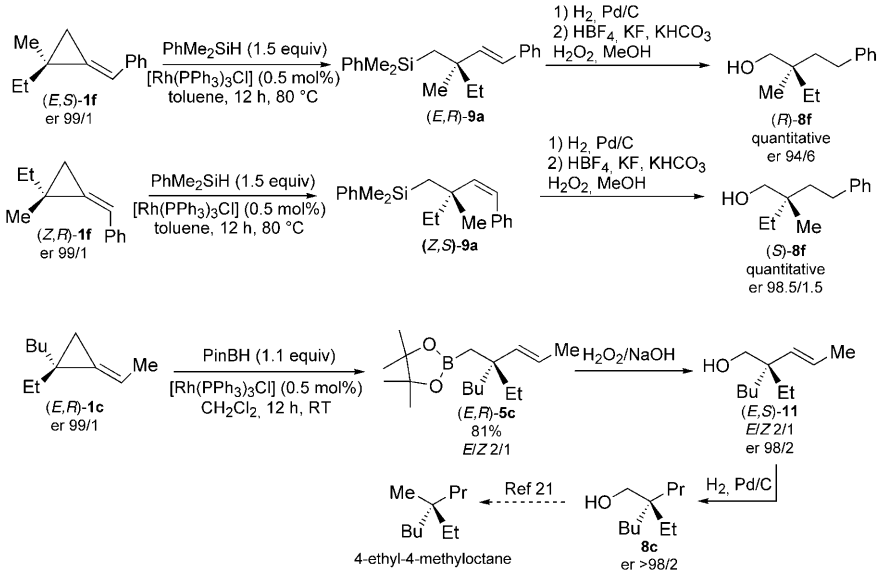
Entry	R^1	R^2	R^3	R^4	Method	E/Z ratio[a]	Yield [%][b]
1 (**1f**)	Me	Et	Ph	H	A	93:7	90 (**9a**)
2 (**1g**)	Me	Bu	Ph	H	A	87:13	93 (**9b**)
3 (**1i**)	Me	Et	*p*-MeAr	H	A	95:5	89 (**9c**)
4 (**1j**)	Me	Ph	*p*-MeAr	H	A	97:3	91 (**9d**)
5 (**1k**)	Me	Bu	*p*-BrAr	H	A	100:0	85 (**9e**)
6 (**1L**)	Bu	Et	*p*-MeAr	H	A	100:0	87 (**9f**)
7 (**1m**)	Bu	Et	*p*-BrAr	H	A	100:0	94 (**9g**)
8 (**1n**)	Bu	Ph	H	H	B	–	90 (**10a**)
9 (**1o**)	Me	Bu	Me	Me	B	–	80 (**10b**)
10 (**1p**)	Me	Bu	Ph	Ph	B	–	93 (**10c**)
11 (**1q**)	Bu	Ph	*p*-MeAr	H	B	100:0	94 (**10d**)
12 (**1r**)	Me	Bu	Ar[c]	H	B	72:28	90 (**10e**)
13 (**1s**)	Me	Ph	Bu	H	B	87:13	91 (**10f**)
14 (**1t**)	Me	Et	Me	H	B	76:24	88 (**10g**)

[a] E/Z ratio determined on the crude ^{1}H NMR spectrum and is identical to the starting E/Z ratio of ACPs **1**. [b] Isolated yields after purification by column chromatography. [c] Ar = 2,4,6-Me_3Ar.

anes **9** correspond to the initial E/Z ratios of the alkylidenecyclopropanes **1**. No traces of hydrosilylation of the *exo*-methylene double bond was detected suggesting that the ring-opening is again faster that the reductive elimination.[17] When MCPs and ACPs **1** were treated with a slight excess (1.3 equiv) of Bu_3SnH in THF in the presence of a catalytic amount of $[Pd(PPh_3)_4]$ (3 mol%, method B),[15] the corresponding homoallylstannanes **10** were also obtained in excellent yields as single ring-opened products (Table 2, entries 8–14). As the ring cleavage preferentially occurs to lead to the primary alkyl metal species **3** in all examined cases (Scheme 2), the integrity of the quaternary stereogenic center should remain unaffected in the process. To confirm our assumption, several enantiomerically pure alkylidenecyclopropane derivatives were prepared by the method that we recently described.[18]

Although the E isomer is largely predominant, the two isomers have opposite absolute configurations. For instance, **1f** was prepared with a E/Z ratio of 93:7, whereby (E)-**1f** has an absolute S configuration and that of (Z)-**1f** is R—each geometric isomer was formed with an enantiomeric ratio >99:1. Accordingly, when the Rh-catalyzed hydrosilylation reaction of enantiomerically pure **1f** ($(E,S)/(Z,R)$ = 93:7) was performed, (E)- and (Z)-homoallylsilanes **9a** were formed with the same E/Z ratio, respectively ((E,R)-**9a**/(Z,S)-**9a** = 93:7). Both isomers were purified and then subjected to hydrogenation of the double bond followed by Tamao–Fleming oxidation.[19] The corresponding saturated alcohols **8f** possessing the quaternary center were obtained in quantitative yields with enantiomeric ratios similar to the starting materials (Scheme 3).[20]

To confirm that such reaction proceeds also with an aliphatic group on the double bond of the alkylidenecyclopropane, **1c** was easily accessed as a single E isomer in an enantiomerically pure form from our reported procedure.[18] When submitted to the Rh-catalyzed hydroboration reaction, a selective ring-opening reaction occurs leading to the corresponding primary alkyl borane **5c** in 81% yield as a mixture of two E/Z isomers. After oxidation, the enantiomeric excess of the homoallylic alcohol **11** possessing the quaternary stereocenter was determined to be higher than 96%, demonstrating again that the stereochemistry of the stereogenic center is retained in the reaction sequence. This simple concept could be used to prepare **8c**, a known precursor of 4-ethyl-4-methyloctane,[21] the simplest chiral saturated hydrocarbon with a quaternary stereocenter (Scheme 3).



Scheme 3. Formation of enantiomerically enriched quaternary stereocenter through selective ring opening.

In conclusion, a selective metal-catalyzed ring opening of alkylidenecyclopropane derivatives leads to various functionalized acyclic derivatives possessing the challenging quaternary sterocenters. The key feature of this transformation is that the ring opening is faster than the reductive elimination and is highly regioselective; a single opened product was always observed and the stereointegrity of the quaternary stereogenic center remains unaffected in the process.

Experimental Section

General procedure for the preparation of homoallyl boranes: [Rh(PPh_3)$_3$Cl] (5 mg, 0.5 mol%) was placed in a dry three-necked flask. The flask was attached to a vacuum pump for 5 min and refilled with argon three times. ACP (1 mmol) was dissolved in CH_2Cl_2 (3 mL; distilled over CaH_2) and added to the flask. The solution was stirred for 15 min and then pinacolborane (PinBH; 1.5 equiv) was added slowly. The reaction was finished after 12 h at room temperature. The solvent was evaporated and the crude product was purified by short column chromatography. Eluent: hexane/ethyl acetate 100:1.

General procedure for the preparation of homoallyl silanes: The ACP derivative (1 mmol) was placed in a dry three-necked flask containing a solution of [Rh(PPh_3)$_3$Cl] (5 mg, 0.5 mol%) in dry toluene (5 mL). Phenyldimethylsilane (0.23 mL, 1.5 mmol) was added slowly to the solution over a period of 15 min and the mixture was heated at 80°C over night. The solvent was evaporated and the crude product was purified by column chromatography. Eluent: hexane.

General procedure for the preparation of homoallyl stannanes: The ACP derivative (1 mmol) was placed in a dry three-necked flask containing dry THF (10 mL). The catalyst [Pd(PPh_3)$_4$] (34 mg, 3 mol%) was added to the solution and the mixture was stirred for 15 min. Then tributyltin hydride (0.44 mL) was added through a syringe pump over a period of one hour. The reaction was monitored by TLC and finished after 30 min. The solute was evaporated and the crude product was purified by column chromatography. Eluent: hexane.

Acknowledgements

This research was supported by a grant from the Israel Science Foundation administrated by the Israel Academy of Sciences and Humanities (70/08). I.M. is holder of the Sir Michael and Lady Sobell Academic Chair.

Keywords: alkylidenecyclopropanes · homogeneous catalysis · hydroboration · hydrosilylation · hydrostannation · palladium · rhodium

[1] E. J. Corey, A. Guzman-Perez, *Angew. Chem.* **1998**, *110*, 2092; *Angew. Chem. Int. Ed.* **1998**, *37*, 388.

[2] a) B. M. Trost, C. Jiang, *Synthesis* **2006**, 369; b) J. Christoffers, A. Baro, *Adv. Synth. Catal.* **2005**, *347*, 1473.

[3] a) J. P. Das, H. Chechik, I. Marek, *Nature Chem.* **2009**, *1*, 128; b) I. Marek, *Chem. Eur. J.* **2008**, *14*, 7460; c) I. Marek, G. Sklute, *Chem. Commun.* **2007**, 1683; d) G. Kolodney, G. Sklute, S. Perrone, P. Knochel, I. Marek, *Angew. Chem.* **2007**, *119*, 9451; *Angew. Chem. Int. Ed.* **2007**, *46*, 9291; e) G. Sklute, I. Marek, *J. Am. Chem. Soc.* **2006**, *128*, 4642; f) G. Sklute, D. Amsallem, A. Shibli, J. P. Varghese, I. Marek, *J. Am. Chem. Soc.* **2003**, *125*, 11776.

[4] For representative recent papers, see: a) A. H. Hoveyda, P. J. Lombardi, R. V. O'Brien, A. R. Zhugralin, *J. Am. Chem. Soc.* **2009**, *131*, 8378; b) E. A. Tiong, J. L. Gleason, *Org. Lett.* **2009**, *11*, 1725; c) R. Yazaki, N. Kumagai, M. Shibasaki, *J. Am. Chem. Soc.* **2009**, *131*, 3195; d) L. Yin, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2009**, *131*, 9610; e) S. E. Denmark, T. W. Wilson, M. T. Burk, J. R. Heemstra, *J. Am. Chem. Soc.* **2007**, *129*, 14864; f) D. A. Kummer, W. J. Chain, M. R. Morales, O. Quiroga, A. G. Myers, *J. Am. Chem. Soc.* **2008**, *130*, 13231; g) A. Wilsily, E. Fillion, *Org. Lett.* **2008**, *10*, 2801; h) S. E. Reisman, A. G. Doyle, E. N. Jacobsen, *J. Am. Chem. Soc.* **2008**, *130*, 7198; i) M. Branca, D. Gori, R. Guillot, V. Alezra, C. Kouklovsky, *J. Am. Chem. Soc.* **2008**, *130*, 5864; j) R. Yazaki, T. Nitabura, N. Kumagai, M. Shibasaki, *J. Am. Chem. Soc.* **2008**, *130*, 14477; k) C. A. Falciola, A. Alexakis, *Chem. Eur. J.* **2008**, *14*, 10615; l) C. E. Stivala, A. Zakarian, *J. Am. Chem. Soc.* **2008**, *130*, 3774; m) S. Jautze, R. Peters, *Angew. Chem.* **2008**, *120*, 9424; *Angew. Chem. Int. Ed.* **2008**, *47*, 9284; n) J. L. Stymiest, V. Bagutski, R. M. French, V. K. Aggarwal, *Nature* **2008**, *456*, 778.

[5] For reviews, see a) I. Marek, S. Simaan, A. Masarwa, *Angew. Chem.* **2007**, *119*, 7508; *Angew. Chem. Int. Ed.* **2007**, *46*, 7364; b) M. Rubin, M. Rubina, V. Gevorgyan, *Chem. Rev.* **2007**, *107*, 3117; c) I. Nakamura, Y. Yamamoto, *Adv. Synth. Catal.* **2002**, *344*, 111; d) A. Brandi, A. Goti, *Chem. Rev.* **1998**, *98*, 589; e) A. de Meijere, S. I. Kozhushkov, A. F. Khlebnikov, *Top. Curr. Chem.* **2000**, *207*, 89; f) L.-X. Shao, M. Shi, *Curr. Org. Chem.* **2007**, *11*, 1135.

[6] For a single report on non-catalyzed hydroboration of ACP derivatives, see: a) K. Utimoto, M. Tamura, M. Tanouti, K. Sisido, *Tetrahedron* **1972**, *28*, 5697. Pd- and Pt-catalyzed silaboration of MCP derivatives, see: b) M. Suginome, T. Matsuda, Y. Ito, *J. Am. Chem. Soc.* **2000**, *122*, 11015; c) T. Ohmura, H. Taniguchi, Y. Kondo, M. Suginome, *J. Am. Chem. Soc.* **2007**, *129*, 3518; d) T. Pohlmann, A. de Meijere, *Org. Lett.* **2000**, *2*, 3877; e) T. Ohmura, H. Taniguchi, M. Suginome, *Org. Lett.* **2009**, *11*, 2880.

[7] For recent reports on metal-catalyzed addition of pinacol borane on different substrates, see: a) D. Imao, B. W. Glasspoole, V. S. Laberge, C. M. Crudden, *J. Am. Chem. Soc.* **2009**, *131*, 5024; b) C. M. Crudden, Y. B. Hleba, A. C. Chen, *J. Am. Chem. Soc.* **2004**, *126*, 9200; c) M. Rubina, M. Rubin, V. Gevorgyan, *J. Am. Chem. Soc.* **2003**, *125*, 7198; For addition of different metal hydrides on cyclopropenes, see d) A. Trofimov, M. Rubina, M. Rubin, V. Gevorgyan, *J. Org. Chem.* **2007**, *72*, 8910.

[8] D. R. Edwards, Y. B. Hleba, C. J. Lata, L. A. Calhoun, C. M. Crudden, *Angew. Chem.* **2007**, *119*, 7945; *Angew. Chem. Int. Ed.* **2007**, *46*, 7799.

[9] C. M. Crudden, D. R. Edwards, *Eur. J. Org. Chem.* **2003**, 4695.

[10] D. A. Evans, G. C. Fu, *J. Org. Chem.* **1990**, *55*, 2280.

[11] For recent metal-catalyzed reactions of MCPs and ACPs, see a) S. I. Kozhushkov, D. S. Yufit, L. Ackermann, *Org. Lett.* **2008**, *10*, 3409; b) P. A. Evans, P. A. Inglesby, *J. Am. Chem. Soc.* **2008**, *130*, 12838; c) R. García-Fandiño, M. Gulías, L. Castedo, J. R. Granja, J. L. Mascareñas, D. J. Cárdenas, *Chem. Eur. J.* **2008**, *14*, 272; d) M. Gulías, J. Durán, L. Castedo, J. L. Mascareñas, *J. Am. Chem. Soc.* **2007**, *129*, 11026; e) E. Smolensky, M. Kapon, M. S. Eisen, *Organometallics* **2005**, *24*, 5495; f) A. I. Siriwardana, I. Nakamura, Y. Yamamoto, *J. Org. Chem.* **2004**, *69*, 3202; g) B. H. Oh, I. Nakamura, Y. Yamamoto, *J. Org. Chem.* **2004**, *69*, 2856; h) M. Shi, Y. Chen, B. Xu, *Org. Lett.* **2003**, *5*, 1225; i) M. Shi, B. Xu, *Tetrahedron Lett.* **2003**, *44*, 3839; j) S. Ma, J. Zhang, *Angew. Chem. Int. Ed.* **2003**, *42*, 184; *Angew. Chem.* **2003**, *115*, 193; k) D. H. Camacho, I. Nakamura, S. Saito, Y. Yamamoto, *J. Org. Chem.* **2001**, *66*, 270; l) I. Nakamura, S. Saito, Y. Yamamoto, *J. Am. Chem. Soc.* **2000**, *122*, 2661; m) D. H. Camacho, I. Nakamura, S. Saito, Y. Yamamoto, *Angew. Chem.* **1999**, *111*, 3576; *Angew. Chem. Int. Ed.* **1999**, *38*, 3365; *Angew. Chem.* **1999**, *111*, 3576; n) M. Lautens, Y. Ren, *J. Am. Chem. Soc.* **1996**, *118*, 10668; o) M. Shi, B.-Y. Wang, J.-W. Huang, *J. Org. Chem.* **2005**, *70*, 5606; p) M. Shi, G.-Q. Tian, J. Li, *Tetrahedron* **2009**, *65*, 3404; q) X.-Y. Tang, M. Shi, *Tetrahedron* **2009**, *65*, 8863.

[12] C. Aïssa, A. Fürstner, *J. Am. Chem. Soc.* **2007**, *129*, 14836.

[13] As two *E* and *Z* isomers were obtained, the reduction of the double bond was performed to have better NMR spectra.

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

[15] a) M. Lautens, C. Meyer, A. Lorenz, *J. Am. Chem. Soc.* **1996**, *118*, 10676; b) M. Lautens, Y. Ren, P. Delanghe, P. Chiu, S. Ma, J. Colucci, *Can. J. Chem.* **1995**, *73*, 1251.

[16] For hydrido-rhodium(I) and Ir^I complex in the ring-opening of MCPS, see a) Y. Nishihara, C. Yoda, M. Itazaki, K. Osakada, *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1469; b) M. Itazaki, Y. Nishihara, K. Osakada, *J. Org. Chem.* **2002**, *67*, 6889 and references therein.

[17] For Pt-catalyzed hydrosilylation reaction without ring-opening of MCPs, see: Y. Nishihara, M. Itazaki, K. Osakada, *Tetrahedron Lett.* **2002**, *43*, 2059.

[18] a) S. Simaan, A. Masarwa, P. Bertus, I. Marek, *Angew. Chem.* **2006**, *118*, 4067; *Angew. Chem. Int. Ed.* **2006**, *45*, 3963; b) A. Masarwa, A. Stanger, I. Marek, *Angew. Chem.* **2007**, *119*, 8185; *Angew. Chem. Int. Ed.* **2007**, *46*, 8039; c) S. Simaan, I. Marek, *Org. Lett.* **2007**, *9*, 2569; d) S. Simaan, I. Marek, *Chem. Commun.* **2009**, 292; e) S. Simaan, A. Masarwa, E. Zohar, A. Stanger, P. Bertus, I. Marek, *Chem. Eur. J.* **2009**, *15*, 8449.

[19] I. Fleming, R. Henning, D. C. Parker, H. E. Plaut, P. E. J. Sanderson, *J. Chem. Soc. Perkin Trans. 1* **1995**, 317.

[20] (*R*)-**8 f**, resulting from the ring-opening of (*E*,*S*)-**1 f**, has an enantiomeric excess slightly lower since we couldn′t completely remove the *Z* isomer of **1 f** [(*Z*,*R*)-**1 f**] that has the opposite absolute configuration.

[21] a) K. Mislow, P. Bickart, *Isr. J. Chem.* **1976**, *15*, 1; b) T. Fujita, K. Obata, S. Kuwahara, N. Miura, A. Nakahashi, K. Monde, J. Decatur, N. Harada, *Tetrahedron Lett.* **2007**, *48*, 4219; c) W. ten Hoeve, H. Wynberg, *J. Org. Chem.* **1980**, *45*, 2754.

Received: September 27, 2009
Published online: November 30, 2009

