

### Metal-Catalyzed Rearrangement of Cyclopropenes to Allenes

Jingwei Li, Chunrui Sun, Silviya Demerzhan, and Daesung Lee\*

Department of Chemistry, University of Illinois at Chicago, 845 West Taylor Street, Chicago, Illinois 60607, United States

Supporting Information

**ABSTRACT:** A novel transition-metal-catalyzed rearrangement of silylated cyclopropenes to the corresponding allenes is described. The presence of both the trimethylsilyl group on the cyclopropene and the platinum catalyst are crucial for this rearrangement.

The rearrangement of cyclopropenes to allenes under thermal and photochemical conditions has been documented extensively, yet the corresponding metal-catalyzed reaction is virtually unprecedented.<sup>1</sup> The metal-catalyzed opening of cyclopropenes leads to various end products,<sup>2,3</sup> typically involving the formation of metallacyclobutene or vinyl alkylidene intermediates. Some of these alkylidenes, such as the Grubbs-type alkylidene complexes, are stable enough to be isolated,<sup>4</sup> whereas many putative gold carbene complexes<sup>5</sup> exist transiently. We surmised that the metal carbenoids derived from opening of silylated cyclopropenes would take a different reaction course to generate new end products, such as allenes, because of the  $\beta$ -cation-stabilizing effect of silicon.<sup>6</sup>

To verify this, we compared the reactions of cyclopropenes 1a and 1b containing a trimethylsilyl substituent with those of the corresponding unsilylated cyclopropenes 1c and 1d (Scheme 1). When treated with a catalytic amount of platinum dichloride (5 mol %) in dichloromethane at 50 °C, silylated cyclopropenes 1a and 1b afforded allenes 2a and 2b, respectively, in good yields, whereas the corresponding unsubstituted cyclopropenes 1c and 1d provided only intractable material without any sign of allenes 2c and 2d. This clearly indicates that the silyl substituent is required for the rearrangement of cyclopropenes to the corresponding allenes.

To further define the structural requirements for this rearrangement of cyclopropenes to allenes, we examined the behavior of silyl-substituted 3,3-diphenylcyclopropene 3 (Scheme 2). In this case, however, only silylated indene 5 was generated, presumably via the formation of vinyl carbenoid 4.<sup>7</sup> On the other hand, silylated cyclopropene 6 containing a benzyl group led to the exclusive formation of allene 7 without any indene 8.

The relatively facile preparation and better reaction profiles of non-C3-substituted silylated cyclopropenes relative to other cyclopropenes prompted us to choose them as the substrate platform for further exploration of the rearrangement of cyclopropenes to allenes. These non-C3-substituted cyclopropenes were prepared by the C–Si bond insertion method recently developed in our laboratory.<sup>8</sup> Herein we describe the first efficient metal-catalyzed rearrangement of silylated cyclopropenes to the corresponding allenes.

To further investigate the scope of the initial rearrangement demonstrated by silylated cyclopropenes 1a, 1b, and 6 to the

#### Scheme 1. Contrasting Reactivities of Silylated and Unsilylated Cyclopropenes toward a Platinum Catalyst



Scheme 2. C–H Functionalization versus Allene Formation from Differently Substituted Silylated Cyclopropenes



corresponding allenes **2a**, **2b**, and 7, we examined other conditions and different catalysts (Table 1). As opposed to the formation of allene **2a** in 95% yield from cyclopropene **1a** using platinum chloride (entry 1),<sup>9</sup> thermal conditions alone over the 50-110 °C range were not effective, and **1a** was recovered intact (entry 2). A cationic gold complex,<sup>10</sup> although not effective at room temperature (entry 3), provided the desired allene **2a** at an elevated temperature in 65% yield along with an unidentified byproduct (entry 4). Other metal complexes such as Rh<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub>, PtCl<sub>2</sub>-(PPh<sub>3</sub>)<sub>2</sub>, and RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> were virtually inert toward the substrate, and the starting material was recovered unconsumed in each case(entries 5–7).

Relying on the reported method,<sup>8</sup> we prepared a variety of silylated cyclopropenes 9a-j and examined their conversion to the corresponding allenes (Table 2). The simple alkyl chain-substituted cyclopropene 9a afforded allene 10a in excellent yield (entry 1), but the reaction of 3-butenyl-substituted cis and trans

 Received:
 May 30, 2011

 Published:
 July 26, 2011

#### Table 1. Catalyst Screening for Allene Formation



isomers of **9b** was not satisfactory (entry 2).<sup>11</sup> Similarly, several byproducts<sup>12</sup> were formed from cyclopropene **9c** containing a geranyl moiety, although the desired allene was also generated (entry 3). These results suggest that the double bond near the reaction center interferes with the rearrangement. To explore the compatibility of unsaturation, we introduced structural variations in the unsaturated moiety and found that cyclic alkenes were tolerated. Thus, cyclopropenes **9d**–**f** all underwent rearrangement to the corresponding allenes **10d**–**f** in good yields (entries 4–6). However, **9g** with a tetrasubstituted exocyclic double bond did not provide the desired allene **10g** (entry 7). Alkenyl and alkynyl substituents at the remote site were tolerated, with cyclopropenes **9h**–**j** providing allenes **10** h–**j** in excellent yields (entries 8–10).<sup>13</sup>

It was observed that a proximal alkene functionality such as that in **9b** interfered with the reaction. We surmised that this is the consequence of a putative interaction between Lewis acidic platinum and the alkene during the reaction. If this is indeed the case, then other basic functionalities (e.g., ether) should interfere with the process in a similar manner. To verify this hypothesis, we prepared cyclopropenes **9k**–**o** containing ether linkages at various distances from the cyclopropene moiety and examined their rearrangements (Table 3). While  $\alpha$ -alkoxy-substituted substrate **9k** did not produce the corresponding allene **10k** (entry 1), the other alkoxy-substituted substrates **9l**–**o** afforded allenes **10l–o** in good yields (entries 2–5).

As a further demonstration of the synthetic utility and effectiveness of the current allene synthesis,<sup>14</sup> a three-step procedure without purification of the intermediates was developed (Scheme 3). With this protocol, hydrocinnamaldehyde **11** could be transformed to the corresponding allene **2a** in 57% overall yield.

In light of the known carbophilic Lewis acidity of the platinum complex,<sup>15</sup> several plausible mechanistic pathways can be proposed (Scheme 4). The  $\beta$ -cation-stabilizing effect of a silyl group would favor the formation of intermediate **12**, which could undergo three different structural reorganization processes. We surmised that the formation of **13** from **12** via a C–C bond migration should be quite reasonable because of the relief of ring strain.<sup>16</sup> A subsequent [1,2]-alkyl shift<sup>17</sup> in **13** would provide the observed allene products. Alternatively, C–Si bond migration leading to **14** followed by a [1,2]-C–C bond shift would also be quite plausible. In another pathway, the formation of **regio**isomeric intermediate **16** via the cycloreversion of **15** followed by a [1,2]-silyl shift<sup>18</sup> would be equally possible.<sup>19</sup>

To gain more insight into the reaction mechanism, isotopically labeled cyclopropene 17 was prepared and subjected to the reaction conditions for allene formation (Scheme 5). This

# Table 2. Rearrangement of Cyclopropenes Containing Unsaturation<sup>a</sup>

$$R \xrightarrow{9} SiMe_3 \xrightarrow{PtCl_2, CH_2Cl_2} R \xrightarrow{SiMe_3} R \xrightarrow{10} R$$



<sup>*a*</sup> A 5 mol % catalyst loading was used. <sup>*b*</sup> Isolated yields. <sup>*c*</sup> *trans*-9b afforded 10b along with an unknown byproduct, but *cis*-9b did not give any allene. <sup>*d*</sup> Allene 10c was contaminated with several unidentifiable byproducts. <sup>*c*</sup> Decomposition of 10e was observed with an extended reaction time. <sup>*f*</sup> Allene 10g was not observed.

exclusively afforded <sup>13</sup>C-labeled allene **18** in which the alkyl group remained connected to the original <sup>13</sup>C-labeled carbon. This clearly rules out the possibility of a [1,2]-alkyl shift involving intermediate **13** and supports the other pathways with intermediates **14** and **16**. Unfortunately, the current experiment with <sup>13</sup>C-labeled cyclopropene **17** could not distinguish the remaining two pathways.

In conclusion, we have developed an efficient metal-catalyzed rearrangement of silylated cyclopropenes to the corresponding allenes. Both the electronic effect of a silyl substituent on the cyclopropene and the presence of the platinum catalyst have been shown to be essential for this reaction. The mild reaction conditions are in stark contrast to those of thermal or photochemical reactions. Good overall functional-group tolerance was also recognized, except for several cases where alkene and oxygen substituents interfered with the reaction. Further mechanistic studies and broadening of the scope of this new rearrangement will be reported in due course.

## Table 3. Rearrangement of Cyclopropenes Containing Ether Linkages<sup>a</sup>





<sup>*a*</sup> A 5 mol % catalyst loading was used. <sup>*b*</sup> Isolated yields. <sup>*c*</sup> Substrate 9k was completely consumed, but allene 10k was not observed.

# Scheme 3. Synthesis of a Silylated Allene Starting from an Aldehyde



Scheme 4. Plausible Pathways for Allene Formation



Scheme 5. <sup>13</sup>C-Labeling Study of Allene Formation



#### ASSOCIATED CONTENT

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

#### AUTHOR INFORMATION

### Corresponding Author

dsunglee@uic.edu

#### ACKNOWLEDGMENT

We especially thank Prof. Vladimir Gevorgyan and Dr. Alexander Trofimov for their donation of compound 1 and helpful discussions. The donors of ACS Petroleum Research Fund and the NSF (CHE 0955972) are gratefully acknowledged for financial support for this work. J.L. is grateful for the Moriarty Fellowship at UIC. We also thank Mr. Furong Sun of the University of Illinois at Urbana-Champaign for high-resolution mass spectrometry data.

#### REFERENCES

(1) For examples of the rearrangement of cyclopropenes to allenes under thermal and photolytic conditions, see: (a) Baird, M. S. Chem. Rev. 2003, 103, 1271. (b) de Meijere, A.; Faber, D.; Heinecke, U.; Walsh, R.; Müller, T.; Apeloig, Y. Eur. J. Org. Chem. 2001, 663. (c) Billups, W. E.; Bachman, R. E. Tetrahedron Lett. 1992, 33, 1825. (d) Walsh, R.; Untiedt, S.; de Meijere, A. Chem. Ber. 1994, 127, 237. (e) Kirms, M. A.; Primke, H.; Stohlmeier, M.; de Meijere, A. Recl. Trav. Chim. Pays-Bas 1986, 105, 462. (f) Karni, M.; Oref, I.; Barzilai-Gilboa, S.; Lifshitz, A. J. Phys. Chem. 1988, 92, 6924. (g) Steinmetz, M. G.; Yen, Y.-P.; Poch, G. K. J. Chem. Soc., Chem. Commun. 1983, 1504. (h) Eckert-Maksic, M.; Golic, M. J. Chem. Soc., Perkin Trans. 2 1993, 2325. (i) Walsh, R. Chem. Soc. Rev. 2005, 34, 714.

(2) For reviews of cyclopropene chemistry, see: (a) Marek, I.;
Simaan, S.; Masarwa, A. Angew. Chem., Int. Ed. 2007, 46, 7364. (b)
Rubin, M.; Rubina, M.; Gevorgyan, V. Chem. Rev. 2007, 107, 3117. (c)
Fox, J. M.; Yan, N. Curr. Org. Chem. 2005, 9, 719. (d) Rubin, M.; Rubina,
M.; Gevorgyan, V. Synthesis 2006, 1221. (e) Nakamura, M.; Isobe, H.;
Nakamura, E. Chem. Rev. 2003, 103, 1295. (f) Boutagy, J.; Thomas, R.
Chem. Rev. 1974, 74, 87. (g) Wadsworth, W. S. Org. React. 1977, 25, 73.
(h) Kelly, S. E. In Comprehensive Organic Synthesis; Trost, B. M.,
Fleming, I., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 1, pp 729–817.

(3) For transition-metal-catalyzed isomerization of cyclopropenes, see:
(a) Padwa, A.; Blacklock, T.; Loza, R. J. Am. Chem. Soc. 1981, 103, 2404.
(b) Cho, S. H.; Liebeskind, L. S. J. Org. Chem. 1987, 52, 2631. (c) Semmelhack, M. F.; Ho, S.; Steigerwald, M.; Lee, M. C. J. Am. Chem. Soc. 1987, 109, 4397. (d) Müller, P.; Pautex, N.; Doyle, M. P.; Baheri, V. Helv. Chim. Acta 1990, 73, 1233. (e) Padwa, A.; Kassir, J.; Xu, S. L. J. Org. Chem. 1991, 56, 6971. (f) Ma, M.; Zhang, J. J. Am. Chem. Soc. 2003, 125, 12386.
(g) Shao, L.-X.; Zhang, Y.-P.; Qi, M.-H.; Shi, M. Org. Lett. 2007, 9, 117. (h) Chuprakov, S.; Gevorgyan, V. Org. Lett. 2007, 9, 4463. (i) Miege, F.; Meyer, C.; Cossy, J. Angew. Chem., Int. Ed. 2011, 50, 5932.

(4) For early development of metal alkylidene complexes, see: (a) Binger, P.; Müller, P.; Benn, R.; Mynott, R. Angew. Chem., Int. Ed. Engl. 1989, 28, 610. (b) Gagne, M. R.; Grubbs, R. H.; Feldman, J.; Ziller, J. W. Organometallics 1992, 11, 3933. (c) Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. J. Am. Chem. Soc. 1993, 115, 8130.

(5) For recent gold-catalyzed transformations of cyclopropenes, see:
(a) Hadfield, M. S.; Lee, A.-L. Chem. Commun. 2011, 47, 1333. (b) Li, C.;
Zeng, Y.; Zhang, H.; Feng, J.; Zhang, Y.; Wang, J. Angew. Chem., Int. Ed.
2010, 49, 6413. (c) Seraya, E.; Slack, E.; Ariafard, A.; Yates, B. F.; Hyland,
C. J. T. Org. Lett. 2010, 12, 4768. (d) Hadfield, M. S.; Bauer, J. T.; Glen,
P. E.; Lee, A.-L. Org. Biomol. Chem. 2010, 8, 4090. (e) Miege, F.; Meyer,
C.; Cossy, J. Org. Lett. 2010, 12, 4144. (f) Seidel, G.; Mynott, R.;

Fürstner, A. Angew. Chem., Int. Ed. 2009, 48, 2510. (g) Li, C.; Zeng, Y.;
Wang, J. Tetrahedron Lett. 2009, 50, 2956. (h) Bauer, J. T.; Hadfield,
M. S.; Lee, A.-L. Chem. Commun, 2008, 6405. (i) Zhu, Z. B.; Shi, M. Chem.—Eur. J. 2008, 14, 10219.

(6) (a) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. J. Am. Chem. Soc. **1985**, 107, 1496. (b) Lambert, J. B.; Wang, G.; Finzel, R. B.; Teramura, D. H. J. Am. Chem. Soc. **1987**, 109, 7838.

(7) For indene formation, see: Padwa, A.; Blacklock, T. J.; Loza, R. J. Org. Chem. **1982**, 47, 3712–3721. Also see refs 3b, 3d, 5b, and 5g.

(8) (a) Li, J.; Sun, C.; Lee, D. *J. Am. Chem. Soc.* **2010**, *132*, 6640. (b) Sun, C.; Li, J.; Demerzhan, S.; Lee, D. ARKIVOC **2011**, No. iv, 17.

(9) The reaction under CO did not show much difference in terms of reaction rate and yield. For the effects of CO on platinum-catalyzed reactions, see: (a) Fürstner, A.; Davies, P. W.; Gress, T. J. Am. Chem. Soc. **2005**, *127*, 8244. (b) Fürstner, A.; Davies, P. W. J. Am. Chem. Soc. **2005**, *127*, 15024. (c) Cho, E.; Lee, D. Eur. J. Org. Chem. **2006**, 3074.

(10) Nieto-Oberhuber, C.; López, S.; Muñoz, M. P.; Cárdenas, D. J.; Buñuel, E.; Nevado, C.; Echavarren, A. M. Angew. Chem., Int. Ed. 2005, 44, 6146.

(11) One of the major byproducts from *cis*-**9b** was identified as a cyclopropanated material derived from a putative carbenoid such as **13**. The <sup>1</sup>H and <sup>13</sup>C NMR signals of this material were identical to those of the cyclopropanated product of *cis*-**9b** catalyzed by the cationic gold complex used in Table 1. In addition, MALDI mass spectroscopy analysis of the products derived from both *cis*- and *trans*-**9b** showed clusters of high molecular masses ranging from 300 up to 1233, implying the formation of oligomers associated with platinum metal.

(12) The formation of at least three inseparable byproducts precluded the unambiguous identification of their structures.

(13) The terminal alkynyl-substituted substrate corresponding to **9**j generated a complex product mixture. The expected allene product was identified in the NMR spectrum but was too unstable to be isolated via purification on silica gel.

(14) For representative examples of the synthesis of allenylsilanes and their use in organic synthesis, see: (a) Danheiser, R. L.; Carini, D. J.; Kwasigroch, C. A. J. Org. Chem. 1986, 51, 3870. (b) Borzilleri, R. M.; Weinreb, S. M.; Parvez, M. J. Am. Chem. Soc. 1994, 116, 9789. (c) Masse, C. E.; Panek, J. S. Chem. Rev. 1995, 95, 1293. (d) Suginome, M.; Matsumoto, A.; Ito, Y. J. Org. Chem. 1996, 61, 4884. (e) Jin, J.; Weinreb, S. M. J. Am. Chem. Soc. 1997, 119, 5773. (f) Myers, A. G.; Zheng, B. Org. Synth. 1999, 76, 178. (g) Hirashima, S.; Aoyagi, S.; Kibayashi, C. J. Am. Chem. Soc. 1999, 121, 9873. (h) Marshall, J. A.; Maxson, K. J. Org. Chem. 2000, 65, 630. (i) Han, J. W.; Tokunaga, N.; Hayashi, T. J. Am. Chem. Soc. 2001, 123, 12915. (j) Evans, D. A.; Sweeney, J. K.; Rovis, T.; Tedrow, J. S. J. Am. Chem. Soc. 2001, 123, 12095. (k) Shen, Q.; Hammond, G. B. J. Am. Chem. Soc. 2002, 124, 6534. (1) Heo, J.-N.; Micalizio, G. C.; Roush, W. R. Org. Lett. 2003, 5, 1693. (m) Daidouji, K.; Fuchibe, K.; Akiyama, T. Org. Lett. 2005, 7, 1051. (n) Wipf, P.; Pierce, J. G. Org. Lett. 2005, 7, 3537. (o) Gonzalez, A. Z.; Soderquist, J. A. Org. Lett. 2007, 9, 1081. (p) Brawn, R. A.; Panek, J. S. Org. Lett. 2007, 9, 2689. (q) Ohmiya, H.; Ito, H.; Sawamura, M. Org. Lett. 2009, 11, 5618. (r) Nishimura, T.; Makino, H.; Nagaosa, M.; Hayashi, T. J. Am. Chem. Soc. 2010, 132, 12865. (s) Williams, D. R.; Shah, A. A. Chem. Commun. 2010, 46, 4297. (t) Ogasawara, M.; Okada, A.; Subbarayan, V.; Sörgel, S.; Takahashi, T. Org. Lett. 2010, 12, 5736. (u) Zheng, J.-C.; Yun, S. Y.; Sun, C.; Lee, N.-K.; Lee, D. J. Org. Chem. 2011, 76, 1086.

(15) For selected examples of PtCl<sub>2</sub>-catalyzed reactions, see: (a) Ting, C.-M.; Wang, C.-D.; Chaudhuri, R.; Liu, R.-S. Org. Lett. 2011, 13, 1702.
(b) Zheng, H.; Zheng, J.; Yu, B.; Chen, Q.; Wang, X.; He, Y.; Yang, Z.; She, X. J. Am. Chem. Soc. 2010, 132, 1788. (c) Kim, S. Y.; Park, Y.; Chung, Y. K. Angew. Chem., Int. Ed. 2010, 49, 415. (d) Sun, J.; Conley, M. P.; Zhang, L.; Kozmin, S. A. J. Am. Chem. Soc. 2006, 128, 9705. (e) Lin, M.-Y.; Das, A.; Liu, R.-L. J. Am. Chem. Soc. 2006, 128, 9340. (f) Prasad, B. A. B.; Yoshimoto, F. K.; Sarpong, R. J. Am. Chem. Soc. 2005, 127, 12468. (g) Harrak, Y.; Blaszykowski, C.; Bernard, M.; Cariou, K.; Mainetti, E.; Mouriès, V.; Dhimane, A.-L.; Fensterbank, L.; Malacria, M. J. Am. Chem. Soc. 2004, 126, 8656.

(16) For a related example, see: Fürstner, A.; Aïssa, C. J. Am. Chem. Soc. 2010, 128, 6306.

(17) For a review of 1,2-alkyl migration, see: Crone, B.; Kirsch, S. F. *Chem.*—*Eur. J.* **2008**, *14*, 3514.

(18) For studies of silyl shifts in metal carbenoids, see: Dudnik, A. S.; Xia, Y.; Li, Y.; Gevorgyan, V. J. Am. Chem. Soc. **2010**, 132, 7645.

(19) The insertion of the metal catalyst into one of the C–C bonds to form a metallacyclobutene (see refs  $3b_3c_3f$ ) followed by its electrocyclic ring opening would be another pathway leading to 13 and 16.