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Metal-Catalyzed Rearrangement of Cyclopropenes to Allenes

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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.[1] The metal-catalyzed opening of cyclopropenes leads to various end products,[2,3] 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,[4] whereas many putative gold carbene complexes[5] 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 β-cation-stabilizing effect of silicon.[6]

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.

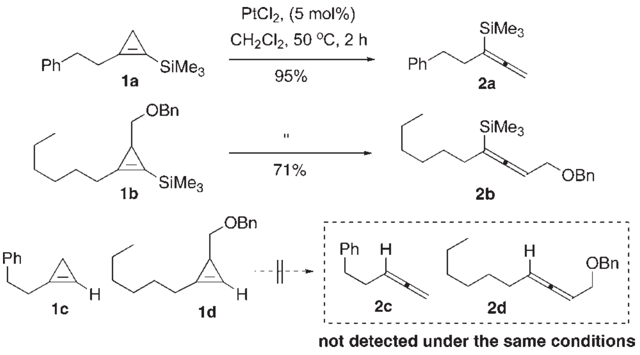
To further define the structural requirements for this rearrangement of cyclopropenes to allenes, we examined the behavior of silyl-substituted 3,3-diphenylcyclopropene **3** (Scheme 2). In this case, however, only silylated indene **5** was generated, presumably via the formation of vinyl carbenoid **4**.[7] 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.[8] 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 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),[9] thermal conditions alone over the 50−110 °C range were not effective, and **1a** was recovered intact (entry 2). A cationic gold complex,[10] 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 $Rh_2(O_2CCF_3)_4$, $PtCl_2(PPh_3)_2$, and $RuCl_2(PPh_3)_3$ were virtually inert toward the substrate, and the starting material was recovered unconsumed in each case(entries 5−7).

Relying on the reported method,[8] 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

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

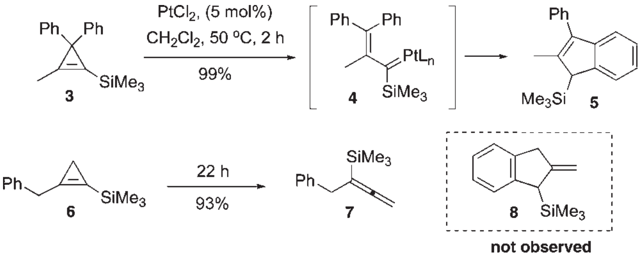


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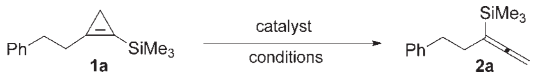
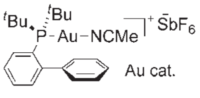
Table 1. Catalyst Screening for Allene Formation

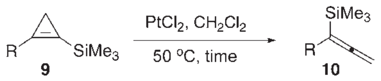


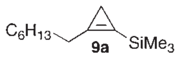
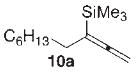
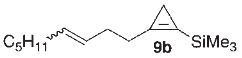
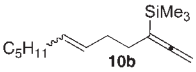
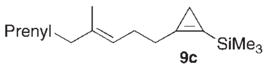
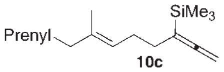
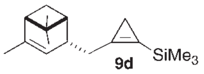
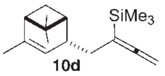
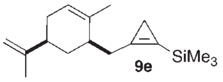
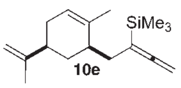
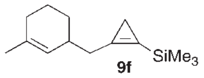
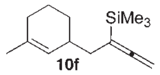
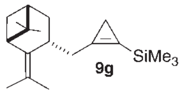
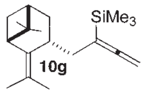
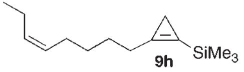
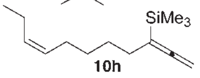
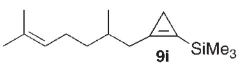
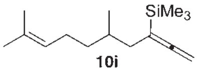
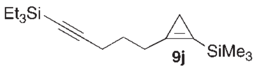
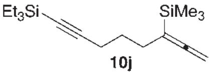
entry	catalyst / conditions	isolated yield (%)
1	$PtCl_2$ (5 mol%), CH_2Cl_2, 50 °C	95
2	DMF, 110 °C	0
3	Au cat. (1 mol%), CH_2Cl_2, rt	0
4	Au cat. (1 mol%), CH_2Cl_2, 50 °C	65
5	$Rh_2(O_2CCF_3)_4$ (5 mol%), CH_2Cl_2, 50 °C	0
6	*cis*-$PtCl_2(PPh_3)_2$ (5 mol%), CH_2Cl_2, 50 °C	0
7	$RuCl_2(PPh_3)_3$ (5 mol%), CH_2Cl_2, 50 °C	0



Au cat.

Table 2. Rearrangement of Cyclopropenes Containing Unsaturation[a]



entry	cyclopropene	time (h)	allene	yield (%)[b]
1	 9a	12	 10a	95
2	 9b	20	 10b	–[c]
3	 9c	1	 10c	–[d]
4	 9d	10	 10d	68
5	 9e	10	 10e	92[e]
6	 9f	10	 10f	78
7	 9g	10	 10g	–[f]
8	 9h	14	 10h	87
9	 9i	10	 10i	74
10	 9j	18	 10j	85

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

isomers of **9b** was not satisfactory (entry 2).[11] Similarly, several byproducts[12] 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).[13]

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 α-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).

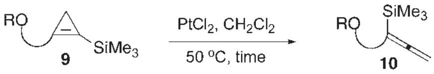
As a further demonstration of the synthetic utility and effectiveness of the current allene synthesis,[14] a three-step procedure without purification of the intermediates was developed (Scheme 3). With this protocol, hydrocinnamaldehyde **11** could be transformed to the corresponding allene **2a**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

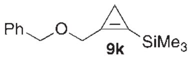
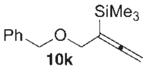
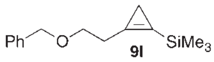
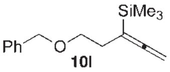
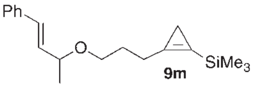
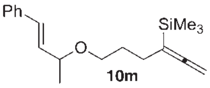
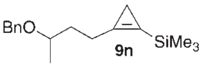
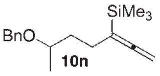
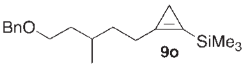
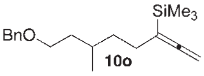
In light of the known carbophilic Lewis acidity of the platinum complex,[15] several plausible mechanistic pathways can be proposed (Scheme 4). The β-cation-stabilizing effect of a silyl group would favor the formation of intermediate **12**, which could undergo three different structural reorganization 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.[16] A subsequent [1,2]-alkyl shift[17] 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 regioisomeric intermediate **16** via the cycloreversion of **15** followed by a [1,2]-silyl shift[18] would be equally possible.[19]

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 exclusively afforded ^{13}C-labeled allene **18** in which the alkyl group remained connected to the original ^{13}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 ^{13}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.

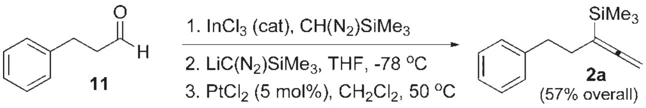
Table 3. Rearrangement of Cyclopropenes Containing Ether Linkages[a]



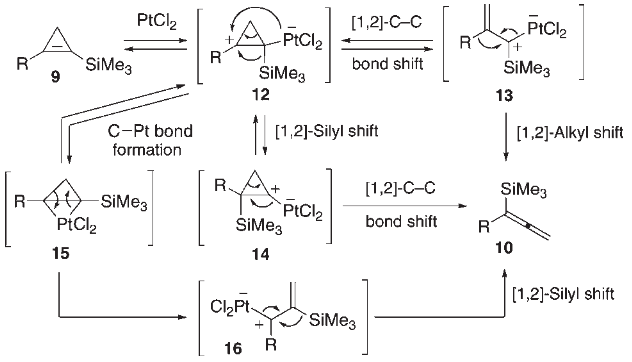
entry	cyclopropene	time (h)	allene	yield (%)[b]
1	 9k	12	 10k	–[c]
2	 9l	10	 10l	74
3	 9m	17	 10m	90
4	 9n	10	 10n	81
5	 9o	10	 10o	82

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

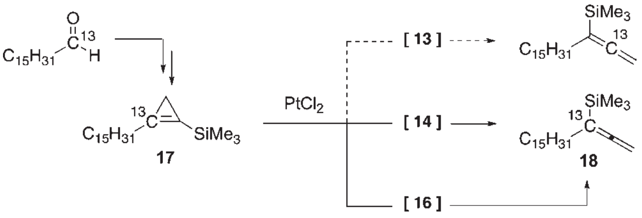
Scheme 3. Synthesis of a Silylated Allene Starting from an Aldehyde



Scheme 4. Plausible Pathways for Allene Formation



Scheme 5. ^{13}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.

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

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