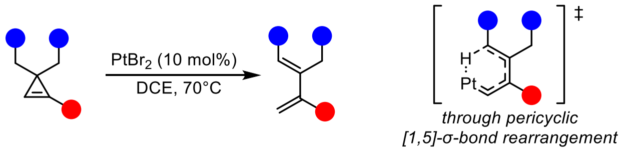
Platinum-catalyzed Isomerization of Cyclopropenes to 1,3-Dienes

Vladyslav Smyrnov, Antonin Homassel, Leander Choudhury, and Jerome Waser*

Laboratory of Catalysis and Organic Synthesis, Institut des Sciences et Ingénierie Chimique, Ecole Polytechnique Fédérale de Lausanne, CH-1015, Lausanne, Switzerland.

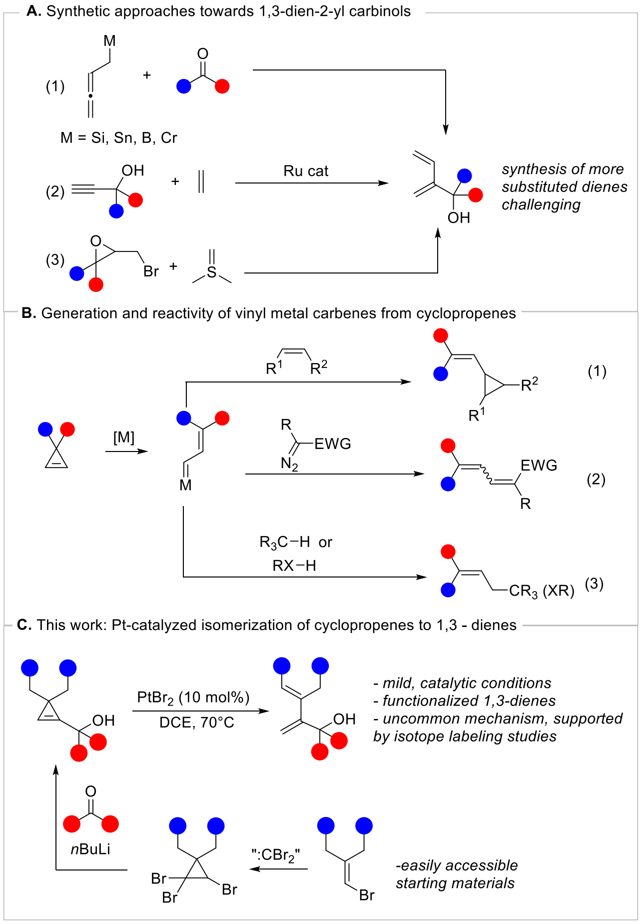


ABSTRACT: Herein we report a platinum-catalyzed isomerization of cyclopropenes to 1,3-dienes. Diverse dienylated alcohols were obtained in 42-98% yield. The synthetic potential of the products was demonstrated by their use in Diels-Alder cycloadditions with various dienophiles. Isotope labelling studies provide strong support for a mechanism involving pericyclic [1,5]-σ-bond rearrangement of a vinyl platinum carbene intermediate.

1,3 – Dienes are important compounds, present in a variety of natural products and bioactive molecules.[1] Moreover, they possess a unique reactivity, which is exploited in a variety of useful transformations such as the Diels-Alder cycloaddition.[2] A variety of methods exist for the construction of 1,3-dienes.[3] However, the synthesis of highly functionalized 1,3-dienes is still challenging. In particular, there are only few general methods for the synthesis of dienes bearing a carbinol function at the β position of the conjugated system, despite the fact that these compounds are versatile building blocks in organic synthesis.[4] One of the main strategies is the addition of organometallic allenyl reagents (M = Si, Sn, B, Cr) to carbonyl compounds (Scheme 1A, Eq. 1).[4c-d, 5] This approach can also be performed enantioselectively. Other reported methods are the enyne metathesis of propargylic alcohols (Scheme 1A, Eq. 2),[6] and the homologation of epoxybromides with sulfur ylides (Scheme 1A, Eq. 3).[7] However, all these methods are mostly used for the synthesis of simple 1,3-butadien-2-yl carbinols, while more substituted dienes are rarely accessible. Therefore, the development of new methods for the synthesis of more substituted dienyl carbinols would be highly desirable.

Cyclopropenes are the smallest cyclic alkenes. Due to the substantial ring strain, they display unique reactivity compared to other strained alkenes. In particular, the ring-opening of cyclopropenes with the formation of vinylmetal carbene intermediates represents an important platform for the development of synthetic methods.[8] These versatile intermediates were shown to undergo a variety of transformations including cyclopropanation of alkenes (Scheme 1B, Eq, 1),[9] carbene-carbene coupling (Scheme 1B, Eq. 2),[10] and C-H and X-H insertions (Scheme 1B, Eq. 3).[11]

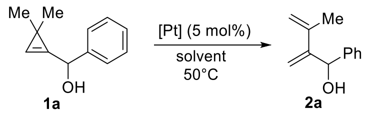
Scheme 1. a) Synthetic approaches towards 1,3-dien-2-yl carbinols. b) Generation and reactivity of vinyl metal carbenes from cyclopropenes. c) Pt-catalyzed isomerization of cyclopropenes to 1,3 – dienes.



1,3-Dienes can be considered as the isomers of cyclopropenes, and are more stable due to the absence of strain. Surprisingly, only few substrate-specific examples for the energetically-favored catalytic isomerization of cyclopropenes to dienes have been reported: Zhi-Bin Zhu and Min Shi reported a cascade isomerization/Diels-Alder cycloaddition of 1-aryl,2-alkenylcyclopropenes.[12] During completion of our work, the group of Ruben observed the isomerization of cyclopropenyl silane to the corresponding diene product under Pt catalysis as an undesired side reaction.[11d] Such isomerization, if performed in a controllable manner, would be highly useful for the synthesis of 1,3-dienes, in particular valuable 1,3-dien-2-yl carbinols. Herein, we report our studies on the platinum-catalyzed isomerization of 3,3-disubstituted cyclopropenylcarbinols, easily accessible from addition of cyclopropenyllithiums to carbonyl compounds,[13] to highly substituted conjugated dienes (Scheme 1C).

Our group recently became interested in the development of new synthetic methods involving cyclopropenes. While exploring reactions of platinum complexes with cyclopropenylcarbinol **1a** we observed the formation of the unexpected diene product **2a** (Table 1, entry 1). Inspired by this result, we decided to optimize this transformation. First, different platinum catalysts were examined, and only $PtBr_2$ gave comparable results (Table 1, Entries 2-5). Then, different solvents were examined for both $PtCl_2$ (for the results see the SI) and $PtBr_2$ (Table 1, Entries 6-8). The reaction using $PtBr_2$ in DCE gave the best yield of 60% (Entry 8). Fine-tuning of the reaction temperature and the concentration resulted in a slight improvement of the yield up to 69% (Table 1, Entry 9). When the reaction was performed with 5 mol% of the catalyst, it was difficult to obtain reproducible results. More reliable yields were obtained using 10 mol% of the catalyst.

Table 1. Optimization of the Pt-catalyzed isomerization of 1a.



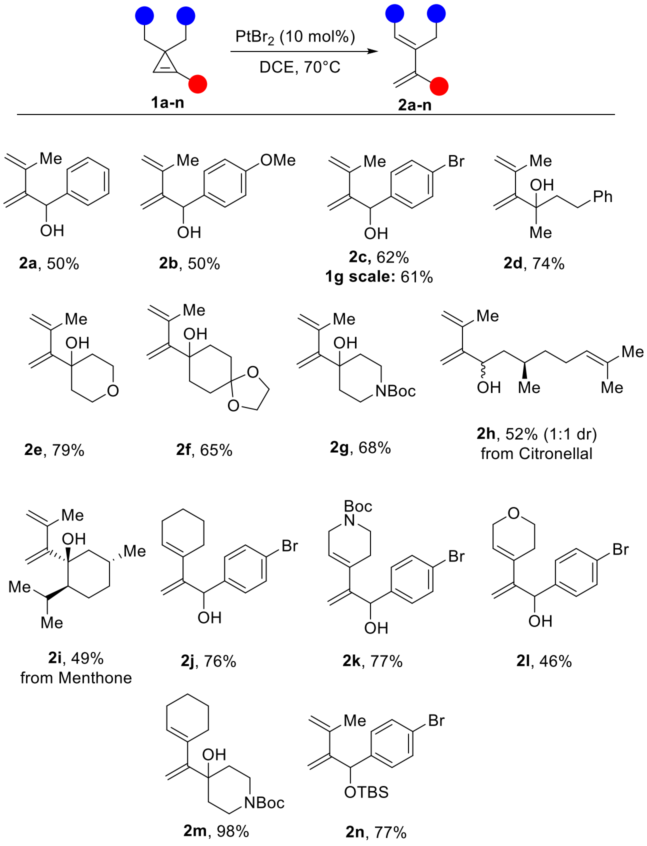
Entry	Catalyst	Solvent	yield[b]
1	$PtCl_2$	Toluene (0.1 M)	55%
2	$PtBr_2$	Toluene (0.1 M)	51%
3	PtI_2	Toluene (0.1 M)	14%
4	$PtCl_4$	Toluene (0.1 M)	6%
5	$PtCl_2(PPh_3)_2$	Toluene (0.1 M)	0%
6	$PtBr_2$	Acetone (0.1 M)	37%
7	$PtBr_2$	MeCN (0.1 M)	44%
8	$PtBr_2$	DCE (0.1 M)	60%
9[c]	$PtBr_2$	DCE (0.05 M)	67%

[a] The reactions were performed on a 0.1 mmol scale. [b]The yield was determined by ^1H NMR of the concentrated reaction mixture using CH_2Br_2 as an internal standard.[c] The reaction was performed at 70 °C.

With the optimized conditions in hand, we moved to the exploration of the scope of the transformation (Scheme 3). First, the reaction of the model substrate **1a** was scale up to a 0.4 mmol scope scale with subsequent isolation of product **2a** by column chromatography. A 17% decrease in yield was observed, speculatively due to instability of the product during purification.

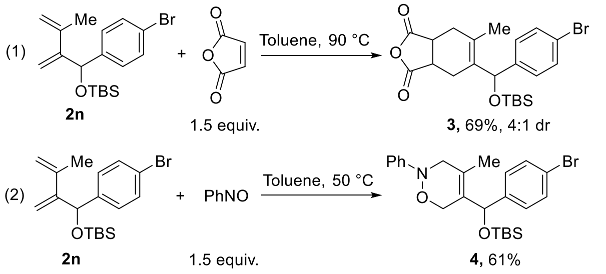
We then decided to vary substitution on the aromatic ring. Product **2b** bearing a methoxy-substituted arene was obtained in 50% yield. Product **2c** arose in 62% yield from bromobenzene substituted cyclopropene **1c**. Remarkably, the reaction starting from 1 gram of **1c** resulted in 61% yield of **2c**. To our delight, aliphatic alcohols also performed well in the reaction. Moreover, the products demonstrated better stability with no losses observed during purification. Products **2d** and **2e** were obtained in 74% and 79% yield respectively. An acetal group was tolerated as shown in the formation of diene **2f**. A Boc-protected amine did not interfere with the reaction, and product **2g** was obtained in 42% yield. Moreover, cyclopropenes **1h** and **1i**, derived from the addition of dimethylcyclopropenyllithium to naturally occurring citronellal and menthone can also be transformed to the corresponding 1,3-dienes **2h** and **2i**. Substitution at the aliphatic carbon of the cyclopropene can also be varied. Starting from various spirocyclic cyclopropenes, more complex dienes **2j-m** were obtained in 46-98% yield. Finally, we could demonstrate that a free alcohol is not necessary for the reaction: TBS-protected dienol **2n** was obtained in 77% yield. It is interesting to note, that the yield of the protected alcohol product is even higher, presumably due to a slower decomosition of the product during the reaction and purification.

Scheme 3. Substrate scope[a]



To demonstrate the utility of the products we performed first a Diels-Alder cycloaddition of diene **2n** with maleic anhydride, resulting in the formation of cyclohexene **3** in 69% yield (Scheme 4, Eq. 1). Furthermore, hetero-Diels-Alder cycloaddition reaction of **2n** with nitrosobenzene gave heterocycle **4** in 61% yield as a single regioisomer (Scheme 4, Eq. 2).

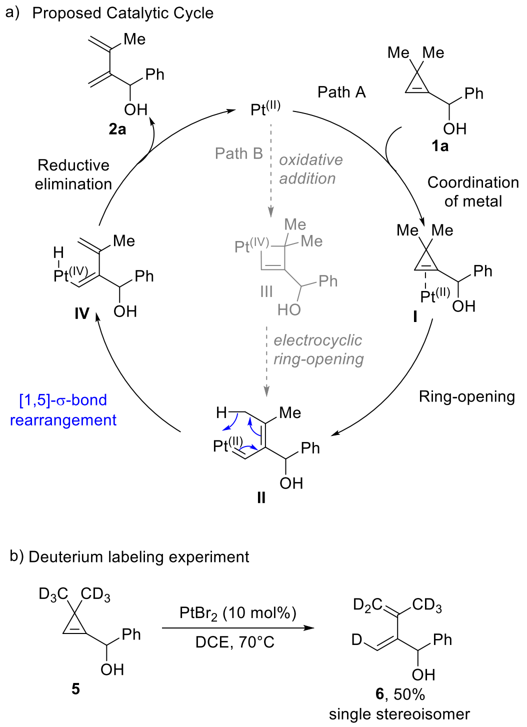
Scheme 4. Product modifications



After careful examination of the literature[14] we propose the following mechanism (Scheme 5a): after coordination of the platinum to the cyclopropene double bond (complex **I**), ring-opening occurs with the formation of vinyl platinum carbene species **II** (Path A).[15] Such sequence appears to be highly probable due to the π-philicity of platinum complexes.[16] However, an oxidative addition of the platinum complex onto the C-C bond, followed by cycloreversion of metallacyclobutane intermediate **III** (Path B), resulting in the same metal carbene intermediate **II** cannot be excluded at this stage.[17] Carbene **II** then undergoes pericyclic [1,5] - σ-bond rearrangement, resulting in platinum hydride intermediate **IV**.[18] Intermediate **IV** finally leads to the product and regenerates the catalyst through reductive elimination. To further support the proposed catalytic cycle, we performed isotope labeling studies. Deuterated cyclopropene **5** was prepared in 6 steps from d^6-acetone (see SI for the preparation) and subjected to the reaction conditions. To our delight, the deuterated product **6** was formed selectively, providing strong support for the proposed mechanism. To the best of our knowledge such pericyclic [1,5]- σ-bond rearrangement is a unique feature of vinyl platinum carbenes, which has not yet been reported with other transition metal complexes.

In summary, a protocol for the Pt-catalyzed isomerization of cyclopropenes to 1,3-dienes is reported. The transformation resulted in the formation of highly substituted 1,3-dienyl carbinols. The utility of the products was demonstrated by two distinct Diels-Alder cycloadditions. Isotope labeling studies supported the formation of a Pt-carbene intermediate, which underwent [1,5]-hydride shift. So far this rearrangement was only reported as a minor and undesired pathway in Pt-catalyzed transformations. We hope, that our work will attract more attention to this unique elementary step, which can be used in the development of diverse synthetic transformations.

Scheme 5. Proposed mechanism and isotope labeling studies



ASSOCIATED CONTENT

Supporting Information

Experimental procedures, optimization data, spectra (PDF)

AUTHOR INFORMATION

Corresponding Author

Jerome Waser - Laboratory of Catalysis and Organic Synthesis, Institut des Sciences et Ingénierie Chimique, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland; orcid.org/0000-0002-4570-914X; Email: jerome.waser@epfl.ch

Co-authors

Vladyslav Smyrnov - Laboratory of Catalysis and Organic Synthesis, Institut des Sciences et Ingénierie Chimique, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland; https://orcid.org/0000-0001-7180-0337; Email: vladyslav.smyrnov@epfl.ch

Antonin Homassel - Laboratory of Catalysis and Organic Synthesis, Institut des Sciences et Ingénierie Chimique, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland; Email: antonin.homassel@cea.fr

Leander Choudhury - Laboratory of Catalysis and Organic Synthesis, Institut des Sciences et Ingénierie Chimique, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland; Email: leander.choudhury@epfl.ch

Author Contributions

V.S designed the project, did preliminary experiments, prepared the experimental part and first draft of the manuscript. A. H. optimized the reaction and performed mechanistic studies. V.S., A.H., and L.C. performed investigations of the scope and product modifications. J. W. supervised the project, edited the manuscript and proofread the experimental part. All authors have given approval to the final version of the manuscript.

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