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Communication

Cross metathesis of Allenes. Mechanistic Analysis and Identi cation of a Ru CAAC as the Most Effective Catalyst

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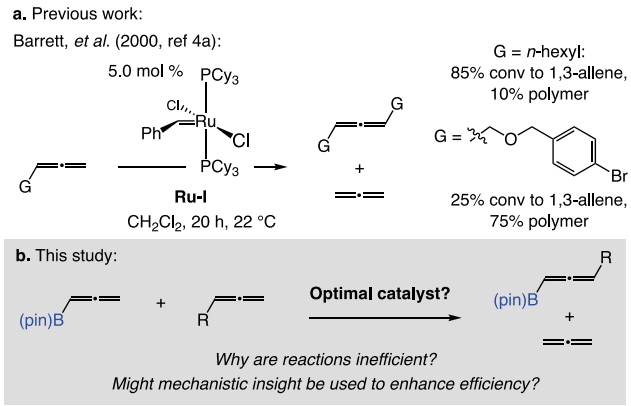
ABSTRACT: The rst examples of cross-metathesis between two different allenes is disclosed. First- and second-generation Ru complexes were found to be ineffective, at most affording only oligomeric products. The exception was a rst-generation complex bearing a bidentate phenyl isopropoxy ligand (i.e., PCy_3 is not released upon initiation), reactions with which afforded a 1,3-disubstituted allenyl boronate in 22 yield. On the basis of mechanistic studies designed to gain deeper understanding of the reasons for the ineffectiveness of different Ru catalysts, it was discovered that phosphine-free Ru-CAAC complexes have the steric and electronic attributes to be highly effective. The results of these investigations pave the way for development of additional ole n metathesis reactions that generate allenes.

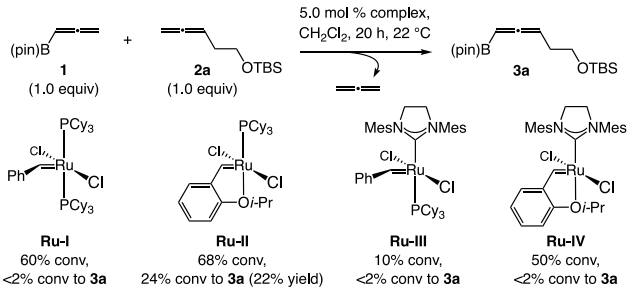
Despite recent progress in catalytic cross-metathesis (CM),[1] there are key processes that remain underdeveloped, notable among which are those affording allenes, moieties found in bioactive compounds,[2] and used with increasing frequency in enantioselective catalysis.[3] The sole relevant disclosure[4] is in regard to homometathesis of monosubstituted allenes, carried out with bis-phosphine complex **Ru-I** (Scheme 1a). Symmetric disubstituted allenes were obtained together with polymeric byproducts. As the rst step to address this shortcoming, we decided to develop transformations that afford boryl-substituted allenes (Scheme 1b). The choice of substrates was for two reasons: the versatility and increasing use of allenyl boronates in organic synthesis,[5] and the likelihood that CM of electronically complementary allenes would be more facile (vs homometathesis).[6]

Scheme 1. Previous Work and the Focus of This Study



We began by probing the reaction between commercially available allenyl-B(pin) (**1**) and **2a** (Scheme 2). None of the desired product (**3a**) was detected with Mo alkylidenes (oligomers only), **Ru-I**, or NHC-containing **Ru-III** and **Ru-IV**. Unexpectedly, though, with monophosphine **Ru-II**, there was 24 conversion to allenyl-B(pin) **3a** (22 yield after puri cation). The key question then was: why would a less active Ru complex be more effective?

Scheme 2. Initial Data



[a]Performed under N_2 atm. Conv (±2) was determined by analysis of the ^1H NMR spectra of the unpuri ed product mixtures. Yield corresponds to puri ed product (±5). See the Supporting Information for details.

In search of an answer, we investigated the fate of **Ru-II** under the reaction conditions. The ^{31}P NMR spectrum of the mixture derived from the reaction between allenes **1** and **2b** indicated rapid Ru complex consumption and formation of two new species, evidenced by the appearance of signals at 35.1 and

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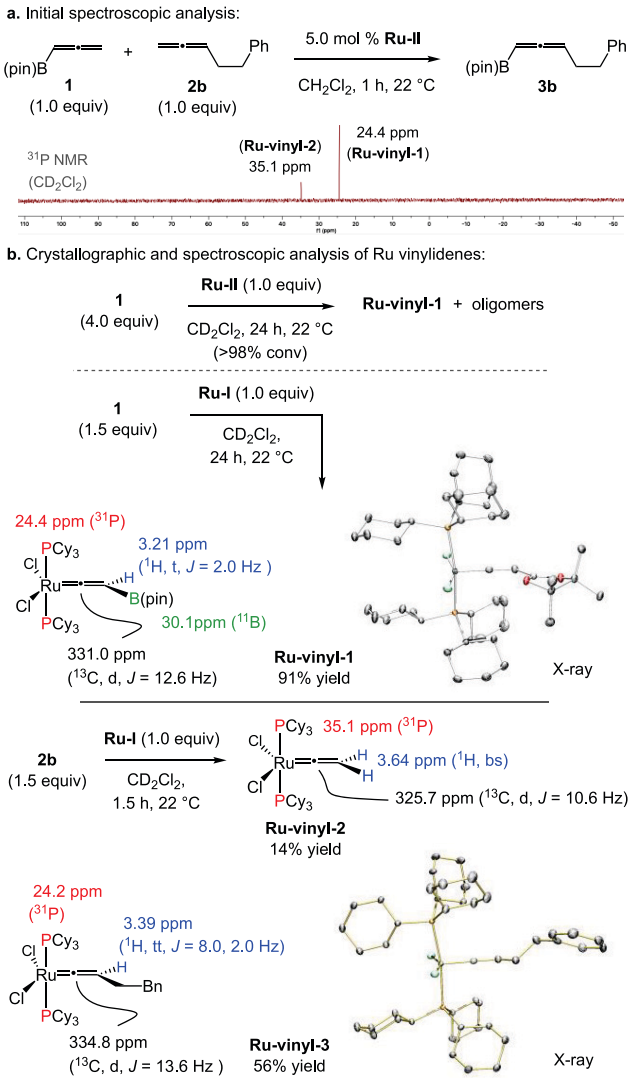
24.4 ppm (Scheme 3a). For insight regarding the identity of the vinylidene complexes formed and the reason for their low

Scheme 3. Studies with Ru-I and Ru-II

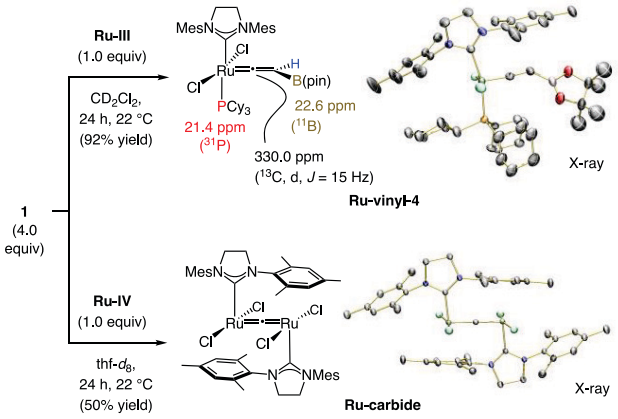


[a]Performed under N_2 atm. See the Supporting Information for details.

reactivity, we rst treated **Ru-II** with 4.0 equiv of **1** (Scheme 3b). A new vinylidene was formed together with decomposition byproducts.[7] On the basis of spectroscopic analysis and X-ray crystallography, the resulting complex was identi ed as **Ru-vinyl-1**. This was con rmed when **Ru-vinyl-1** was generated in 91 yield by reaction of **Ru-I** and allenyl-B(pin) (1.5 equiv). A similar process involved alkyl-allene **2b**, affording **Ru-vinyl-2** and **Ru-vinyl-3** (mixture; 14 and 56 yield, respectively). These ndings suggested that formation of the more electron-de cient allenyl-B(pin) is more favorable (vs an alkyl-allene). Control experiments showed that Ru-vinylidene complexes are less effective than **Ru-II** in promoting CM (e.g., ~10 conv to **3b** with 5.0 mol **Ru-vinyl-1** or **Ru-vinyl-2**/**Ru-vinyl-3**, mostly oligomerization).

Parallel experiments were carried out with NHC-containing **Ru-III** and **Ru-IV** (Scheme 4). The reaction with monophosphine **Ru-III** produced **Ru-vinyl-4** in 92 yield (Scheme 4). The transformation between allenyl-B(pin) and phosphine-

Scheme 4. Studies Involving Ru-III and Ru-IV



[a]Performed under N_2 atm. See the Supporting Information for details.

free **Ru-IV**, on the other hand, revealed a different decomposition mode: **Ru-carbide**[8] was obtained in 50 yield (Scheme 4). An X-ray structure was secured, but spectroscopic analysis was precluded by the complex s low solubility.

Next, we performed DFT studies (Scheme 5) to obtain further information vis-a-vis the productive pathways and those leading to inactive complexes, such as **Ru-vinyl-1** **4** and **Ru-carbide**. Catalyst initiation likely occurs via **ts-i** and **mcb-i** to give **vinyl-i** (catalytically active, unlike bis-phosphine **Ru-vinyl-1**).[9] Reaction of **vinyl-i** with the second allene then affords the CM product and unsubstituted vinylidene complex **vinyl-ii** (via **ts-ii** **mcb-ii**, and **ts-iii**). Ensuing transformation involving **vinyl-ii** and allenyl-B(pin) **1** regenerates **vinyl-i** via **ts-iv**, completing a productive catalytic cycle. Another energetically competitive route for **vinyl-ii** entails its homometathesis via **ts-v** to yield **mcb-iv**. Cyclo-reversion of **mcb-iv** then leads to a carbide complex, which is likely considerably lower in energy (32.1 and 22.2 kcal/mol for **Ru-carbide** with L = PCy_3 and NHC, respectively).

DFT investigations revealed that catalyst initiation is the most energetically demanding stage of the transformation (**Ru-II** or **Ru-IV** **ts-i** **mcb-i** **vinyl-i**, Scheme 5). Furthermore, in the case of phosphine-free **Ru-IV**, the barrier for carbide formation is competitive with the productive route (see **vinyl-ii** **ts-iv** vs **vinyl-ii** **ts-v**). In connection to **Ru-II**, bisphosphine vinylidene formation likely occurs by interception of **vinyl-i** or **vinyl-ii** with PCy_3 (**Ru-vinyl-1** or **Ru-vinyl-2**, respectively). DFT studies indicated that bisphosphine formation is nearly barrierless and highly exergonic (19.0 and 14.5 kcal/mol for **Ru-vinyl-1** or **Ru-vinyl-2**, respectively).[10] Regarding reactions with **Ru-II**, which typically do not generate PCy_3, it might be suggested that bisphosphine vinylidene generation entails intramolecular phosphine transfer in a complex such as **mcb-iv** (L = PCy_3). Nonetheless, computational studies indicate that such pathways, as well as loss of PCy_3 from the intermediates illustrated in Scheme 5, are unfavorable.[11] This suggests that, when **Ru-II** is used, a likely source of free phosphine is catalyst decomposition. A more detailed picture will require further mechanistic exploration.

The above ndings indicated that a more efficient Ru complex would be one that instead of a phosphine contains a ligand that is signi cantly more sterically demanding than a

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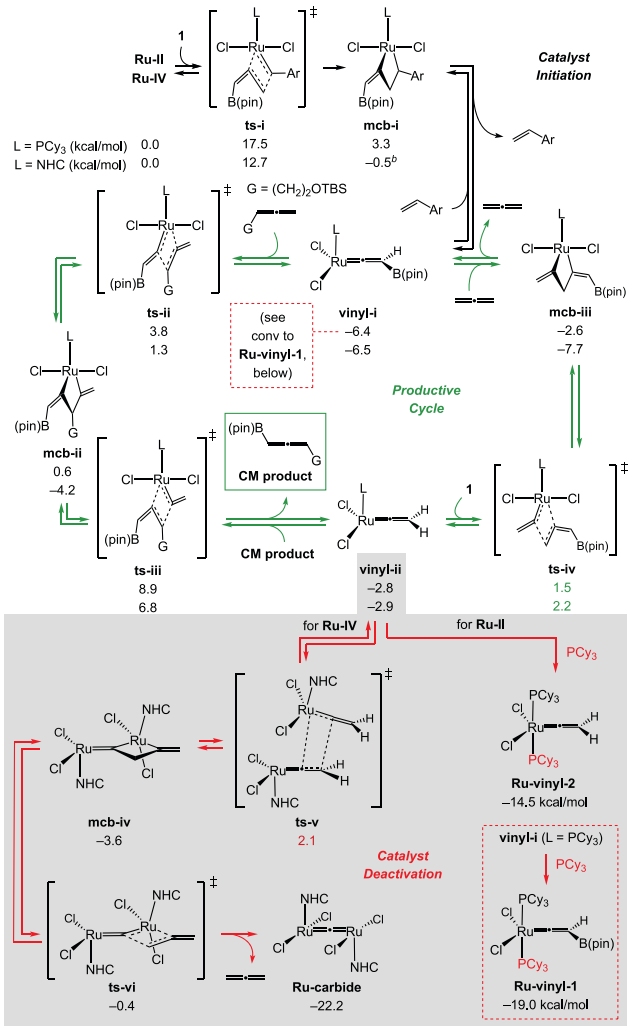
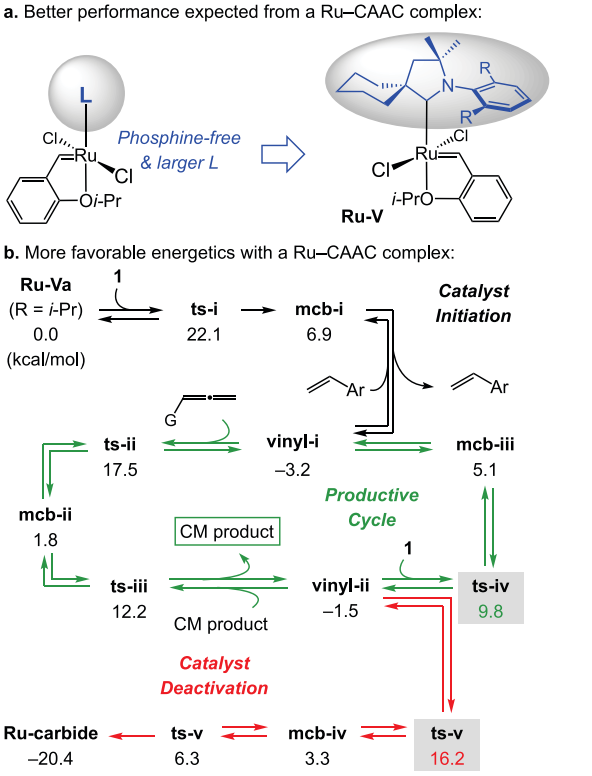
Scheme 5. Pathways for Catalyst Initiation Productive Cycles and Catalyst Deactivation



[a]Performed with B97X-D/6-311++G(d,p)-SDD(Ru), SMD-(CH_2Cl_2)//B3LYP-D3/6-31G(d)-SDD(Ru). See the Supporting Information for details. [b]Ether dissociation is calculated to require 16.1 kcal/mol, the highest point in the reaction with **Ru-IV** (L = NHC).

PCy_3 or NHC so that two vinylidenes cannot readily react (see **mcb-iv**, Scheme 5) to generate an inactive carbide. These considerations led us to cyclic (alkyl) (amino) carbenes (CAAC)[12] as potential ligands (Scheme 6a). This was partly because the quaternary carbon in a CAAC ligand causes the space around the transition metal to be notably more hindered compared to an NHC unit with a more sizable *N*-aryl or *N*-alkyl group (referred to as a "wall" vs an "umbrella" shape, respectively[12]). DFT studies (Scheme 6b) indicated that catalyst initiation and the productive catalytic cycle would require higher energy (e.g., 22.1 vs 17.5 and 12.7 kcal/mol **ts-i** and 17.5 vs 3.8 and 1.3 kcal/mol **ts-ii** for **Ru-Va**, **Ru-II**, and **Ru-IV**, respectively). However, the difference in activation barriers at the crucial juncture, determining the preference for a productive cycle versus carbide formation (**vinyl-ii** **ts-iv** vs **vinyl-ii** **ts-v**), was calculated to be higher (e.g., 9.8 vs 16.2 kcal/mol for **Ru-Va** compared to 2.2 vs 2.1 kcal/mol for **Ru-IV**, respectively).

Scheme 6. Energetics of Reactions with Ru-CAAC



[a]DFT studies with B97X-D/6-311++G(d,p)-SDD(Ru), SMD-(CH_2Cl_2)//B3LYP-D3/6-31G(d)-SDD(Ru). See the Supporting Information for details.

When **Ru-Va** (prepared in one step from **Ru-II**)[13] was subjected to allenyl-B(pin) and phenanthroline (**4**; to help capture an otherwise unstable species; Scheme 7a), **Ru-vinyl-5**[14] was formed in 82 yield along with detectable amounts of diborylallene **5** (≤25 ; unstable). A likely pathway to **Ru-vinyl-5** entails reaction of the initially generated (pin)B-substituted Ru vinylidene with **1**, pointing to greater longevity of a Ru-CAAC vinylidene. Without diamine **4**, **1** was consumed completely (20 h, 45 °C), affording ~15 **5**, with ~80 unreacted **Ru-Va**. None of the derived carbide complex was detected. What is more, with 5.0 mol **Ru-Va** CM between **1** and **2a** (Scheme 7b) proceeded to 93 conversion, allowing us to isolate **3a** in 67 yield.

With an effective catalyst identi ed, we prepared 1,3-disubstituted allenyl-B(pin) products **3a** **h** and **3j** **l** in 40 71 yield (Scheme 7b). When performed at larger scale (1.0 mmol), **3b** was isolated in 65 yield (85 conv). The presence of a terminal alkyne led to the formation of a mixture of unidenti able byproducts (compare **3i** and **3j**), and reaction with cyclohexyl allene afforded **3m** in only 21 yield. Use of less hindered complexes **Ru-Vb** **c**, an effective strategy in reactions of sizable ole ns resulted in reduced efficiency. The lower yield for **3m** is likely caused by greater steric repulsion between the B(pin) and Cy groups in **ts-iii** (Scheme 5 and 6b). Here, the size of L is unlikely to be influential, with reaction between two unsubstituted Ru-vinylidenes (see **vinyl-ii**) and carbide formation becoming faster. Finally, the following points merit note: (1) CM reactions proceed with complete chemoselectivity in the presence of a monosubstituted ole n (**3h**). (2) As might be expected,[6] CM between two

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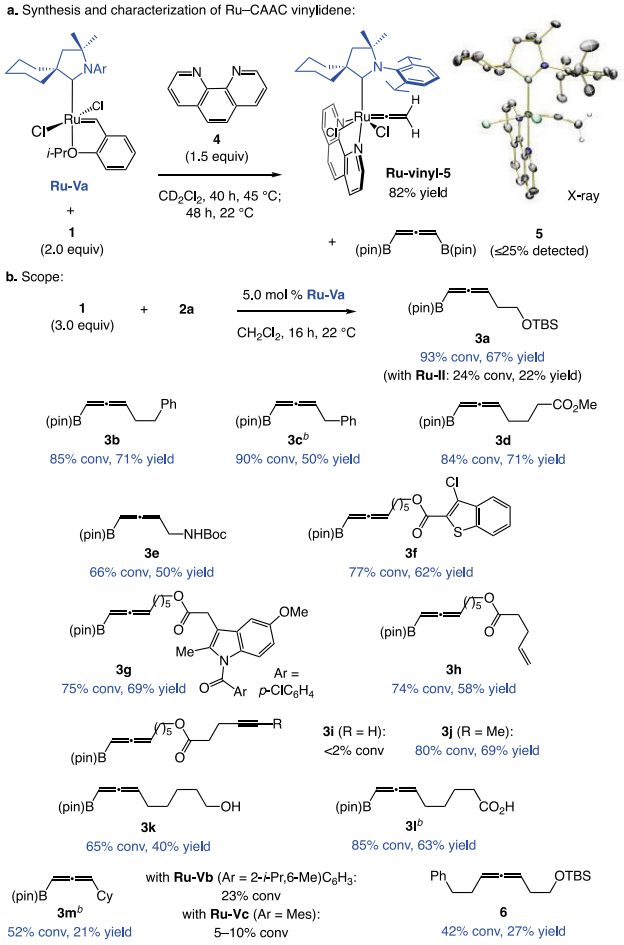
Scheme 7. Ru-CAAC Complexes for Allene CM



[a]Performed under N_2 atm. Conv (±2) refers to the desired product generated, determined by analysis of the ^{1}H NMR spectra of unpuri ed mixtures. Yields of pure product (±5). Discrepancy between conv and yield is mostly due to product instability. [b]10 mol **Ru-Va** was used.

electronically similar alkyl-substituted allenes led to signi cant amount of homocoupling (e.g., **6**). (3) Disubstituted allenyl-B(pin) compounds can be converted to other allenes by the use of a variety of established methods.[15]

To summarize, we nd that Ru-CAAC complexes are distinctively effective in promoting CM between allenes. We have been able to gain insight regarding catalyst decomposition pathways when Ru-PCy_3 or Ru-NHC complexes are involved. Additionally, features that render Ru-vinylidenes distinct from the more widely studied carbenes have been outlined. The newly acquired knowledge sheds light on some of the more recent ndings and should prove to be of value to future initiatives,[16] including those intended to be diastereo- and/or enantioselective.[17]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c11453.

Experimental and analytical details (PDF)

Accession Codes

CCDC 2116550 2116554 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing nancial interest.

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(10) Similarly, favorable phosphine association was calculated for reactions involving **Ru-III** (i.e., **vinyl-i** **Ru-vinyl** **4** = 16.1 kcal/mol).

(11) See the Supporting Information, section 5.2, for details.

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