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## Catalytic Hydroalkylation of Allenes\*\*

Mitchell Lee, Mary Nguyen, Chance Brandt, Werner Kaminsky and Gojko Lalic\*

**Abstract:** We have developed a catalytic method for hydroalkylation of allenes using alkyl triflates as electrophiles and silane as a hydride source. The reaction has an excellent substrate scope and is compatible with a wide range of functional groups, including esters, aryl halides, aryl boronic esters, sulfonamides, alkyl tosylates, and alkyl bromides. We found evidence for the reaction mechanism that involves unusual dinuclear copper ally complexes as catalytic intermediates. The unusual structure of these complexes provides rationale for their unexpected reactivity.

Reductive cross-coupling reactions of unsaturated compounds have been extensively studied over the last decade and have been developed into a powerful tool for the formation of carboncarbon bonds. These reactions obviate the need for the stoichiometric preparation of reactive organometallic intermediates and allow direct use of unsaturated compounds as coupling partners.<sup>[1]</sup> As a result, reductive cross-coupling reactions often provide a more efficient alternative to the traditional cross coupling of organometallic reagents and organic electrophiles.

Most reductive cross-coupling reactions involve  $\pi$ -electrophiles, such as aldehydes,<sup>[2]</sup> ketones,<sup>[3]</sup> imines,<sup>[4]</sup> and activated alkenes.<sup>[5]</sup>  $\pi$ -Electrophiles can be generated in situ from suitable precursors, as demonstrated by Krische et al. For example, primary<sup>[6]</sup> and secondary<sup>[7]</sup> alcohols can be used as coupling partners in reactions with a range of unsaturated compounds. Reactions with  $\sigma$ -electrophiles are generally significantly more challenging and less common. Notable early examples of such reactions are the reductive cross-coupling of alkynes with epoxides developed by Jamison et al,[8] and the reductive crosscoupling of functionalized alkenes with alkyl zinc reagents developed by Sigman et al.<sup>[9]</sup> More recently, several inter molecular hydroalkylation reactions have been developed using alkyl halides of sulfonate esters as coupling partners.<sup>[10]</sup> In 2015, Kambe et al. reported copper-catalyzed hydroalkylation of 1,3dienes.<sup>[11]</sup> The same year, our group reported E-selective hydroalkylation of terminal alkynes,[12] while the Z-selective hydroalkylation of aryl alkynes was reported by Hu et al.[13] In 2016, Fu et al reported Markovnikov hydroalkylation of terminal alkynes using a nickel catalyst.<sup>[14]</sup> Despite these developments hydroalkylation of alkynes and certain in alkenes. hydroalkylations of allenes are still relatively rare.

The most general method for reductive cross-coupling of allenes is a recently reported hydroallylation with allylic chlorides as

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coupling partners.<sup>[15]</sup> However, hydroalkylation reactions with simple  $\sigma$ -electrophiles remain limited to intramolecular reactions of specific classes of functionalized allenes,<sup>[16]</sup> with no general methods for intermolecular hydroalkylation of simple allenes.

In this communication, we report copper-catalyzed hydroalkylation of allenes using alkyl triflates as electrophiles. We describe the reaction development and the exploration of the substrate scope. We propose a reaction mechanism and describe the isolation, structure, and reactivity of a new catalytic intermediate.

Using our previous work on hydroalkylation of alkynes as a starting point,<sup>[12]</sup> we developed a method for hydroalkylation of allenes shown in Scheme 1. The best results in the reaction were obtained using alkyl triflates as electrophiles, SIPrCuOTf as a catalyst, (Me<sub>2</sub>HSi)<sub>2</sub>O as a hydride source and CsF as a turnover reagent. The hydroalkylation product was formed as a single regioisomer.



Scheme 1. Copper-catalysed hydroalkylation of allenes

In the process of the reaction development we made several observations summarized in Table 1. The changes in the stoichiometry of the substrates are well-tolerated, and a high yield (91%) of the desired product can be obtained even when neither coupling partner is used in excess. IPrCuF can also be used as a catalyst with a relatively small decrease in yield.

The use of  $(Me_2HSi)_2O$  is essential for the success of the reaction, and even closely related silanes provide lower yields of the hydroalkylation product. High yields are obtained when fewer equivalents of silane or CsF are used in the reaction, while less than 5% of the product is obtained with KF as a turnover reagent. The reaction can be performed at a high concentration of alkyl triflate without decrease in yield. Finally, in addition to 1,4-dioxane, the reaction can also be performed in Et<sub>2</sub>O, while the use of other common organic solvents leads to lower yields.

Table 1. Reaction development.

Bn % yield
Yield <sup>[a]</sup>
99%
99%
91%
81%
91%
66%
91%

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8	2.0 equiv of CsF	98%
9	KF instead of CsF	1%
10	0.5 M ROTf vs 0.1 M ROTf	99%
11	Et <sub>2</sub> O	96%
12	THF	46%
13	CH <sub>2</sub> Cl <sub>2</sub>	77%
14	toluene	66%

<sup>[a]</sup> GC yields are reported. All reactions performed on 0.1 mmol scale.



Hydroalkylation can be accomplished with a range of allenes and alkyl triflates. In all cases, only one regioisomer of the product is obtained. The reaction can be performed in the presence of a variety of functional groups, including esters (7), silyl ethers (9), aryl iodides (4), aryl bromides (13), aryl boronic esters (6), alkyl bromides (8), tosylates (11), and sulfonamides (10, 12). 1,1-Disubstituted allenes provide compounds containing a quaternary carbon center (16). With silyl-substituted allenes, the alkenyl silane product is obtained in high yield, as a single diastereoisomer (17).<sup>[17]</sup> Finally, we found that on the large preparative scale (4 mmol) the hydroalkylation product is obtained in good yield (see 3, Table 2).

Table 2. Substrate scope<sup>[a]</sup>



<sup>[a]</sup> All reactions performed on 0.5 mmol scale. Yields of pure isolated products are reported. <sup>[b]</sup> NMR yield. <sup>[c]</sup> IPrCuF used as a catalyst. Reaction performed at 45 °C.

Overall, the exploration of the substrate scope demonstrates that the new hydroalkylation reaction provides access to a wide range of substituted terminal alkenes and vinyl silanes, and is compatible with a variety of functional groups. The hydroalkylation complementary to  $S_N2'$  allylic substitution

reactions,<sup>[18]</sup> which require alkyl organometallic reagents as coupling partners. The reversed polarity of the hydroalkylation reaction allows the alkylation with substrates that carry highly electrophilic functional groups, such as alkyl bromides (8) and sulfonate esters (11). To provide a better understanding of the underlining chemistry and enable further development of the hydroalkylation reaction, we explored the mechanism of the reaction.

There are two plausible mechanisms of the hydroalkylation reaction (Scheme 2). The mechanism shown in Scheme 2a is based on the generally accepted mechanism for most coppercatalyzed hydrofunctionalization reactions reported so far.<sup>[19]</sup> According to this proposal, copper hydride formation is followed by hydrocupration of the allene and alkylation of the allyl copper intermediate. An alternative mechanism featuring dinuclear cationic complexes [(NHCCu)<sub>2</sub>( $\mu$ -X)]OTf (X=F, H, allyl) (**22**, **23**, **24**) is based on the mechanism of a related hydroalkylation of alkynes recently reported by our group.<sup>[12b]</sup><sup>[20]</sup> The two plausible mechanisms shown in Scheme 2 are closely related, and the major difference is that all mononuclear copper complexes that are intermediates in the first proposal are replaced by cationic dinuclear intermediates in the second proposal.



Scheme 2. Plausible mechanisms

One of the key differences between the two mechanisms is the difference in the reactivity of the copper hydride responsible for the hydrocupration of the allene. We have previously established that dinuclear [(NHCCu)<sub>2</sub>( $\mu$ -H)]OTf (**23**) does not react with alkyl triflates, while the NHCCuH reacts quickly to give alkanes.<sup>[12b]</sup> As a result, an important implication of the first proposal is that hydrocupration of allenes needs to be faster than the reduction of alkyl triflates by SIPrCuH (**20**). We performed a stoichiometric competition experiment shown in Scheme 3a, and observed the formation of the hydroalkylation product (**3**) in 84% yield and the reduction of the alkyl triflate in just 6% yield. This result confirms that the hydroalkylation of allenes is faster than the reduction of

alkyl triflates and confirms the plausibility of the mechanism shown in Scheme 2a.



Scheme 3. Stoichiometric experiments (mechanism a)

Next, we explored the formation of the allyl copper intermediate and its reaction with alkyl triflates. We isolated the SIPrCu(allyl) complex **25** from a stoichiometric hydrocupration reaction (Scheme 3b). It is interesting to note the Z configuration of the alkene in the X-ray crystal structure of the copper allyl complex shown in Figure 1. In a stoichiometric reaction, SIPrCu(allyl) complex **25** reacts with alkyl triflate to produce the desired product in 94% yield (Scheme 3c). The S<sub>E</sub>2' regioselectivity of the alkylation is surprising in light of the S<sub>E</sub>2 reactivity of allylcopper complexes with allylic chlorides previously reported.



Figure 1. ORTEP of mononuclear copper allyl complex closely related to  ${\bf 25}$  with thermal ellipsoids at the 50% probability level.

In the stoichiometric alkylation of 25, we noticed that while the first 50% of the product is formed within the first 6 min, it takes 4 h to reach 87% yield. The significant decrease in the rate of the reaction is consistent with the idea that the SIPrCu(allyl) complex is sequestered by SIPrCuOTf formed as a byproduct of the alkylation reaction. Such formation of the dinuclear [(SIPrCu)<sub>2</sub>(µ-allyl)]OTf (26) complex from SIPrCuOTf with SIPrCu(allyl) (25) can be replicated in a stoichiometric reaction (Scheme 4a). The same complex can also be prepared by a reaction of dinuclear [(SIPrCu)<sub>2</sub>(µ-H)]OTf with allene 2 (Scheme 4b). Access to the dinuclear allyl complex allowed us to explore its reactivity toward alkyl triflates. The stoichiometric reaction of 26 with alkyl triflate 1 yields the expected alkylation product at a significantly lower rate than the reaction of the mononuclear complex under the same reaction conditions. The successful alkylation of the dinuclear [(SIPrCu)<sub>2</sub>(µ-allyl)]OTf complex is surprising considering that the analogous [(NHCCu)<sub>2</sub>(µ-

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alkenyl)]OTf complex does not react with alkyl triflates under a variety of conditions.  $\ensuremath{^{[12b]}}$ 



Scheme 4. Stoichiometric experiments (mechanism b)

The results of experiments shown in Scheme 3 and 4 demonstrate the feasibility of key elementary steps of both catalytic cycles shown in Scheme 2. However, we favor mechanism b shown in Scheme 2b. In previous work, we have shown that in related reduction of alkyl triflates and hydroalkylation of alkynes the catalyst turnover (step IVa in Scheme 2a) is rate limiting, most likely because of the slow phase transfer of the fluoride. One consequence of the slow entry of fluoride into the catalytic cycle is a relatively high concentration of NHCCuOTf, which forces the formation of the dinuclear intermediates. Considering that the elementary steps involved in mechanism a (hydrocupration and alkylation of the organocopper intermediate) are faster with allenes than with alkynes, the formation of SIPrCuF is most likely still rate limiting and would force the shift towards mechanism b.

The mechanism shown in Scheme 2b features dinuclear copper allyl complexes (24) as key intermediates. These complexes are related to the cationic dinuclear alkenyl complexes previously described by Sadighi and later by us. However, they have never been reported or characterized before. Attempts to obtain crystals of 26 were not successful, and we focused on crystallization of a closely related complex that contains a *para*bromobenzene moiety (27, Fig. 2a). After considerable effort, we obtained an X-ray crystal structure of 27, which shows surprising structural features distinct from those found in dinuclear alkenyl copper complexes.<sup>[21]</sup>

The crystal structure of **27** (Fig. 2a) contains two configurations (Fig. 2b and 2c), with the Z double bond preserved in both. It is interesting to note that the <sup>1</sup>H NMR of **26** and **27** features broad signals consistent with a dynamic structure. The minor configuration in the X-ray structure contains symmetrically arranged metal centers bonded to a  $\pi$ -allyl fragment from the opposite faces (Fig. 2b). This structural arrangement is very unusual for late transition metal complexes, with no other examples of ally fragments sandwiched between two metal centers available in The Cambridge Crystallographic Data Centre.

In the major configuration (Fig. 2c), the two metal centers distort from the symmetrical arrangement towards the opposite ends of the allyl fragment. In the resulting arrangement of copper atoms, one is  $\sigma$ -bonded to the allyl fragment, while the other is  $\pi$ bonded to the alkene. This bonding arrangement contrasts with

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dinuclear alkenyl copper complexes, in which metal centers do not interact with the alkene and instead form a three-center-twoelectron bond with the alkenyl carbon. This structural difference is consistent with the difference in reactivity of two types of dinuclear complexes. The nonsymmetrical configuration of the dinuclear allyl copper complex with the  $\sigma$ -bonded allyl copper fragment offers a plausible explanation for the much higher reactivity of these complexes towards alkyl triflates relative to the reactivity of analogous alkenyl complexes.





b)



C)



Figure 2. X-ray crystal structure of complex **27**. The counterion and most hydrogen atoms were removed for clarity a) schematics of complex **27**. b) ORTEP of the minor configuration with thermal ellipsoids at 40% probability level. c) ORTEP of the major configuration with thermal ellipsoids at 40% probability level.

The results of our studies of the hydroalkylation of allenes and alkynes point to several important differences in the reactivity of these classes of compounds. First, while the hydrocupration of allenes by SIPrCuH is faster than the reduction of alkyl triflates, the opposite is true for the reaction of alkynes. This is in line with the generally higher reactivity of allenes. The second difference is the much higher reactivity of dinuclear [(SIPrCu)<sub>2</sub>(µ-allyl)]OTf complexes, which react with alkyl triflates. The analogous [(NHCCu)<sub>2</sub>(µ-alkenyl)]OTf complexes do not react with alkyl triflates under a wide range of reaction conditions. These differences in the reactivity of allenes and alkynes point to opportunities for taking different approaches to the development of reactions for their hydrofunctionalization.

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### Entry for the Table of Contents (Please choose one layout)

Layout 2:

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Mitchell Lee, Mary Nguyen, Chance SIPrCuF (5 mol%) Brandt, Werner Kaminsky, Gojko Lalic\* (Me<sub>2</sub>HSi)<sub>2</sub>O, CsF  $R^1$ R<sup>2</sup>-OTf R  $R^1$ Page No. – Page No. 1,4-dioxane  $R^2$ 25 °C, 16 h Catalytic Hydroalkylation of Allenes Text for Table of Contents