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Remarkable Ligand Effect on Rh-Catalyzed C–H-Active [3 + 2] Annulation of Ketimines and Alkynes

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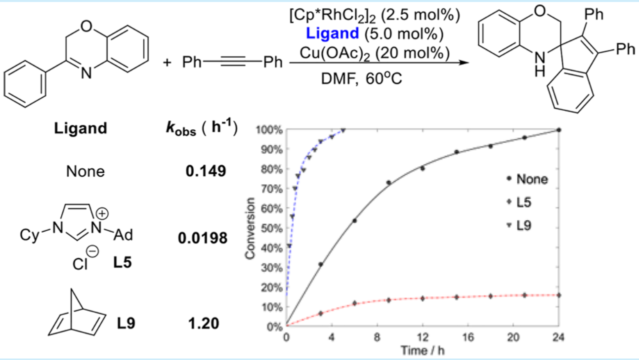
Cite This: https://dx.doi.org/10.1021/acs.orglett.0c01768 Read Online

ABSTRACT: Externally added ligands were first found to have a significant impact on the Rh-catalyzed C–H-active [3 + 2] annulation of ketimines and alkynes. Olefin ligands have shown remarkable promotion effect for this reaction. The olefin promoted the reaction by increasing both the turnover rate and conversion of $[Cp^*RhCl_2]_2$ in the formation of rhodacycle in the C–H activation step.

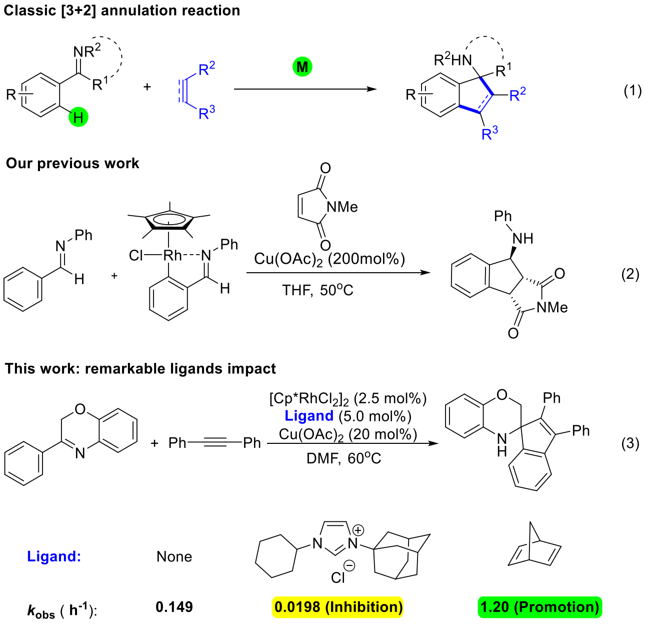


C–H activation triggered [3 + 2] annulation reactions have been conceptually established as a new class of annulation reactions by applying this emerging synthetic strategy to substrates having no acidic protons. Several successful protocols[1−6] including enantioselective versions[7,8] have been reported. Of these, transition-metal-catalyzed [3 + 2] annulations of aromatic ketimines/aldimines with unsaturated hydrocarbon electrophiles have received great interest, and significant advances have been achieved due to the high importance of the indenyl/indanyl amine skeleton that was constructed via these protocols (see eq 1, Scheme 1).[1−5,8] Owing to the high stability of rhodium catalyst, particularly intense efforts have been spent on the rhodium-catalyzed [3 + 2] annulation reactions.[5,8]

Of all these transformations that use rhodium metal as the catalyst, a rhodium complex with a Cp ring or Cp rings with different substituting groups is almost the only type of catalyst.[9] Moreover, the challenges in the Cp ring modification make it difficult to introduce ligands with various elements that having diverse structures and properties. Thus, although several reports with regard to the impact of the substituent group on the Cp ring have been studied by Rovis,[10] Cramer,[11] and others,[12] compared with the rhodium catalysts using phosphine-, nitrogen-, and even carbon-based ligand, the rhodium–Cp complexes are largely less developed in terms of either quantities or structural diversities.

Therefore, if the catalytic performance of the single Cp Rh-type catalysts could be manipulated by an externally added ligand, it could provide a highly efficient strategy to improve the reaction considering the challenge in the modification of Cp ligand. Moreover, there is great importance in discovering

Scheme 1. Transition-Metal-Catalyzed [3 + 2] Annulation Reactions



Received: May 25, 2020

new chemistry for this new strategy which could potentially bring new insight or new ideas.[13]

In our previous report, we observed that the single rhodacycle complex of an imine did not react with an electron-deficient olefin to yield the desired product; instead, an extra molecule of imine was needed to make the reaction proceed (eq 2, Scheme 1).[14] We assumed that either the free imine or the imine in the rhodacycle served as a required ligand to evolve the reaction, although there is a lack of solid evidence.

In this study, we found the externally added ligands have a dramatic impact on the reaction rate in a $[Cp^*RhCl_2]_2$-catalyzed [3 + 2] annulation reaction of a new combination of aromatic ketimines and alkynes (eq 3, Scheme 1).

Our study started with the 2-phenyl-2*H*-benzo[*b*][1,4]-oxazine **1a** as substrate and 1,2-diphenylacetylene **2a** as electrophile. The optimized condition is still the combination of $[Cp^*RhCl_2]_2$ and $Cu(OAc)_2$ in DMF.[14] The results also suggested that $Cu(OAc)_2$ was still crucial additive in this reaction despite the electrophile is alkyne.[15]

However, this condition is far from ideal because of the long reaction time even with 5 mol % rhodium metal loadings (53% conversion at 5 h (see Figure 1) and 24 h to complete the reaction (see the SI)). As mentioned previously, we assumed that an externally added ligand for the rhodium could be very influential to the reaction. Thus, different types of ligands were tested, and the results are shown in Figure 1.

First, molecules containing a C═N bond were tested. When py-box ligand **L1** was added to the reaction, the 5 h conversion dropped from 53% to 40%. Then chiral py-box ligands **L2** and **L3** were used and the 5 h conversions dropped further to 34% for **L2** and 32% for **L3**, respectively. However, no enantioselective excess was observed in both cases despite both chiral ligands showing a strong impact on the activity of the catalyst.

Next, the phosphine-based ligand (**L4**) showed the smallest inhibition effect on the reaction rate compared with other ligands. This may be explained by either the oxidation of phosphine ligand[16] by copper acetate or the competitive coordination of the ligand to copper. Carbon-based precarbene ligands **L5** and **L6** almost inhibited the reaction completely.[17] The conversions of these two ligands were as low as 10% and 9%, respectively.

Gratifyingly, a 95% conversion was achieved with **L7**, which is a significant contrast to the reaction that has no ligand (53%). **L8**, a chiral diene ligand developed by Hayashi,[18] showed a similar impact with regard to the reaction rate (97% conversion) as **L7**. However, there is still no enantioselective induction despite the remarkable promotion of reaction rate given by **L8**. The best result was achieved on norbornadiene **L9**, which afforded a >99% conversion in 5 h. Monodentate olefins norbornene (**L10**, 98%) and cyclohexene (**L11**, 92%) showed that they also could promote the reaction effectively.

To quantify the impacts of the ligands on the reaction, kinetic analysis of reactions using **L5−10** and no ligand were carried out. The resulting kinetic profiles are shown in Figure 2, from which the dramatic ligand effects on the reaction can be seen more clearly.

In general, it took 24 h to complete the reaction without any ligand, but it only took ~4 h to finish the reaction that with the presence of 5 mol % norbornadiene (**L9**) in the reaction. A remarkable rate promotion effect was also observed with diene ligands **L7**, **L8**, and **L10**, which could accelerate the reaction to a full conversion within 5 h. On the other hand, **L5** allowed the reaction to slowly progress to 10% conversion in the first 8 h and almost stopped after that. **L6** also showed a strong inhibition effect initially, but the conversion has an unexpected increase after 16 h.

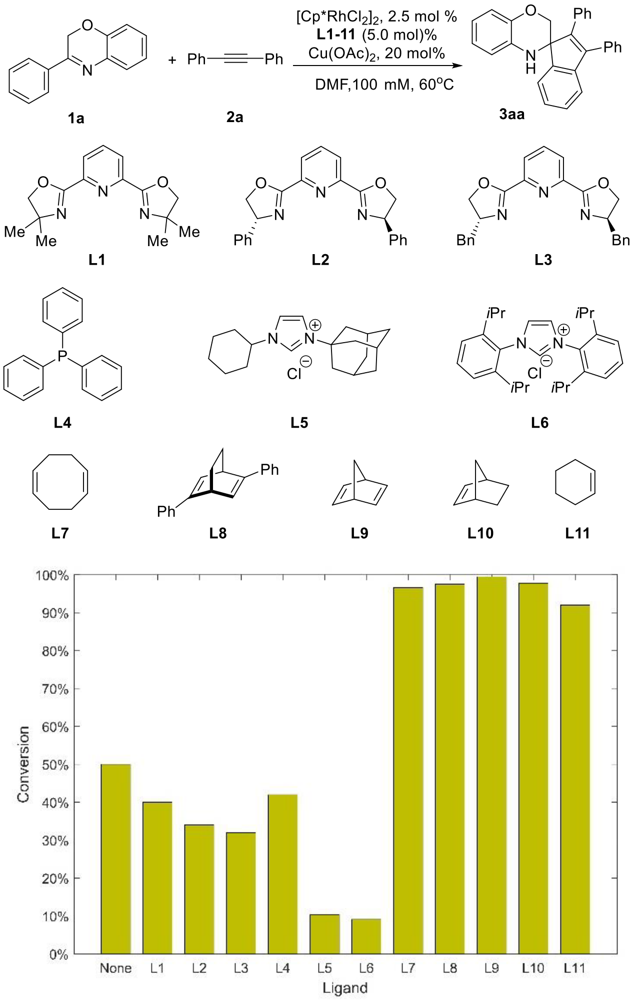


Figure 1. Five-hour conversion of the reactions with the presence of the various ligands. Reaction conditions: 0.3 mmol of **1a**, 0.36 mmol of **2a**, 7.5 μmol of $[Cp^*RhCl_2]_2$, ligand (15 μmol if added), and 0.06 mmol of $Cu(OAc)_2$ in 3 mL of DMF and heated to 60 °C for 5 h. All conversions were obtained from NMR analysis based on the ratio of **1a** and **3aa**. See the SI for details.

The kinetic constants of the reactions in Figure 2 were calculated, and the results were shown in Table 1. The observed k_{obs} appeared to be the first-order reaction, suggesting that there is at least one slow step in this complex reaction. It can be seen that **L9** has the highest reaction rate constant (1.20 h^{-1}), which is 8-fold of the reaction with no ligand (0.149 h^{-1}). The precarbene ligand **L5** almost inhibited the reaction (0.0198 h^{-1}). To the best of our knowledge, this is the first time such a pronounced phenomenon has been observed where the external catalytic amount ligand could promote the reaction rate dramatically in the $[Cp^*RhCl_2]_2$-catalyzed functionalization reaction.

In the next reaction, the ligand promotion effect was examined with cross-reaction of various substrates with three representative types of alkynes. The results (Scheme 2) showed that this new catalytic strategy could generally work

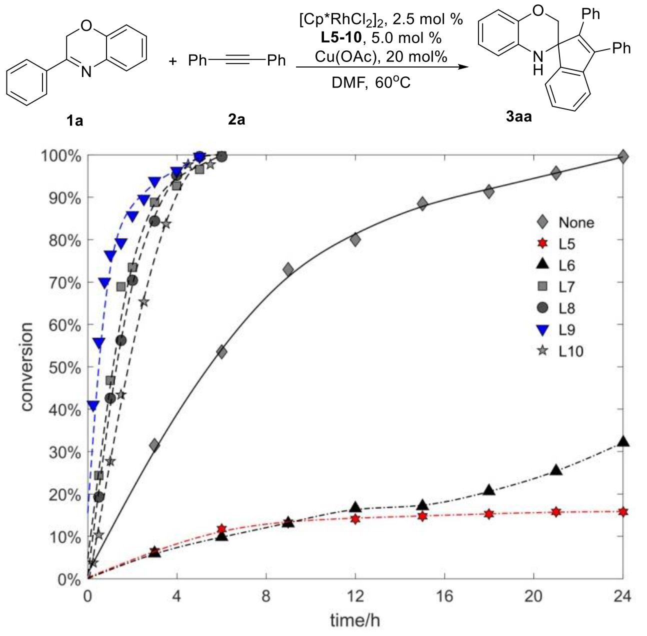


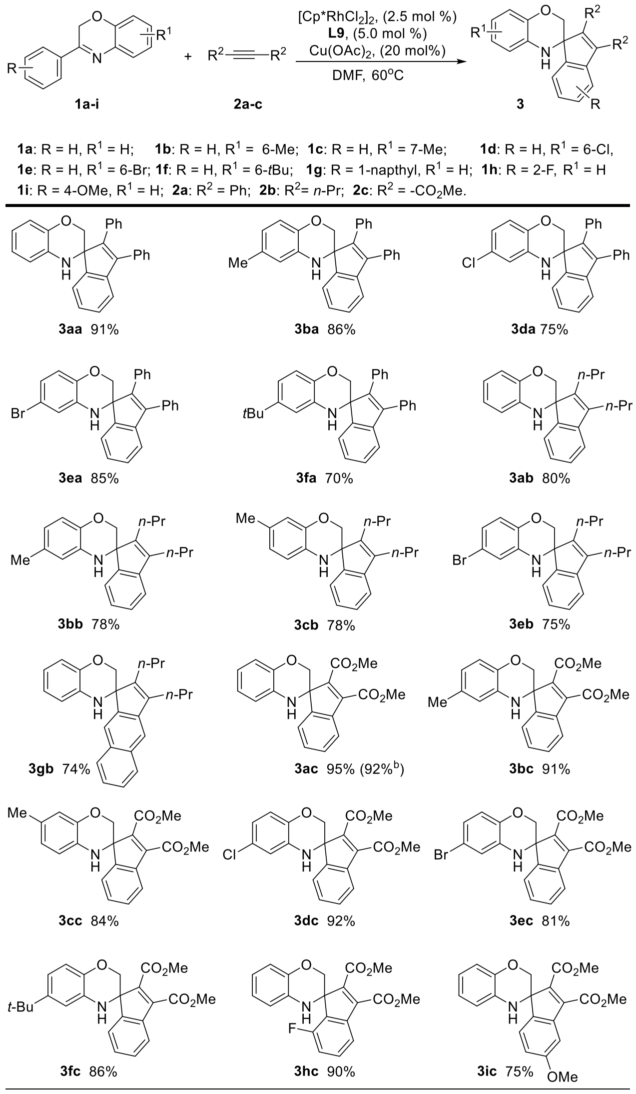
Figure 2. Kinetic profiles of selected ligands. The reaction was carried out as the following: the starting concentration of catalyst and other ingredients: [**Rh**] = 5 mM, [**Ligand**] = 5 mM (if added), $[\mathbf{1a}]_0$ = 100 mM, $[\mathbf{2a}]_0$ = 100 mM. For experimental details, see the SI.

Table 1. Kinetic Analysis of Reactions in Figure 2

entry	ligand	k_{obs}[a] (h^{-1})
1	none	**0.149 ± 0.002**
2[b]	**L5**	0.0198 ± 0.0007
3[c]	**L6**	
4	**L7**	0.771 ± 0.001
5	**L8**	0.659 ± 0.008
6	**L9**	**1.20 ± 0.002**
7	**L10**	0.658 ± 0.002

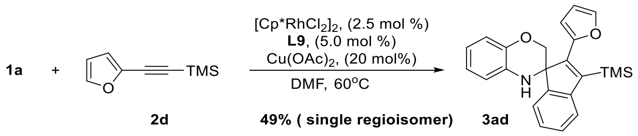
[a] The rate equations of all reactions were in agreement with the first-order reactions after solving the differential equations of each curve in Figure 2. [b] The curve between 0−7 h was used for the calculation of the kinetic constant. [c] The kinetic constant was not calculated due to the unexpected increase after 16 h.

Scheme 2. Scope of Substrates and Alkynes[a]



[a] The reaction condition is same as that used in the Figure 1 and with the addition of 5 mol % of **L9**. All reaction was stopped at 5 h. All yields are isolated yields. [b] Yield of a 2.0 mmol scale reaction.

Scheme 3. Reaction with Functionalized Alkyne[a]



[a] The reaction conditions are same as those used in Scheme 2.

with ketimines having different substituting groups and different types of alkynes in a very efficient way and afford the products in good to excellent yields. For all examples, a yield range of 74−95% was achieved and the average yield is over 80%. In general, the alkynes having an aryl (**3aa**−**3fa**) or electron-withdrawing ester group (**3ac**−**3ic**) have an apparently higher yield than the alkyl-substituted alkyne (**3ab**−**3gb**). This is reasonable because the alkyl alkyne is electronically richer so a higher energy barrier in insertion step is required.

Highly functionalized asymmetrical alkyne **2d**, containing a heterocyclic ring and functionalizable silyl group, was attempted and afforded the product **3ad** with single regioisomeric selectivity, which showed great potential in synthetic application (Scheme 3). The moderate yield was perhaps due to the labile property of **2d** under the reaction conditions (**1a** was not fully consumed even with **3** equiv of **2d**.).

To probe the promotion mechanism of the olefin ligand, reactions with significantly biased ratio of starting materials were carried out and their kinetic constants were measured (Figure 3 and Table2). The results shown that the kinetic constants with regard to the alkyne (**A1**: 0.158, **A2**: 0.180) are significantly smaller than those with regard to imine (**B1**: 0.839, **B2**: 2.127), which suggested that either the carborhodation or cyclization is the rate-determine step. This also explained why the reaction in Table 2 appeared to be the first-order reaction.

Experimental evidence[20] showed that the ligand effectively accelerated the reaction rate of the C−H activation step and push the equilibrium in the way of forming more rhodacycle,

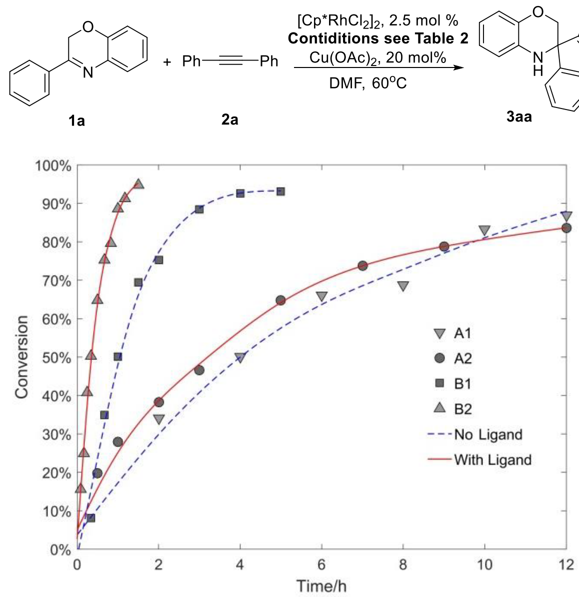


Figure 3. Kinetic profiles of reactions with different ratio in starting material.

Table 2. Kinetic Analysis of Reactions in Figure 3

reaction[a]	$[\mathbf{1a}]_0$ (M)	$[\mathbf{2a}]_0$ (M)	ligand[b]	k_{obs}[c] (h^{-1})
A1	2.00	0.20	none	0.158 ± 0.001
A2	2.00	0.20	**L9**	0.180 ± 0.001
B1	0.20	**2.00**	none	**0.839 ± 0.007**
B2	0.20	**2.00**	**L9**	**2.127 ± 0.005**

[a] For all reactions [Rh] = 2.50 mM. [b] [Ligand] = 2.50 mM (if added). For experimental details, see the SI. [c] The rate equations of all reactions were in agreement with the first-order reactions after solving the differential equations of each curve in Figure 3.

which reached 76% conversion while the control reaction is only 13%. Therefore, olefin promoted the reaction by increasing the content of the effective catalyst.

Although how the olefin impacts the reaction remains unclear, an interaction of olefin with rhodium metal should be expected. Stirring $[Cp^*RhCl_2]_2$ with norbornene[19] afforded a mixture which contains free $[Cp^*RhCl_2]_2$ and probably partially coordinated complex $[Cp^*Rh(norbornene)Cl_2]$ according to NMR analysis.[20] This hypothetical complex, containing only 6 mol % in the residue if the assumed structure is correct, could complete the reaction less than 3 h using the standard reaction conditions in Figure 1.[20]

In conclusion, a remarkable ligand impact on the $[Cp^*RhCl_2]_2$-catalyzed [3 + 2] annulation reaction was discovered first in this research. Various ligands, consisting of different elements and having diverse structures and properties, have been used. The results showed that nitrogen-based ligands could apparently retard the reaction. The carbon-based ligand, which coordinates the metal with σ-bond, could almost kill the reactivity. On the contrary, olefin ligands, which coordinate the metal with π-bond, showed a significant promotion effect on the reaction rate, of which the kinetic constant is 8-fold of that without ligand. A set of substrates and different alkynes were cross reacted using this new protocol, and the results showed that it is a very general strategy. Preliminary experiments supported the olefin effectively promoting this reaction by changing the equilibrium of the C−H activation step. More importantly, the discovery of this unique phenomenon did not just provide the positive result achieved from the olefin ligands but also could bring new ideas to study the $[Cp^*RhCl_2]_2$-catalyzed C−H functionalizations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01768.

Experiment procedures, compounds data, and spectra (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Hefei University of Technology, NSFC (Project No. 21401037 and 21672049) and Fthe undamental Research Funds for the Central Universities of China (Nos. PA2019GDPK0056, PA2020GDPKC0011) for financial support for this work.

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(20) See the SI for details.