A Journal of the Gesellschaft Deutscher Chemiker

Angewandte International Edition GDCh Chemie

www.angewandte.org

## Accepted Article

**Title:** Visible Light-Induced Bifunctional Rhodium Catalysis for Decarbonylative Coupling of Imides with Alkynes

**Authors:** Xiang-Ting Min, Ding-Wei Ji, Yu-Qing Guan, Shi-Yu Guo, Yan-Cheng Hu, Boshun Wan, and Qing-An Chen

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

**To be cited as:** *Angew. Chem. Int. Ed.* 10.1002/anie.202010782

**Link to VoR:** https://doi.org/10.1002/anie.202010782

WILEY-VCH

10.1002/anie.202010782

COMMUNICATION

WILEY-VCH

# Visible Light-Induced Bifunctional Rhodium Catalysis for Decarbonylative Coupling of Imides with Alkynes

Xiang-Ting Min, Ding-Wei Ji, Yu-Qing Guan, Shi-Yu Guo, Yan-Cheng Hu, Boshun Wan, Qing-An Chen*

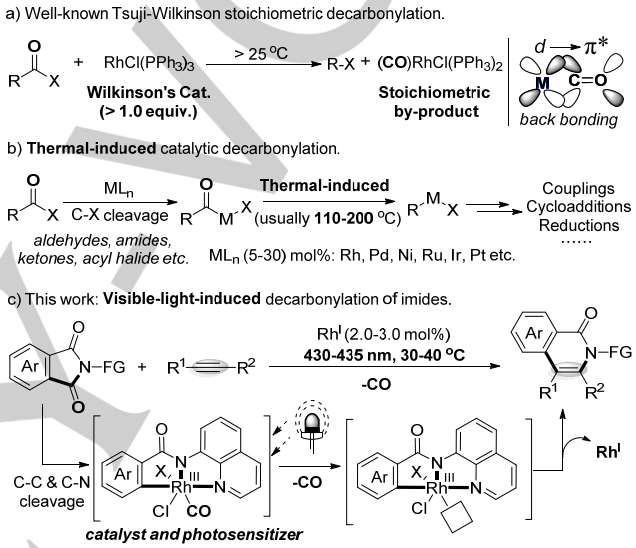
[a] X. T. Min, D. W. Ji, Y. Q. Guan, S. Y. Guo, Dr. Y. C. Hu, Prof. Dr. B. Wan, Prof. Dr. Q. A. Chen.
Dalian Institute of Chemical Physics, Chinese Academy of Sciences
457 Zhongshan Road, Dalian 116023, China
E-mail: qachen@dicp.ac.cn, Homepage: http://www.lbcs.dicp.ac.cn
[b] X. T. Min, D. W. Ji.
University of Chinese Academy of Sciences
Beijing 100049, China

Supporting information for this article is given via a link at the end of the document.

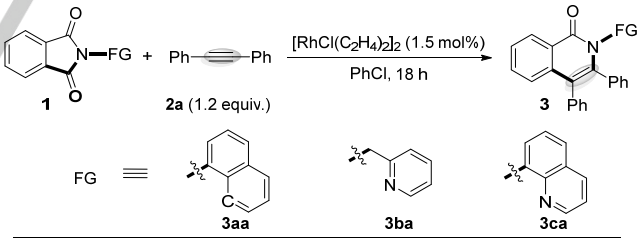
**Abstract:** Transition metal-catalyzed decarbonylation offers a distinct synthetic strategy for new chemical bond formation. However, the π-backbonding between CO π* orbitals and metal center *d*-orbitals impedes ligand dissociation to regenerate catalyst under mild condition. Herein, we developed a visible light-induced rhodium catalysis for decarbonylative coupling of imides with alkynes under ambient conditions. Initial mechanistic studies suggest that the rhodium complex simultaneously serves as the catalytic center and photosensitizer for decarbonylation. This visible light-promoted catalytic decarbonylation strategy offers new opportunities for reviewing old transformations with ligand dissociation as a rate determining step.

Well known ligand dissociation is a common and important step in transition metal catalysis.[1] This fundamental step spares vacant coordination sites and simultaneously affects the steric and electronic properties on the metal center.[2] Dissociation of the product or by-product usually either regenerates the starting catalyst or generates a species that will be converted to the starting catalyst. Conversely, transition metal reagent must be used in stoichiometric quantities instead of a catalyst.[3] For example, Tsuji and Ohno reported the famous Tsuji-Wilkinson decarbonylation reaction of the aldehydes with stoichiometric amounts Wilkinson's complex $RhCl(PPh_3)_3$ (Scheme 1a).[4] As one of the most strongly π-accepting ligand, carbon monoxide (CO), the π-backbonding between CO and Rh impedes the ligand dissociation step to regenerate Wilkinson's catalyst under mild condition.[5] Through a compromise approach, scientists have taken advantage of thermal dissociation (usually 110-200 °C)[6] of CO from resting state of catalyst to facilitate the catalytic decarbonylation using various transition metals (Rh,[7] Pd,[8] Ni,[9] Ru,[10] Pt,[11] Ir[12] etc.[6]) (Scheme 1b). Therefore, it is of great interest to develop mild methods for the catalytic decarbonylation.[6]

As an alternative approach, photochemically induced ligand dissociation has been employed for the simple metal carbonyl complexes $Cr(CO)_6$,[13] $Fe(CO)_5$,[13] and $Ni(CO)_4$[13] etc. under ultraviolet light irradiation. Inspired by these stoichiometric precedents in combination with growing field of photo-induced catalysis,[14,15] we envisioned developing a catalytic decarbonylation promoted by photochemically induced CO dissociation using visible light. Herein, we demonstrated a visible light-driven bifunctional rhodium catalysis for decarbonylative coupling of imides with alkynes under mild condition (Scheme 1c).




**Scheme 1.** Transition metal-catalyzed decarbonylation.




| | 3aa | 3ba | 3ca |
|---|---|---|---|
| **Thermal induced (150 °C)** | NR | 11% | 45% |
| **Photo induced (40 °C, 450-455 nm)** | NR | NR | 80% |

**Scheme 2.** Initial investigation on thermal- or photo-induced Rh-catalyzed decarbonylative coupling.

To verify our proposal, we chose decarbonylative coupling of imides with alkynes as model reaction (Scheme 2). Matsubara and our group have previously demonstrated that this transformation could be realized under Ni[16] or Co[17] catalysis (10–20 mol%) via a thermally induced approach (110–130 °C). Given the unique property of Rh on decarbonylation reactions,[7, 15g] we were curious about its performance on decarbonylative coupling of imides with alkynes. An initial investigation suggested the functional group on the nitrogen atom of imide **1** plays an important role on reaction outcomes (Scheme 2). Under thermally induced conditions (150 °C), low yields (11–


This article is protected by copyright. All rights reserved.

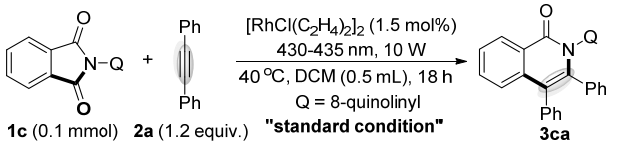
Accepted Manuscript

10.1002/anie.202010782



45%) could be obtained using pyridyl or quinolinyl as functional group. Switching to photo-induced condition (450–455 nm, 40 °C), we observed a dramatic functional group effect where only quinolinyl-substituted substrate **1c** delivered the expected cross coupling product in 80% yield. These initial results indicated that the functional group plays a bifunctional role as a directing group and as an energy transfer promoter.

**Table 1.** Selected optimization studies.




**1c** (0.1 mmol) **2a** (1.2 equiv.) **3ca**

| entry | deviation from standard conditions | **3ca** yield[a] |
|---|---|---|
| 1 | *none* | 90%[b] |
| 2 | without $[RhCl(C_2H_4)_2]_2$ | NR |
| 3 | 40 °C without light | NR |
| 4 | 130 °C without light | 26% |
| 5 | 3.0 mol% $Rh(acac)(CO)_2$ as catalyst | 84% |
| 6 | 1.5 mol% $[RhCl(CO)_2]_2$ as catalyst | 80% |
| 7 | 1.5 mol% $[RhOH(COD)]_2$ as catalyst | 80% |
| 8 | 1.5 mol% $[RhCl(COD)]_2$ as catalyst | 88% |
| 9 | 3.0 mol% $RhCl(PPh_3)_3$ as catalyst | NR |
| **10** | **DCE instead of DCM** | **95%[b]** |
| 11 | PhCl instead of DCM | 95%[b] |
| 12 | 380-385 nm instead of 430-435 nm | 75%[c] |
| 13 | 450-455 nm instead of 430-435 nm | 79%[c] |
| 14 | 30 °C instead of 40 °C | 95%[b,c] |
| 15 | 1.0 mol% $[RhCl(C_2H_4)_2]_2$ as catalyst | 92%[b,c,d] |
| 16 | $Ni(COD)_2$ 5.0 mol% | NR[c] |
| 17 | $Co_2(CO)_8$ 2.5 mol% | NR[c] |
| 18 | $Pd(PPh_3)_4$ 5.0 mol% | NR[c] |

[a]Determined by $^1$H NMR analysis of crude mixture. [b]Isolated yield. [c]DCE was used as solvent. [d]36 h.

To further improve the reactivity, a systematic optimization of this photo-induced cross coupling reaction was carried out (Table 1 and Table S1-S2 in Supporting Information). After careful evaluation of the reaction conditions, isoquinolone **3ca** was formed in 90% yield using $[RhCl(C_2H_4)_2]_2$ as the catalyst precursor under blue light irradiation (430–435 nm) at 40 °C (Table 1, entry 1). Control experiments confirmed the essential roles of the rhodium and the visible light (entries 2 and 3). It was found that photoreaction showed higher efficiency than thermal induced reaction (entry 4). Except for Wilkinson's catalyst $RhCl(PPh_3)_3$, other $Rh^I$ precursor, such as $Rh(acac)(CO)_2$, $[RhCl(CO)_2]_2$, $[RhOH(COD)]_2$ and $[RhCl(COD)]_2$ showed comparable reactivity (entries 5–9). Both DCE and PhCl could serve as competent solvents (entries 10 and 11). Further screening of wavelengths revealed that 430–435 nm was the optimal wavelengths for this protocol, may be related to the maximum absorption wavelength of rhodium intermediates (entries 12 and 13). To our delight, the decarbonalytion reaction proceeded well at 30 °C, which suggested that the light induced reaction could be carried out at room temperature (entry 14). A high yield was also obtained at lower catalyst loadings (1.0 mol%) with a prolonged reaction time (entry 15). Notably, other commonly used transition-metal catalysts for decarbonylation, such as $Ni(COD)_2$,[9a-d, 9g] $Co_2(CO)_8$,[18] $Pd(PPh_3)_4$,[8] did not afford any desired product, which indicates the unique property of Rh in the photo-induced decarbonylative reactions (entries 16–18).

Considering the mild nature of the photo-induced decarbonylative coupling, a light on/off experiment was carried out to get the reactivity profile of this reaction (see Table S3 and Figure S1 in Supporting Information for light on/off experiment). It revealed that constant irradiation was required for effective product formation versus light on/off experiment. No background product formation during dark exposure supports that the current protocol does not involve a light-initiated radical chain pathway.

With the optimized conditions in hand, the generality of alkyne substrates was subsequently tested. As depicted in Table 2a, various symmetrical diarylacetylenes bearing either electron-withdrawing or electron-donating substituents all successfully afforded isoquinolones with moderate to excellent yields (**3ca**-**3cf**). Notably, a bromo-bearing aryl-alkyne could be well tolerated and delivered isoquinolone **3cb** in 95% yield. Interestingly, an alkyne with a cyano-functional group at the para-position of the phenyl ring was a bit sluggish in this protocol (**3cd**). This presumably ascribed to the coordinated ability of cyano-groups to rhodium. Due to the steric hindrance of ortho-substituted diarylalkyne, isoquinolinone **3cf** was isolated as a 5:1 rotamer mixture in 67% yield. To our delight, dialkyl acetylenes were also applicable under this visible light-induced rhodium catalysis conditions and led to **3cg**-**3ci** in 63–83% yields. Encouraged by these promising results, a series of aryl-substituted terminal alkynes were further examined in this transformation. To our delight, these reactions exclusively produced isoquinolones **3cj**-**3cm** in 28–42% yields, which is uncommon due to the existence of a dominant [2+2+2] cycloaddition side reaction.[19] For alkyl-substituted terminal alkynes such as acetylene, cyclohexylacetylene, 1-decyne, no product was formed under the photo-induced condition (see Scheme S1 in Supporting Information). Furthermore, unsymmetric alkynes were also suitable substrate to generate **3cn**-**3ct** in moderate to high yields with acceptable regioselectivities. It is noteworthy that ethyl 3-phenylpropynoate (**2u**) led to 4-substituted isoquinolone **3cu** in 36% yield. This unique regioselectivity is probably due to electron-withdrawing ability of the ester group. No expected decarbonylative coupling was observed for alkene substrates such as phenylmaleimide, methyl cinnamate or styrene (see Scheme S1 in Supporting Information).

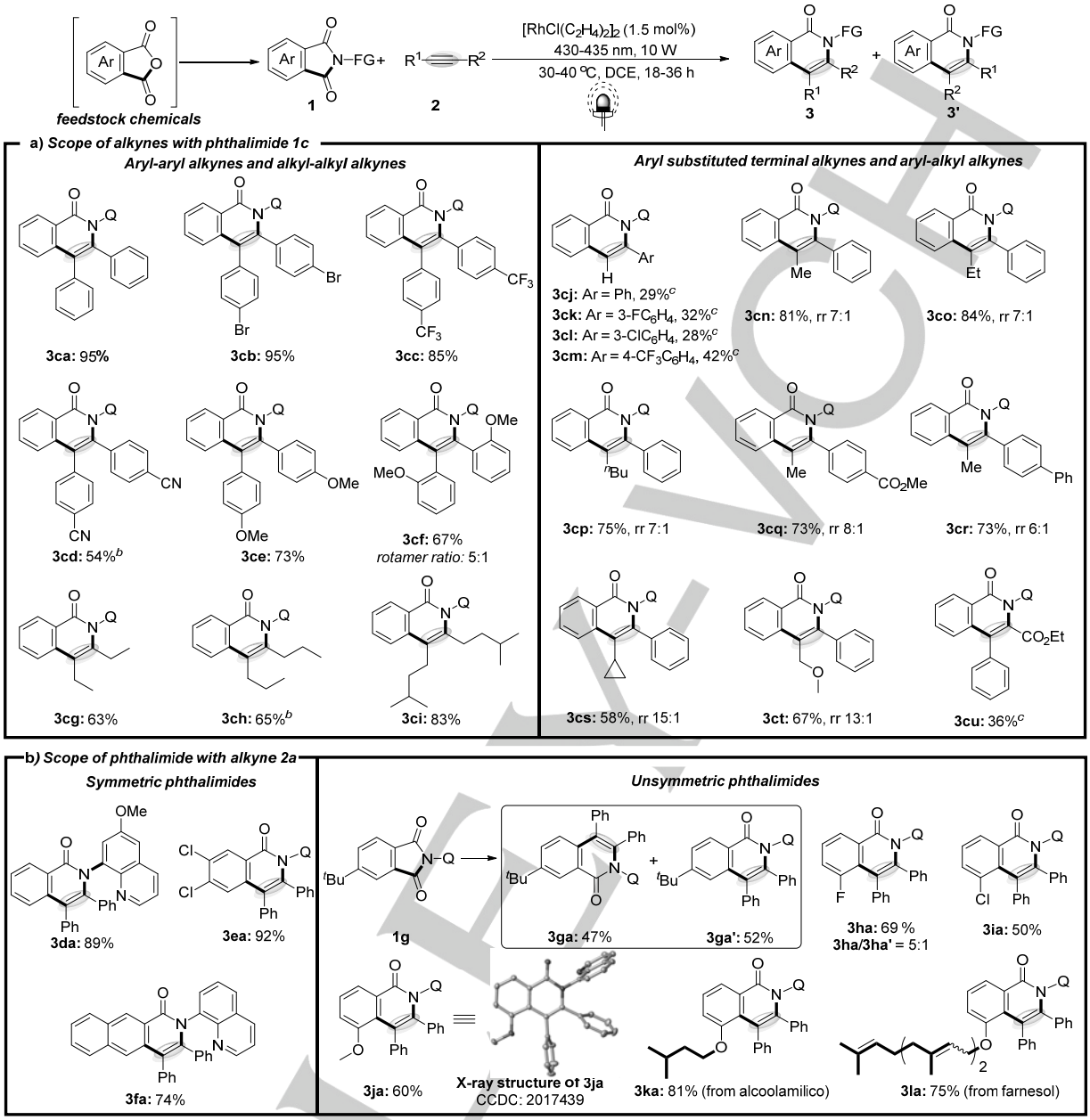
Next, we further investigated the scope of phthalimides (Table 2b). Substrate possessing methoxy group on the 6-position of quinoline ring successfully furnished the desired product **3da** in 89% yield. Symmetric phthalimides reacted with **2a** smoothly in this process, providing the corresponding products **3ea** and **3fa** in 74–92% yields. Substrate bearing *tert*-butyl group at the 4-position (**1g**) exhibited good reactivity via this decarbonylation process, although gave a mixture of two regioisomers **3ga** and **3ga'** in approximate 1:1 ratio. In the case of 3-fluorine substituted phthalimide, the product **3ha** was isolated in 69% yield, together with a 5:1 regiomeric ratio. Remarkably, phthalimides having substitutents at the 3-position, such as 3-chloride and 3-alkoxy groups, all worked well to give



Accepted Manuscript

This article is protected by copyright. All rights reserved.

**Table 2.** Substrate scope for photo-induced decarbonylative coupling of imides with alkynes.[a]




[a]**1** (0.10 mmol), **2** (0.12 mmol), $[RhCl(C_2H_4)_2]_2$ (1.5 mol%), 40 °C , 36 h. Regiomeric ratio (rr) was determined by $^1$H NMR analysis of crude mixture. Unless noted, the rr is greater than 20:1. [b]30 °C, 18 h. [c]**2** (0.1 mmol) was used.

regiospecific isoquinolones **3ia**-**3la** in 50–81% yields. The molecular structure of **3ja** was confirmed by X-ray crystallography. Of particular interest is that these reactions all exclusively occurred at the adjacent positions of the corresponding substituents, which offers an important complement for the reported C–H activation strategy in the synthesis of 5-substituted isoquinolinones.[20]

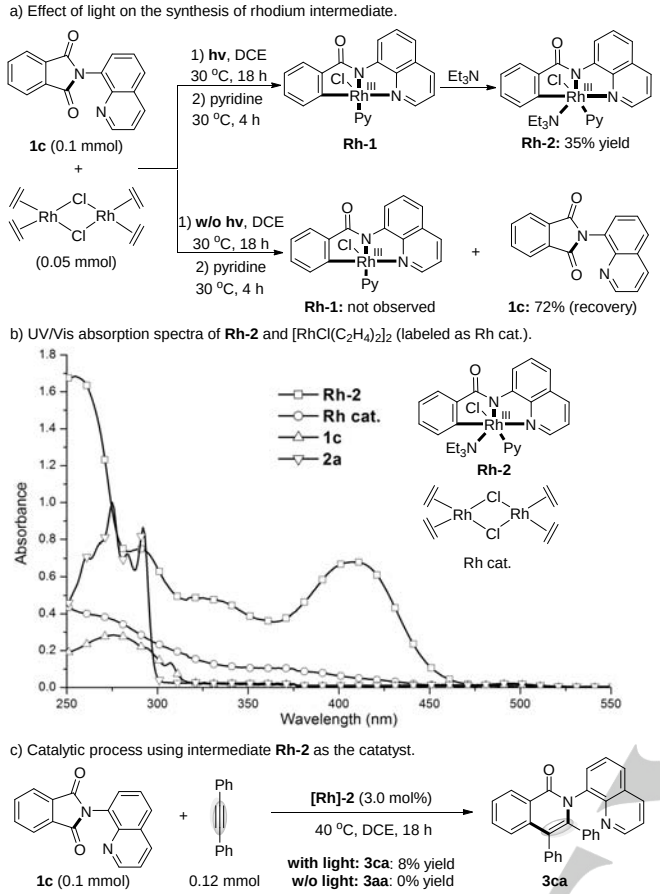
Regarding mechanistic features, a key question is elucidating the role of visible light. First, the effect of light on the synthesis rhodium intermediate was investigated (Scheme 3a). Under light irradiation, the reaction of $[RhCl(C_2H_4)_2]_2$ with phthalimide **1c** slowly generated a red solid precipitate which was then treated with excess pyridine to form a more stable speculative complex **Rh-1**. The subsequent purification of **Rh-1** (16-electron) gave an unexpected coordination saturated complex **Rh-2** (18-electron). The structure of **Rh-2** was fully characterized by $^1$H, $^{13}$C NMR and HRMS (See Supporting Information). In the absence of visible light irradiation, no red precipitate was formed and only phthalimide **1c** was recovered in 72% yield. The UV/Vis absorption spectra of the **Rh-2** showed a strong absorbance in the region of 390–420 nm (Scheme 3b). The catalytic performance of **Rh-2** complex was evaluated for the decarbonylative coupling of imide **1c** with alkyne **2a** (Scheme 3c). No desired product was observed in the absence of light. Under light irradiation, **3ca** was obtained in 8% yield with 2.7 turn over number (TON). The low yield probably results from the different coordination environment between **Rh-2** complex and real Rh catalyst. Overall, these above results suggest that



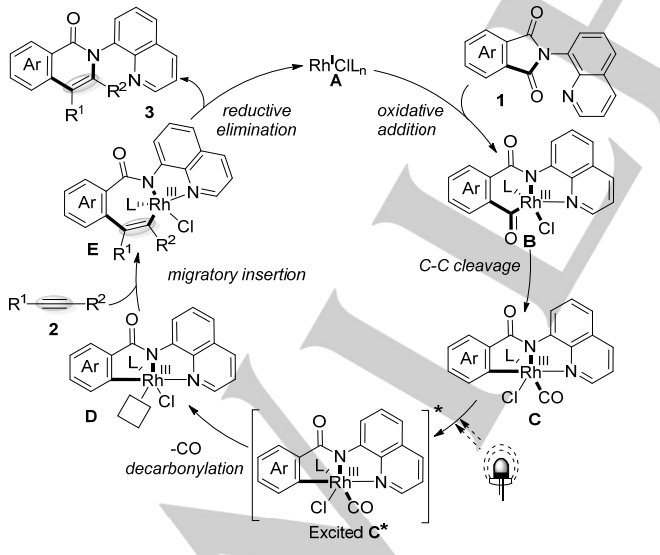
This article is protected by copyright. All rights reserved.

Accepted Manuscript

rhodium complex simultaneously serves as the catalytic center and photosensitizer for decarbonylation.




**Scheme 3.** Mechanistic studies on reaction intermediate.




**Scheme 4.** Proposed mechanism for decarbonylative coupling.

Based on the above results and literature precedents on decarbonylative reactions,[16-17] a possible catalytic cycle is shown in Scheme 4. With the assistance of the quinoline group, the reaction is initiated from the oxidative addition of the $Rh^{I}$ species **A** into the C–N bond in the phthalimide **1** to form $Rh^{III}$ intermediate **B**. A subsequent deinsertion of carbon monoxide cleaves the C–C bond to give Rh-complex **C**. Under visible light irradiation, it generates the excited state Rh-complex **C*** where the transfer of an electron from the π-backbonding Rh-CO orbital into an antibonding orbital decreases the bond dissociation energy of the Rh–CO bond. This leads to the subsequent CO extrusion under mild conditions to give a Rh intermediate **D** with a vacant coordination site. The coordination and migratory insertion of the alkyne **2** with **D** delivers a seven-membered rhodacycle **E**, which undergoes reductive elimination to form the isoquinolone **3** and regenerates the $Rh^{I}$ catalyst **A**.

In summary, we have developed a visible light-induced rhodium catalysis for decarbonylative coupling of imides with alkynes under ambient conditions. The main advantages include mild conditions, good regioselectivity, and wide functional group tolerance. Initial mechanistic studies suggest that rhodium complex simultaneously serves as the catalytic center and photosensitizer for decarbonylation. This visible light-promoted catalytic decarbonylation strategy offers new opportunities for reviewing old transformations with ligand dissociation as a rate determining step.

## Acknowledgements

We thank Prof. Yong-Gui Zhou (DICP) and Prof. Daniel K. Kim (Temple University) for helpful discussion and paper revisions. Financial support from the National Natural Science Foundation of China (21971234, 21772194, 21572225), China Postdoctoral Science Foundation (2019M661137) and Liaoning Revitalization Talents Program (XLYC1807181) is acknowledged.

**Keywords:** visible light • bifunctional rhodium catalysis • C-N bond cleavage • decarbonylative coupling • alkynes

[1] J. F. Hartwig, *Organotransition Metal Chemistry: From Bonding to Catalysis*, Lineworks, **2010**.

[2] R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals: Sixth Edition*, John Wiley & Sons, **2014**.

[3] a) M. Murakami, H. Amii, Y. Ito, *Nature* **1994**, *370*, 540; b) M. Murakami, H. Amii, Y. Ito, *J. Am. Chem. Soc.* **1996**, *118*, 8285; c) S. E. Havlik, J. M. Simmons, V. J. Winton, J. B. Johnson, *J. Org. Chem.* **2011**, *76*, 3588; d) T. Morioka, A. Nishizawa, T. Furukawa, M. Tobisu, N. Chatani, *J. Am. Chem. Soc.* **2017**, *139*, 1416; e) E. M. Heyboer, R. L. Johnson, M. R. Kwiatkowski, T. C. Pankratz, M. C. Yoder, K. S. DeGlopper, G. C. Ahlgrim, J. M. Dennis, J. B. Johnson, *J. Org. Chem.* **2020**, *85*, 3757.

[4] a) J. Tsuji, K. Ohno, *Tetrahedron Lett.* **1965**, *6*, 3969; b) J. Tsuji, K. Ohno, *Tetrahedron Lett.* **1967**, *8*, 2173; c) K. Ohno, J. Tsuji, *J. Am. Chem. Soc.* **1968**, *90*, 99.

[5] a) E. J. Garcia-Suarez, K. Kahr, A. Riisager, *Rhodium Catalyzed Decarbonylation, Vol. 61*, Springer International Publishing Ag, Cham, **2018**; b) L. Guo, M. Rueping, *Acc. Chem. Res.* **2018**, *51*, 1185; c) C. Liu, M. Szostak, *Org. Biomol. Chem.* **2018**, *16*, 7998.

[6] H. Lu, T.-Y. Yu, P.-F. Xu, H. Wei, *Chem. Rev.* **2020**, dio: 10.1021/acs.chemrev.0c00153.

[7] a) P. Fristrup, M. Kreis, A. Palmelund, P.-O. Norrby, R. Madsen, *J. Am. Chem. Soc.* **2008**, *130*, 5206; b) Q. Shuai, L. Yang, X. Guo, O. Baslé, C.-J. Li, *J. Am. Chem. Soc.* **2010**, *132*, 12212; c) Z.-Q. Lei, H. Li, Y. Li, X.-S. Zhang, K. Chen, X. Wang, J. Sun, Z.-J. Shi, *Angew. Chem., Int. Ed.* **2012**, *51*, 2690; *Angew. Chem.* **2012**, *124*, 2744; d) P.-H. Chen, T. Xu, G. Dong, *Angew. Chem., Int. Ed.* **2014**, *53*, 1674; *Angew. Chem.* **2014**,*126*, 1700; e) Z.-Q. Lei, F. Pan, H. Li, Y. Li, X.-S. Zhang, K. Chen,



This article is protected by copyright. All rights reserved.

Accepted Manuscript

X. Wang, Y.-X. Li, J. Sun, Z.-J. Shi, *J. Am. Chem. Soc.* **2015**, *137*, 5012; f) S. K. Murphy, J.-W. Park, F. A. Cruz, V. M. Dong, *Science* **2015**, *347*, 56; g) T.-T. Zhao, W.-H. Xu, Z.-J. Zheng, P.-F. Xu, H. Wei, *J. Am. Chem. Soc.* **2018**, *140*, 586; h) G. Tan, Y. Wu, Y. Shi, J. You, *Angew. Chem., Int. Ed.* **2019**, *58*, 7440; *Angew. Chem.* **2019**, *131*, 7518.

[8] a) G. Meng, M. Szostak, *Angew. Chem., Int. Ed.* **2015**, *54*, 14518; *Angew. Chem.* **2015**,*127*, 14726; b) Y.-Y. Meng, X.-J. Si, Y.-Y. Song, H.-M. Zhou, F. Xu, *Chem. Commun.* **2019**, *55*, 9507; c) S. Shi, M. Szostak, *ACS Omega* **2019**, *4*, 4901.

[9] a) P. Mi, P. Liao, T. Tu, X. Bi, *Chem. -Eur. J.* **2015**, *21*, 5332; b) J. Hu, Y. Zhao, J. Liu, Y. Zhang, Z. Shi, *Angew. Chem., Int. Ed.* **2016**, *55*, 8718; *Angew. Chem.* **2016**, *128*, 8860; c) X. Liu, H. Yue, J. Jia, L. Guo, M. Rueping, *Chem. -Eur. J.* **2017**, *23*, 11771; d) H. Yue, L. Guo, H.-H. Liao, Y. Cai, C. Zhu, M. Rueping, *Angew. Chem., Int. Ed.* **2017**, *56*, 4282; *Angew. Chem.* **2017**, *129*,4346; e) C. A. Malapit, J. R. Bour, C. E. Brigham, M. S. Sanford, *Nature* **2018**, *563*, 100; f) C. A. Malapit, J. R. Bour, S. R. Laursen, M. S. Sanford, *J. Am. Chem. Soc.* **2019**, *141*, 17322; g) T. Morioka, S. Nakatani, Y. Sakamoto, T. Kodama, S. Ogoshi, N. Chatani, M. Tobisu, *Chem. Sci.* **2019**, *10*, 6666.

[10] a) D. V. Gribkov, S. J. Pastine, M. Schnürch, D. Sames, *J. Am. Chem. Soc.* **2007**, *129*, 11750; b) X. Guo, J. Wang, C.-J. Li, *J. Am. Chem. Soc.* **2009**, *131*, 15092; c) Y.-C. Yuan, R. Kamaraj, C. Bruneau, T. Labasque, T. Roisnel, R. Gramage-Doria, *Org. Lett.* **2017**, *19*, 6404.

[11] F. Yamashita, H. Kuniyasu, J. Terao, N. Kambe, *Org. Lett.* **2008**, *10*, 101.

[12] a) T. Iwai, T. Fujihara, Y. Tsuji, *Chem. Commun.* **2008**, *46*, 6215; b) E. P. Olsen, R. Madsen, *Chem. -Eur. J.* **2012**, *18*, 16023; c) S. Kusumoto, T. Tatsuki, K. Nozaki, *Angew. Chem., Int. Ed.* **2015**, *54*, 8458; *Angew. Chem.* **2015**, *127*, 8578.

[13] a) E. J. Baerends., A. Rosa., *Coordin. Chem. Rev.* **1997**, *177*, 97; b) C. Long, *Photophysics of CO Loss from Simple Metal Carbonyl Complexes, Vol. 29*, **2010**; c) M. A. Wright, J. A. Wright, *Dalton Trans.* **2016**, *45*, 6801.

[14] a) C. K. Prier, D. A. Rankic, D. W. MacMillan, *Chem. Rev.* **2013**, *113*, 5322; b) A. B. Beeler, *Chem. Rev.* **2016**, *116*, 9629; c) M. D. Karkas, J. A. Porco, Jr., C. R. Stephenson, *Chem. Rev.* **2016**, *116*, 9683; d) D. Staveness, I. Bosque, C. R. Stephenson, *Acc. Chem. Res.* **2016**, *49*, 2295; e) Y. Wei, S. Liu, M.-M. Li, Y. Li, Y. Lan, L. Q. Lu, W. J. Xiao, *J. Am. Chem. Soc.* **2019**, *141*, 133; f) J. Zheng, W. B. Swords, H. Jung, K. L. Skubi, J. B. Kidd, G. J. Meyer, M. H. Baik, T. P. Yoon, *J. Am. Chem. Soc.* **2019**, *141*, 13625; g) Q.-Q. Zhou, Y.-Q. Zou, L.-Q. Lu, W.-J. Xiao, *Angew. Chem., Int. Ed.* **2019**, *58*, 1586; *Angew. Chem.* **2019**, *131*,1600; h) Q. L. Zhang, Q. Xiong, M. M. Li, W. Xiong, B. Shi, Y. Lan, L. Q. Lu, W. J. Xiao, *Angew. Chem., Int. Ed.* **2020**, DOI: 10.1002/anie.202005313; *Angew. Chem.* **2020**, DOI: 10.1002/ange.202005313.

[15] a) S. E. Creutz, K. J. Lotito, G. C. Fu, J. C. Peters, *Science* **2012**, *338*, 647; b) C. Uyeda, Y. Tan, G. C. Fu, J. C. Peters, *J. Am. Chem. Soc.* **2013**, *135*, 9548; c) D. T. Ziegler, J. Choi, J. M. Muñoz-Molina, A. C. Bissember, J. C. Peters, G. C. Fu, *J. Am. Chem. Soc.* **2013**, *135*, 13107; d) D. C. Fabry, J. Zoller, S. Raja, M. Rueping, *Angew. Chem., Int. Ed.* **2014**, *53*, 10228; *Angew. Chem.* **2014**, *126*, 10392; e) P. Gandeepan, J. Koeller, K. Korvorapun, J. Mohr, L. Ackermann, *Angew. Chem., Int. Ed.* **2019**, *58*, 9820; *Angew. Chem.* **2019**, *131*, 9925; f) A. Sagadevan, M. F. Greaney, *Angew. Chem., Int. Ed.* **2019**, *58*, 9826; *Angew. Chem.* **2019**, *131*, 9931; g) J. Thongpaen, R. Manguin, V. Dorcet, T. Vives, C. Duhayon, M. Mauduit, O. Basle, *Angew. Chem., Int. Ed.* **2019**, *58*, 15244; *Angew. Chem.* **2019**, *131*,15388.

[16] a) Y. Kajita, S. Matsubara, T. Kurahashi, *J. Am. Chem. Soc.* **2008**, *130*, 6058; b) K. Fujiwara, T. Kurahashi, S. Matsubara, *Org. Lett.* **2010**, *12*, 4548; c) T. Shiba, T. Kurahashi, S. Matsubara, *J. Am. Chem. Soc.* **2013**, *135*, 13636.

[17] X.-T. Min, D.-W. Ji, H. Zheng, B.-Z. Chen, Y.-C. Hu, B. Wan, Q.-A. Chen, *Org. Lett.* **2020**, *22*, 3386.

[18] M. M, A. H, S. K, I. Y, *J. Am. Chem. Soc.* **1996**, *118*, 8285.

[19] Z. Zhu, X. Li, S. Chen, P.-H. Chen, B. A. Billett, Z. Huang, G. Dong, *ACS Catal.* **2018**, *8*, 845.

[20] a) C. Wang, X. Li, F. Wu, B. Wan, *Angew. Chem., Int. Ed.* **2011**, *50*, 7162; *Angew. Chem.* **2011**, *123*, 7300; b) M. Neumeier, U. Chakraborty, D. Schaarschmidt, V. de la Pena O'Shea, R. Perez-Ruiz, A. Jacobi von Wangelin, *Angew. Chem., Int. Ed.* **2020**, DOI: 10.1002/anie.202000907. *Angew. Chem.* **2020**, DOI: 10.1002/ange.202000907.

[21] a) L. Grigorjeva, O. Daugulis, *Angew. Chem., Int. Ed.* **2014**, *53*, 10209; *Angew. Chem.* **2014**, *126*, 10373; b) D. Kalsi, S. Dutta, N. Barsu, M. Rueping, B. Sundararaju, *ACS Catal.* **2018**, *8*, 8115; c) S. Tang, D. Wang, Y. Liu, L. Zeng, A. Lei, *Nat. Commun.* **2018**, *9*, 798; d) P. Gandeepan, T. Muller, D. Zell, G. Cera, S. Warratz, L. Ackermann, *Chem. Rev.* **2019**, *119*, 2192.

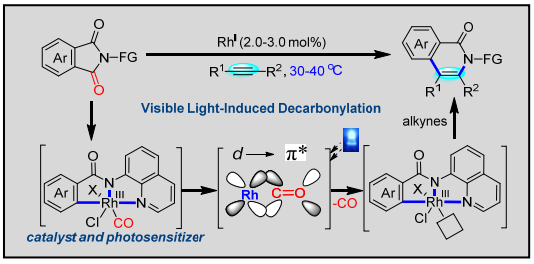


This article is protected by copyright. All rights reserved.

Accepted Manuscript

10.1002/anie.202010782






A visible light-induced rhodium catalysis has been developed for decarbonylative coupling of imides with alkynes under ambient conditions. Initial mechanistic studies suggest that the rhodium complex simultaneously serves as the catalytic center and photosensitizer for decarbonylation.

# Visible Light-Induced Bifunctional Rhodium Catalysis for Decarbonylative Coupling of Imides with Alkynes

Xiang-Ting Min, Ding-Wei Ji, Yu-Qing Guan, Shi-Yu Guo, Yan-Cheng Hu, Boshun Wan, Qing-An Chen*

WILEY-VCH

Accepted Manuscript



This article is protected by copyright. All rights reserved.