Organic LETTERS

Letter

Cite This: Org. Lett. XXXX, XXX, XXX−XXX

pubs.acs.org/OrgLett

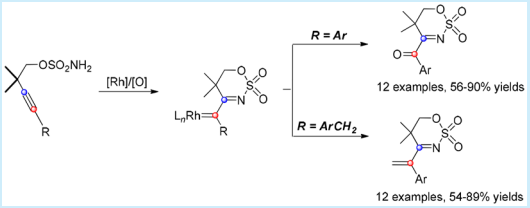
Rh(II)-Catalyzed Chemoselective Oxidative Amination and Nucleophilic Trapping of *gem*-Dimethyl Alkynyl-Tethered Sulfamates

Dong Pan, Yin Wei, and Min Shi*

State Key Laboratory of Organometallic Chemistry, Center for Excellence in Molecular Synthesis, University of Chinese Academy of Sciences, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China

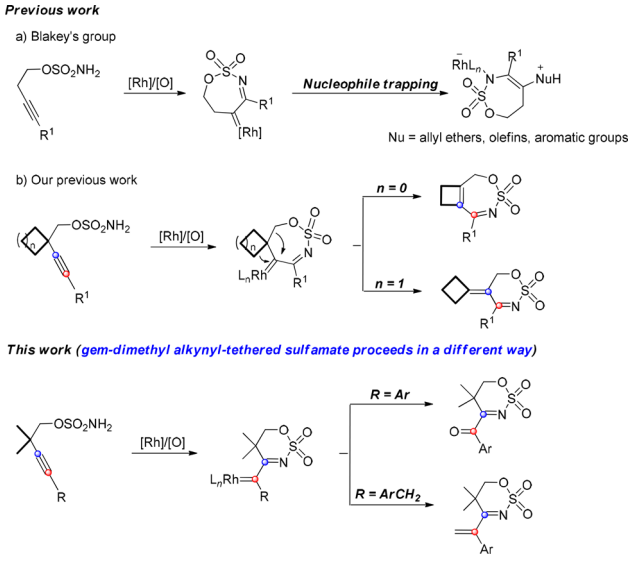
Supporting Information

ABSTRACT: A Rh(II)-catalyzed chemoselective oxidative amination and nucleophilic trapping of *gem*-dimethyl sulfamates has been presented. For 2,2-dimethyl-4-arylbut-3-yn-1-yl sulfamates, the reactions underwent a metallonitrene-initiated alkyne oxidation along with nucleophilic trapping of H_2O upon oxidation, giving aroyl group containing heterocycles. For 2,2-dimethyl-4-arylpent-3-yn-1-yl sulfamates, the α-iminometal carbene intermediate was trapped by aryl group migration, delivering a styryl group containing heterocycles.



Catalytically generated metallocarbenes, primarily obtained by metal-catalyzed decomposition of α-diazocarbonyl compounds, have been extensively investigated over the past decades and have demonstrated broad applications in modern organic synthetic chemistry for strategic C−C, C−O, and C−N bond formation through a variety of well-defined reaction mechanisms.[1] Since nitrogen atom is prevalent in biologically and pharmaceutically relevant molecules, much attention has been paid to the development of methodologies for the development of synthetic methods for its incorporation into organic molecules in recent years.[2] The metallonitrene chemistry would broaden the strategic methods to build structurally complex nitrogen-containing molecules.[3] With the pioneering works by Du Bois,[4] practical conditions involving iodine(III) oxidants for the generation of metallonitrenes now make catalytic C−H amination[5] and alkene aziridination[6] general methods for the preparation of nitrogen-containing molecules. While cyclopropenation of alkynes is a well-established method for the preparation of cyclopropenes,[7] the addition of nitrenes to alkynyl derivatives has rarely been explored.[8] It has been known that α-imino gold carbene intermediates could be generated via addition of iminopyridium ylides onto gold-activated alkynes and followed by elimination of the neutral pyridines.[9] Moreover, Blakey and co-workers recently developed a new method to generate α-iminometal carbenes through metallonitrene/alkyne metathesis.[10] They showed that α-iminometal carbenes could be generated via Rh-catalyzed metallonitrene-initiated alkyne oxidation, and the α-iminometal carbenes could be terminated in an array of reactions, such as oxygen-ylide formation, [2,3]-Wittig rearrangement, aromatic substitution, and cyclopropanation as well as intermolecular trapping by a variety of allyl ethers (Scheme 1a). With these termination methods of carbene/alkyne cascade alkyl migration process and on the basis of our ongoing investigation on the chemical transformations of strained small rings, we reported a Rh(II)-catalyzed chemoselective oxidative amination and cyclization cascade of 1-(arylethynyl)cycloalkyl)-methyl sulfamates (Scheme 1b). For cyclopropyl or cyclobutyl moiety containing alkynyl sulfamates, the reactions underwent a metallonitrene initiated alkyne oxidation along with cyclopropyl ring expansion or alkoxyl moiety migration to give cyclobutane-fused or methylenecyclobutane containing heterocycles.[11]

Scheme 1. Previous Work and This Work



After the investigation on these cycloalkyl sulfamates, we then simultaneously attempted to examine the corresponding *gem*-dimethyl sulfamates such as 2,2-dimethyl-4-arylbut-3-yn-1-yl

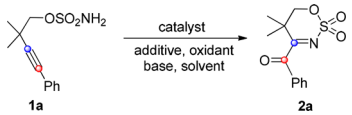
Received: November 3, 2017

DOI: 10.1021/acs.orglett.7b03425
Org. Lett. XXXX, XXX, XXX−XXX

sulfamates and 2,2-dimethyl-5-arylpent-3-yn-1-yl sulfamates in this transformation. However, we observed totally different results from our previous cycloalkyl sulfamates and Blakey's work. When R = Ar, the α-iminometal carbene intermediate was trapped by water and then oxidized by iodine(III) oxidants to give benzoyl group containing heterocycles. When R = $ArCH_2$, the α-iminometal carbene intermediate was trapped by aryl migration rather than β-H migration to give a styryl group containing heterocycles (Scheme 1c).[12] Herein, we wish to report these new findings.

First, we utilized the sulfamic ester **1a** for the initial examination using $[Rh_2(esp)_2]$ (2.5 mol %) as the catalyst and $PhI(OPiv)_2$ (2.3 equiv) as the oxidant with 4.6 equiv of CaO as a base at room temperature in dichloromethane (DCM) under argon atmosphere. We were pleased to find that the desired product **2a** was given in 66% NMR yield within 24 h (Table 1, entry 1). This result inspired us to further explore the better conditions for this reaction, and the results are summarized in Table 1. First, we screened various rhodium catalysts such as $[Rh_2(Oct)_4]$, $[Rh_2(OAc)_4]$, $[Rh_2(O_2C^tBu)_4]$, and $[Rh_2(TFA)_4]$ (Table 1, entries 1−5). $[Rh_2(esp)_2]$ was found to be the best one for this cascade reaction. Then, $PhI(O_2C^tBu)_2$ was identified as the more efficient oxidant than $PhI(OAc)_2$ and PhIO (Table 1, entries 6 and 7). With the addition of 4 Å MS (50 mg for 0.2 mmol of **1a**), **2a** could be obtained in 48% yield (Table 1, entry 8). The yield of **2a** was 68% under O_2 atmosphere (Table 1, entry 9). Next, different equiv of H_2O was used as the additive for this reaction, and we identified that adding 5.0 equiv of H_2O afforded **2b** in 87% NMR yield and 85% isolated yield (Table 1, entries 10−13). The examination of solvent effects revealed that DCM was the best choice (Table 1, entries 14−16).

Table 1. Optimization of the Reaction Conditions[a]



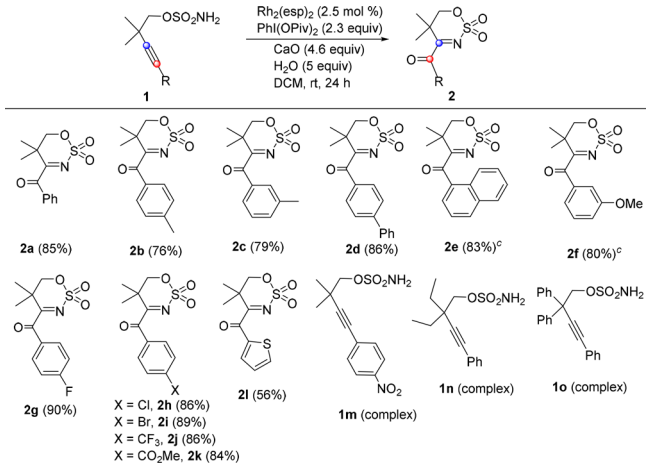
1a 2a

entry	cat. (mol %)	oxidant	additive	solvent	yield (%)[b]
1	$Rh_2(esp)_2$	$PhI(OPiv)_2$		DCM	66
2	$Rh_2(Oct)_4$	$PhI(OPiv)_2$		DCM	<5
3	$Rh_2(OAc)_4$	$PhI(OPiv)_2$		DCM	<5
4	$Rh_2(OPiv)_4$	$PhI(OPiv)_2$		DCM	<5
5	$Rh_2(TFA)_4$	$PhI(OPiv)_2$		DCM	<5
6	$Rh_2(esp)_2$	PhIO		DCM	<5
7	$Rh_2(esp)_2$	$PhI(OAc)_2$		DCM	<5
8[c]	$Rh_2(esp)_2$	$PhI(OPiv)_2$	4 Å MS	DCM	48
9[d]	$Rh_2(esp)_2$	$PhI(OPiv)_2$	O_2	DCM	68
10[e]	$Rh_2(esp)_2$	$PhI(OPiv)_2$	H_2O (1.0)	DCM	73
11[f]	$Rh_2(esp)_2$	$PhI(OPiv)_2$	H_2O (2.0)	DCM	80
12[g]	$Rh_2(esp)_2$	$PhI(OPiv)_2$	H_2O (5.0)	DCM	87 (85)[i]
13[h]	$Rh_2(esp)_2$	$PhI(OPiv)_2$	H_2O (10)	DCM	77
14[g]	$Rh_2(esp)_2$	$PhI(OPiv)_2$	H_2O (5.0)	THF	<5
15[g]	$Rh_2(esp)_2$	$PhI(OPiv)_2$	H_2O (5.0)	CH_3CN	<5
16[g]	$Rh_2(esp)_2$	$PhI(OPiv)_2$	H_2O (5.0)	toluene	63

[a]Unless otherwise specified, all reactions were carried out using **1a** (0.2 mmol), oxidant (0.46 mmol), catalyst (2.5 mol %), CaO (0.92 mmol), and additive in solvent (4.0 mL), rt, 24 h. [b]The yield was determined by ^1H NMR spectroscopic data using mesitylene as an internal standard. [c]50 mg of 4 Å MS was added. [d]1.0 atm O_2. [e]1.0 equiv of H_2O was added. [f]2.0 equiv of H_2O was added. [g]5.0 equiv of H_2O was added. [h]10 equiv of H_2O was added. [i]Isolated yield.

With the optimal conditions in hand, we next investigated the generality of this reaction using a variety of substrates **1b**−**1l** (Scheme 2). Regardless of whether electron-donating or electron-withdrawing groups were introduced on the aromatic R group, the reactions proceeded smoothly, affording the desired products **2b**−**2l** in moderate to good yields. The electron-donating group could be a methyl group at the *para*- or *meta*-position as well as phenyl group or methoxyl group, affording the corresponding products **2b**, **2c**, **2d**, and **2f** in 76, 79, 86, and 80% yields, respectively. Naphthyl moiety was also compatible, giving **2e** in 83% yield. The halogen substituents were also tolerated, furnishing the desired products **2g**, **2h**, and **2i** in good yields at room temperature. Substrate **1j** with a strongly electron-withdrawing trifluoromethyl group and substrate **1k** having an ester moiety could also provide the desired products **2j** and **2k** in 86 and 84% yields. Furthermore, substrate **1k** having a thiophene moiety gave the corresponding product **2k** in 56% yield under the standard conditions. With substrate **1m** bearing a nitryl group, the reaction gave a complex mixture. For substrates **1n** and **1o**, none of the desired products were obtained. The structure of **2a** was further confirmed by X-ray diffraction, and the ORTEP drawing is shown in the Supporting Information.

Scheme 2. Substrate Scope of 1[a,b]

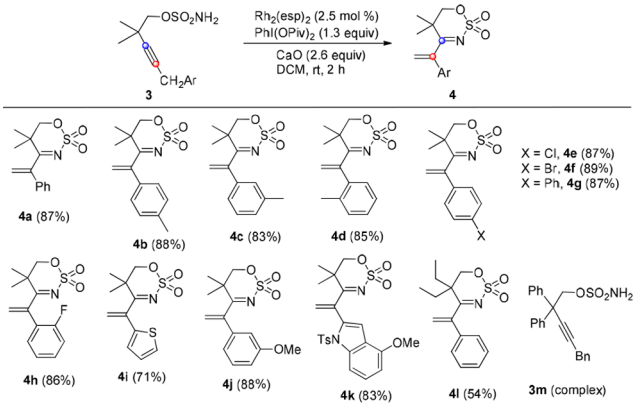


[a]Unless otherwise specified, all reactions were carried out using **1** (0.2 mmol), $PhI(OPiv)_2$ (0.46 mmol), $Rh_2(esp)_2$ (2.5 mol %), H_2O (1.0 mmol), and CaO (0.92 mmol) in DCM (4.0 mL), rt, 24 h. [b]Isolated yields are provided. [c]No water was added.

The further examination of substrates **3** containing an arylmethyl moiety was also conducted. At first, we conducted the reaction of **3a** under the same conditions as that of **1**, and we were pleased to find that the aryl migration could take place via α-iminometal carbene, giving the styryl group containing heterocyclic product **4a** in good yield rather than the H_2O-trapping product or H migration product. The structure of **4f** was further confirmed by X-ray diffraction. This result indicates the special reaction property of α-iminometal carbene derived from sulfamates with alkyne. We found that using 1.3 equiv of $PhI(O_2C^tBu)_2$ as the oxidant, 2.5 mol % of $[Rh_2(esp)_2]$ as the catalyst, and 2.6 equiv of CaO as a base and carrying out the reaction at room temperature in DCM for 2 h gave the desired product **4a** in 87% isolated yield. The substrate scope was also explored. As summarized in Scheme 3, the reactions proceeded smoothly with various substrates **3b**−**3l**, allowing the facile synthesis of product **4** in moderate to good yields. The substrates

DOI: 10.1021/acs.orglett.7b03425
Org. Lett. XXXX, XXX, XXX−XXX

Scheme 3. Substrate Scope of 3[a,b]



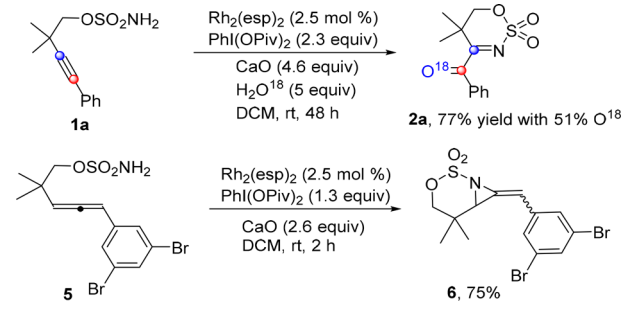
[a]Unless otherwise specified, all reactions were carried out using **3** (0.2 mmol), $PhI(OPiv)_2$ (0.26 mmol), $Rh_2(esp)_2$ (2.5 mol %), and CaO (0.52 mmol) in DCM (4.0 mL), rt, 2 h. [b]Isolated yields are provided.

bearing electron-withdrawing or electron-donating group on the aromatic ring underwent the cascade cyclization efficiently to deliver the desired products **4b**−**4h** in yields ranging from 83 to 89%. Of note, for substrates **3c** and **3d** with a methyl substituent at the *meta*-position or *ortho*-position, the corresponding products **4c** and **4d** were formed in 83 and 85% yields. Substrates **3i** and **3k** having heteroaromatic moiety were tolerable in this reaction, affording the desired products **4i** and **4k** in 71 and 77% yields, respectively. In addition, for substrate **3l**, in which methyl group was replaced by ethyl group, the reaction could also take place, affording **4l** in 54% yield. However, when both of the two methyl groups were replaced by phenyl groups, such as substrate **3m**, none of the desired product was obtained.

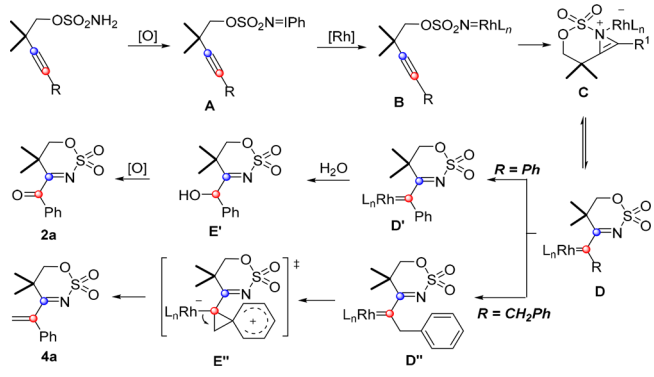
To identify the source of O in product **2**, we conducted the O^{18} labeling experiment with the addition of 5.0 equiv of H_2O^{18} into the reaction mixture and found that the obtained product incorporated 51% O^{18} content, suggesting that oxygen atom in product **2** was derived from H_2O. For the aryl migration, alkyne bearing a benzyl group could be transformed to allene under the basic condition. To exclude the possible allenic intermediate in the pathway, we synthesized the allenic compound **5** and found that the corresponding cycloaddition product **6** was formed in 75% under the standard conditions rather than the aryl migration product **4**, rendering unlikely the involvement of allenic intermediate (Scheme 4).[13]

On the basis of the previous reports and the control experiments mentioned above, a plausible reaction mechanism has been outlined in Scheme 5 to account for the different reaction outcomes. The oxidation of substrate **1a** or **3a** initiates

Scheme 4. Mechanistic Experiments



Scheme 5. Proposed Reaction Mechanism



the formation of iminoiodinane intermediate **A**, which undergoes exchange with dirhodium catalyst to generate the metallonitrene intermediate **B**. Then intramolecular metallonitrene/alkyne addition cascades afford intermediate **C** or its α-iminometal carbene **D**. The Thorpe−Ingold effect of *gem*-dimethyl groups facilitated the formation of 6-*exo* α-iminometal carbene intermediate **D** and did not favor 7-*endo* cyclization, thereby exclusively affording the six-membered ring products.[10] For substrate **1a** (R = Ph), intermediate **D′** undergoes nucleophilic attack of H_2O to form intermediate **E′**, which furnishes the desired product **2a** upon oxidation with $PhI(OPiv)_2$. However, in the case of **3a** ($R = PhCH_2$), the corresponding intermediate **D″** undergoes the aryl group migration through intermediate **E″**.[14] The elimination of Rh catalyst from **E″** gives product **4a**.

In summary, we have disclosed a novel chemoselective oxidative amination and nucleophilic trapping of *gem*-dimethyl sulfamates in the presence of Rh(II) catalyst. For 2,2-dimethyl-4-arylbut-3-yn-1-yl sulfamates, the reactions underwent a metallonitrene-initiated alkyne oxidation along with nucleophilic attacking of H_2O to give aroyl group containing heterocycles in moderate to good yields depending on the substituents under mild conditions. For 2,2-dimethyl-4-arylpent-3-yn-1-yl sulfamates, the α-iminometal carbene intermediate was trapped by aryl migration, affording styryl group containing heterocycles in good yields. Further investigations on expanding the scope and applications of this method for the synthesis of diversified nitrogen-containing heterocyclic products are ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b03425.

Experimental procedure and characterization data for all compounds (PDF)

Accession Codes

CCDC 1493128 and 1525668 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.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: mshi@mail.sioc.ac.cn.

DOI: 10.1021/acs.orglett.7b03425
Org. Lett. XXXX, XXX, XXX−XXX

ORCID

Yin Wei: 0000-0003-0484-9231
Min Shi: 0000-0003-0016-5211

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for the financial support from the National Basic Research Program of China ((973)-2015CB856603), the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB20000000), and the National Natural Science Foundation of China (20472096, 21372241, 21572052, 20672127, 21421091, 21372250, 21121062, 21302203, 20732008, and 21772037).

■ REFERENCES

(1) (a) Pena-Lopez, M.; Beller, M. *Angew. Chem., Int. Ed.* **2017**, *56*, 46. (b) Che, J.; Xing, D.; Hu, W. *Curr. Org. Chem.* **2015**, *20*, 41. (c) Zhou, S.; Li, J.; Schlangen, M.; Schwarz, H. *Acc. Chem. Res.* **2016**, *49*, 494. (d) Xu, X.; Doyle, M. P. *Acc. Chem. Res.* **2014**, *47*, 1396. (e) Guo, X.; Hu, W. *Acc. Chem. Res.* **2013**, *46*, 2427. (f) Xiao, Q.; Zhang, Y.; Wang, J. *Acc. Chem. Res.* **2013**, *46*, 236. (g) Zhu, S.-F.; Zhou, Q.-L. *Acc. Chem. Res.* **2012**, *45*, 1365. (h) Doyle, M. P.; Duffy, R.; Ratnikov, M.; Zhou, L. *Chem. Rev.* **2010**, *110*, 704.

(2) (a) Hu, F.; Xia, Y.; Ma, C.; Zhang, Y.; Wang, J. *J. Org. Chem.* **2016**, *81*, 3275. (b) Liu, X.; Cong, T.; Liu, P.; Sun, P. *J. Org. Chem.* **2016**, *81*, 7256. (c) Xia, Y.; Chen, L.; Qu, P.; Ji, G.; Feng, S.; Xiao, Q.; Zhang, Y.; Wang, J. *J. Org. Chem.* **2016**, *81*, 10484. (d) Min, H.; Palani, T.; Park, K.; Hwang, J.; Lee, S. *J. Org. Chem.* **2014**, *79*, 6279. (e) Wang, X.; Cheng, G.; Shen, J.; Yang, X.; Wei, M.-e.; Feng, Y.; Cui, X. *Org. Chem. Front.* **2014**, *1*, 1001. (f) Ren, W.; Liu, J.; Chen, L.; Wan, X. *Adv. Synth. Catal.* **2010**, *352*, 1424.

(3) (a) Darses, B.; Rodrigues, R.; Neuville, L.; Mazurais, M.; Dauban, P. *Chem. Commun.* **2017**, *53*, 493. (b) Dequirez, G.; Pons, V.; Dauban, P. *Angew. Chem., Int. Ed.* **2012**, *51*, 7384. (c) Gephart, R. T.; Warren, T. H. *Organometallics* **2012**, *31*, 7728. (d) Roizen, J. L.; Harvey, M. E.; Du Bois, J. *Acc. Chem. Res.* **2012**, *45*, 911. (e) Collet, F.; Lescot, C.; Dauban, P. *Chem. Soc. Rev.* **2011**, *40*, 1926. (f) Driver, T. G. *Org. Biomol. Chem.* **2010**, *8*, 3831.

(4) (a) Varela-Álvarez, A.; Yang, T.; Jennings, H.; Kornecki, K. P.; Macmillan, S. N.; Lancaster, K. M.; Mack, J. B. C.; Du Bois, J.; Berry, J. F.; Musaev, D. G. *J. Am. Chem. Soc.* **2016**, *138*, 2327. (b) Bess, E. N.; DeLuca, R. J.; Tindall, D. J.; Oderinde, M. S.; Roizen, J. L.; Du Bois, J.; Sigman, M. S. *J. Am. Chem. Soc.* **2014**, *136*, 5783. (c) Olson, D. E.; Su, J. Y.; Roberts, D. A.; Du Bois, J. *J. Am. Chem. Soc.* **2014**, *136*, 13506. (d) Harvey, M. E.; Musaev, D. G.; Du Bois, J. *J. Am. Chem. Soc.* **2011**, *133*, 17207. (e) Zalatan, D. N.; Du Bois, J. *J. Am. Chem. Soc.* **2009**, *131*, 7558. (f) Wehn, P. M.; Du Bois, J. *J. Am. Chem. Soc.* **2002**, *124*, 12950.

(5) (a) Fukui, Y.; Liu, P.; Liu, Q.; He, Z.-T.; Wu, N.-Y.; Tian, P.; Lin, G.-Q. *J. Am. Chem. Soc.* **2014**, *136*, 15607. (b) Hennessy, E. T.; Betley, T. A. *Science* **2013**, *340*, 591. (c) Huckins, J. R.; Bercot, E. A.; Thiel, O. R.; Hwang, T.-L.; Bio, M. M. *J. Am. Chem. Soc.* **2013**, *135*, 14492. (d) Colby, D. A.; Tsai, A. S.; Bergman, R. G.; Ellman, J. A. *Acc. Chem. Res.* **2012**, *45*, 814. (e) Song, G.; Wang, F.; Li, X. *Chem. Soc. Rev.* **2012**, *41*, 3651. (f) Ye, B.; Cramer, N. *Science* **2012**, *338*, 504. (g) Stang, E. M.; White, M. C. *J. Am. Chem. Soc.* **2011**, *133*, 14892. (h) Hyster, T. K.; Rovis, T. *J. Am. Chem. Soc.* **2010**, *132*, 10565.

(6) (a) Grigg, R. D.; Rigoli, J. W.; Pearce, S. D.; Schomaker, J. M. *Org. Lett.* **2012**, *14*, 280. (b) Bonge, H. T.; Hansen, T. *Tetrahedron Lett.* **2010**, *51*, 5298.

(7) (a) Liu, Z.; Li, Q.; Liao, P.; Bi, X. *Chem. - Eur. J.* **2017**, *23*, 4756. (b) Muller, D. S.; Marek, I. *Chem. Soc. Rev.* **2016**, *45*, 4552. (c) Cui, X.; Xu, X.; Lu, H.; Zhu, S.; Wojtas, L.; Zhang, X. P. *J. Am. Chem. Soc.* **2011**, *133*, 3304. (d) Uehara, M.; Suematsu, H.; Yasutomi, Y.; Katsuki, T. *J. Am. Chem. Soc.* **2011**, *133*, 170. (e) Briones, J. F.; Hansen, J.; Hardcastle, K. I.; Autschbach, J.; Davies, H. M. L. *J. Am. Chem. Soc.* **2010**, *132*, 17211. (f) Nowlan, D. T., III; Singleton, D. A. *J. Am. Chem. Soc.* **2005**, *127*, 6190. (g) Lou, Y.; Horikawa, M.; Kloster, R. A.; Hawryluk, N. A.; Corey, E. J. *J. Am. Chem. Soc.* **2004**, *126*, 8916. (h) Perez, P. J.; Brookhart, M.; Templeton, J. L. *Organometallics* **1993**, *12*, 261. (i) Protopopova, M. N.; Doyle, M. P.; Mueller, P.; Ene, D. *J. Am. Chem. Soc.* **1992**, *114*, 2755.

(8) Yeom, H.-S.; Shin, S. *Acc. Chem. Res.* **2014**, *47*, 966.

(9) (a) Ling, H.-B.; Chen, Z.-S.; Yang, F.; Xu, B.; Gao, J.-M.; Ji, K. *J. Org. Chem.* **2017**, *82*, 7070. (b) Ruan, P.-P.; Li, H.-H.; Liu, X.; Zhang, T.; Zuo, S.-X.; Zhu, C.; Ye, L.-W. *J. Org. Chem.* **2017**, *82*, 9119. (c) Harris, R. J.; Widenhoefer, R. A. *Chem. Soc. Rev.* **2016**, *45*, 4533. (d) Huple, D. B.; Ghorpade, S.; Liu, R.-S. *Adv. Synth. Catal.* **2016**, *358*, 1348. (e) Jin, H.; Huang, L.; Xie, J.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2016**, *55*, 794. (f) Shu, C.; Wang, Y.-H.; Shen, C.-H.; Ruan, P.-P.; Lu, X.; Ye, L.-W. *Org. Lett.* **2016**, *18*, 3254. (g) Yu, Y.; Chen, G.; Zhu, L.; Liao, Y.; Wu, Y.; Huang, X. *J. Org. Chem.* **2016**, *81*, 8142. (h) Schulz, J.; Jasikova, L.; Skriba, A.; Roithova, J. *J. Am. Chem. Soc.* **2014**, *136*, 11513.

(10) (a) Mace, N.; Thornton, A. R.; Blakey, S. B. *Angew. Chem., Int. Ed.* **2013**, *52*, 5836. (b) Thornton, A. R.; Blakey, S. B. *J. Am. Chem. Soc.* **2008**, *130*, 5020. (c) Thornton, A. R.; Martin, V. I.; Blakey, S. B. *J. Am. Chem. Soc.* **2009**, *131*, 2434.

(11) Pan, D.; Wei, Y.; Shi, M. *Org. Lett.* **2017**, *19*, 3584.

(12) (a) Candeias, N. R.; Paterna, R.; Gois, P. M. P. *Chem. Rev.* **2016**, *116*, 2937. (b) Xiao, F.; Wang, J. *J. Org. Chem.* **2006**, *71*, 5789. (c) Keating, A. E.; Garcia-Garibay, M. A.; Houk, K. N. *J. Phys. Chem. A* **1998**, *102*, 8467.

(13) (a) Rigoli, J. W.; Weatherly, C. D.; Alderson, J. M.; Vo, B. T.; Schomaker, J. M. *J. Am. Chem. Soc.* **2013**, *135*, 17238. (b) Rigoli, J. W.; Weatherly, C. D.; Vo, B. T.; Neale, S.; Meis, A. R.; Schomaker, J. M. *Org. Lett.* **2013**, *15*, 290. (c) Adams, C. S.; Boralsky, L. A.; Guzei, I. A.; Schomaker, J. M. *J. Am. Chem. Soc.* **2012**, *134*, 10807. (d) Stoll, A. H.; Blakey, S. B. *J. Am. Chem. Soc.* **2010**, *132*, 2108.

(14) (a) Xiao, T.; Peng, P.; Xie, Y.; Wang, Z.-y.; Zhou, L. *Org. Lett.* **2015**, *17*, 4332. (b) Jiang, N.; Wang, J. *Synlett* **2002**, *2002*, 0149. (c) Jiang, N.; Qu, Z.; Wang, J. *Org. Lett.* **2001**, *3*, 2989.

DOI: 10.1021/acs.orglett.7b03425
Org. Lett. XXXX, XXX, XXX−XXX