ACS Catalysis

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Nonmetathesis Heterocycle Formation by Ruthenium-Catalyzed Intramolecular [2 + 2] Cycloaddition of Allenamide-enes to Azabicyclo[3.1.1]heptanes

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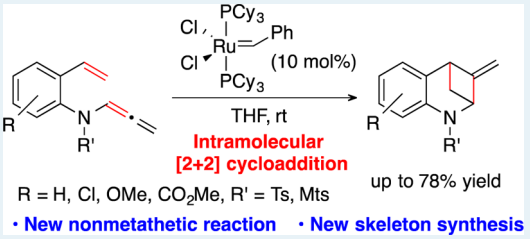
Supporting Information

ABSTRACT: We have developed a novel nonmetathesis reaction, namely, ruthenium-catalyzed intramolecular [2 + 2] cycloaddition of allenamide-enes, to give heterocycles (i.e., azabicyclo[3.1.1]heptanes). This is the first example of [2 + 2] cycloaddition using a ruthenium carbene catalyst. The reaction proceeds at room temperature, but not under thermal or radical conditions.



KEYWORDS: *metathesis, heterocycles, ruthenium, cycloaddition, allenamide*

Olefin metathesis using a ruthenium carbene catalyst (see Figure 1, compounds **A**–**G**) is a versatile carbon–carbon

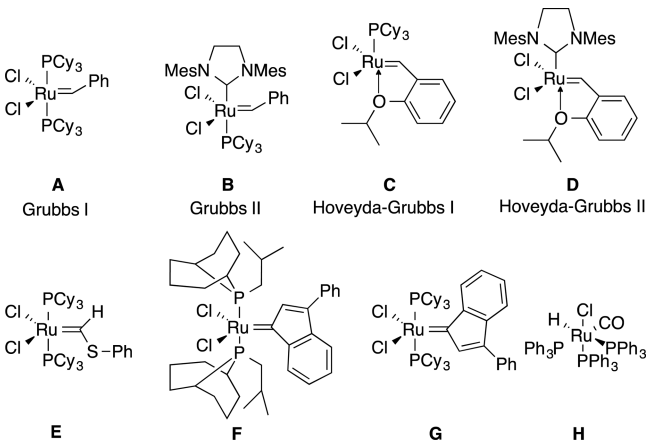


Figure 1. Ruthenium catalysts.

double-bond-forming reaction; it is widely used to prepare complex organic compounds.[1] Ruthenium alkylidenes such as **A**,[2] **B**,[3] **C**,[4] and **D**,[5] which are widely used for olefin metathesis, have been shown to function as procatalysts[6] in olefin isomerizations,[7] hydrogenations,[8] radical reactions,[9] activation of silanes,[10] cyclopropanations,[11] cyclopropane epimerizations,[12] oxidations,[13] hydrovinylations,[14] [4 + 2] cycloadditions,[15] [3 + 2] cycloadditions,[16] [2 + 2 + 2] cycloadditions,[17] and cycloisomerizations.[18]

We have made several contributions to this research field and have already reported several nonmetathesis reactions, i.e., isomerizations[7n] of terminal olefins, cycloisomerizations,[18a,c] and one-pot metathesis and subsequent nonmetathesis reactions to give novel heterocyclic dyes.[16c]

Allenamides are important functional groups in organic synthesis, and many allenamides reactions have been developed.[20] Allenamides reactions using organometallic catalysts have been reported, but nonmetathesis reactions with ruthenium carbene catalysts are limited to isomerizations and cycloisomerizations (see eqs 1[19] and 2[18b] in Scheme 1).[21] These reactions both proceed via a ruthenium hydride species with a nitrogen-containing heterocyclic carbene ligand generated from a Grubbs II catalyst.

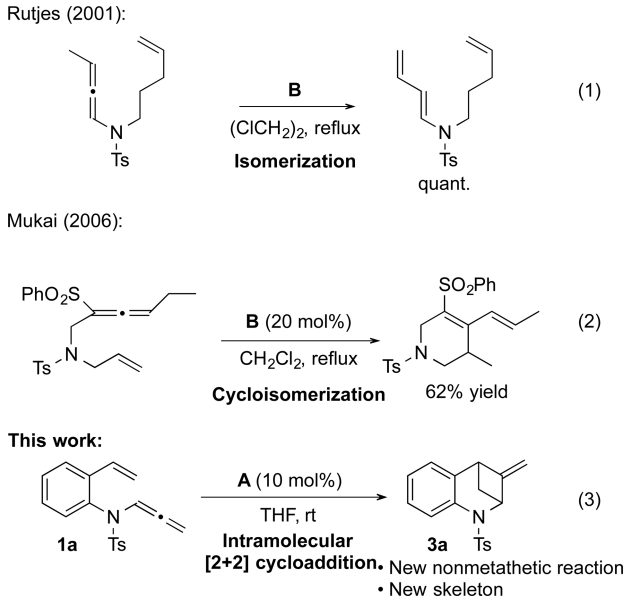
Here, we report intramolecular [2 + 2] cycloadditions of terminal allenes, *N*-allenyl-*o*-vinylaniline (**1**), at room temperature, catalyzed by Grubbs I, to give novel bicyclic heterocycles: azabicyclo[3.1.1]heptanes. The reaction does not proceed under thermal or radical conditions or via ruthenium hydride species. As far as we know, there have been no reports of [2 + 2] cycloadditions involving a nonmetathesis reaction.[22]

Compound **2a** was treated with ^{t}BuOK (0.5 equiv) in THF at 0 °C for 10 min to form **1a**, which was treated, without purification, with a catalytic amount of one of the ruthenium carbene catalysts in Figure 1 for 1.5 h. The [2 + 2] cycloaddition proceeded at room temperature with Grubbs I

Received: March 1, 2016
Revised: March 30, 2016

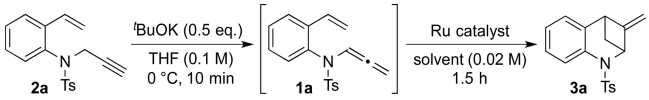
DOI: 10.1021/acscatal.6b00628
ACS Catal. 2016, 6, 3168−3171

Scheme 1. Reactions of Allenes Using Ruthenium Carbene Catalysts



catalyst **A** to give **3a** in 62% yield in two steps (Table 1, entry 1). The crystal structure of **3a** was determined using single-crystal X-ray diffraction (XRD); it contained four planar rings (Figure 2).[23] Only catalyst **A** was effective in this novel nonmetathesis reaction, and other ruthenium carbene catalysts in Figure 1, including Grubbs II catalyst (**B**), Hoveyda–Grubbs I catalyst (**C**), Hoveyda–Grubbs catalyst II (**D**), and $RuHCl(CO)(PPh_3)_3$ (**H**), did not work well (see Table 1, entries 2–8). Solvent screening was performed, and we obtained **3a** from **2a** in 76% yield, in two steps, when we used THF as the solvent in the second step, i.e., the [2 + 2] cycloaddition (entry 11). Although [2 + 2] cycloadditions proceed under heating or radical conditions, control experiments (Table 1, entries 9 and 12) clearly showed that our [2 + 2] cycloaddition does not require thermal or radical conditions.

Table 1. Reaction of *N*-allenyl-*o*-vinylaniline 1a with a Ruthenium Carbene Catalyst



entry	"Ru" (mol %)	solvent	temp[a] (°C)	yield of **3a** (%, two steps)[b]
1	**A** (10)	toluene	rt	62
2	**B** (10)	toluene	rt	0
3	**C** (10)	toluene	rt	14
4	**D** (10)	toluene	rt	0
5	**E** (10)	toluene	rt	10
6	**F** (10)	toluene	rt	3
7	**G** (10)	toluene	rt	31
8	**H** (10)	toluene	rt	0
9		toluene	110	0
10	**A** (10)	CH_2Cl_2	rt	56
11	**A** (10)	THF	rt	76
12[c]	**A** (10)	THF	rt	71

[a]The abbreviation "rt" denotes room temperature. [b]Isolated yield (two steps). [c]Here, galvinoxyl (10 mol %) was added.

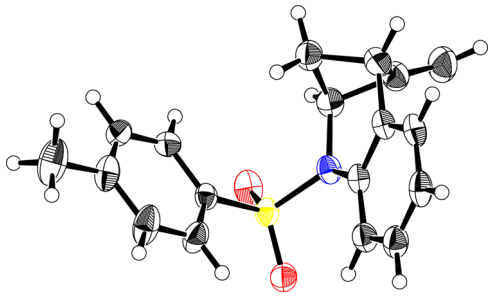
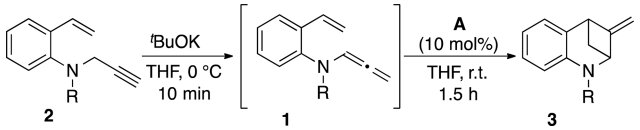


Figure 2. X-ray structure of **3a**. (Space group: $P21/n$. $R1$ [$I > 2.0\sigma(I)$]: 4.60%. wR [all data]: 12.13%. Goodness of fit (GOF): 1.033.)

Based on these results, we next examined the effect of a substituent on nitrogen (Table 2). A 2-mesitylenesulfonyl (Mts) derivative **2b** and methanesulfonyl (Ms) derivative **2c** gave the corresponding [2 + 2] cycloadducts in yields of 78% and 43%, respectively; the yield difference is probably the result of steric effects. Derivatives with weaker electron-withdrawing groups on nitrogen, i.e., acetyl derivative **1d** and *tert*-butoxycarbonyl derivative **1e**, did not take part in this reaction; **1d** was unchanged and **1e** was converted to **3e** in 23% yields. In these experiments, we observed that allenamides with weaker electron-withdrawing groups gradually decomposed.

The effects of substituents on the benzene ring are summarized in Table 3; the data show the scope, limitation, and mechanism of this [2 + 2] cycloaddition. All the substrates

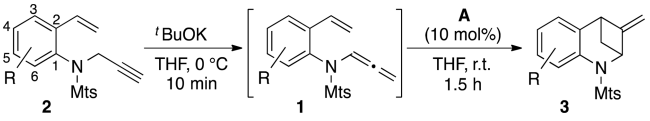
Table 2. Effect of the Nitrogen-Protecting Group



entry	substrate	R	yield of **3** (%, two steps)[b]
1	**2a**	Ts	76
2	**2b**	Mts[a]	78
3	**2c**	Ms	43
4	**2d**	Ac	0
5	**2e**	Boc	23

[a]Mts = 2,4,6-trimethylphenylsulfonyl. [b]Isolated yield (two steps).

Table 3. Effect of Benzene Ring Substituents



entry	substrate	R	yield (%, two steps)[a]
1	**2b**	H	78
2	**2f**	3-OMe	70
3	**2g**	4-OMe	69
4	**2h**	5-OMe	73
5	**2i**	6-OMe	16
6	**2j**	3-Cl	68
7	**2k**	4-Cl	70
8	**2l**	5-Cl	69
9	**2m**	6-Cl	0[b]
10	**2n**	4-CO_2Me	63

[a]Isolated yield (two steps). [b]Starting material was recovered.

DOI: 10.1021/acscatal.6b00628
ACS Catal. 2016, 6, 3168–3171

2b−**2n** were prepared as Mts amides and were subjected to the reaction conditions used for Table 1, entry 7 (see Table 3). Allenamides **2f**, **2g**, and **2h** and allenamides **2j**, **2k**, and **2l**, which have a substituent at the 3-, 4-, or 5-position, respectively, were converted to the corresponding [2 + 2] cycloadducts **3** in good yields. However, allenamides **1i** and **1m**, with a substituent at the 6-position, were respectively converted to **3i** in 16% yield and unchanged (see Table 3, entries 5 and 9). There were sharp contrasts between 1,2,3-trisubstituted and 1,2,6-trisubstituted substrates, although both have substituents at the *ortho* position. These results suggest that some ruthenium species[24] react with the allene moiety faster than the styrene moiety on allenamide **1** in this [2 + 2] cycloaddition.

Finally, we used NMR spectroscopy to obtain information on the active ruthenium species in this [2 + 2] cycloaddition. We compared the ^{1}H and ^{31}P NMR spectra in C_6D_6 of catalyst **A** and the reaction mixture for the [2 + 2] cycloaddition. For catalyst **A**, we observed signals for the benzylidene proton at 20.6 ppm in the ^{1}H NMR spectrum, and tricyclohexylphosphine at 36.82 ppm in the ^{31}P NMR spectrum (Figure 3). In

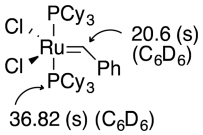


Figure 3. Summary of NMR spectroscopic data for catalyst **A**.

the spectra of the [2 + 2] cyclization reaction mixture, these peaks disappeared within 5 min (Figure S1 in the Supporting Information). New peaks appeared in the ^{31}P NMR spectrum, at 10.4 ppm[25] and 5.4 ppm. No peak typical of Ru−H, at approximately −20 ppm, was observed in the ^{1}H NMR spectrum. These results and those of the control experiments shown in Table 1 suggest that this [2 + 2] cycloaddition proceeds via a ruthenium catalyst derived from catalyst **A**, but not a ruthenium hydride. A plausible reaction mechanism of this reaction was drawn in Figure 4.

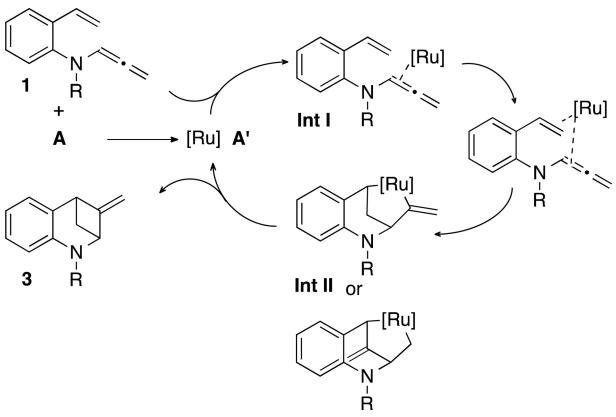


Figure 4. Schematic of a plausible reaction mechanism.

In conclusion, we have developed a ruthenium-catalyzed intramolecular [2 + 2] cycloaddition of allenamide-enes to give azabicyclo[3.1.1]heptanes. This transformation uses a ruthenium carbene catalyst (i.e., Grubbs I), proceeds at room temperature, and does not involve radical species. This is another example of a nonmetathesis reaction using a ruthenium carbene catalyst. It will be of interest because ruthenium carbene catalysts are widely used in functional molecular synthesis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b00628.

Experimental procedures and full characterizations of compounds (PDF)

X-ray structure report for compound **3a** (PDF)

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Author Contributions

†T.N. and Y.Y. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology, Japan, ACT-C from the Japan Science and Technology Agency, and the Takeda Science Foundation.

■ REFERENCES

(1) (a) Cossy, J. In *Olefin Metathesis: Theory and Practice*; Grela, K., Ed.; Wiley: Hoboken, NJ, 2014; p 287. (b) Cossy, J.; Arseniyadis, S.; Meyer, C.; Grubbs, R. H. In *Metathesis in Natural Product Synthesis: Strategies, Substrates and Catalysts*; Wiley−VCH: Weinheim, Germany, 2010; p 1.

(2) (a) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039−2041. (b) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 960−961.

(3) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953−956.

(4) Harrity, J. P. A.; La, D. S.; Cefalo, D. R.; Visser, M. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1998**, *120*, 2343−2351.

(5) Kingsbury, J. S.; Harrity, J. P. A., Jr.; Bonitatebus, P. J.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 791−799.

(6) For reviews, see: (a) Alcaide, B.; Almendros, P. *Chem.—Eur. J.* **2003**, *9*, 1258−1262. (b) Schmidt, B. *Eur. J. Org. Chem.* **2004**, *2004* (9), 1865−1880. (c) Arisawa, M.; Terada, Y.; Takahashi, K.; Nakagawa, M.; Nishida, A. *Chem. Rec.* **2007**, *7*, 238−253. (d) Alcaide, B.; Almendros, P.; Luna, A. *Chem. Rev.* **2009**, *109*, 3817−3858.

(7) (a) Miller, S. J.; Blackwell, H. E.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 9606−9614. (b) Hu, Y.-J.; Dominique, R.; Das, S. K.; Roy, R. *Can. J. Chem.* **2000**, *78*, 838−845. (c) Wipf, P.; Rector, S. R.; Takahashi, H. *J. Am. Chem. Soc.* **2002**, *124*, 14848−14849. (d) Wipf, P.; Spencer, S. R. *J. Am. Chem. Soc.* **2005**, *127*, 225−235. (e) Alcaide, B.; Almendros, P.; Alonso, J. M.; Aly, M. F. *Org. Lett.* **2001**, *3*, 3781−3784. (f) Cadot, C.; Dalko, P. I.; Cossy, J. *Tetrahedron Lett.* **2002**, *43*, 1839−1841. (g) Alcaide, B.; Almendros, P.; Alonso, J. M. *Tetrahedron Lett.* **2003**, *44*, 8693−8695. (h) Alcaide, B.; Almendros, P.; Alonso, J. M. *Chem.—Eur. J.* **2003**, *9*, 5793−5799. (i) Fürstner, A.; Thiel, O. R.; Ackermann, L.; Schanz, H.-J.; Nolan, S. P. *J. Org. Chem.* **2000**, *65*, 2204−2207. (j) Braddock, D. C.; Wildsmith, A. J. *Tetrahedron Lett.* **2001**, *42*, 3239−3242. (k) Gurjar, M. K.; Yakambram, P. *Tetrahedron Lett.* **2001**, *42*, 3633−3636. (l) Braddock, D. C.; Matsuno, A. *Tetrahedron Lett.* **2002**, *43*, 3305−3308. (m) Bourgeois, D.; Pancrazi, A.; Nolan, S. P.; Prunet, J. *J. Organomet. Chem.* **2002**, *643*−*644*, 247−252. (n) Arisawa, M.; Terada, Y.; Nakagawa, M.; Nishida, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 4732−4734. (o) Sworen, J. C.; Pawlow, J. H.;

DOI: 10.1021/acscatal.6b00628
ACS Catal. 2016, 6, 3168−3171

Case, W.; Lever, J.; Wagener, K. B. *J. Mol. Catal. A: Chem.* **2003**, *194*, 69−78. (p) Edlin, C. D.; Faulkner, J.; Fengas, D.; Knight, C. K.; Parker, J.; Preece, I.; Quayle, P.; Richards, S. N. *Synlett* **2005**, 572−576. (q) Schmidt, B. *J. Mol. Catal. A: Chem.* **2006**, *254*, 53−57. (r) Kotha, S.; Mandal, K.; Tiwari, A.; Mobin, S. M. *Chem.—Eur. J.* **2006**, *12*, 8024−8038. (s) Hanessian, S.; Giroux, S.; Larsson, A. *Org. Lett.* **2006**, *8*, 5481−5484. (t) Sutton, A. E.; Seigal, B. A.; Finnegan, D. F.; Snapper, M. L. *J. Am. Chem. Soc.* **2002**, *124*, 13390−11391. (u) Schmidt, B. *Eur. J. Org. Chem.* **2003**, *2003*, 816−819. (v) Schmidt, B. *Chem. Commun.* **2004**, 742−743. (w) Schmidt, B. *J. Org. Chem.* **2004**, *69*, 7672−7687. (x) Schmidt, B. *Synlett* **2004**, *9*, 1541−1544. (y) Fustero, S.; Sánchez-Roselló, M.; Jiménez, D.; Sanz-Cervera, J. F.; del Pozo, C.; Aceña, J. L. *J. Org. Chem.* **2006**, *71*, 2706−2714. (z) Arisawa, M.; Terada, Y.; Takahashi, K.; Nakagawa, M.; Nishida, A. *J. Org. Chem.* **2006**, *71*, 4255−4261. (aa) Donohoe, T. J.; O'Riordan, T. J. C.; Rosa, C. P. *Angew. Chem., Int. Ed.* **2009**, *48*, 1014−1017.

(8) (a) Louie, J.; Bielawski, C. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 11312−11313. (b) Bielawski, C. W.; Louie, J.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 12872−12873. (c) Schmidt, B.; Pohler, M. *Org. Biomol. Chem.* **2003**, *1*, 2512−2517. (d) Menozzi, C.; Dalko, P. I.; Cossy, J. *Synlett* **2005**, 2449−2452. (e) Poeylaut-Palena, A. A.; Testero, S. A.; Mata, E. G. *Chem. Commun.* **2011**, *47*, 1565−1567.

(9) (a) Tallarico, J. A.; Malnick, L. A.; Snapper, M. L. *J. Org. Chem.* **1999**, *64*, 344−345. (b) Simal, F.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **1999**, *40*, 5689−5693. (c) Schmidt, B.; Pohler, M.; Costisella, B. *J. Org. Chem.* **2004**, *69*, 1421−1424. (d) Lee, B. T.; Schrader, T. O.; Martín-Matute, B.; Kauffman, C. R.; Zhang, P.; Snapper, M. L. *Tetrahedron* **2004**, *60*, 7391−7396. (e) Seigal, B. A.; Fajardo, C.; Snapper, M. L. *J. Am. Chem. Soc.* **2005**, *127*, 16329−16332. (f) Faulkner, J.; Edlin, C. D.; Fengas, D.; Preece, I.; Quayle, P.; Richards, S. N. *Tetrahedron Lett.* **2005**, *46*, 2381−2385. (g) Quayle, P.; Fengas, D.; Richards, S. *Synlett* **2003**, 1797−1800. (h) Simal, F.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **1999**, *40*, 5689−5693. (i) Faulkner, J.; Edlin, C. D.; Fengas, D.; Preece, I.; Quayle, P.; Richards, S. N. *Tetrahedron Lett.* **2005**, *46*, 2381−2385. (k) Edlin, C. D.; Faulkner, J.; Quayle, P. *Tetrahedron Lett.* **2006**, *47*, 1145−1151.

(10) (a) Maifeld, S. V.; Miller, R. L.; Lee, D. *Tetrahedron Lett.* **2002**, *43*, 6363−6366. (b) Aricó, C. S.; Cox, L. R. *Org. Biomol. Chem.* **2004**, *2*, 2558−2562. (c) Maifeld, S. V.; Tran, M. N.; Lee, D. *Tetrahedron Lett.* **2005**, *46*, 105−108. (d) Menozzi, C.; Dalko, P. I.; Cossy, J. *J. Org. Chem.* **2005**, *70*, 10717−10719. (e) Bokka, A.; Hua, Y.; Berlin, A. S.; Jeon, J. *ACS Catal.* **2015**, *5*, 3189−3195.

(11) (a) Kim, B. G.; Snapper, M. L. *J. Am. Chem. Soc.* **2006**, *128*, 52−53. (b) Peppers, B. P.; Diver, S. T. *J. Am. Chem. Soc.* **2004**, *126*, 9524−9525.

(12) Zeng, X.; Wei, Z.; Farina, V.; Napolitano, E.; Xu, Y.; Zhang, L.; Haddad, N.; Yee, N. K.; Grinberg, N.; Shen, S.; Senanayake, C. H. *J. Org. Chem.* **2006**, *71*, 8864−8875.

(13) (a) Beligny, S.; Eibauer, S.; Maechling, S.; Blechert, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 1900−1903. (b) Scholte, A. A.; An, M. H.; Snapper, M. L. *Org. Lett.* **2006**, *8*, 4759−4762. (c) Chen, Q. H.; Ganesh, T.; Jiang, Y.; Banerjee, A.; Sharma, S.; Bane, S.; Snyder, J. P.; Kingston, D. G. I. *Chem. Commun.* **2010**, *46*, 2019−2021. (d) Schmidt, B.; Krehl, S. *Chem. Commun.* **2011**, *47*, 5879−5881. (e) Kato, H.; Ishigame, T.; Oshima, N.; Hoshiya, N.; Shimawaki, K.; Arisawa, M.; Shuto, S. *Adv. Synth. Catal.* **2011**, *353*, 2676−2680. (f) Dornan, P. K.; Wickens, Z. K.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2015**, *54*, 7134−7138.

(14) Gavenonis, J.; Arroyo, R. V.; Snapper, M. L. *Chem. Commun.* **2010**, *46*, 5692−5694.

(15) (a) Rosillo, M.; Casarrubios, L.; Domínguez, G.; Pérez-Castells, J. *Tetrahedron Lett.* **2001**, *42*, 7029−7031. (b) Rosillo, M.; Domínguez, G.; Casarrubios, L.; Amador, U.; Pérez-Castells, J. *J. Org. Chem.* **2004**, *69*, 2084−2093.

(16) (a) López, F.; Delgado, A.; Rodríguez, J. R.; Castedo, L.; Mascarenas, J. L. *J. Am. Chem. Soc.* **2004**, *126*, 10262−10263. (b) Takagi, R.; Yamamoto, K.; Hiraga, Y.; Kojima, S.; Abe, M. *J. Organomet. Chem.* **2013**, *723*, 171−175. (c) Arisawa, M.; Fujii, Y.; Kato, H.; Fukuda, H.; Matsumoto, T.; Ito, M.; Abe, H.; Ito, Y.; Shuto, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 1003−1007.

(17) Desroy, N.; Robert-Peillard, F.; Toueg, J.; Hénaut, C.; Duboc, R.; Rager, M.-N.; Savignac, M.; Genêt, J.-P. *Synthesis* **2004**, *2004*, 2665−2671.

(18) (a) Terada, Y.; Arisawa, M.; Nishida, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 4063−4067. (b) Mukai, C.; Itoh, R. *Tetrahedron Lett.* **2006**, *47*, 3971−3974. (c) Arisawa, M.; Terada, Y.; Takahashi, K.; Nakagawa, M.; Nishida, A. *J. Org. Chem.* **2006**, *71*, 4255−4261. (d) Boyer, F.-D.; Hanna, I. *Eur. J. Org. Chem.* **2006**, *2006*, 471−482.

(19) Kinderman, S. S.; van Maarseveen, J. H.; Schoemaker, H. E.; Hiemstra, H.; Rutjes, F. P. J. T. *Org. Lett.* **2001**, *3*, 2045−2048.

(20) (a) Lu, T.; Lu, Z.; Ma, Z.-X.; Zhang, Y.; Hsung, R. P. *Chem. Rev.* **2013**, *113*, 4862−4904. (b) Wei, L.-I.; Xiong, H.; Hsung, R. P. *Acc. Chem. Res.* **2003**, *36*, 773−782.

(21) Allene cross metathesis; see: Ahmed, M.; Arnauld, T.; Barrett, A. G. M.; Braddock, D. C.; Flack, K.; Procopiou, P. A. *Org. Lett.* **2000**, *2*, 551−553.

(22) Transition metal-catalyzed intramolecular [2 + 2] cycloaddition between allenes and alkenes; see: (a) Noucti, N. N.; Alexanian, E. J. *Angew. Chem., Int. Ed.* **2015**, *54*, 5447−5450 (for [Ni]). (b) Gulías, M.; Collado, A.; Trillo, B.; López, F.; Onate, E.; Esteruelas, M. A.; Mascarenas, J. L. *J. Am. Chem. Soc.* **2011**, *133*, 7660−7663 (for [Ru]). (c) Luzung, M. R.; Mauleón, P.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 12402−12403 (for [Au]).

(23) CCDC 1451275 contains the supplementary crystallographic data for **3a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(24) After the experiment in Figure 4, authors understand that this ruthenium species came from catalyst **A**, rather than ruthenium hydride.

(25) It is reported that tricyclohexylphosphine has a peak at 10.4 ppm in ^{31}P NMR. A peak at 0 ppm is attributed to a reference, H_3PO_4. See: Lummiss, J. A. M.; McClennan, W. L.; McDonald, R.; Fogg, D. E. *Organometallics* **2014**, *33*, 6738−6741.

DOI: 10.1021/acscatal.6b00628
ACS Catal. 2016, 6, 3168−3171