Organic LETTERS

Letter

pubs.acs.org/OrgLett

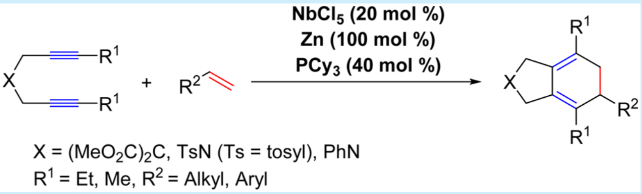
NbCl$_5$/Zn/PCy$_3$-System-Catalyzed Intramolecular [2 + 2 + 2] Cycloadditions of Diynes and Alkenes To Form Bicyclic Cyclohexadienes

Keisuke Watanabe, Yasushi Satoh, Motofumi Kamei, Hirohisa Furukawa, Maito Fuji, and Yasushi Obora*

Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita, Osaka 564-8680, Japan

Ⓢ *Supporting Information*

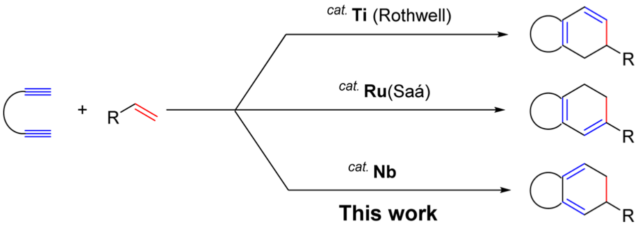
ABSTRACT: A NbCl$_5$, Zn, and PCy$_3$ catalytic system that generated low-valent Nb species is used for the synthesis of bicyclic cyclohexadienes from diynes and simple alkenes. A phosphine ligand is important for stabilizing low-valent Nb in the cycloaddition. The bicyclic cyclohexadiene skeleton is important in transition-metal-catalyzed intramolecular cycloadditions.



Low-valent early transition metals are efficient in organic syntheses because of their electron-rich and Lewis acidic properties;[1] for example, Ti−alkyne complexes react with ketones to give allyl alcohols[1a] and Zr−alkyne complexes produce benzene derivatives.[1b,e−h] However, these low-valent species need to be generated at low temperatures (−78 to 0 °C). Low-valent Nb species have greater thermal stability than other early transition-metal species and can be used in organic syntheses under ambient conditions.[2] Previously, we reported the Nb-mediated synthesis of indenes from aliphatic ketones and aromatic internal alkynes.[3] We also reported Nb−alkyne complex mediated coupling reactions of aryl iodides.[4] Recently, the use of early transition metals in many catalytic organic reactions, e.g., cycloaddition,[5] reductive coupling,[6] and C−H bond activation,[7] have been reported. We previously developed Nb-catalyzed intermolecular [2 + 2 + 2] cycloadditions of alkynes with alkenes or nitriles and isocyanates.[8,9] In these reactions, Nb-catalyzed cycloadditions of alkynes and alkenes produce cyclohexadienes with high chemo- and regioselectivities.[8,9a] A few examples of transition-metal-catalyzed intermolecular cycloadditions to give cyclohexadienes have been reported.[10]

The selectivities of transition-metal-catalyzed intramolecular cycloadditions are easier to control than those of intermolecular cycloadditions.[11] However, the chemo- and regioselective preparation of bicyclic cyclohexadienes from diynes and alkenes is difficult because cyclohexadiene aromatization or double-bond migration can occur.[12] Enynes and alkynes[13] or diynes and cyclic alkenes[12b,14] are used for transition-metal-catalyzed syntheses of bicyclic cyclohexadienes to prevent these processes. Rothwell[5a] and Saá[14a,b] reported the formation of bicyclic cyclohexadienes from diynes and terminal alkenes using Ti and Ru catalysts, respectively. These cyclohexadiene skeletons are formed via double-bond migration (Scheme 1). There are some reports on intramolecular cycloaddition of diynes and terminal alkenes for preparing bicylic cyclohexadienes without double-bond migration. For example, Ni-catalyzed reaction of diynes and α,β-enones[12a] and Ti-mediated reaction of diynes and homoallylic alcohols[1c] were reported. Therefore, to the best of our knowledge, there is no report of selective synthesis of bicyclic cyclohexadienes from intramolecular [2 + 2 + 2] cycloaddition between diynes and simple alkenes, such as aliphatic- and aromatic alkenes, without double-bond migration.

Scheme 1. Synthesis of Bicyclic Hexadiene Derivatives from Diynes and Terminal Alkenes



In this paper, we report the intramolecular [2 + 2 + 2] cycloaddition of diynes and simple alkenes catalyzed by low-valent Nb species formed from NbCl$_5$/Zn/tricyclohexylphosphine (PCy$_3$) to give bicyclic cyclohexadienes in high yields and with high selectivities, without C═C bond migration (Scheme 1). In this reaction, the phosphine ligand significantly affects the cycloaddition. Ti−phosphine catalysts have been used in organic synthesis,[15] but this is the first reported example of the use of a Nb−phosphine catalyst in organic synthesis.

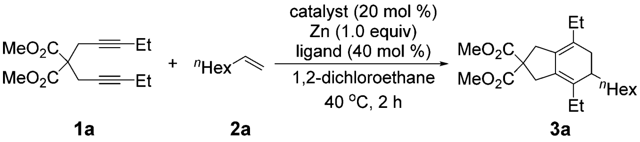
Initially, dimethyl 2,2-di(pent-2-ynyl)malonate (**1a**) and 1-octene (**2a**) were used as model substrates for optimization of

Received: August 28, 2017

DOI: 10.1021/acs.orglett.7b02672
Org. Lett. XXXX, XXX, XXX−XXX

the cycloaddition reaction conditions; the results are shown in Table 1. We investigated various phosphine ligands. When **1a** (0.5 mmol) was reacted with **2a** (3 mmol) in the presence of $NbCl_5$ (0.2 mmol), Zn (0.5 mmol), and PCy_3 (0.2 mmol) in 1,2-dichloroethane (2 mL) at 40 °C for 2 h, the reaction provided bicyclic cyclohexadiene **3a** in 82% yield (entry 1). It is noteworthy that side products, such as cyclotrimerization products of alkynes, in the aromatization of **3a** are not obtained. Takai and co-workers reported that $NbCl_5$/Zn catalysis is effective for generating low-valent Nb species in situ.[2c] We therefore used $NbCl_5$ and Zn in this reaction; however, **3a** was not obtained, and none of the diyne was converted (entry 2).

Table 1. $NbCl_5$/Zn/PCy_3-Catalyzed Reaction of Diyne 1a with 1-Octene (2a) under Various Conditions[a]



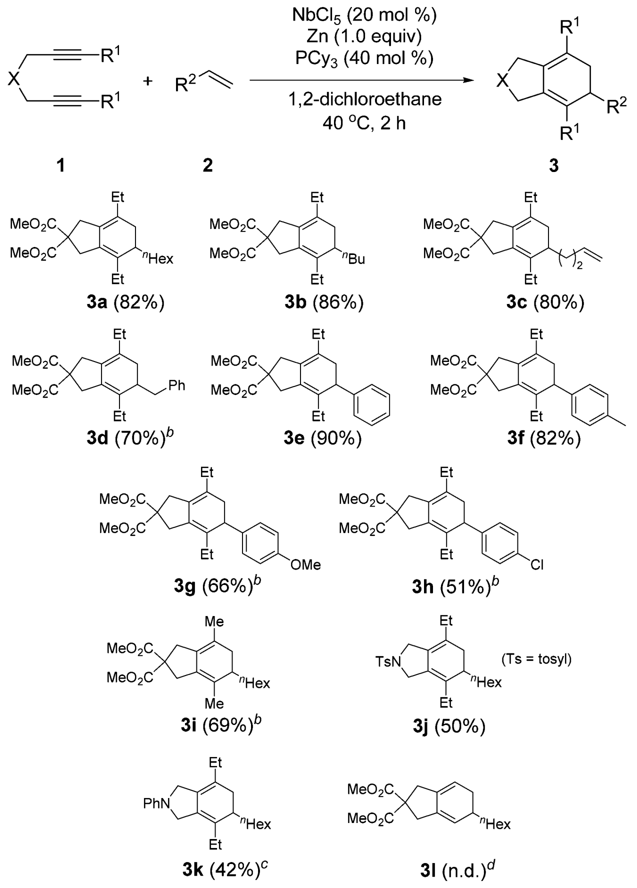
entry	catalyst	ligand[b]	yield of 3a[c] (%)
1	$NbCl_5$	PCy_3	83 (82, 84[d])
2	$NbCl_5$	none	nd[e]
3	$NbCl_5$	PPh_3	24
4	$NbCl_5$	$P(Oct)_3$	nd[e]
5	$NbCl_5$	dppe	3
6[f]	$NbCl_5$	PCy_3	nd[e]
7[g]	$NbCl_5$	PCy_3	40
8[h]	$NbCl_5$	PCy_3	46
9[i]	$NbCl_5$	PCy_3	71
10[j]	$NbCl_5$	PCy_3	73
11[k]	$NbCl_5$	PCy_3	9
12	$NbCl_3$(DME)	PCy_3	nd[e]
13	$TaCl_5$	PCy_3	nd[e]
14	$ZrCl_4$	PCy_3	nd[e]

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (3.0 mmol), catalyst (0.1 mmol, 20 mol %), Zn (0.5 mmol), and ligand (0.6 mmol) in 1,2-dichloroethane (2 mL) at 40 °C for 2 h under Ar. [b] Cone angle (deg): PCy_3 (170), PPh_3 (132); see ref 16. [c] Yields were determined by GC based on **1a** used. GC yields, except the value in parentheses. The numbers in parentheses show isolated yields. [d] Isolated yield from larger scale reaction (**1a**: 1.0 mmol). [e] Not detected by GC. [f] Without Zn. [g] Zn (0.25 mmol) was used. [h] **2a** (0.5 mmol) was used. [i] **2a** (1.0 mmol) was used. [j] **2a** (2.0 mmol) was used. [k] $NbCl_5$ (0.05 mmol), Zn (0.25 mmol), and PCy_3 (0.1 mmol) were used.

We then investigated the effects of other phosphine ligands, namely PPh_3, $P(n\text{-}Oct)_3$, and 1,2-bis(diphenylphosphino)ethane (dppe) (compare entries 1 and 3–5). When PCy_3 was used for the cycloaddition, the reaction proceeded quantitatively. Other phosphine ligands were not efficient in the reaction. These ligand-screening results imply that the cone angle[16] affects stabilization of the low-valent Nb species and the reactivity of the cycloaddition. Recently, we found that $NbCl_5$/Zn/$Ph_2Si(OMe)_2$ catalyzes the cycloaddition of alkynes and nitriles to give pyridines.[9b] However, $Ph_2Si(OMe)_2$ was used instead of PCy_3 in the reaction, and a complex mixture of isomers was obtained. When the reaction was performed without Zn, the cycloaddition did not proceed (entry 6). This shows that Zn is necessary to activate the catalyst. Compounds **1a** and **2a** reacted in a 1:1 stoichiometric ratio to give the product in moderate yield (entry 8). When a **2a**:**1a** stoichiometric ratio of 2:1 and 4:1 was used, **3a** was obtained in good yields (71% and 73%, respectively, entries 9–10). The product yield was poor when the catalyst loading was 10 mol % (entry 11). The substrate was not converted when other early transition-metal compounds, i.e., $NbCl_3$(DME), $TaCl_5$, and $ZrCl_4$, were used (entries 12–14).

The reactions of various alkenes **2** under the optimum conditions, shown in Table 1, entry 1, were investigated (Scheme 2, **3a**–**h**). Alkyne **1a** was reacted with various aliphatic alkenes (**2a**–**d**) using the optimum catalytic system (Scheme 2, **3a**–**d**).

Scheme 2. $NbCl_5$/Zn/PCy_3-Catalyzed Cycloadditions of Diynes 1 and Alkenes 2[a]



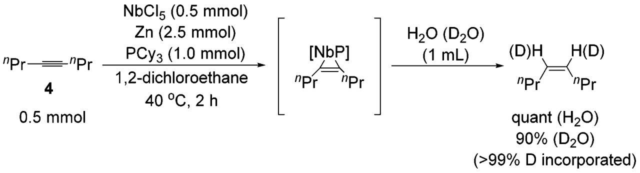
[a] Reaction conditions: see optimum conditions (Table 1, entry 1). [b] Reaction temperature was 60 °C. [c] $P(o\text{-tolyl})_3$ was used as ligand. [d] Not detected by GC.

The 1-alkene 1-hexene (**2b**), *α*,*ω*-diene 1,5-hexadiene (**2c**), and an aliphatic alkene bearing a benzene ring, i.e., allylbenzene (**2d**), gave the corresponding bicyclic cyclohexadienes **3b**–**d** in 70–86% yields, with excellent chemo- and regioselectivities. Various styrene derivatives (**2e**–**h**) were tolerated in the cycloaddition. Styrene (**2e**) and *p*-methylstyrene (**2f**) provided the desired products **3e** and **3f** in excellent yields. When styrene derivatives with functional groups, e.g., *p*-methoxystyrene (**2g**) and *p*-chlorostyrene (**2h**), were used in the reaction, the bicyclic hexadienes **3g** and **3h** were obtained in 66% and 51% yields, respectively. Internal alkenes, e.g., *cis*-4-octene and cyclohexene, did not give any cycloadducts.

We next investigated the scope of the reaction using various diynes (Scheme 2, **3i**–**l**). When an ethyl group on the alkyne skeleton was changed to a methyl group [**1b**, dimethyl 2,2-di(but-2-ynyl)malonate], the reaction afforded the corresponding product **3i** in 69% yield. Similarly, the sulfonamide- and aniline-substituted diynes **1c** and **1d**, respectively, reacted with **1a** to provide the desired products **3j** and **3k** in moderate yields. However, in the reaction of an α,ω-diyne [**1e**, dimethyl 2,2-di(prop-2-ynyl)malonate] with **2a** under the standard conditions, the desired product was not obtained and the diyne was converted to intractable oligomeric products. We have recently reported that the $NbCl_5$/Zn/alkoxysilane system indicated high catalytic activity to intermolecular cycloaddition of *tert*-butylacetylene and benzonitrile to afford pyridine derivatives.[9b] However, the reaction was sluggish, and no catalytic activity was observed by using the present $NbCl_5$/Zn/PCy_3 system under these conditions.

In previous studies, the low-valent Nb complex $NbCl_3$(DME) reacted with internal alkynes to give *cis*-alkenes by hydrolysis via a Nb−alkyne complex.[2a,b,3,4] We therefore examined the stoichiometric reaction of $NbCl_5$, Zn, and PCy_3 with 4-octyne (**4**) (0.5 mmol); *cis*-4-octene was obtained by hydrolysis or deuteriolysis.[9c] This result suggests that $NbCl_5$, Zn, and PCy_3 efficiently generated low-valent Nb species in situ (Scheme 3).

Scheme 3. Hydrolysis/Deuteriolysis of Low-Valent Niobium Complex Generated from $NbCl_5$/Zn/PCy_3 and 4-Octyne (4)



In addition, we observed the presence of PCy_3 coordinated to a low-valent Nb−alkyne (**4**) complex using ^{13}C and ^{31}P NMR spectroscopies. The alkyne carbon peaks of the Nb−alkyne complexes were observed at 239.7 and 229.5 ppm in the ^{13}C NMR spectrum along with the peaks at 251.2 ppm which were assignable to the $NbCl_3$−alkyne complex reported by our group (lit.[9c] 250.9 ppm) (Figure S1). In addition, the ^{31}P NMR spectrum showed peaks at around the range of 30 ppm, which are comparable to the peaks reported for the phosphine-ligated Nb species,[17] along with other unassignable peaks (Figure S2). These results imply that a bulky phosphine ligand such as PCy_3 stabilizes and activates the low-valent Nb species in the synthesis of bicyclic cyclohexadienes. However, we could not determine the full structure of the expected phosphine-ligated niobium complexes.

A possible reaction pathway is as follows: the initial step is generation of a low-valent Nb species from $NbCl_5$, in which Zn[18] acts as a reductant. This active low-valent Nb species can also be stabilized by PCy_3.[17] The oxidative cycloaddition of diynes to low-valent [Nb] then takes place and forms the niobacyclopentadiene intermediate **A**.[18a,19] Niobacyclopentadiene **A** undergoes a Diels−Alder-type alkene insertion to give niobanorbornene intermediate **B**. Lastly, bicyclic cyclohexadiene **3** is formed by reductive fragmentation of low-valent Nb (Figure S3). All attempts to isolate and characterize the niobium intermediates in the catalytic cycle were unsuccessful.

In conclusion, we have developed a low-valent-Nb-catalyzed [2 + 2 + 2] intramolecular cycloaddition reaction between diynes and simple alkenes to give bicyclic cyclohexadiene derivatives. A phosphine ligand is critical in promoting the intramolecular cycloaddition. This is the first example of the transition-metal-catalyzed synthesis of bicyclic cyclohexadienes from the reaction of various diynes with terminal alkenes without double-bond migration. Further investigations regarding the scope and application of this reaction are underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b02672.

Experimental procedures and compound characterization (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: obora@kansai-u.ac.jp.

ORCID

Yasushi Obora: 0000-0003-3702-9969

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported partly by JSPS KAKENHI Grant No. 16K05784. High-resolution mass spectra were performed at the Global Facility Center, Hokkaido University.

■ REFERENCES

(1) (a) Sato, F.; Urabe, H.; Okamoto, S. *Chem. Rev.* **2000**, *100*, 2835. (b) Takahashi, T.; Xi, Z.; Yamazaki, A.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1998**, *120*, 1672. (c) Sung, M. J.; Pang, J. H.; Park, S. B.; Cha, J. K. *Org. Lett.* **2003**, *5*, 2137. (d) Rassadin, V. A.; Nicolas, E.; Six, Y. *Chem. Commun.* **2014**, *50*, 7666. (e) Takahashi, T.; Tsai, F. Y.; Li, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1999**, *121*, 11093. (f) Ren, S.; Igarashi, E.; Nakajima, K.; Kanno, K.; Takahashi, T. *J. Am. Chem. Soc.* **2009**, *131*, 7492. (g) Dumond, Y. R.; Negishi, E. *Tetrahedron* **2004**, *60*, 1345. (h) Takahashi, T.; Liu, Y.; Iesato, A.; Chaki, S.; Nakajima, K.; Kanno, K. *J. Am. Chem. Soc.* **2005**, *127*, 11928. (i) Satoh, Y.; Yasuda, K.; Obora, Y. *Organometallics* **2012**, *31*, 5235. (j) Yasuda, K.; Obora, Y. *J. Organomet. Chem.* **2015**, *775*, 33. (k) Ferrand, L.; Tang, Y.; Aubert, C.; Fensterbank, L.; Mouriès-Mansuy, V.; Petit, M.; Amatore, M. *Org. Lett.* **2017**, *19*, 2062. (l) Sato, F.; Okamoto, S. *Adv. Synth. Catal.* **2001**, *343*, 759 and references cited therein.

(2) (a) Roskamp, E. J.; Pedersen, S. F. *J. Am. Chem. Soc.* **1987**, *109*, 6551. (b) Hartung, J. B., Jr.; Pedersen, S. F. *J. Am. Chem. Soc.* **1989**, *111*, 5468. (c) Kataoka, Y.; Miyai, J.; Oshima, K.; Takai, K.; Utimoto, K. *J. Org. Chem.* **1992**, *57*, 1973 and references cited therein.

(3) Obora, Y.; Kimura, M.; Tokunaga, M.; Tsuji, Y. *Chem. Commun.* **2005**, 901.

(4) Obora, Y.; Kimura, M.; Ohtake, T.; Tokunaga, M.; Tsuji, Y. *Organometallics* **2006**, *25*, 2097.

(5) Selected examples of early transition-metal-catalyzed [2 + 2 + 2] cycloaddition: (a) Johnson, E. S.; Balaich, G. J.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 7685. (b) Du Plessis, J. A. K.; Viljoen, J. S.; Du Toit, C. J. *J. Mol. Catal.* **1991**, *64*, 269. (c) Simon, C.; Amatore, M.; Aubert, C.; Petit, M. *Org. Lett.* **2015**, *17*, 844.

(6) Selected examples of reductive coupling reactions: (a) Diéguez, H. R.; López, A.; Domingo, V.; Arteaga, J. F.; Dobado, J. A.; Herrador, M. M.; Moral, J. F. Q.; Barrero, A. F. *J. Am. Chem. Soc.* **2010**, *132*, 254. (b) Feurer, M.; Frey, G.; Luu, H. T.; Kratzert, D.; Streuff, J. *Chem.*

Commun. **2014**, *50*, 5370. (c) Frey, G.; Hausmann, J. N.; Streuff, J. *Chem. - Eur. J.* **2015**, *21*, 5693.

(7) Selected examples of early transition-metal-catalyzed C−H activations: (a) Tsurugi, H.; Yamamoto, K.; Nagae, H.; Kaneko, H.; Mashima, K. *Dalton. Trans.* **2014**, *43*, 2331. (b) Fuchibe, K.; Akiyama, T. *J. Am. Chem. Soc.* **2006**, *128*, 1434.

(8) Examples of Nb-catalyzed [2 + 2 + 2] cycloaddition to form cyclohexadienes: (a) Obora, Y.; Takeshita, K.; Ishii, Y. *Org. Biomol. Chem.* **2009**, *7*, 428. (b) Obora, Y.; Satoh, Y.; Ishii, Y. *J. Org. Chem.* **2010**, *75*, 6046. (c) Satoh, Y.; Obora, Y. *Org. Lett.* **2011**, *13*, 2568. (d) Satoh, Y.; Obora, Y. *J. Org. Chem.* **2011**, *76*, 8569. (e) Kamei, M.; Watanabe, K.; Fuji, M.; Obora, Y. *Chem. Lett.* **2016**, *45*, 943.

(9) Selected examples of Nb-catalyzed [2 + 2 + 2] cycloaddition: (a) Satoh, Y.; Obora, Y. *Eur. J. Org. Chem.* **2015**, *2015*, 5041. (b) Satoh, Y.; Obora, Y. *J. Org. Chem.* **2013**, *78*, 7771. (c) Ozaki, M.; Obora, Y.; Tada, Y.; Ishii, Y. *J. Organomet. Chem.* **2013**, *741−742*, 109.

(10) Selected examples of transition-metal-catalyzed intermolecular [2 + 2 + 2] cycloaddition to form cyclohexadienes: (a) Hilt, G.; Paul, A.; Harms, K. *J. Org. Chem.* **2008**, *73*, 5187. (b) Hara, J.; Ishida, M.; Kobayashi, M.; Noguchi, K.; Tanaka, K. *Angew. Chem., Int. Ed.* **2014**, *53*, 2956. (c) Ikeda, S.; Kondo, H.; Arii, T.; Odashima, K. *Chem. Commun.* **2002**, 2422. (d) Yoshida, T.; Tajima, Y.; Kobayashi, M.; Masutomi, K.; Noguchi, K.; Tanaka, K. *Angew. Chem., Int. Ed.* **2015**, *54*, 8241.

(11) Selected examples of transition-metal-catalyzed [2 + 2 + 2] cycloaddition reviews: (a) Chopade, P. R.; Louie, J. *Adv. Synth. Catal.* **2006**, *348*, 2307. (b) Domínguez, G.; Castells, J. P. *Chem. Soc. Rev.* **2011**, *40*, 3430. (c) Amatore, M.; Aubert, C. *Eur. J. Org. Chem.* **2015**, *2015*, 265. (d) Shibata, T.; Tsuchikama, K. *Org. Biomol. Chem.* **2008**, *6*, 1317. (e) Domínguez, G.; Pérez-Castells, J. In *Comprehensive Organic Synthesis II*; Knochel, P., Molander, G. A., Eds.; Elsevier: Amsterdam, 2014; Vol. 5, pp 1537−1581. (f) Domínguez, G.; Pérez-Castells, J. *Chem. - Eur. J.* **2016**, *22*, 6720.

(12) (a) Ikeda, S.; Watanabe, H.; Sato, Y. *J. Org. Chem.* **1998**, *63*, 7026. (b) Kezuka, S.; Tanaka, S.; Ohe, T.; Nakaya, Y.; Takeuchi, R. *J. Org. Chem.* **2006**, *71*, 543. (c) Aida, Y.; Tooriyama, S.; Kimura, Y.; Hara, H.; Shibata, Y.; Tanaka, K. *Eur. J. Org. Chem.* **2016**, *2016*, 132.

(13) (a) Evans, P. A.; Sawyer, J. R.; Inglesby, P. A. *Angew. Chem., Int. Ed.* **2010**, *49*, 5746. (b) Ventre, S.; Simon, C.; Rekhroukh, F.; Malacria, M.; Amatore, M.; Aubert, C.; Petit, M. *Chem. - Eur. J.* **2013**, *19*, 5830. (c) Evans, P. A.; Sawyer, J. R.; Lai, K. W.; Huffman, J. C. *Chem. Commun.* **2005**, 3971. (d) Shibata, T.; Otomo, M.; Tahara, Y.; Endo, K. *Org. Biomol. Chem.* **2008**, *6*, 4296. (e) Evans, P. A.; Lai, K. W.; Sawyer, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 12466. (f) Kezuka, S.; Okado, T.; Niou, E.; Takeuchi, R. *Org. Lett.* **2005**, *7*, 1711. (g) Shibata, T.; Arai, Y.; Tahara, Y. *Org. Lett.* **2005**, *7*, 4955. (h) Dachs, A.; Roglans, A.; Solà, M. *Organometallics* **2011**, *30*, 3151.

(14) (a) Varela, J. A.; Rubín, S. G.; González-Rodríguez, C.; Castedo, L.; Saá, C. *J. Am. Chem. Soc.* **2006**, *128*, 9262. (b) Garcia-Rubín, S.; Varela, J. A.; Castedo, L.; Saá, C. *Chem. - Eur. J.* **2008**, *14*, 9772. (c) Wu, M. S.; Rayabarapu, D. K.; Cheng, C. H. *Tetrahedron* **2004**, *60*, 10005. (d) Yamamoto, Y.; Kitahara, H.; Ogawa, R.; Itoh, K. *J. Org. Chem.* **1998**, *63*, 9610. (e) Yamamoto, Y.; Kitahara, H.; Ogawa, R.; Kawaguchi, H.; Tatsumi, K.; Itoh, K. *J. Am. Chem. Soc.* **2000**, *122*, 4310.

(15) (a) Gianino, J. B.; Ashfeld, B. L. *J. Am. Chem. Soc.* **2012**, *134*, 18217. (b) Fleury, L. M.; Kosal, A. D.; Masters, J. T.; Ashfeld, B. L. *J. Org. Chem.* **2013**, *78*, 253. (c) Lepore, A. J.; Pinkerton, D. M.; Ashfeld, B. L. *Adv. Synth. Catal.* **2013**, *355*, 1500. (d) Campos, C. A.; Gianino, J. B.; Ashfeld, B. L. *Org. Lett.* **2013**, *15*, 2656. (e) Gianino, J. B.; Campos, C. A.; Lepore, A. J.; Pinkerton, D. M.; Ashfeld, B. L. *J. Org. Chem.* **2014**, *79*, 12083.

(16) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(17) Morancais, J. L.; Hubert-Pfalzgraf, L. G. *Transition Met. Chem.* **1984**, *9*, 130.

(18) (a) Kataoka, Y.; Miyai, J.; Oshima, K.; Takai, K.; Utimoto, K. *J. Org. Chem.* **1992**, *57*, 1973. (b) Oh, K.; Knabe, W. E. *Tetrahedron* **2009**, *65*, 2966. (c) Arai, S.; Takita, S.; Nishida, A. *Eur. J. Org. Chem.* **2005**, *2005*, 5262.

(19) Oshiki, T.; Nomoto, H.; Tanaka, K.; Takai, K. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1009 and references cited therein.