Generation of Active Ruthenium Catalysts for Hydroarylation of C–C Multiple Bonds from Isolated Ru(IV)=O Species Supported on CeO_2

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Abstract

This paper reports that the treatment of Ru/CeO_2 with PPh_3 and HCHO in 2-methoxyalcohol was an efficient way to generate the catalytically active Ru species for hydroarylation of C-C multiple bonds. A variety of alkenes was applicable toward the title reactions. The solid Ru/CeO_2 could be recycled for several times.

Keywords: Ruthenium | Hydroarylation | Solid catalyst

1. Introduction

From the perspective of sustainable chemistry, the development of greener and environmentally-benign catalytic processes for the synthesis of organic molecules has attracted considerable attention in the 21st century.[1] The use of supported metal catalysts is promising for decreasing environmental load because of simple preparation, high stability and facile recyclability, as well as minimal contamination of the products by metallic species.[2] However, highly selective organic transformation with supported catalysts is still a challenge, since the electronic and steric control of active metal species on the surface of the solid support is much more difficult than with homogeneous complex catalysts. Against this background, in our previous studies, the properties of Ru/CeO_2 catalysts toward organic syntheses and the fine structure of Ru species on CeO_2 have been investigated.[3a–3c] The specific feature of Ru/CeO_2 is the formation of Ru(IV)-oxo species on the surface of CeO_2, and the Ru(IV)-oxo species could be transformed into low-valent Ru species, which showed high activities for various types of organic transformations.[3] In contrast, other Ru catalysts supported on SiO_2, Al_2O_3, TiO_2 or MgO did not show any activities for the reactions due to the absence of Ru(IV)-oxo species on the metal oxides. These results indicate that different types of active Ru species could be generated from Ru(IV)-oxo species on CeO_2 through the appropriate choice of additives or pretreatment conditions. On the other hand, transition metal-catalyzed C–C bond-forming reactions that involve the cleavage and subsequent transformation of less-reactive C–H bonds are central issues in modern synthetic chemistry.[4] In particular, the direct addition of aromatic C–H bonds to carbon–carbon multiple bonds (hydroarylation) is one of the most straightforward and atom-efficient methods for the synthesis of alkylated or alkenylated arenes.[5] Since the pioneering works with homogeneous Ru complexes by Murai, Kakiuchi, et al.,[6] various effective transition-metal-catalyzed hydroarylations of unsaturated molecules have been developed.[7] As described in our previous reports, Ru/CeO_2 that have been pretreated under a hydrogen atmosphere in the presence of PPh_3 (PPh_3-modified Ru/CeO_2) showed excellent catalytic activities for the addition of aromatic C–H bonds to alkoxyvinylsilanes[3b] as well as the direct arylation of aromatic C–H bonds with aryl chlorides.[3c] However, in our previous catalytic system for hydroarylation, recycling of the catalysts was unfeasible due to the irreversible deposition of siliceous residues derived from vinylsilanes on surface Ru species. Moreover, the catalytic system could not be applied to the reaction of unsaturated compounds other than alkoxyvinylsilanes.[3c]

In this paper, we describe the transformation of Ru(IV)-oxo species on CeO_2 to active Ru catalysts for the hydroarylation of unsaturated compounds. This catalytic system showed much higher efficiency than our previous PPh_3-modified Ru/CeO_2 catalysts, and a variety of unsaturated compounds could be used. Furthermore, the solid Ru catalysts could be easily recycled and used several times without a significant loss of activity.

2. Experimental

2.1 Materials and Methods. All manipulations were performed under an argon atmosphere using standard Schlenk techniques. Ruthenium(III) acetylacetonate (Aldrich), all of the aromatic ketones, alkenes and alkynes (TCI) and potassium hydroxide, cerium(III) nitrate hexahydrate, tetrahydrofuran (THF; Wako) were obtained commercially and used without further purification. Ceria was prepared by treating a solution of cerium(III) nitrate hexahydrate (12.6 g, 29 mmol) in 400 mL of deionized water with 40 mL of 3M KOH aqueous solution with stirring for 1 h at room temperature. The resulting precipitates were collected by centrifugation and then dried overnight at 80 °C. The product was heated in a box furnace at a rate of 10 °C min^{-1} and maintained at 400 °C for 30 min to afford ceria in an excellent ceramic yield. Zirconium oxide and magnesium oxide were prepared from zirconium(IV) dinitrate oxide and magnesium nitrate by a method similar to that used to obtain ceria. Titania (JRC-TIO-4), γ-alumina (JRC-ALO-8) and silica (Cabosil) were used as received.

2.2 Physical and Analytical Measurements. The products of catalytic runs were analyzed by GC-MS (Shimadzu GC-MS Parvum 2, Zebron ZB-1 capillary column, i.d. 0.25 mm, length 30 m, at 50–250 °C) and gas chromatography (GL Sciences GC353, Inertcap 17 capillary column, i.d. 0.25 mm, length 30 m at 50–250 °C). NMR spectra were recorded on a JEOL JNM-EX-400 (FT, 400 MHz (^1H), 100 MHz (^{13}C)) instrument. Chemical shifts (δ) are referenced to $SiMe_4$.

The oxide catalysts were analyzed by FT-IR and XAFS. Diffuse reflectance IR spectra were recorded using a Nicolet Magna-IR 560 FT-IR spectrometer with DRIFT optical configuration. Ru K-edge XAFS measurements were performed at BL01B1 beam line at SPring-8 operated at 8 GeV using a Si(311) two-crystal monochromator. XAFS spectra were taken at room temperature. XANES and EXAFS were analyzed using the REX2000 version 2.5 program (Rigaku). Leaching of ruthenium species from the catalysts during the reaction was investigated by ICP atomic emission spectroscopic analysis by using a Shimadzu ICPS-1000III analyzer.

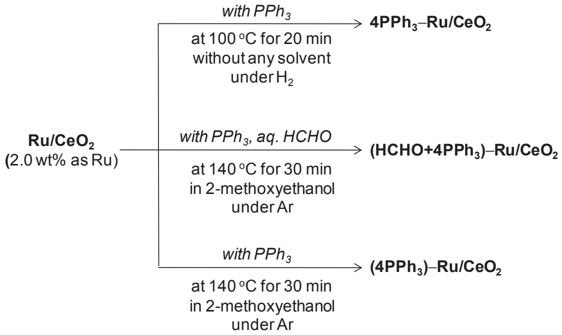
2.3 A typical Method for the Preparation of Ru/Support Catalysts. Supported catalysts were prepared by the impregnation method. 1.0 g of a support was added to a solution of $Ru(acac)_3$ (79.5 mg, 0.20 mmol) in 10 mL of THF in air at room temperature. After impregnation, the resulting powder was calcined in air for 30 min to afford the Ru(2.0 wt%)/Support catalyst.

2.4 Preparation of $4PPh_3$–Ru/CeO_2. Ru/CeO_2 (125 mg, 0.025 mmol as Ru) was stirred in the presence of PPh_3 (26.3 mg, 0.10 mmol) at 100 °C under a hydrogen atmosphere (1 bar) on a hot stirrer with a cooling block for 20 min to give $4PPh_3$–Ru/CeO_2.

2.5 Preparation of $(HCHO+4PPh_3)$–Ru/CeO_2 Catalyst. Ru/CeO_2 (125 mg, 0.025 mmol as Ru) was stirred in the presence of PPh_3 (26.3 mg, 0.10 mmol) and 36% aq. HCHO (0.25 mL) in 2-methoxyethanol (2 mL) at 140 °C under an argon atmosphere on a hot stirrer with a cooling block for 30 min. The resulting solvents and HCHO were removed under reduced pressure at room temperature to give $(HCHO+4PPh_3)$–Ru/CeO_2. The treated catalyst was used for the catalytic reaction without exposure to open air.

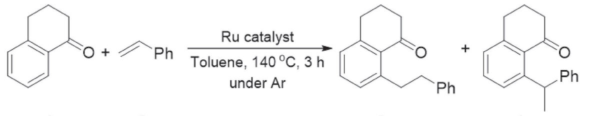
3. Results and Discussion

3.1 Addition of Aromatic C–H Bonds to Alkenes by Modified Ru/CeO_2 Catalysts. The methods for the preparation of supported Ru catalysts are summarized in Scheme 1. CeO_2-supported Ru catalysts (Ru/CeO_2) were prepared by impregnation of a solution of $Ru(acac)_3$, followed by calcination in air at 400 °C for 30 min. The Ru/CeO_2 catalyst was then heated at 100 °C for 20 min under a hydrogen atmosphere (1 atm) without any solvent in the presence of PPh_3 (4 molar equivalents to Ru) to give a phosphine-modified Ru/CeO_2 catalyst ($4PPh_3$–Ru/CeO_2). On the other hand, Ru/CeO_2 catalysts were treated in 2-methoxyethanol in the presence of PPh_3 with



Scheme 1. Method for the preparation of supported Ru catalysts.

Table 1. Hydroarylation of styrene in the presence of supported Ru catalysts[a]

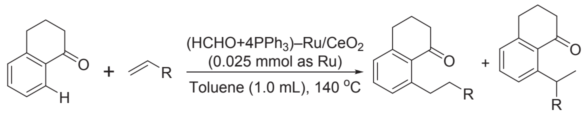


1a **2a** **3aa** **4aa**

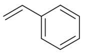
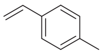
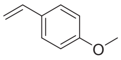
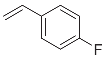
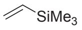
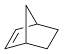
Entry	Ru catalyst	Additive	Total yield of **3aa** and **4aa**(%)[b]	Selectivity (**3aa** : **4aa**)[c]
1	Ru/CeO$_2$	PPh$_3$[d]	0	-
2	4PPh$_3$–Ru/CeO$_2$	-	0	-
3	(HCHO+4PPh$_3$)–Ru/CeO$_2$	-	85	75 : 25
4	(4PPh$_3$)–Ru/CeO$_2$	-	0	-
5	Ru/CeO$_2$	PPh$_3$[d] aq. HCHO[e]	0	-

[a] *Reaction conditions*: **1a** (1.0 mmol), **2a** (3.0 mmol), toluene (2.0 mL), Ru catalyst (0.050 mmol as Ru), at 140 °C for 3 h under Ar. [b] Total yield of **3aa** and **4aa** after silica gel chromatography. [c] Molar ratio of isomers determined by ^{1}H NMR. [d] 0.20 mmol of PPh$_3$ was added. [e] 0.50 mL of aq. HCHO was added.

Table 2. Hydroarylation of alkenes catalyzed by (HCHO+4PPh$_3$)–Ru/CeO$_2$[a]

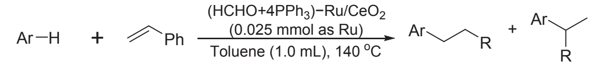


1a (0.50 mmol) **2** (1.5 mmol) **3** **4**

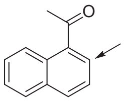
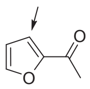
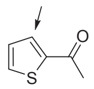
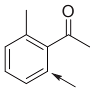
 **3aa**, **4aa** 85% (75 : 25) 3 h	 **3ab**, **4ab** 90% (75 : 25) 3 h	 **3ac**, **4ac** 99% (74 : 26) 4 h	 **3ad**, **4ad** 94% (70 : 30) 4 h
 **3ae** 99% (100 : 0) 0.5 h	 **3af** 99% (100 : 0) 3 h	 **3ag** 74% (100 : 0) 24 h	 **3ah** 78%, 6 h

[a] Molar ratio of **3** : **4** are shown in parentheses.

Table 3. Addition of aromatic compounds to styrene by (HCHO+4PPh$_3$)–Ru/CeO$_2$ catalysts.[a]



1 (0.50 mmol) **2a** (1.5 mmol) **3** **4**

 **3ba**, **4ba** 99% (25 : 75) 3 h	 **3ca**, **4ca** 75% (75 : 25) 6 h	 **3da**, **4da** 98% (75 : 25) 3 h	 **3ea**, **4ea** 67% (77 : 23) 3 h

[a] Molar ratio of **3**: **4** are shown in parentheses.

or without formaldehyde (36% aqueous solution; aq. HCHO) at 140 °C for 30 min, followed by removal of the solvent under reduced pressure to afford (HCHO+4PPh$_3$)–Ru/CeO$_2$ or (4PPh$_3$)–Ru/CeO$_2$, respectively.

In our previous study, the irreversible deposition of siliceous residues derived from vinylsilanes on surface Ru species hampered recycling of the solid catalysts.[3c] Therefore, efforts were made to realize the addition of aromatic C–H bonds with simple unsaturated hydrocarbons. An attempt to add α-tetralone (**1a**) to styrene (**2a**) in the presence of Ru/CeO$_2$ and PPh$_3$ (4 equivalents to Ru) resulted in no formation of the desired adduct (Table 1, Entry 1). 4PPh$_3$–Ru/CeO$_2$ showed excellent activity for the addition to triethoxyvinylsilane,[3c] while no reaction of **2a** also take place (Entry 2). On the other hand, (HCHO+4PPh$_3$)–Ru/CeO$_2$ showed excellent activity to give alkylated aromatic ketones **3a** and **4a** in a yield of 85% as a mixture of regioisomers (linear:branch = 3:1) (Entry 3). In contrast, (4PPh$_3$)–Ru/CeO$_2$, which was treated in alcohol in the absence of HCHO, was not at all effective (Entry 4). The reaction did not occur with Ru/CeO$_2$ in the presence PPh$_3$ and aq. HCHO as external additives (Entry 5). These results indicated that pretreatment in 2-methoxyethanol with aq. HCHO is essential for the transformation of Ru(IV)-oxo species to active Ru catalysts for the hydroarylation of styrene. Other Ru catalysts supported on SiO$_2$, Al$_2$O$_3$, TiO$_2$ or MgO treated with PPh$_3$ and HCHO in 2-methoxyethanol gave no products at all. Note that the amount of Ru species leached into the solution after the reaction of **1a** with **2a** by (HCHO+4PPh$_3$)–Ru/CeO$_2$ catalyst was estimated to be 7.4% of the Ru species in the fresh catalyst.

(HCHO+4PPh$_3$)–Ru/CeO$_2$ showed high catalytic activity for the hydroarylation of a wide range of alkenes (Table 2). Styrene derivatives **2b–2d** efficiently coupled with **1a** to afford alkylated aromatic ketones in high yields. The linear selectivities of the products **3ab**, **3ac** and **3ad** were around 75%. The catalytic system also showed excellent activities in the reaction of **1a** with vinylsilanes. The reaction of triethoxyvinylsilane (**2e**) went to completion within 30 min, although the previous 4PPh$_3$–Ru/CeO$_2$ catalysts needed 90 min to finish the reaction.[3c] Furthermore, other vinylsilanes without an alkoxy substituent could be used in the present catalytic system and the products **3af** and **3ag** were obtained in excellent yields. Hydroarylation of 2-norbornene (**2h**) also occurred and led to the product in a high yield, whereas 1-hexene **2i** was not a good substrate under the present reaction conditions.

The scope of aromatic compounds that could be used in this catalytic system was also examined (Table 3). The addition of aromatic ketones **1b** and **1c** to **2a** took place in the presence of (HCHO+4PPh$_3$)–Ru/CeO$_2$. The reactions of heterocyclic ketones **1d** and **1e** gave the corresponding products **3da** and **3ea** in high yields. However, ester and cyano groups did not participate as an effective directing group for the C–H functionalization by the present catalytic system.

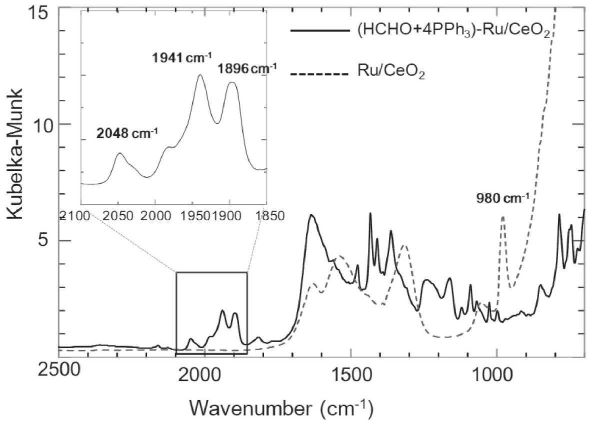


Figure 1. DRIFT spectrum of $(HCHO+4PPh_3)$–Ru/CeO_2.

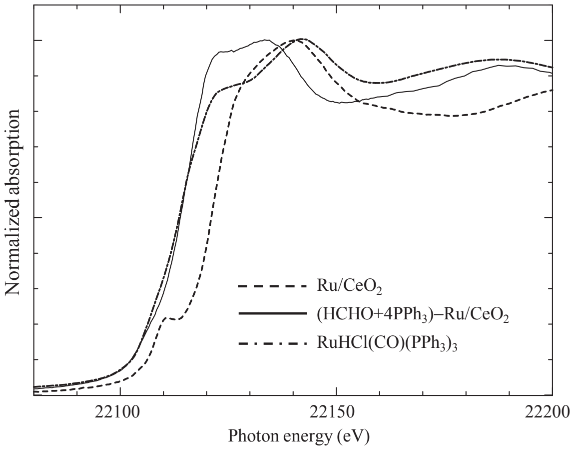
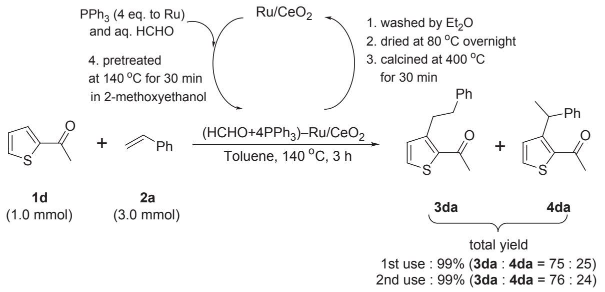


Figure 2. XANES spectra of Ru/CeO_2 before and after the treatment.

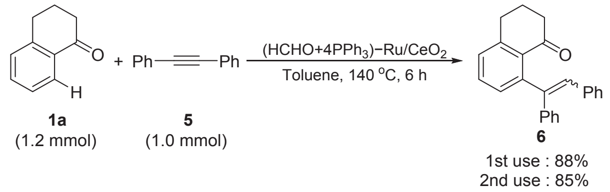
To elucidate the state of the active Ru species in the present catalytic system, $(HCHO+4PPh_3)$–Ru/CeO_2 was characterized by spectroscopic analyses. The diffuse reflectance infrared Fourier transform (DRIFT) spectrum of the Ru/CeO_2 catalyst after treatment with PPh_3 and aq. HCHO is shown in Figure 1. Whereas a peak due to a Ru=O bond was observed at 980 cm^{-1} in the spectrum of Ru/CeO_2 as described in our previous reports, this peak disappeared in the spectrum of $(HCHO+4PPh_3)$–Ru/CeO_2. On the other hand, small peaks that could be assigned to Ru-CO or Ru-H species were observed at around 1900–2050 cm^{-1}.

Figure 2 shows the X-ray absorption near-edge structure (XANES) spectra of Ru catalysts. The absorption-edge of the $(HCHO+4PPh_3)$–$RuCeO_2$ catalyst shifted to a lower energy than that of Ru/CeO_2 before treatment and was very close to that of a Ru(II) complex with PPh_3 and CO ligand, whereas the shape of the spectrum was significantly different. This result indicates that the treatment of Ru(IV)=O on CeO_2 with PPh_3 and HCHO in 2-methoxyethanol produced Ru(II) species.

A recent mechanistic investigation of the alkylation of aromatic C–H bonds with homogeneous Ru complex catalysts revealed the importance of a CO ligand coordinating active Ru(0) species.[7e] Hiraki et al. reported that the reaction of a low-valent Ru complex with alkoxyvinylsilanes produced Ru-CO species via the oxidative addition of Ru accompanying the cleavage of a Si-O bond of alkoxyvinylsilanes, followed by abstraction of β-hydride from the alkoxo ligand and decarbonylation of the resulting aldehyde.[8] In previous catalytic systems that used untreated Ru/CeO_2 together with PPh_3 or PPh_3–Ru/CeO_2 as catalysts, alkoxyvinylsilanes could act as a source of CO ligand, which might explain the absence of any activity for the reaction of alkenes except for alkoxyvinylsilanes. On the other hand, in the present catalytic system, treatment with PPh_3 and HCHO in alcohol is deduced to generate Ru(II) species coordinated by CO and PPh_3, which are transformed, at the initial stage of the reactions, to active Ru(0) species that are effective for the catalytic addition of aromatic C–H bonds to unsaturated carbon–carbon bonds.[7c]



Scheme 2. Recycling of Ru/CeO_2 catalysts.



Scheme 3. Hydroarylation of alkyne by $(HCHO+4PPh_3)$–Ru/CeO_2.

One major advantage of solid catalysts is their high recyclability. After the reaction, the present solid Ru catalyst was washed with diethyl ether, dried in air at 80 °C, and then calcined in air at 400 °C to be recovered as Ru/CeO_2. The thus-obtained solid was re-treated with PPh_3 and HCHO in 2-methoxyethanol to give the reproduced $(HCHO+4PPh_3)$–Ru/CeO_2 for the next catalytic run (Scheme 2).

With the recycled catalysts, the reaction of **1d** with **2a** successfully proceeded to give the corresponding products **3da** and **4da** in a high total yield. Unlike the reaction of vinylsilanes, the surface state of the original Ru/CeO_2 catalysts after the reaction of unsaturated hydrocarbons was restored by washing and re-calcination in air. Thus, the recycled catalysts showed high activities for hydroarylation without a significant loss of activity.

Multi-substituted alkenes are important organic molecules in material science. Hydroarylation of alkynes is the most atom-economical method for the synthesis of these compounds and a $(HCHO+4PPh_3)$–Ru/CeO_2 catalyst was found to be effective for the hydroarylation of alkyne (Scheme 3). The reaction of **1a** with diphenylacetylene (**5**) in the presence of a $(HCHO+4PPh_3)$–Ru/CeO_2 catalyst proceeded efficiently to give triaryl-substituted alkene **6** in 88% yield. Furthermore, the catalyst, recycled by the same method as described above, was also effective for the hydroarylation of alkyne **5** to afford **6** in a high yield.

4. Conclusion

In summary, a novel procedure for the generation of highly active and recyclable catalysts that are effective for the addition of aromatic C–H bonds to unsaturated compounds was described. The treatment of Ru(IV)-oxo species on CeO_2 with PPh_3 and HCHO in 2-methoxyethanol transformed them to active Ru species, which showed high activities for the hydroarylation of various alkenes and alkynes. The present catalytic system is very attractive from practical and environmental points of view because of its simple handling, high recyclability and low contamination of the products by metallic species.

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Supporting Information

This material is available on http://dx.doi.org/10.1246/bcsj.20180144.

References

1 For green chemistry, see: a) P. T. Anastas, J. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, New York, **1998**. b) R. A. Sheldon, R. S. Downing, *Appl. Catal., A* **1999**, *189*, 163. c) B. M. Trost, *Acc. Chem. Res.* **2002**, *35*, 695.

2 For representative reviews, see: a) See ref 1b. b) R. Schlögl, *Angew. Chem., Int. Ed.* **2015**, *54*, 3465. c) P. T. Anastas, D. T. Allen, *ACS Sustainable Chem. Eng.* **2016**, *4*, 5820.

3 a) H. Miura, K. Wada, S. Hosokawa, M. Sai, T. Kondo, M. Inoue, *Chem. Commun.* **2009**, 4112. b) H. Miura, K. Wada, S. Hosokawa, M. Inoue, *Chem.—Eur. J.* **2010**, *16*, 4186. c) H. Miura, K. Wada, S. Hosokawa, M. Inoue, *ChemCatChem* **2010**, *2*, 1223. d) M. Nishiumi, H. Miura, K. Wada, S. Hosokawa, M. Inoue, *Adv. Synth. Catal.* **2010**, *352*, 3045. e) H. Miura, S. Shimura, S. Hosokawa, S. Yamazoe, K. Wada, M. Inoue, *Adv. Synth. Catal.* **2011**, *353*, 2837. f) S. Shimura, H. Miura, K. Wada, S. Hosokawa, S. Yamazoe, M. Inoue, *Catal. Sci. Technol.* **2011**, *1*, 1340. g) M. Nishiumi, H. Miura, K. Wada, S. Hosokawa, M. Inoue, *ACS Catal.* **2012**, *2*, 1753. h) H. Miura, K. Wada, S. Hosokawa, M. Inoue, *Chem.—Eur. J.* **2013**, *19*, 861. i) K. Wada, H. Miura, S. Hosokawa, M. Inoue, *J. Jpn. Pet. Inst.* **2013**, *56*, 69. j) H. Miura, K. Tsutsui, K. Wada, T. Shishido, *Chem. Commun.* **2015**, *51*, 1654. k) H. Miura, K. Takeuchi, T. Shishido, *Angew. Chem., Int. Ed.* **2016**, *55*, 278.

4 For recent reviews of C–H functionalization, see: a) G. Dyker, *Angew. Chem., Int. Ed.* **1999**, *38*, 1698. b) V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731. c) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174. d) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624. e) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147. f) L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315. g) R. H. Crabtree, A. Lei, *Chem. Rev.* **2017**, *117*, 8481, and references cited therein.

5 a) G. Jia, T. Kitamura, Y. Fujiwara, *Acc. Chem. Res.* **2001**, *34*, 633. b) C. Nevado, A. M. Echavarren, *Synthesis* **2005**, 167. c) F. Kakiuchi, S. Murai, *Acc. Chem. Res.* **2002**, *35*, 826. d) D. J. Gorin, F. D. Toste, *Nature* **2007**, *446*, 395. e) F. Kakiuchi, T. Kochi, *Synthesis* **2008**, 3013.

6 a) S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani, *Nature* **1993**, *366*, 529. b) F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani, S. Murai, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 62.

7 a) R. Martinez, R. Chevalier, S. Darses, J.-P. Genet, *Angew. Chem., Int. Ed.* **2006**, *45*, 8232. b) R. Martinez, J.-P. Genet, S. Darses, *Chem. Commun.* **2008**, 3855. c) R. Martinez, M.-O. Simon, R. Chevalier, C. Pautigny, J.-P. Genet, S. Darses, *J. Am. Chem. Soc.* **2009**, *131*, 7887. d) M.-O. Simon, J.-P. Genet, S. Darses, *Org. Lett.* **2010**, *12*, 3038. e) F. Kakiuchi, T. Kochi, E. Mizushima, S. Murai, *J. Am. Chem. Soc.* **2010**, *132*, 17741. f) K. Gao, N. Yishikai, *Angew. Chem., Int. Ed.* **2011**, *50*, 6888.

8 K. Hiraki, T. Ishimoto, H. Kuwano, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2099.