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Ruthenium-Catalyzed Transformation of Aryl and Alkenyl Triflates to Halides

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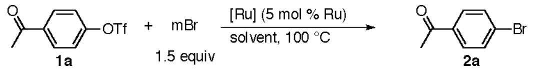
Supporting Information

ABSTRACT: Aryl triflates were transformed to aryl bromides/iodides simply by treating them with LiBr/NaI and [Cp*Ru(MeCN)$_3$]OTf. The ruthenium complex also catalyzed the transformation of alkenyl sulfonates and phosphates to alkenyl halides under mild conditions. Aryl and alkenyl triflates undergo oxidative addition to a ruthenium(II) complex to form η^1-arylruthenium and 1-ruthenacyclopropene intermediates, respectively, which are transformed to the corresponding halides.

Aryl halides are versatile substrates under transition-metal catalysis[1] and convenient precursors for arylmagnesium/lithium reagents[2] and aryl radicals.[3] Simple aryl halides are conventionally prepared by electrophilic aromatic substitution with halogens[4] or the Sandmeyer reaction[5] under relatively harsh conditions. For the synthesis of relatively complicated ones, a three-step scheme starting from phenols and consisting of trifluoromethanesulfonylation,[6] palladium-catalyzed stannylation/borylation, and halogenolysis has been widely used as a reliable method.[7−10] As a straightforward method, Buchwald and co-workers have recently developed a palladium-catalyzed direct transformation of aryl and alkenyl triflates to the corresponding bromides and chlorides.[11] However, it is not applicable to the synthesis of aryl iodides. On the other hand, we had already reported that low-valent ruthenium complexes generated, for example, from Ru(acac)$_3$ and EtMgBr catalyze the transformation of alkenyl triflates to halides, though aryl triflates are unreactive under the ruthenium catalysis.[12] Here we report that Cp*Ru (Cp* = $C_5Me_5^-$) complexes efficiently catalyze the transformation of aryl triflates to aryl bromides and iodides. The Cp*Ru complexes were found to be much more catalytically active than the low-valent ruthenium complexes in the transformation of alkenyl triflates to halides.

Treatment of 4-acetylphenyl triflate (**1a**) with [Cp*Ru(MeCN)$_3$]OTf (5 mol %) and LiBr (1.5 equiv) in 1,3-dimethyl-2-imidazolidinone (DMI) at 100 °C for 12 h gave a 98% yield of 4′-bromoacetophenone (**2a**) (Table 1, entry 1).[13] The reaction also proceeded in high yield in *N*-methyl-2-pyrrolidone (NMP) and *N*,*N*-dimethylformamide (DMF) (entries 2 and 3). In contrast, almost no reaction took place in 1,4-dioxane or dimethyl sulfoxide (DMSO) (entries 4 and 5). NaBr and Bu$_4$NBr also worked as bromide sources, whereas KBr was less effective (entries 6−8). The use of [(C$_5$Me$_4$CF$_3$)Ru(MeCN)$_3$]OTf as the catalyst, in which C$_5$Me$_4$CF$_3$ has steric and electronic effects similar to those of Cp* and Cp, respectively,[14] resulted in slow conversion (entry 9), indicating that strong electron-donating character of the Cp* ligand is crucial. [Cp*RuCl]$_4$ and [Cp*RuCl$_2$]$_2$ also catalyzed the bromination, though contamination with 4′-chloroacetophenone was observed (entries 10 and 11). The catalytic activities of the Cp*Ru complexes were compared using the yields of **2a** in a short reaction period (2 h) (entries 12−14). Moderate conversion was observed with [Cp*Ru(MeCN)$_3$]OTf or [Cp*RuCl]$_4$, whereas only a 5% yield of **2a** was produced with [Cp*RuCl$_2$]$_2$. It is likely that the catalytically active species is a Ru(II) complex and that reluctant reduction of Ru(III) to Ru(II) caused the induction period with [Cp*RuCl$_2$]$_2$.

Table 1. Ruthenium-Catalyzed Transformation of 4-Acetylphenyl Triflate to 4′-Bromoacetophenone[a]



entry	[Ru]	solvent	mBr	time (h)	yield (%)[b]
1	[Cp*Ru(MeCN)$_3$]OTf	DMI	LiBr	12	98
2	[Cp*Ru(MeCN)$_3$]OTf	NMP	LiBr	12	97
3	[Cp*Ru(MeCN)$_3$]OTf	DMF	LiBr	12	89
4	[Cp*Ru(MeCN)$_3$]OTf	DMSO	LiBr	12	0
5	[Cp*Ru(MeCN)$_3$]OTf	1,4-dioxane	LiBr	12	4
6	[Cp*Ru(MeCN)$_3$]OTf	DMI	NaBr	12	98
7	[Cp*Ru(MeCN)$_3$]OTf	DMI	Bu$_4$NBr	12	98
8	[Cp*Ru(MeCN)$_3$]OTf	DMI	KBr	12	56
9	[(C$_5$Me$_4$CF$_3$)Ru(MeCN)$_3$]PF$_6$	DMI	LiBr	12	36
10	[Cp*RuCl]$_4$	DMI	LiBr	12	96 (2)[c]
11	[Cp*RuCl$_2$]$_2$	DMI	LiBr	12	95 (1)[c]
12	[Cp*Ru(MeCN)$_3$]OTf	DMI	LiBr	2	74
13	[Cp*RuCl]$_4$	DMI	LiBr	2	48 (<1)[c]
14	[Cp*RuCl$_2$]$_2$	DMI	LiBr	2	5 (<1)[c]

[a] The reaction was carried out in a solvent (1.0 mL) under a nitrogen atmosphere using **1a** (0.25 mmol) and mBr (0.38 mmol) in the presence of a ruthenium complex (12.5 μmol of Ru). [b] Determined by ^{1}H NMR analysis. [c] The yield of 4′-chloroacetophenone is shown in parentheses.

A wide variety of aryl triflates were converted into the corresponding bromides under the conditions for entry 1 of Table 1. Phenyl triflates having an electron-withdrawing group such as acetyl, ethoxycarbonyl, nitro, or cyano at the para position reacted in high yields (Table 2, entries 1−4). Electron-rich aryl triflates were less reactive. The use of twice the amounts

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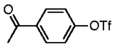
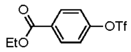
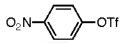
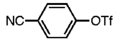
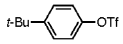
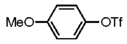
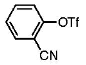
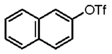
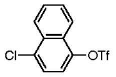
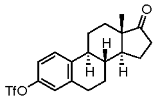
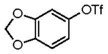
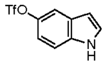
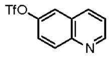
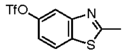
Table 2. Transformation of Aryl Triflates to Halides[a]

$$\underset{\mathbf{1}}{\mathrm{ArOTf}} + \underset{1.5\ \text{equiv}}{\mathrm{mX}} \xrightarrow[\text{DMI, 100 °C}]{[\mathrm{Cp^*Ru(MeCN)_3}]\mathrm{OTf}\ (5\ \text{mol}\ \%)} \underset{\mathbf{2}\ (\mathrm{X = Br})\ \text{or}\ \mathbf{3}\ (\mathrm{X = I})}{\mathrm{ArX}}$$

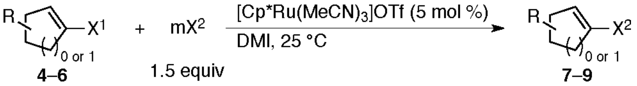
entry	ArOTf		mX	time (h)	yield (%)[b]	prod.
1		**1a**	LiBr	12	96	**2a**
2		**1b**	LiBr	12	97	**2b**
3		**1c**	LiBr	12	91	**2c**
4		**1d**	LiBr	12	92	**2d**
5[c,d,e]		**1e**	LiBr	48	87	**2e**
6[d,e]		**1f**	LiBr	24	70	**2f**
7		**1g**	LiBr	12	83	**2g**
8		**1h**	LiBr	6	91	**2h**
9		**1i**	LiBr	6	90	**2i**
10[c,f,g]		**1j**	LiBr	24	93	**2j**
11		**1k**	LiBr	12	94	**2k**
12[c,d]		**1l**	LiBr	24	88	**2l**
13[c,d,e]		**1m**	LiBr	24	91	**2m**
14		**1n**	LiBr	24	96	**2n**
15[c,e]	**1a**		NaI	12	95	**3a**
16[c,d,e]	**1g**		NaI	24	84	**3g**
17[c,e]	**1h**		NaI	3	94	**3h**
18[c,f,g]	**1e**		NaI	48	56	**3e**

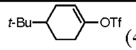
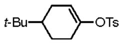
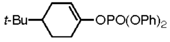
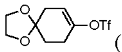
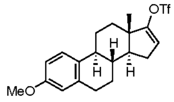
[a]The reaction was carried out in DMI (1.0 mL) at 100 °C under a nitrogen atmosphere using **1** (0.25 mmol) and mX (0.38 mmol) in the presence of [Cp*Ru(MeCN)$_3$]OTf (12.5 μmol). [b]Isolated yields. [c]At 120 °C. [d][Cp*Ru(MeCN)$_3$]OTf (25 μmol) was used. [e]mX (0.75 mmol) was used. [f][Cp*Ru(MeCN)$_3$]OTf (37.5 μmol) was used. [g]mX (1.5 mmol) was used.

of the ruthenium catalyst and LiBr was required to convert *tert*-butyl- and methoxy-substituted triflates to bromides within acceptable reaction periods (entries 5 and 6). *o*-Cyanophenyl triflate (**1g**) underwent the bromination (entry 7). Naphthyl triflates were readily transformed to naphthyl bromides (entries 8 and 9). Chloroarene, ketone, and acetal moieties remained intact (entries 9–11). Heteroaryl triflates were converted into bromides (entries 12–14). In contrast to the observation that the palladium catalysis does not afford aryl iodides,[11a,b] the ruthenium catalysis gave aryl iodides when NaI was used instead of LiBr (entries 15–18). Electron-rich aryl triflates also showed low reactivities for the iodination (entry 18).

Alkenyl triflates were transformed to halides much more smoothly than in our previous report.[12a] In the presence of [Cp*Ru(MeCN)$_3$]OTf (5 mol %), 4-*tert*-butylcyclohexen-1-yl triflate (**4a**) was transformed to bromide **7a** in 10 min at 25 °C (Table 3, entry 1). In contrast, 12 h was required when a low-valent ruthenium complex was used, even at 60 °C (entry 2).[12a] Transformations of **4a** to the iodide and chloride also took place in high yields (entries 3 and 4). In addition, –OTs and –OPO(OPh)$_2$, which are poorer leaving groups than –OTf, were converted to –Br (entries 5 and 6). These leaving groups have economical advantages over triflate. Cyclic alkenyl bromides having an acetal or steroidal moiety also were obtained (entries 7 and 8).

Table 3. Transformation of Alkenyl Esters to Halides[a]

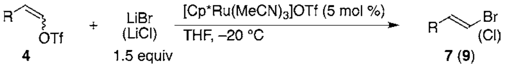


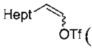
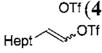
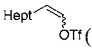
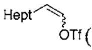
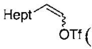
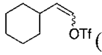
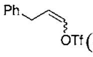
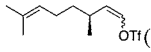
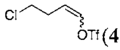
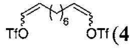
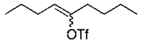
entry	4–6	mX^2	time	yield (%)[b]	prod.
1	 (**4a**)	LiBr	10 min	97	**7a**
2[c]	**4a**	LiBr	12 h	99	**7a**
3	**4a**	NaI	10 min	96	**8a**
4	**4a**	LiCl	10 min	98	**9a**
5	 (**5a**)	LiBr	10 min	94	**7a**
6[d]	 (**6a**)	LiBr	12 h	77	**7a**
7	 (**4b**)	LiBr	10 min	94	**7b**
8	 (**4c**)	LiBr	2 h	97	**7c**

[a]The reaction was carried out in DMI (1.0 mL) at 25 °C under a nitrogen atmosphere using **4–6** (0.25 mmol) and mX (0.38 mmol) in the presence of [Cp*Ru(MeCN)$_3$]OTf (12.5 μmol). [b]Isolated yields. [c]The reaction was carried out in THF (1.0 mL) at 60 °C using Ru(acac)$_3$ (12.5 μmol), EtMgBr (50 μmol), and 1,10-phenanthroline (12.5 μmol). [d]LiBr (1.5 mmol) was used.

Interestingly, both (*E*)- and (*Z*)-1-octen-1-yl triflate (**4d**) were transformed to (*E*)-1-bromo-1-octene (**7d**) upon reaction at –20 °C for 1 h (Table 4, entries 1 and 2). At 25 °C, *E*/*Z*

Table 4. Stereoselective Transformation of Acyclic Alkenyl Triflates to Halides[a]



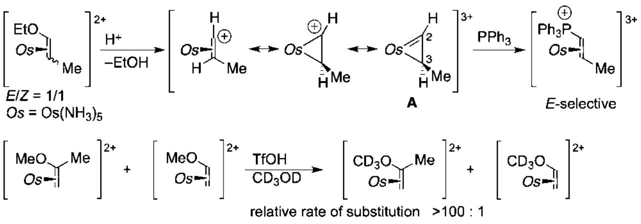
entry		*E*/*Z* of **4**	time	yield (%)[b]	*E*/*Z* of **7**
1	 (**4d**)	17/83	1 h	90	97/3
2	 (**4d**)	95/5	1 h	91	97/3
3[c]	 (**4d**)	17/83	10 min	92	90/10
4[c]	 (**4d**)	17/83	4 d	98	37/63
5[c]	 (**4d**)	17/83	7 d	96	36/64
6	 (**4e**)	20/80	1 h	98	99/1
7	 (**4f**)	13/87	20 min	92	97/3
8	 (**4g**)	16/84	1 h	94	99/1
9	 (**4h**)	36/64	1 h	89	95/5
10[d]	 (**4i**)	3/28/69[e]	1 h	93	96/4/<1[e]
11[f]	 (**4j**)	38/62	1.5 h	96 (**9j**)	97/3 (**9j**)

[a]The reaction was carried out in THF (1.0 mL) at –20 °C under a nitrogen atmosphere using **4** (0.25 mmol) and LiBr (0.38 mmol) in the presence of [Cp*Ru(MeCN)$_3$]OTf (12.5 μmol). [b]Isolated yields. [c]At 25 °C. [d]LiBr (0.75 mmol) and [Cp*Ru(MeCN)$_3$]OTf (25 μmol) were used. [e](*E*,*E*)/(*E*,*Z*)/(*Z*,*Z*). [f]LiCl (0.38 mmol) was used instead of LiBr, and the alkenyl chloride (**9j**) was obtained.

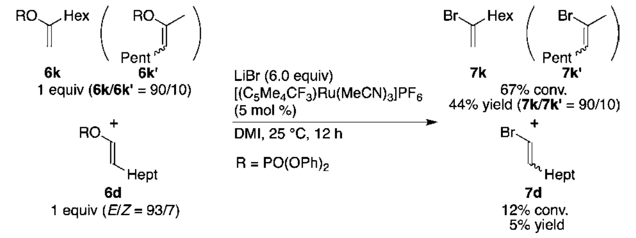
isomerization of **7d** occurred, and the *E*/*Z* ratio became constant at 36/64 (entries 3−5). These results indicate that (*E*)-**7d** is the kinetically favored product and that it is generated from the same intermediate in the reactions of both (*E*)-**4d** and (*Z*)-**4d**. The isomerization is ascribed to reentry of the product into the ruthenium catalysis. 1-Alken-1-yl triflates are much more easily prepared as mixtures of the stereoisomers than in an *E*-pure form.[15] Thus, this transformation is especially useful for the preparation of (*E*)-haloalkenes. Stereoisomeric mixtures of alkenyl triflates having a cycloalkane, benzene, alkene, or chloroalkane moiety were transformed to (*E*)-alkenyl bromides in the reaction at −20 °C (entries 6−9). A ditriflate underwent dibromination (entry 10). An *α*,*β*-disubstituted (*E*)-vinyl chloride also was obtained (entry 11).

A similar characteristic stereochemical outcome has been reported in osmium-mediated substitution reactions of alkenyl ethers.[16] Thus, both (*E*)- and (*Z*)-1-ethoxypropenes coordinated to osmium undergo acid-promoted substitution of EtO with PPh_3 to give (*E*)-propenylphosphonium salts (Scheme 1). The exclusive formation of the *E* isomer is ascribed to the intermediacy of 1-osmacyclopropene **A**, which accepts attack of PPh_3 at cationic C2 selectively from the opposite site of Me on C3. The result that 2-methoxypropene was much more reactive than methoxyethene in substitution in the coordination sphere of osmium can also be rationally understood by the involvement of a 1-osmacyclopropene, which would be stabilized by an *α*-alkyl substituent. A similar substituent effect was observed in the ruthenium-catalyzed transformation of alkenyl triflates to halides (Scheme 2). *α*-Alkyl vinyl phosphate **6k** was preferentially consumed over non-*α*-substituted vinyl phosphate **6d** in a competition reaction.

Scheme 1. Osmium-Mediated Substitution Reaction of Alkenyl Ethers

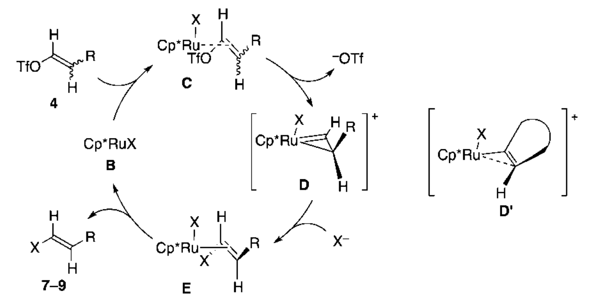


Scheme 2. Competition Reaction of Alkenyl Phosphates



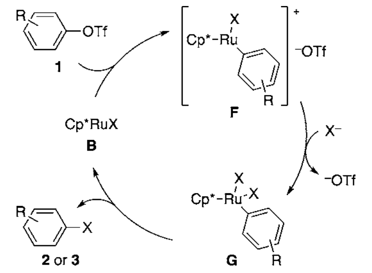
The observed similarities prompt us to propose that the present reaction also proceeds through a 1-metallacyclopropene intermediate, as shown in Scheme 3. Coordination of alkenyl triflate **4** to ruthenium to give **C** followed by oxidative addition upon elimination of ^{-}OTf gives 1-ruthenacyclopropene **D**. Attack on **D** by an outer sphere X^{-} or a 1,2-shift of X^{-} from Ru to C within **D** gives ruthenium−haloalkene complex **E**, which undergoes elimination to give alkenyl halide **7−9**, regenerating **B**. For cyclic alkenyl triflates, η^2-alkenylruthenium(IV) complex **D′** rather than **D** is considered to be the intermediate,[17] taking into account high ring strain probably induced in a form of **D**.

Scheme 3. Plausible Mechanism for the Transformation of Alkenyl Triflates to Halides

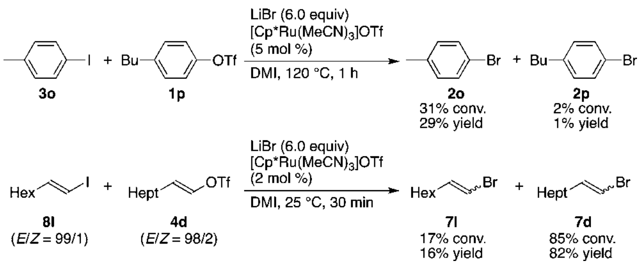


On the other hand, the transformation of aryl triflates is unlikely to include **D** or **D′** because the loss of aromaticity upon its formation would be unsuitable.[18] Alternatively, activation of aryl triflates through a different mode of oxidative addition to Ru(II) could possibly be operative. Thus, a catalytic cycle including η^1-arylruthenium(IV) triflate **F** (Scheme 4) is a possibility.[19] Oxidative addition of ArOTf **1** to Cp*RuX **B** generates **F**.[20,21] After coordination of X^{-} to **F**, reductive elimination of aryl halide **2**/**3** from η^1-arylruthenium(IV) complex **G** regenerates **B**. The higher reactivities of electron-deficient aryl triflates compared with electron-rich ones (Table 2) are consistent with this type of oxidative addition. The result that aryl iodide **3o** was more reactive than triflate **1p** in the competition reaction (Scheme 5) is in good agreement with the general reactivity order observed in oxidative addition of aryl electrophiles to transition-metal complexes such as palladium(0) complexes.[22] The opposite reactivity order was observed with alkenyl electrophiles, where alkenyl iodide **8l** was less reactive than triflate **4d**.[23] These results support the conclusion that the reaction mechanism with aryl triflates is different from that with alkenyl triflates.

Scheme 4. Plausible Mechanism for the Transformation of Aryl Triflates to Halides



Scheme 5. Effect of Leaving Groups



In conclusion, we have developed a ruthenium-catalyzed transformation of aryl and alkenyl triflates to the corresponding bromides and iodides. The strong electron-donating character of the Cp* ligand likely contributes to the high catalytic activity by facilitating oxidative addition of aryl and alkenyl triflates to ruthenium(II) complexes to give arylruthenium(IV) and 1-ruthenacyclopropene complexes, respectively.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and characterization data for all the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(13) The most efficient conditions found in the previous study[12a] [Ru(acac)$_3$ (3 mol %), EtMgBr (12 mol %), and 3,4,7,8-tetramethyl-1,10-phenanthroline (3 mol %) in 1,4-dioxane at 120 °C] were totally ineffective for the transformation of **1a** to **2a**. Also, bromide **2a** was not produced at all in the reaction in DMI.

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(15) Mixtures of stereoisomers can readily be obtained from aldehydes simply by treatment with Tf_2O and a base such as 2,6-di-*tert*-butyl-4-methylpyridine. See ref 6 and: (a) Stang, P. J.; Treptow, W. *Synthesis* **1980**, 283. (*E*)-1-Alken-1-yl triflates can be synthesized from the corresponding silyl enolates in a stereoretentive manner. However, the stereoselective synthesis of (*E*)-silyl enolates is generally not facile. See: (b) Matsuzawa, S.; Horiguchi, Y.; Nakamura, E.; Kuwajima, I. *Tetrahedron* **1989**, *45*, 349. (c) Ohmura, T.; Yamamoto, Y.; Miyaura, N. *Organometallics* **1999**, *18*, 413.

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(17) The existence of an apparent border between 1-metallacyclopropenes and η^2-alkenylmetals has been debated. See: (a) Casey, C. P.; Brady, J. T.; Boller, T. M.; Weinhold, F.; Hayashi, R. K. *J. Am. Chem. Soc.* **1998**, *120*, 12500. (b) Frohnapfel, D. S.; Templeton, J. L. *Coord. Chem. Rev.* **2000**, *206−207*, 199. To the best of our knowledge, no reports of the observation of 1-ruthenacyclopropenes or η^2-alkenylrutheniums are available. However, both of these have been proposed as intermediates in antihydrosilylation of alkynes catalyzed by $[Cp^*Ru(MeCN)_3]^+$ on the basis of DFT calculations. See: (c) Chung, L. W.; Wu, Y.-D.; Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2003**, *125*, 11578.

(18) Naphthyl triflates are more reactive than phenyl triflates, probably because a 10-π-electron (10π) aromatic system is much less susceptible to the loss of π-bond character than a 6π system. Naphthyl triflates are likely to be transformed via **D′** in a similar manner as alkenyl triflates.

(19) The result that [Cp*Ru(η^6-**1e**)]OTf showed no catalytic activity under the conditions of Table 2, entry 5 excludes S_NAr pathways accelerated by π complexation with the metal. Ruthenium complexes are known to catalyze or mediate S_NAr reactions of aryl halides through ruthenium−η^6-haloarene complexes. See: (a) Otsuka, M.; Endo, K.; Shibata, T. *Chem. Commun.* **2010**, *46*, 336. (b) Otsuka, M.; Yokoyama, H.; Endo, K.; Shibata, T. *Synthesis* **2010**, 2601. (c) Dembek, A. A.; Fagan, P. J. *Organometallics* **1996**, *15*, 1319. (d) West, C. W.; Rich, D. H. *Org. Lett.* **1999**, *1*, 1819.

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