

# Oxidative Arylation of Ethylene with Benzene to Produce Styrene

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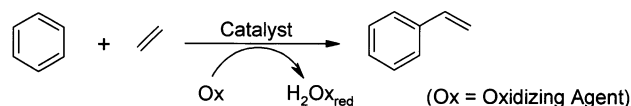
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Rh complexes were found to work as catalysts for oxidative arylation of ethylene with benzene to produce styrene by addition of acetylacetone and O<sub>2</sub> without any oxidizing agent like Cu salt. Vinylacetate was not formed at all in spite of coexistence of acetic acid.

Much work has been done at olefin oxidation catalyzed by group VIII metal complexes. In presence of an oxidant, Pd catalyzes partial oxidation of ethylene, namely well-known Wacker reaction to form acetaldehyde<sup>1</sup> and oxidative vinylation of acetic acid to produce vinylacetate.<sup>2</sup> Numerous efforts related to homogeneous C–H bond activation in aromatic compounds by discrete transition metal complexes through various mechanisms have also been reported.<sup>3</sup> Derivatives from aromatic compounds such as alkylbenzene, phenol, aniline and naphthalene are the large-quantity chemicals manufactured by chemical industries. Especially styrene holds a majority in the derivatives from benzene. Fujiwara et al. have reported significant work for direct formation of styrene by oxidative arylation of ethylene catalyzed by Pd complexes combining arene activation with oxidation.<sup>4</sup> Hong and Yamazaki have also reported direct formation of styrene by another approach using Rh(0) complex, whereas 3-pentanone is simultaneously produced, and the mechanism is completely different from Fujiwara's.<sup>5</sup> Since the current industrialized process to produce styrene consists of two parts, which are the alkylation of benzene with ethylene to form ethylbenzene and the dehydrogenation of ethylbenzene to afford styrene,<sup>6</sup> the attempt on direct formation of styrene from benzene and ethylene through C–H bond activation is an attractive field, which has enough room to be developed from the industrial point of view. Group VIII metal complexes can be employed for the series of oxidation reactions such as Wacker reaction, oxidative vinylation of acetic acid and oxidative arylation of ethylene. However, an oxidizing agent such as Cu salt, Ag salt or heteropoly acid is required in order to proceed the reactions catalytically. Namely, the oxidizing agent reoxidizes the group VIII metal complex reduced in the reaction, and then oxygen reoxidizes the oxidizing agent in reduced form. Accordingly, the oxidizing agent works as a co-catalyst.

Herein we report oxidative arylation of ethylene to produce styrene catalyzed by Rh complexes with no oxidizing agent like Cu salt by addition of acetylacetone (acacH), in which oxygen directly drive the catalytic cycle. The reaction, catalyzed by Rh complex, is assumed to occur by the C–H activation of benzene. The comparison study of reaction condition and catalysts for arylation of ethylene is shown in Table 1. The typical reaction procedure is as follows (Entry 3); a 10-mL stainless steel autoclave equipped with a glass insert and a magnetic stir bar was charged with 3 mL of catalyst / benzene / acetic acid / acacH solution which contained 1.0 mM of Rh(acac)(CO)<sub>2</sub> (1),

10.6 M of benzene and 0.67 M of acacH. The reactor was degassed with N<sub>2</sub>, pressurized with 1.55 MPa of ethylene, sequentially pressurized with O<sub>2</sub> up to 2.10 MPa and heated to 180 °C with stirring for 20 min. The liquid phase was analyzed by GC (FID) at the end of the reaction. Styrene was obtained (TOF = 188 × 10<sup>−4</sup> s<sup>−1</sup>, TN = 23; Table 1, Entry 3). Although the arylation of ethylene using Cu(OAc)<sub>2</sub> as a co-catalyst also resulted in styrene (TOF = 248 × 10<sup>−4</sup> s<sup>−1</sup>) coupled with formation of vinyl acetate (VA) (TOF = 83 × 10<sup>−4</sup> s<sup>−1</sup>; Entry 1), the reaction was not catalyzed by 1 without Cu(OAc)<sub>2</sub> (Entry 2). The addition of acacH made oxidative arylation directly forced by O<sub>2</sub> possible. Furthermore, in spite of coexistence of acetic acid in the reaction medium, no formation of vinyl acetate was observed in the system of O<sub>2</sub> / benzene / acetic acid / acacH.



**Table 1.** Oxidative arylation of ethylene with benzene<sup>a</sup>

Entry	Catalyst	Oxidant	Additive <sup>b</sup>	TOF/10 <sup>−4</sup> s <sup>−1</sup>	
				VA	Styrene
1	1	O <sub>2</sub> / Cu(OAc) <sub>2</sub> <sup>c</sup>	----	83	248
2	1	O <sub>2</sub>	----	0	0
3	1	O <sub>2</sub>	acacH	0	188
4	2	O <sub>2</sub> / Cu(OAc) <sub>2</sub> <sup>c</sup>	----	34	34
5	2	O <sub>2</sub>	----	0	13
6	2	O <sub>2</sub>	acacH	0	180
7	Pd(OAc) <sub>2</sub>	O <sub>2</sub> / Cu(OAc) <sub>2</sub> <sup>c</sup>	----	365	328
8	Pd(OAc) <sub>2</sub>	O <sub>2</sub>	acacH	121	482
9	1	O <sub>2</sub>	tmhd <sup>d</sup>	0	159
10	1	O <sub>2</sub>	hfacacH <sup>e</sup>	0	4
11	1	O <sub>2</sub>	aabe <sup>f</sup>	0	17

<sup>a</sup>Reactions were proceeded at 180 °C for 20 minutes in benzene/acetic acid solution (10.6 M of benzene). <sup>b</sup>670 mM of additive was introduced. <sup>c</sup>50 mM of Cu(OAc)<sub>2</sub> was added. <sup>d</sup>2,2,6,6-Tetramethyl-3,5-heptanedione. <sup>e</sup>1,1,1,5,5,5-Hexafluoro-2,4-pentanedione. <sup>f</sup>Acetoacetic acid tert-butylester.

[Rh(NBD)(DPPB)]BF<sub>4</sub> (NBD = bicyclo[2.2.1]hepta-2,5-diene, DPPB = 1,4-bis(diphenylphosphino)butane) (2) also catalyzed oxidative arylation of ethylene to afford styrene (TOF = 180 × 10<sup>−4</sup> s<sup>−1</sup>, TN = 22; Entry 6) and no vinyl acetate by addition of acacH and O<sub>2</sub>. Though the TOF for styrene formation with Pd(OAc)<sub>2</sub> using Cu(OAc)<sub>2</sub> was larger than that with 1, vinyl acetate production was preferable to styrene formation with Pd(OAc)<sub>2</sub> (Entries 1 and 7). When acacH and O<sub>2</sub> were

added, styrene was produced with smaller amount of vinyl acetate (Entry 8) than  $\text{O}_2/\text{Cu}(\text{OAc})_2$  case. However, in contrast to the reaction catalyzed by complex **1**, vinyl acetate was still afforded with  $\text{Pd}(\text{OAc})_2$ .

As a comparison study of additives, 2,2,6,6-tetramethyl-3,5-heptanedione, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione and acetoacetic acid *tert*-butylester were respectively introduced into the reaction catalyzed by **1** instead of *acacH* (Entries 9, 10 and 11). Among these additives, *acacH* and 2,2,6,6-tetramethyl-3,5-heptanedione showed much higher activity for this reaction than others which have electron-withdrawing groups.

**Table 2.** Oxidative arylation of ethylene with benzene by addition of *acacH* and  $\text{O}_2^a$

Entry	Catalyst	Starting Oxidation State	TOF <sup>b</sup> / $10^{-4} \text{ s}^{-1}$	
			VA	Styrene
12	$\text{Rh}(\text{acac})(\text{ethylene})_2$	Rh(I)	0	183
13	$[\text{Rh}(\text{COD})\text{Cl}]_2$	Rh(I)	0	175
14	$\text{RhCl}(\text{PPh}_3)_3$	Rh(I)	0	179
15	$[\text{Rh}(\text{Cp}^*)\text{Cl}_2]_2$	Rh(III)	0	8
16	$[\text{Rh}(\text{ppy})_2\text{Cl}]_2$	Rh(III)	0	22

<sup>a</sup>Reactions were proceeded at 180 °C for 20 minutes in benzene / acetic acid / *acacH* solution (10.6 M of benzene and 670 mM of *acacH*). <sup>b</sup>TOF was based on Rh.

We also studied the reaction by other various Rhodium catalysts in presence of *acacH* and  $\text{O}_2$ . The results were shown in Table 2. Rh complexes,  $\text{Rh}(\text{acac})(\text{ethylene})_2$ ,  $[\text{Rh}(\text{COD})\text{Cl}]_2$  and  $\text{RhCl}(\text{PPh}_3)_3$ , which were introduced into the reaction as catalysts in Rh(I) oxidation state at the beginning of the reaction, showed almost same activities as those for **1** and **2** to produce styrene and no vinylacetate. On the other hand, The rates with Rh(III) complexes,  $[\text{Rh}(\text{Cp}^*)\text{Cl}_2]_2$  and  $[\text{Rh}(\text{ppy})_2\text{Cl}]_2$ , were almost one order of magnitude slower than those with Rh(I) complexes.

**Table 3.** H-D exchange between  $\text{C}_6\text{H}_6$  and  $\text{AcOD}$  catalyzed by **1**<sup>a</sup>

Entry	Oxidant	Additive	TOF/ $10^{-4} \text{ s}^{-1}$
17	----	----	0
18	$\text{O}_2$	----	0
19	$\text{O}_2$	<i>acacH</i> <sup>b</sup>	1,486

<sup>a</sup>Reactions were proceeded at 160 °C for 20 minutes in benzene/ $\text{AcOD}$  solution (6.0 M of benzene). <sup>b</sup>670 mM of *acacH* was introduced.

We propose that the reaction occurs in five main steps: A) aromatic CH bond activation by the Rh(III) center (possibly formed by in-situ oxidation) to produce an Rh–phenyl intermediate species, B) olefin insertion to produce an Rh–alkyl, C) product loss from the metal center with  $\beta$ -hydride elimination, D)  $\text{H}^+$  release by reductive elimination and E) reoxidation of reduced metal center. Although the mechanism has not been fully elucidated yet, benzene seemed to be activated by Rh center. To learn whether C–H bond activation of benzene was occurring, we examined the effect of reaction environment in catalyzing proton exchange (generally a good test for reversible C–H bond activation) between  $\text{C}_6\text{H}_6$  and  $\text{CH}_3\text{COOD}$  in which

benzene was activated through electrophilic substitution. Without *acacH* and  $\text{O}_2$ , complex **1** didn't show any activity for H–D exchange at all. In contrast to this, by the combination of complex **1**, *acacH* and  $\text{O}_2$ , deuterium incorporation was observed in  $\text{C}_6\text{H}_6/\text{CH}_3\text{COOD}$  (6.0 M of benzene) at 160 (TOF =  $1,486 \times 10^{-4} \text{ s}^{-1}$ ; Table 3, Entry 19), which corresponded with the result that the combination was available for styrene formation.

In summary, we report that various Rh(I) complexes worked as catalysts for oxidative arylation of ethylene to produce styrene without any oxidizing agent like Cu salt by addition of *acacH* and  $\text{O}_2$ . Moreover, in this reaction environment, namely the combination of Rh(I), *acacH* and  $\text{O}_2$ , H–D Exchange between  $\text{C}_6\text{H}_6$  and  $\text{AcOD}$  was catalyzed by complex **1**. Therefore, it is obvious that this catalysis occurs through C–H bond activation of benzene.

## References and Notes

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