

Transition metal catalyzed oxidative arene alkenylation: the impact of oxidant identity on reaction rate and selectivity

Alquenilación oxidativa de arenos catalizada por metales de transición: influencia de la naturaleza del oxidante en la velocidad y la selectividad de la reacción

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KEYWORDS:

Arene
Alkenylation
Alkylation
Late transition metal
Rhodium

ABSTRACT:

Rh-, Pd-, Ir-, and Ru-based catalysts for the oxidative conversion of olefins and arenes to alkenyl arenes have been reported. Proposed mechanisms often invoke arene C–H activation, olefin insertion into M–aryl bonds, β -hydride elimination, and reaction of M–H intermediates with an oxidant. Of central importance is identification of oxidants that do not generate oxidized transition metal complexes that are catalytically inactive. Herein, we overview reported oxidants for arene alkenylation reactions catalyzed by homogeneous late transition metal complexes and their influence on reaction rate and selectivity. This review is limited to reactions involving hydrocarbon olefins and arenes without functionalized directing groups and will not cover the extensive literature on directed arene alkenylation reactions.

PALABRAS CLAVE:

Areno
Alquenilación
Alquilación
Metales del final de las series de transición
Rodio

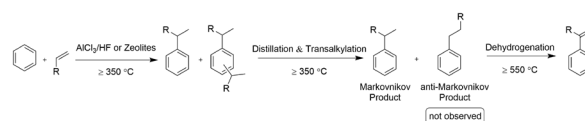
RESUMEN:

Se han descrito catalizadores que contienen Rh, Pd, Ir y Ru para la conversión oxidativa de olefinas y arenos en alquenilarenos. Los mecanismos propuestos suelen incluir la activación del enlace C–H del areno, la inserción de la olefina en los enlaces M–arilo, la β -eliminación de hidrógeno y la reacción de los intermedios M–H con un oxidante. Es de vital importancia identificar oxidantes que no generen productos de reacción catalíticamente inactivos. En este artículo, recogemos ejemplos de oxidantes descritos para las reacciones de alquenilación de arenos catalizadas por complejos de metales del final de las series de transición, y de su influencia en la velocidad de reacción y la selectividad. Esta revisión se limita a las reacciones en las que intervienen olefinas hidrocarbonadas y arenos no funcionalizados con grupos directores, y no abarca la extensa bibliografía sobre reacciones de alquenilación de arenos con dichos grupos directores.

Introduction

Alkenyl and alkyl arenes are fundamental building blocks for various materials such as plastics, fragrances and pharmaceuticals.^[1–3] In 2024, 42 million tons of styrene were produced, and these numbers are expected to grow over the next ten years.^[4] The production of styrene is energy intensive, first requiring the alkylation of benzene and ethylene via Friedel-Crafts catalysis or a zeolite-catalyzed reaction to produce ethylbenzene (Scheme 1).^[5] Benzene alkylation and product purification via distillation is followed by an energy intensive dehydrogenation.^[6] There are many disadvantages to these commercial processes including over alkylation, the production of halogenated waste, the inability to form styrene from benzene in a single step, and catalyst dictated selectivity for reactions of substituted arenes and olefins (Scheme 1).^[7–11]

Transition metal catalyzed oxidative coupling of arenes and olefins to alkenyl arenes offers potential advantages to current



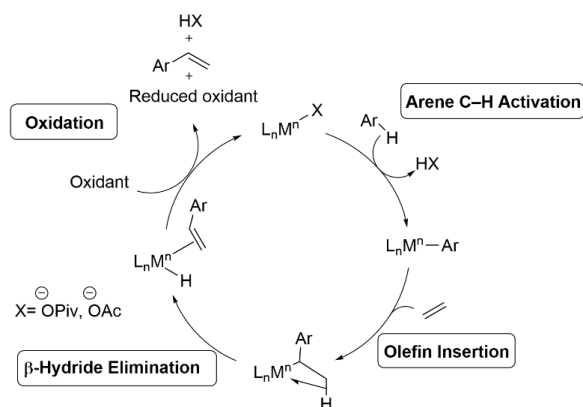
Scheme 1. General synthesis of alkenyl arenes via Friedel-Crafts alkylation followed by dehydrogenation, presenting challenges such as harsh conditions, high temperature, polyalkylation, and non-selectivity for linear alkylated arenes.

commercial routes. Our group and others have reported Rh,^[12–33] Pd,^[8,14,25,31,34,35] Pt,^[36–39] Ru,^[31,40,41] and Ir catalysts for this transformation.^[31,42] Often, these catalysts have been proposed to operate via C–H activation, olefin insertion, β -hydride elimination, and reaction of M–H intermediates with an in-situ oxidant to regenerate the starting catalyst (Scheme 2).

Our group has shown that oxidant identity can impact reaction kinetics and selectivity for arene alkenylation.^[43] For example,

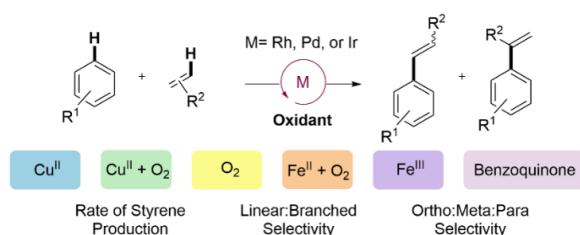
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Scheme 2. General mechanism that is often proposed for transition metal catalyzed oxidative coupling of arenes and olefins to form alkenyl arenes. The stoichiometry of the balanced overall reaction and of some steps in the catalytic cycle depend on the oxidant identity. Thus, it is not possible to show correct stoichiometric for all variations.

in addition to impact on reaction rate for arene alkenylation, when using mono-substituted olefins such as propylene, differences in Markovnikov versus anti-Markovnikov selectivity, also referred to as linear:branched selectivity, based on oxidant identity have been quantified (Scheme 3). Further, when using mono-substituted arenes, *ortho*:*meta*:*para* regioselectivity for arene alkenylation can also vary with oxidant identity (Scheme 3).



Scheme 3. Oxidant identity impacts the rate of arene alkenylation, linear:branched selectivity when using mono-substituted olefins and *ortho*:*meta*:*para* selectivity for alkenylation of mono-substituted arenes.

This review will focus on the effect of in situ oxidant identity on reaction rate and product selectivity. Primarily, we discuss Rh-based catalysis since the majority of detailed mechanistic studies are for such reactions, but we include results from different catalysts as warranted.

Overview of oxidants

We will discuss Cu(II) carboxylates, dioxygen, Fe(III) carboxylates, and benzoquinones as oxidants for transition metal catalysis. While the use of dioxygen as the ultimate oxidant is likely required for the economic viability of any commercial process, there are several potential disadvantages to using it as the sole oxidant including the formation of off-cycle species with low valent metal centers,^[44-46] and the kinetically challenging oxidation of metal hydrides.^[21,47] Thus, use of in situ oxidants that can be recycled by dioxygen is a common strategy. A successful example is the commercial Wacker process in which CuCl₂ is the operative oxidant, and CuCl and HCl are converted back to CuCl₂.^[48] In addition to the Wacker process, Cu(II) carboxylates have been used as oxidants in transition metal catalyzed arene alkenylation reactions including the Fujiwara-Moritani reaction.^[49] Given the precedence for commercial use of Cu(II) for catalytic

ethylene oxidation, we investigated Cu(II) carboxylates under both aerobic and anaerobic conditions for Rh-catalyzed arene alkenylation. Fe(III) has been studied as a catalyst for hydrocarbon oxidation reactions.^[50-53] Additionally, some complexes of Fe(II) are known to undergo oxidation upon reactivation with dioxygen.^[50-54] The oxidative coupling of arenes and electron-deficient olefins catalyzed by Pd(OAc)₂ using benzoquinones as oxidant has been reported by the Bäckvall and Fujiwara groups.^[50-56]

Rate of styrene production

We have quantified the kinetics of benzene ethenylation for each oxidant using 0.001 mol% of the catalyst precursor $[(\eta^2\text{-C}_2\text{H}_4)_2\text{Rh}(\mu\text{-OAc})_2]$ (relative to benzene per single Rh atom), 960 equiv of HOPIV (relative to single Rh atom), and 70 psig of ethylene at 150 °C.^[25] When using 480 equiv of Cu(OPiv)₂, an initial turnover frequency (TOF) of 0.101(9) s⁻¹ was observed (Table 1, entry 1), which is the highest TOF observed for any oxidant that we studied for Rh-catalyzed styrene formation. When 1 atm of O₂ is added with Cu(OPiv)₂, thus rendering Cu(III) catalytic rather than stoichiometric, the TOF is ~3-fold slower (entry 2). We speculate that the slower rate of catalysis in the presence of O₂ could be due to O₂ reacting with Rh to form off-cycle and catalytically inactive Rh species. When 1 atm O₂ and 480 equiv of Fe(OAc)₂ is used, a TOF of 0.0084(3) s⁻¹ was observed (entry 3), similar to the rate using anaerobic Fe(III) (see below), indicating that dioxygen is not as detrimental as it is with Cu(OPiv)₂. Use of 80 equiv Fe₆(μ-OH)₂(μ₃-O)₂(μ₂-OPiv)₁₂(HOPIV)₂ under anaerobic conditions resulted in a TOF of 0.0073(7) s⁻¹ (entry 4). Use of 1 atm of O₂ as the sole oxidant gave the lowest TOF of 0.0006(1) s⁻¹ (entry 5). We attribute the slow rate to be due in part to the Rh-H oxidation step being kinetically challenging.^[43] Use of Pd catalysis was also compared to Rh using 480 equiv Cu(OPiv)₂ and 960 equiv HOPIV at 120 °C. It was found that using Pd(OAc)₂ as the catalyst precursor is > 20-fold slower than Rh and has 82% selectivity towards styrene, compared to 98% for Rh (entries 6 and 7).

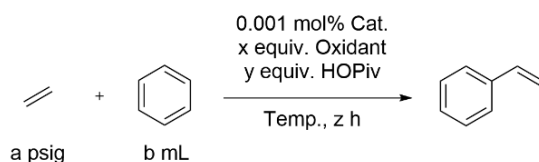
Kinetics of styrene production using benzoquinones was also studied using 0.001 mol% of the catalyst precursor $[(\eta^2\text{-C}_2\text{H}_4)_2\text{Rh}(\mu\text{-OPiv})_2]$, 960 equiv HOPIV, 70 psig of ethylene, and 240 equiv of benzoquinone derivatives at 170 °C.^[30] We demonstrated that *ortho*-benzoquinones exhibit a faster rate of styrene production than *para*-benzoquinones with the fastest styrene production observed using 1,2-naphthoquinone (entries 8 and 9).

The formation of undesirable side products during styrene production was quantified for each oxidant (Table 2). Use of Cu(OPiv)₂ resulted in 93% selectivity towards styrene with vinyl pivalate, biphenyl, phenyl pivalate, and *trans*-stilbene formed as side products.^[43] When using Cu(OPiv)₂ under aerobic conditions, selectivity towards styrene decreases and more phenyl pivalate is formed in comparison to anaerobic conditions (Entries 1 and 2). The decreased selectivity for styrene is likely due to the suppressed rate of formation of styrene while having less impact on rate of phenyl pivalate formation when using Cu(OPiv)₂/O₂ compared to anaerobic Cu(OPiv)₂.^[57] Use of only O₂ gave the highest selectivity towards styrene, 95%, with the most significant side products observed being benzaldehyde and biphenyl. Use of Fe(OAc)₂ as the oxidant under aerobic conditions results in the elimination of phenyl acetate or phenyl pivalate as a side product, although benzaldehyde production is observed (Entry 4). Use of Fe₆(μ-OH)₂(μ₃-O)₂(μ₂-OPiv)₁₂(HOPIV)₂ as the oxidant under anaerobic conditions results in significant biphenyl production (Entry 5), which is much more prominent than with use of Fe under aerobic conditions.

Table 1. Kinetics of benzene ethenylation to styrene as a function of metal catalyst and oxidant identity. Eq. 1.

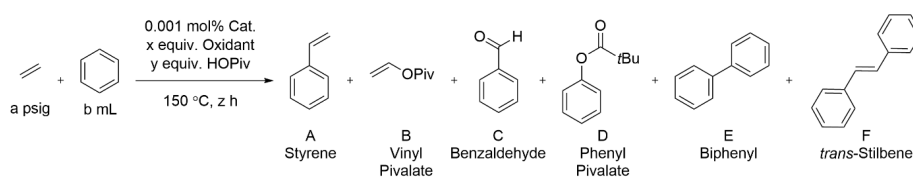
Entry	Catalyst precursor	Oxidant	oxidant (equiv)	O ₂ (atm)	HOPiv (equiv)	Ethylene pressure (psig)	Benzene amount (mL)	Temp (°C)	TOF (s ⁻¹)
1	Rh ¹	Cu(OPiv) ₂	480	–	480	70	7.5	150	0.101(9)
2	Rh ¹	Cu(OPiv) ₂ /O ₂	480	1	480	70	7.5	150	0.045(4)
3	Rh ¹	Fe(OAc) ₂ /O ₂	480	1	480	70	7.5	150	0.0084(6)
4	Rh ¹	Fe ₆ (μ-OH) ₂ (μ ₃ -O) ₂ (μ-OPiv) ₁₂ (HOPiv) ₂	80	–	480	70	7.5	150	0.0073(7)
5	Rh ¹	O ₂	–	1	480	70	7.5	150	0.0006(1)
6	Pd(OAc) ₂	Cu(OPiv) ₂	480	–	960	50	10	120	0.0026(1)
7	Rh ¹	Cu(OPiv) ₂	480	–	960	50	10	120	0.0561(7)
8	Rh ²	1,2-naphthoquinone	240	–	960	70	7.5	170	0.04
9	Rh ²	<i>para</i> -chloranil	240	–	960	70	7.5	170	0.0028

Rh¹ = [(η²-C₂H₄)₂Rh(μ-OAc)]₂; Rh² = [(η²-C₂H₄)₂Rh(μ-OPiv)]₂. Detailed reaction conditions can be found in original publications. Each TOF value represents the average of at least three independent experiments, and the values in parentheses represent the standard deviation in the final digit(s).

**Equation 1.****Table 2.** Product selectivity for benzene ethenylation as a function of catalyst precursor and oxidant identity. Eq. 2.

Entry	Catalyst precursor	Oxidant	% Selectivity					
			A	B	C	D	E	F
1	Rh ¹	Cu(OPiv) ₂	93	4	nd	<1	<1	2
2	Rh ¹	Cu(OPiv) ₂ /O ₂	90	1	1	3	1	2
3	Rh ¹	O ₂	95	nd	2	nd	2	nd
4	Rh ¹	Fe(OAc) ₂ /O ₂	92	1	2	nd	1	3
5	Rh ¹	Fe ₆ (μ-OH) ₂ (μ ₃ -O) ₂ (μ-OPiv) ₁₂ (HOPiv) ₂	92	<1	1	nd	5	<1
6	Rh ¹	Cu(OPiv) ₂	97	3	nd	nd	nd	nd
7	Pd(OAc) ₂	Cu(OPiv) ₂	96	4	nd	nd	nd	nd

Rh¹ = [(η²-C₂H₄)₂Rh(μ-OAc)]₂; Rh² = [(η²-C₂H₄)₂Rh(μ-OPiv)]₂; Ir¹ = [Ir(μ-Cl)(coe)]₂; Fe₆ = Fe₆(μ-OH)₂(μ₃-O)₂(μ-OPiv)₁₂(HOPiv)₂. Detailed reaction conditions can be found in original publications. Use of "nd" indicates that the individual product selectivity's were not reported. L:B ratios represent the average of at least three independent experiments, and the values in parentheses represent the standard deviation in the final digit(s).

**Equation 2.**

Anti-Markovnikov to Markovnikov selectivity for benzene alkenylation using propylene

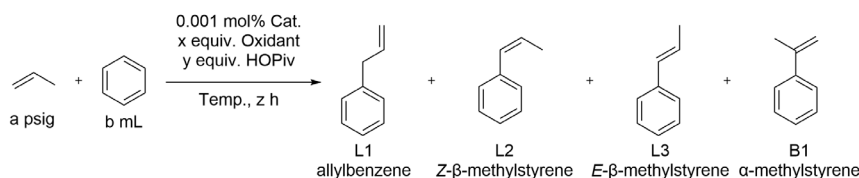
When using propylene as the olefin for alkenylation of benzene, the regioselectivity of propylene insertion into a metal-phenyl bond can dictate whether the Markovnikov (branched) or anti-Markovnikov (linear) product is formed (Scheme 2). Using a 0.001 mol% loading of $[\eta^2\text{-C}_2\text{H}_4]_2\text{Rh}(\mu\text{-OAc})_2$ as the catalyst precursor and 960 equiv of HOPiv at 150 °C, we probed linear to branched selectivity with 50 psig of propylene as the olefin.^[43] Using 480 equiv of $\text{Cu}(\text{OPiv})_2$ as the sole oxidant (i.e., anaerobic), a linear:branched of 11.0(2):1 was observed (Table 3). The selectivity for linear products significantly decreases to

5.7(1):1 at otherwise identical conditions but in the presence of 1 atm of dioxygen. This finding provides evidence that the active Rh catalyst and/or reaction pathway are likely changed upon introduction of dioxygen. We speculated that this might be attributable to formation of dioxygen-coordinated intermediates. Use of dioxygen as the sole oxidant results in a linear:branched selectivity of 4.6(6):1, indicating the possibility of a distinct active species from the one formed in the presence of $\text{Cu}(\text{OPiv})_2$. In the presence of 1 atm of dioxygen and 480 equiv of $\text{Fe}(\text{OAc})_2$, a linear:branched ratio of 2.21(3):1 was observed, which is substantially lower than observed with the other oxidants. Use of $\text{Fe}_6(\mu\text{-OH})_2(\mu_3\text{-O})_2(\mu\text{-OPiv})_{12}(\text{HOPiv})_2$ as the oxidant

Table 3. Linear to branched selectivity for benzene propenylation as a function of catalyst precursor and oxidant identity. Eq. 3.

Entry	Catalyst precursor	Oxidant	Temp (°C)	% Selectivity				L:B
				L1	L2	L3	B1	
1	Rh ¹	$\text{Cu}(\text{OPiv})_2$	150	44	7	41	8	11.0(2):1
2	Rh ¹	$\text{Cu}(\text{OPiv})_2/\text{O}_2$	150	44	7	34	15	5.7(1):1
3	Rh ¹	$\text{Fe}(\text{OAc})_2/\text{O}_2$	150	7	14	47	32	2.21(3):1
4	Rh ¹	Fe_6	150	8	14	46	32	2.15(1):1
5	Rh ¹	O_2	150	42	7	35	16	4.6(6):1
6	Ir ¹	$\text{Cu}(\text{OHex})_2$	150	–	–	–	–	89(2):1
7	Rh ²	3,5-di- <i>tert</i> -butyl- <i>ortho</i> -benzoquinone	170	19	9	54	18	4.7(4):1
8	Rh ²	<i>o</i> -naphthoquinone	170	19	5	59	17	4.8(1):1
9	Rh ²	9,10-phenanthrenequinone	170	30	3	44	23	3.2(1):1
10	Rh ²	<i>o</i> -chloranil	170	28	11	33	28	2.6(1):1
11	Rh ²	anthraquinone	170	23	8	44	25	3.0(1):1
12	Rh ²	tetramethylquinone	170	34	32	14	20	4.1(4):1
13	Rh ²	2,5-di- <i>tert</i> -butyl- <i>p</i> -quinone	170	14	7	46	33	2.1(1):1
14	Rh ²	<i>p</i> -benzoquinone	170	27	9	38	26	2.85(4):1
15	Rh ²	2-chloroquinone	170	26	11	39	24	3.1(1):1
16	Rh ²	2,5-dichloro- <i>p</i> -benzoquinone	170	26	9	40	25	3.1(1):1
17	Rh ²	<i>p</i> -chloranil	170	27	12	34	27	2.65(7):1
18	Rh ²	<i>p</i> -fluoranil	170	10	5	35	50	1.03(9):1

Rh¹ = $[\eta^2\text{-C}_2\text{H}_4]_2\text{Rh}(\mu\text{-OAc})_2$; Rh² = $[\eta^2\text{-C}_2\text{H}_4]_2\text{Rh}(\mu\text{-OPiv})_2$; Ir¹ = $[\text{Ir}(\mu\text{-Cl})(\text{coe})_2]_2$; Fe_6 = $\text{Fe}_6(\mu\text{-OH})_2(\mu_3\text{-O})_2(\mu\text{-OPiv})_{12}(\text{HOPiv})_2$. Detailed reaction conditions can be found in original publications. Use of “–” indicates that the individual product selectivity's were not reported. L:B ratios represent the average of at least three independent experiments, and the values in parentheses represent the standard deviation in the final digit(s).



Equation 3.

under anaerobic conditions gives a similar linear:branched selectivity of 2.15(1):1. The observation that no significant variance in selectivity was observed for processes with Fe-based oxidants under aerobic versus anaerobic conditions could indicate that the active species is likely not sensitive to dioxygen, which contrasts to catalytic reactions using $\text{Cu}(\text{OPiv})_2$.

Linear:branched selectivity was also studied with *tert*-butyl ethylene, styrene and methyl acrylate, and a similar trend in linear:branched selectivity to that observed with propylene was found, linear:branched selectivity changes as a function of oxidant: $\text{Cu}(\text{II}) > \text{Cu}(\text{II})/\text{O}_2 > \text{O}_2 > \text{Fe}(\text{III})/\text{O}_2 \approx \text{Fe}(\text{III})$. While $\text{Cu}(\text{OPiv})_2$ and dioxygen produced trace branched product with electronically biased methyl acrylate or styrene as the olefin, use of $\text{Fe}(\text{III})$ yielded more significant branched product formation.^[43]

Using $\text{Ir}(\text{I})$ in place of $\text{Rh}(\text{I})$ as catalyst precursor results in a significant increase in linear:branched ratio, albeit with a significantly reduced reaction rate. With 0.005 mol% of $[\text{Ir}(\text{COE})_2\text{Ir}(\mu\text{-Cl})_2]$ as the catalyst precursor in benzene and 240 equiv of $\text{Cu}(\text{OHex})_2$ (OHex = 2-ethylhexanoate) (relative to single Ir atom), 960 equiv of HOHex and 30 psig of propylene, a linear:branched selectivity of 18(1.3):1 was observed after heating for three hours at 150 °C.^[42] Upon heating for 42 hours, the selectivity increased to 42(2):1.^[42] After control experiments indicated that the observed increase was not the result of an isomerization or selective decomposition of the branched product, we speculated that an increase in $\text{Cu}(\text{OPiv})$ concentration as the reaction progresses might be the origin of this observation. Use of an initial $\text{Cu}(\text{I}):\text{Cu}(\text{II})$ of 4:1 resulted in a linear:branched selectivity of 65(3):1 after 18 h, and no statistically significant variation was observed over time. From these results, we hypothesized that hetero-multimetallic species of $\text{Cu}(\text{II})$ and/or $\text{Cu}(\text{I})$ can form with Ir and the $\text{Cu}(\text{I})$ containing complexes more selectively form linear propenylbenzene products.^[42] This mirrors findings with Rh ,^[23,25,43] and Pd catalysis that hetero multi-metallic species with $\text{Cu}(\text{II})$ form under the reaction conditions and serve as the likely active catalysts.

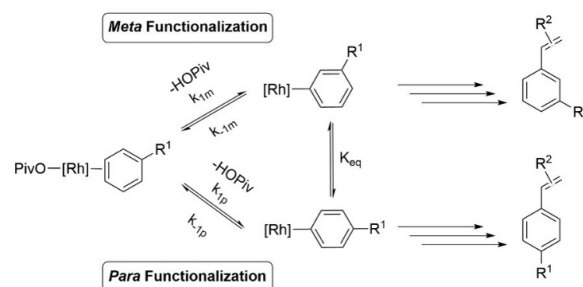
We studied the use of benzoquinone and impact on linear:branched selectivity using $[\text{Ir}(\text{C}_2\text{H}_4)_2\text{Rh}(\mu\text{-OPiv})_2]$ at 170 °C using 240 equiv of *ortho*-benzoquinone derivatives as the in-situ oxidant in the presence of 960 equiv of HOPiv and 50 psig of propylene.^[30] Use of *ortho*-chloranil as the oxidant results in a linear:branched of 2.6(1):1, 9,10-phenanthrene dione gives a selectivity of 3.2(1):1, 1,2-naphthoquinone, 1,2-naphthoquinone 4.8(1):1 and 3,5-di-*tert*-butyl-*ortho*-benzoquinone 4.7(4):1 (Table 3). Since benzoquinone derivatives can react with $\text{Rh}(\text{I})$ to form catecholate or semiquinone complexes, we speculated that ligand effects of the quinones might be the origin of the selectivity variation. Quinone donor ability was approximated using DFT-calculated $\text{p}K_{\text{a1}}$ values, and it was found that linear selectivity increases as ligand donor ability is increased.^[58] Notably, the selectivity did not correlate with quinone oxidizing ability, indicating that ligand effects, rather than Rh-H oxidation kinetics, likely dictate selectivity patterns.^[30] With *para*-benzoquinones, a linear:branched selectivity between ~1:1 and 4:1 were determined with no clear trend as a function of benzoquinone donor or oxidizing ability. We attributed this observation to *para*-benzoquinones either not

coordinating to Rh or not having a significant influence on linear:branched selectivity if coordinated.^[30]

Regioselectivity for alkenylation of mono-substituted arenes

Toluene ethenylation reactions were studied at 150 °C using 0.112 mM of $[\text{Ir}(\text{C}_2\text{H}_4)_2\text{Rh}(\mu\text{-OAc})_2]$ (relative to single Rh atom) as the catalyst precursor with 480 equiv of HOPiv and 45 psig of ethylene.^[43] With each oxidant, trace *ortho*-functionalization was observed. In the presence of 240 equiv of $\text{Cu}(\text{OPiv})_2$ under anaerobic conditions, a meta:para ratio of 1.4(1):1 was observed, and addition of 1 atm of air in combination with $\text{Cu}(\text{OPiv})_2$ results in a 1.1(1):1 meta:para ratio (Table 4). Consistent with studies of linear:branched selectivity using mono-substituted olefins (see above), the difference between aerobic and anaerobic conditions with $\text{Cu}(\text{OPiv})_2$ is significant. Use of 1 atm dioxygen as the sole oxidant yielded a 1.4(1):1 meta:para ratio. In the combination of $\text{Fe}(\text{OAc})_2$ and 1 atm dioxygen, a meta:para of 1.6(1):1 was observed, while use of $\text{Fe}_6(\mu\text{-OH})_2(\mu_3\text{-O})_2(\mu\text{-OPiv})_2(\text{HOPiv})_2$ under anaerobic conditions gave a 1.9(1):1 ratio.^[28] Similar trends were observed with *tert*-butylbenzene and chlorobenzene: trace or no *ortho* functionalization with meta:para ratios between ~1:1 and 2:1 were observed. With anisole as the olefin, $\text{Cu}(\text{II})$ carboxylates gave more significant *ortho* functionalization, possibly as a result of a weak directing effect from the oxygen atom.^[28]

In a previous report, we found that meta:para selectivity using $\text{Cu}(\text{OPiv})_2$ as the oxidant with $[\text{Ir}(\text{C}_2\text{H}_4)_2\text{Rh}(\mu\text{-OAc})_2]$ as the catalyst precursor for the alkenylation of mono-substituted arenes (e.g., toluene, ethylbenzene, *tert*-butylbenzene) with mono-substituted olefins (e.g., ethylene, propylene, vinyl cyclohexane) under anaerobic conditions is likely controlled by a combination of thermodynamic and kinetic contributions (Scheme 4).^[24] Since arene C-H activation is reversible, under conditions with high $[\text{HOPiv}]$ and low $[\text{C}_2\text{H}_4]$, an equilibrium between meta and para Rh-aryl intermediates likely contributes to the observed *ortho*:meta:para regioselectivity with ratios close to ~2:1. In contrast, reactions performed with low $[\text{HOPiv}]$ and high $[\text{C}_2\text{H}_4]$ give meta:para ratios close to ~1:1. We attributed this to para C-H activation being kinetically favored due to sterics with higher ethylene concentration decreasing the reversibility of toluene C-H activation by increasing the rate of ethylene insertion.^[24] This effect was particularly pronounced with anisole as the arene, which we studied in detail in a subsequent study.^[26]

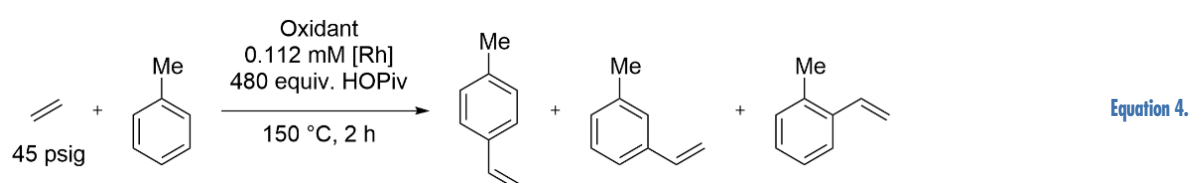


Scheme 4. Proposed equilibria and reactions that contribute to *ortho*:meta:para regioselectivity for Rh catalyzed alkenylation of mono-substituted arenes.

Table 4. *meta:para* regioselectivity for toluene ethenylation reactions under different conditions with different oxidants. Eq. 4.

Entry	Catalyst precursor	Oxidant	% Selectivity		
			<i>Ortho</i> functionalization	<i>Meta</i> functionalization	<i>Para</i> functionalization
1	Rh ^I	Cu(OPiv) ₂	Trace	58	42
2	Rh ^I	Cu(OPiv) ₂ /O ₂	Trace	52	48
3	Rh ^I	Fe(OAc) ₂ /O ₂	Trace	61.5	38.5
4	Rh ^I	Fe ₆	Trace	65.5	34.5
5	Rh ^I	O ₂	Trace	58	42
6	Pd(OAc) ₂	Cu(OPiv) ₂	20	40	40

Rh^I = $[\eta^2\text{-C}_2\text{H}_4]_2\text{Rh}(\mu\text{-OAc})_2$; Fe₆ = Fe₆(μ-OH)₂(μ₃-O)₂(μ-OPIV)₁₂(HOPIV)₂. Detailed reaction conditions can be found in original publications.

**Table 5.** Comparison of *ortho:meta:para* regioselectivity in reported Pd(OAc)₂-catalyzed nondirected C–H alkenylation of toluene with acrylate coupling partners. Detailed reaction conditions can be found in original publications.

Entry	Arene	Olefin	Catalyst precursor	Oxidant	Ligand/Additive	Time (h)	Temp (°C)	<i>o:m:p</i> ratio
1	toluene	ethyl acrylate	Pd(OAc) ₂	PhCO ₃ tBu	Pyridine	6	100	1:1.2:1.3
2	toluene	ethyl acrylate	Pd(OAc) ₂	<i>t</i> -BuOOH & Benzoquinone	–	12	90	1:1:3
3	toluene	butyl acrylate	Pd(OAc) ₂	Benzoquinone/O ₂	Fe(II) phthalocyanine	24	90	1:1:2.5
4	toluene	methyl acrylate	Pd(OAc) ₂	(NH ₄) ₂ S ₂ O ₈	–	24	rt	1.3:1:2.9

Using Pd(OAc)₂ as the catalyst precursor under otherwise identical conditions to the Rh catalysis with Cu(OPiv)₂ as the oxidant was performed in the presence of 1 atm of air. For the reaction of toluene with ethylene an *ortho:meta:para* selectivity of ~0.5:1.0:1.0 was observed. The greater predilection towards *ortho* functionalization observed for Pd catalysis was attributed to the C–H activation step containing significant electrophilic character for Pd, whereas Rh catalysis possibly activates C–H bonds through an oxidative addition pathway, a rationalization that is consistent with Density Functional Theory (DFT) calculations.^[25] The Sanford group studied toluene alkenylation with ethyl acrylate using Pd(OAc)₂ as the catalyst precursor in the presence of pyridine ligands using PhCO₃tBu as the oxidant and observed an *ortho:meta:para* ratio of ~1:1.2:1.3, a greater predilection towards *ortho*-functionalization than observed with Cu(OPiv)₂ as the oxidant.^[11] Fujiwara and coworkers reported Pd(OAc)₂ catalyzed arene alkenylation in the presence of *tert*-butylhydroperoxide and benzoquinone with a reported 1:1:3 *ortho:meta:para* ratio for alkenylation of toluene with ethyl acrylate.^[56] Similarly, with Pd(OAc)₂ as the catalyst precursor, Bäckvall and coworkers reported around a 1:1:2.5 selectivity for reaction of butyl acrylate with toluene using benzoquinone as the direct oxidant and Fe(II) phthalocyanine as a catalyst

to re-oxidize hydroquinone to benzoquinone with dioxygen.^[55] You and coworkers reported Pd(OAc)₂-catalyzed conversion of arenes with electron-deficient olefins using (NH₄)₂S₂O₈ as the oxidant, and observed around a 1.3:1.0:2.9 *ortho:meta:para* ratio for reaction of toluene with methyl acrylate.^[59]

Meta to *para* regioselectivity with quinones was studied with *tert*-butylbenzene as the arene substrate and ethylene as the olefin using 0.112 mM of $[\eta^2\text{-C}_2\text{H}_4]_2\text{Rh}(\mu\text{-OPiv})_2$ as the catalyst precursor, 240 equiv of quinone (relative to single Rh atom), 70 psig of ethylene and 960 equiv of HOPIV at 170 °C.^[30] Variation of *para*-benzoquinone identity resulted in *meta:para* selectivity between 1.31(2):1 and 1.78(6):1 with no observation of *ortho* product. These ratios did not strongly correlate with quinone oxidizing ability or donor ability of putative Rh-coordinated ligands. In contrast, *meta* selectivity with *ortho*-benzoquinones increased as quinone donor ability increased. Use of *ortho*-chloranil as the oxidant resulted in a *meta:para* of 1.49(4):1, 9,10-phenanthrene dione gave 2.03(7):1 selectivity, 1,2-naphthoquinone 2.0(1):1 and 3,5-di-*tert*-butyl-*ortho*-benzoquinone 2.8(1):1. We attributed this to an *ortho*-chloranil semi-quinone or catecholate ligand forming an electron-deficient Rh complex, which results in a more electrophilic C–H activation process, favoring the *para* position. In contrast to the case

of *ortho*-chloranil, a comparatively electron-rich Rh complex forms upon reaction with 3,5-di-*tert*-butyl-*ortho*-benzoquinone, and a classical concerted metalation-deprotonation could occur, favoring the meta position.^[30]

To provide more definitive evidence for differences in C–H activation mechanism, our group has performed intermolecular competition arene ethenylation experiments with equimolar quantities of toluene and *a,a,a*-trifluorotoluene.^[25,30,43] For Rh catalysis using Cu(II) carboxylates as the oxidant under both anaerobic and aerobic conditions, toluene and *a,a,a*-trifluorotoluene undergo ethenylation at statistically identical rates.^[25,43] In contrast, for catalysis using Pd(OAc)₂ as catalyst precursor, toluene reacts ~10-fold faster than electron-deficient *a,a,a*-trifluorotoluene, strengthening evidence for the C–H activation containing electrophilic character for the Pd-based catalysis.^[25] For Rh catalysis with dioxygen as the oxidant, toluene reacts more rapidly than *a,a,a*-trifluorotoluene, also consistent with its C–H activation step containing at least some electrophilic character. Use of Fe(OAc)₂ under aerobic conditions results in *a,a,a*-trifluorotoluene reacting slightly faster than toluene, which is potentially consistent with a classical concerted metalation-deprotonation, which favors acidic C–H bonds, occurring.^[43] Similarly, with 3,5-di-*tert*-butyl-*ortho*-benzoquinone as the oxidant, *a,a,a*-trifluorotoluene reacts faster than toluene, indicating significant deprotonation character in the C–H activation step. Use of 9,10-phenanthrene dione results in approximately identical rates of toluene and *a,a,a*-trifluorotoluene alkenylation, and *ortho*-chloranil ethenylated toluene faster than *a,a,a*-trifluorotoluene. These results indicate that when coordinated to Rh, *ortho*-quinone ligands can control C–H activation mechanism on a continuum from concerted metalation deprotonations with electrophilic character to those without electrophilic character.^[30,60,61]

Conclusions

Herein, we have overviewed the effect of oxidant identity on catalytic arene alkenylation with a primary focus on our group's studies of Rh-catalyzed arene alkenylation and added discussion of Pd- and Ir-based catalysis. We discussed Cu(II) carboxylates, Fe(III) carboxylates, dioxygen and benzoquinones and their influence on reaction rate and selectivity. Overall, we conclude:

- The rate of styrene production follows the trend Cu(II) > Cu(II)/O₂ > Fe(III)/O₂ = Fe(III) > O₂ for Rh-catalysis. Selectivity for styrene follows the trend O₂ > Cu(II) > Fe(III)/O₂ > Fe(III) > Cu(II)/O₂. In addition, *ortho*-benzoquinones generally give a faster rate of catalysis compared to *para*-benzoquinones.
- For Pd-catalysis with a Cu(II) oxidant, styrene production is increased under aerobic conditions; however selectivity for styrene decreases.
- Linear:branched selectivity follows the trend Cu(II) > Cu(II)/O₂ > O₂ > Fe(III)/O₂ ≈ Fe(III) for Rh-catalysis when using propylene as the olefin. *Ortho*-benzoquinones gave linear:branched selectivities ranging between 2.6:1-4.8:1, while *para*-benzoquinones ranged between 1:1-4:1.
- With Ir-catalysis with a Cu(II) oxidant an increase in linear:branched ratio is observed over time, which we speculate is due to the increase in Cu(II) concentration as the reaction progresses. As a result, Cu(II)-containing hetero multi-metallic complexes are thought to form under the reaction conditions and favor the production of linear alkenyl arenes.
- For Rh-catalyzed alkenylation of mono-substituted arenes, distinct *ortho*/*meta*/*para* regioselectivity is observed as a function of oxidant identity. Cu(II) and Cu(II)/O₂ have sig-

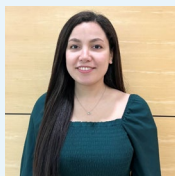
nificantly different regioselectivities, indicating there is a difference in mechanistic pathway and/or catalyst identity. With Pd catalysis, the regioselectivity for alkenylation of substituted olefins is more sensitive to arene substituent than Rh catalysis, and greater *ortho* and *para* functionalization is observed with electron-rich arenes compared to Rh catalysis.

- For mono-substituted arenes, meta selectivity increases as *ortho*-quinone donor ability increases.

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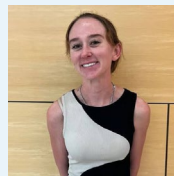
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