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Catalytic Synthesis of Superlinear Alkenyl Arenes Using a Rh(I) Catalyst Supported by a "Capping Arene" Ligand: Access to Aerobic Catalysis

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S Supporting Information

ABSTRACT: Alkyl and alkenvl arenes are used in a wide range of products. However, the synthesis of 1-phenylalkanes or their alkenyl variants from arenes and alkenes is not accessible with current commercial acid-based catalytic processes. Here, it is reported that an air-stable Rh(I) complex, $(5-FP)Rh(TFA)(\eta^2-C_2H_4)$ (5-FP = 1,2-bis(N-7-azaindolyl)benzene; TFA = trifluoroacetate), serves as a catalyst precursor for the oxidative conversion of arenes and alkenes to alkenyl



arenes that are precursors to 1-phenylalkanes upon hydrogenation. It has been demonstrated that coordination of the 5-FP ligand enhances catalyst longevity compared to unligated Rh(I) catalyst precursors, and the 5-FP-ligated catalyst permits in situ recycling of the Cu(II) oxidant using air. The 5-FP ligand provides a Rh catalyst that can maintain activity for arene alkenylation over at least 2 weeks in reactions at 150 °C that involve multiple Cu(II) regeneration steps using air. Conditions to achieve >13 000 catalytic turnovers with an 8:1 linear:branched (L:B) ratio have been demonstrated. In addition, the catalyst is active under aerobic conditions using air as the sole oxidant. At 80 °C, an 18:1 L:B ratio of alkenyl arenes has been observed, but the reaction rate is substantially reduced compared to 150 °C. Quantum mechanics (QM) calculations compare two predicted reaction pathways with the experimental data, showing that an oxidative addition/reductive elimination pathway is energetically favored over a pathway that involves C-H activation by concerted metalation-deprotonation. In addition, our QM computations are consistent with the observed selectivity (11:1) for linear alkenyl arene products.

INTRODUCTION

Billions of pounds of alkyl and alkenyl arenes are produced each year, and they serve as precursors for plastics, elastomers, detergents, and pharmaceuticals.¹⁻⁵ For example, the global production of ethylbenzene is over 20 million tons annually with approximately 98% of ethylbenzene converted to styrene.^{1,6-9} Currently, ethylbenzene is produced from benzene alkylation with ethylene either using Friedel-Crafts catalysis with AlCl₃ and a Brønsted acid or using acidic zeolite catalysts.^{5,10} These acid-based catalysts often produce polyalkylated products, which results in the need for distillation followed by catalytic transalkylation of the polyalkyl arenes with arene to optimize the yield of monoalkyl arene product (for example, processes for ethylbenzene production).¹ Longchain alkylbenzenes are converted to alkylbenzenesulfonates, which are the active component in detergents, through alkyl benzenesulfonation. In the 1960s, branched alkylbenzenesulfonates (BASs), produced by sulfonation of branched alkyl benzenes (Chart 1), were used widely as raw materials for domestic detergents. However, their low rate of biodegradation led to pollution.¹¹ Linear alkylbenzenes (LABs) were introduced in the mid-1960s as a precursor for making linear alkylbenzenesulfonates (LASs), which provided the environmental benefit of more facile biodegradations. Since then, LASs have gradually replaced BASs and have become the main component in modern detergents.^{11,12} Currently, LABs are produced from benzene alkylation with terminal olefins using acidic catalysts.¹¹ These acid-based methods generate carbocationic intermediates that undergo electrophilic aromatic substitution. As a result, the major fractions of LABs are 2- and 3-phenyl alkanes.⁵ The production of 1-phenyl alkanes, or the alkenyl analogs, is not possible with current commercial acid-based catalysts.¹³ To differentiate the 1-phenyl alkanes from the predominantly 2-substituted LABs, we have labeled the former superlinear alkyl benzenes (SLABs, Chart 1) or superlinear alkenyl benzenes for their unsaturated variants.

Transition metal mediated olefin hydroarylation or oxidative olefin hydroarylation can circumvent the formation of carbocationic intermediates and presents a potential alternative to acid-based catalysis for alkyl or alkenyl arene synthesis. Transition metal catalyzed olefin hydroarylation reactions often combine olefin insertion into metal-aryl bonds with metal-mediated C-H activation $^{14-28}$ and offer possible

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Scheme 1. Current Processes for the Synthesis of Styrene, Linear Alkyl Benzenes (LABs) and Reported Processes for the Synthesis of Alkane Benzenes That Can Be Hydrogenated to Form Superlinear Alkyl Benzenes (SLABs)



Scheme 2. Illustration of Our Concept of Using the "Capping Arene" Ligand 5-FP to Inhibit the Air Oxidation of Rh(I) to Rh(III)



advantages over acid-based processes including (1) direct oxidative alkenylation (as opposed to alkylation), (2) production of 1-aryl alkanes or alkene precursors, and (3) control over the regioselectivity for alkylation or alkenylation of substituted arenes. By controlling the regioselectivity of the olefin insertion step (i.e., 1,2- vs 2,1-insertion), it is possible to selectively produce 1-phenyl alkanes or their unsaturated alkenyl variants (Scheme 1). For example, Ru(II) and Ir(III) catalysts have been reported to convert benzene and α -olefins such as propylene or 1-hexene to alkyl arenes with \sim 1.6:1 linear:branched (L:B) ratios.^{16,18,29,30} In contrast, Pt complexes have been shown to catalyze olefin hydroarylation slightly favoring the generation of branched products.³¹⁻³⁴ However, similar to the Ru(II) and Ir(III) catalysts, one example of a Pt catalyst that achieves a L:B ratio of 1.6:1 with 1-hexene as olefin has been reported.³² It has been demonstrated that a Ni(II) complex can mediate olefin hydroarylation with trifluoromethyl-substituted arenes with a L:B ratio up to 19:1, but these transformations are stoichiometric in Ni.³⁵ In a different approach, 1-aryl alkanes have been prepared through dehydrogenation of alkyl arenes followed by olefin cross-metathesis.^{36,37} In addition, Kim and co-workers showed that a Rh complex could generate linear products using heterofunctionalized 2-phenylpyridine and terminal alkenes.³⁸ Thus, to the best of our knowledge, the

L:B selectivity for catalytic benzene alkylation when using simple α -olefins (e.g., propene, 1-hexene) either favors branched products or is only modestly selective for linear products with at best 1.6:1 L:B ratios.

Recently, our group reported that $(^{FI}DAB)Rh(TFA)(\eta^2$ - C_2H_4) (^{FI}DAB = N_1N' -bis(pentafluorophenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene; TFA = trifluoroacetate) serves as a catalyst precursor for the oxidative hydrophenylation of ethylene to produce styrene using Cu(II) salts as the in situ oxidant.^{39,40} We also reported that the simple Rh complex $[Rh(\mu-OAc)(\eta^2-C_2H_4)]_2$ is a catalyst precursor to convert α olefins and arenes to alkenyl arenes with high anti-Markovnikov selectivity (up to a 10:1 L:B ratio).⁴¹ An advantage of these processes is that the reduced Cu(I) product can be easily regenerated to Cu(II) upon mixing with air, a transformation that is well known and has been industrially used for Pd-catalyzed ethylene oxidation. $^{42-45}$ However, under our previously reported conditions, these two Rh catalysts can only maintain catalytic activity under an inert atmosphere that avoids air or oxygen. Thus, in situ air regeneration of the Cu(II) oxidant was not demonstrated. More ideal would be air-tolerant catalysts for which the Cu(II) oxidant could be easily regenerated in situ or the Cu(II) could be replaced with air or oxygen. Yet, accessing air-stable Rh catalysts is a challenge since the conversion of Rh(I) to Rh(III) peroxide

complexes is often facile.⁴⁶⁻⁴⁸ We speculated that issues regarding oxidative degradation of previously reported Rh catalysts were a result of this facile aerobic oxidation. Thus, we sought to design a ligand that would thermodynamically and/ or kinetically suppress the oxidation of Rh(I). Oxidation from Rh(I) to Rh(III) is generally favored by formation of octahedral products that provide electronically saturated 18electron complexes. We speculated that the ligand 5-FP [5-FP = 1,2-bis(N-7-azaindoly)benzene], which we have termed a "capping arene" ligand, would prevent the coordination of a sixth strongly donating ligand to the metal center upon its oxidation to Rh(III) and, hence, stabilize Rh(I) against oxidation by oxygen and permit catalysis under aerobic conditions (Scheme 2). $^{49-51}$ Using this design, we report a new Rh catalyst precursor that achieves efficient oxidative olefin hydroarylation using air either to recycle Cu(II) oxidants or as the sole oxidant. The new Rh complex, (5-FP)Rh- $(TFA)(n^2-C_2H_4)$ (1), catalyzes the conversion of benzene and propylene to linear alkenyl arenes in the presence of oxygen or using air as the *in situ* oxidant. Turnovers (TOs) > 13 000 with an 8:1 L:B ratio of alkenyl arenes have been achieved with no evidence of catalyst decomposition after 2 weeks at 150 °C. At 80 °C, a L:B ratio of ~18:1 has been observed. Although the source of the catalytic enhancement is not experimentally demonstrated, our studies indicate that this approach has led to an improved catalytic process.

RESULT AND DISCUSSION

The ligand 1,2-bis(N-7-azaindolyl)benzene was synthesized according to a published procedure.⁵² The Rh(I) complex 1 was synthesized by mixing 5-FP and $[Rh(\mu-TFA)(\eta^2-C_2H_4)]_2$ in tetrahydrofuran (THF). Complex 1 has been characterized by multinuclear NMR spectroscopy, elemental analysis, and a single-crystal X-ray diffraction study. As anticipated, the ¹³C and ¹H NMR data of 1 are consistent with an asymmetric complex. For coordinated ethylene, the ¹H NMR spectrum reveals two broad peaks, which is consistent with rapid rotation of ethylene on the time scale of the NMR experiment.⁵³ A small coupling constant (~1.5 Hz) is observed between Rh and all hydrogens on the C6 arene ring of the ligand in the ¹H NMR spectrum, which indicates weak coordination of the arene moiety to Rh. The structure of complex 1 was confirmed by single-crystal X-ray diffraction. Figure 1 depicts an ORTEP of complex 1. The coordinated ethylene is oriented approximately perpendicular to the Rh square plane, as is typical for four-coordinate and d⁸ η^2 -olefin complexes.^{53–58} The arene ring of the ligand is positioned with Rh-C8 and Rh–C13 distances of 3.002(3) and 3.008(3) Å, respectively. As expected, these distances are longer than a typical Rh-C single bond, ^{54,59-61} which indicates weak coordination between Rh and the arene moiety. When compared with a similar crystal structure reported by our group in which the ligand has a quinoline other than the 7-azaindole group,⁵⁰ the distance between Rh and the benzene ring center is longer for complex 1 (3.354 vs 3.019 Å, Figure 2). The distance is measured by calculating a centroid with six carbon atoms of the benzene ring and then measuring the distance between the Rh atom and the centroid. Thus, the five-membered nitrogen heterocycle of the 7-azaindole group likely weakens the Rharene bonding interaction by positioning the arene group farther from the Rh center than the six-membered ring of the quinoline-based ligand. This feature seemingly provides an ability to fine-tune the Rh-arene interaction, which could be



Figure 1. OPTEP of (5-FP)Rh $(TFA)(\eta^2\text{-}C_2H_4)$ (1). Ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Rh1–C21 2.101(3), Rh1–C22 2.096(3), C8–Rh1 3.002(3), C13–Rh1 3.008(3), N1–Rh1 2.134(2), N4–Rh1 2.022(2). Selected bond angles (deg): C5–N2–C8 127.0(2), C17–N3–C13 128.4(2), N1–Rh1–N4 86.94(9), C22–Rh1–C21 38.8(1).

important to future efforts to control Rh-based redox chemistry.

We investigated complex 1 as a catalyst precursor for the oxidative hydrophenylation of ethylene to probe reactivity and optimize the reaction conditions. Table 1 summarizes the results. Heating a 10 mL benzene solution of complex 1 (0.001 mol % relative to benzene) with 50 psig ethylene and $Cu(OPiv)_2$ (240 equiv relative to 1, OPiv = pivalate) at 150 °C affords 114(1) TOs of styrene after 1 h (for all catalytic reactions the average TOs and standard deviations based on at least three separate experiments are given). The percent yields in Table 1 are based on $Cu(OPiv)_2$ as the limiting regent with two equivalents of Cu(II) required per equivalent of styrene. Trace amounts of phenyl pivalate (PhOPiv) and biphenyl were observed as side products but were not quantified. Biphenyl likely forms from a Rh-mediated oxidative benzene coupling reaction, and the generation of PhOPiv results from a slow background reaction that occurs upon heating $Cu(OPiv)_2$ to 150 °C in benzene.⁶² The conversion of benzene, ethylene, and $Cu(OPiv)_2$ to styrene using complex 1 can achieve a >90% yield with high selectivity for styrene. Under most conditions, small amounts of trans-stilbene from the hydrophenylation of styrene were also detected as shown in Table 1.

We investigated the influence of temperature on the reaction (Table 1, entries 1–4). The reaction time is reduced by raising the temperature from 120 °C to 180 °C; however, the yield decreases at 180 °C with an increase in production of *trans*-stilbene (0.6 TOs vs 5.2 TOs) and PhOPiv.⁶³ Under the conditions studied, the optimal temperature is 150 °C, which provides a 95% yield of styrene. Higher ethylene pressure can facilitate the reaction (Table 1, entries 3, 5–7), as indicated by a reduction in time to achieve a >90% yield from 4 h at 15 psig of ethylene (entry 5) to 1 h at 70 psig of ethylene (entry 7).

Entries 8–10 in Table 1 demonstrate that the addition of pivalic acid can benefit the reaction. The reaction rate is enhanced, and the over 90% yield can still be achieved. For example, at 50 psig of ethylene at 150 °C without added pivalic acid, the reaction requires about 1 h to reach >90% yield (entry 3), but with added pivalic acid the time to achieve a >90% yield is reduced to 0.5 h (entries 8–10). We suggest that pivalic acid has two possible benefits. First, acid increases the solubility of the Cu(OPiv)₂ in benzene. Second, it is known that Cu(OAc) and water undergo reaction to generate acetic



Figure 2. Structure comparison between $(5-FP)Rh(TFA)(\eta^2-C_3H_4)$ (1) and former reported "capping arene" complex.⁵⁰

Table 1. Results for Oxidative Hydrophenylation of Ethylene Using $(5-FP)Rh(TFA)(\eta^2-C_2H_4)$ (1) as Catalyst Precursor



					products/ 1 Os			
	temp/°C	acid ^a /equiv	$C_2H_4/psig$	time/h	styrene	trans-stilbene	% yield styrene ^b	
1	120		50	16	109(9)	0.6	91	
2	130		50	10	107(3)	0.2	89	
3	150		50	1	114(1)	1.3	95	
4	180		50	0.5	83(8)	5.2	69	
5	150		15	4	113(7)	0.4	94	
6	150		25	2	108(3)	1.0	90	
7	150		70	1	109(4)	0.2	91	
8	150	240	50	0.5	109(2)	1.6	91	
9	150	480	50	0.5	108(1)	2.0	90	
10	150	2400	50	0.5	108(6)	2.2	90	
11 ^c	150	2400	50	7	671(42)	124(12)	56	
12 ^{<i>c</i>,<i>d</i>}	150		500	6	632(5)	4	53	
13 ^e	150	480	50	40	96(5)	1.4	80	

^{*a*}Acid additive is HOPiv for entries 8–11, HOAc for entry 13. ^{*b*}Yields are relative to the limiting reagent Cu(II) oxidant. ^{*c*}2400 equiv of Cu(OPiv)₂ was used in the reaction. ^{*d*}The reaction is carried out in a stainless steel Parr reactor. ^{*e*}240 equiv of Cu(OAc)₂ was used in the reaction.

acid and a Cu oxide.⁶⁴ Oxidation of Cu(I) salts and acid (pivalic or acetic acid) to Cu(II) produces water. Thus, the Cu(I)/H₂O reaction becomes important to the longevity of the catalytic process, as the addition of acid (e.g., pivalic or acetic) can inhibit the water-induced decomposition of Cu(OAc) or Cu(OPiv) (see below for studies of catalyst longevity).

Using a large amount of Cu(II) (2400 equiv relative to 1, entry 11) results in a decreased yield of styrene (\sim 56%) due to the formation of *trans*-stilbene. Importantly, when using 500 psig of ethylene in order to promote the formation of styrene, the reaction can achieve a >99:1 selectivity for styrene over *trans*-stilbene (entry 12). Thus, using high olefin concen-

trations can effectively suppress the formation of "double" arylation products. However, only a ~50% yield is observed with high ethylene pressure. This could be due to the production of vinyl pivalate at higher ethylene concentrations. In addition, the reaction in entry 12 used stainless steel reactors, which gives rise to a difference in heating compared to the glass Fischer–Porter vessels. The use of Cu(II) acetate reduces the yield from ~90% with Cu(OPiv)₂ to ~80% (entries 9 and 13, Table 1).

Next, we probed the use of 1 for the oxidative hydrophenylation of propylene (Table 2). Heating 10 mL of a benzene solution of complex 1 (0.001 mol % relative to benzene) to 150 °C with 30 psig of propylene with $Cu(OPiv)_2$



^{*a*}Acid additive is HOPiv for entries 1–6, HOAc for entry 7. ^{*b*}Yield is relative to Cu(II). ^{*c*}2400 equiv of $Cu(OPiv)_2$ was added to the reaction. ^{*d*}240 equiv of $Cu(OAc)_2$ was added to the reaction.

(240 equiv relative to 1) and HOPiv (480 equiv relative to 1) over 0.5 h affords 86 TOs with a L:B ratio of ~11:1. The L:B ratio is determined based on the *n*-propylbenzene to cumene ratio that would result from hydrogenation of the alkenyl products (i.e., it is the ratio of allylbenzene and β -methylstyrenes vs α -methylstyrene; see Table 2). The L:B ratio of products increases to 18:1 when the temperature is decreased from 150 °C to 80 °C, but catalyst activity is decreased (Table 2, entries 1–5). No alkenyl benzene products were observed after 110 h when the temperature is 60 °C.

In order to test the catalyst longevity, a large amount of $Cu(OPiv)_2$ (2400 equiv relative to 1) was used in the conversion of benzene and propylene. This resulted in 900 TOs (79% yield) after 10 h. The yield is similar to lower Cu(II) oxidant loading (Table 2, entries 1 and 6). For the oxidative hydrophenylation of ethylene to produce styrene under similar conditions (Table 1, entry 11), only 671 TOs are produced with >120 TOs of stilbene production. But, for the oxidative hydrophenylation of propylene, only ~20 TOs of 1,1'-(*E*)-1-propene-1,3-diylbis[benzene] are formed compared to the amount of *trans*-stilbene from the reaction with ethylene. It may that the steric bulk of propenyl arenes inhibits a second hydrophenylation; however, electronic influences might also be important.

One of the drawbacks of our previously reported Rh catalysts is that under the reported conditions catalytic activity is only maintained under an inert atmosphere.³⁹⁻⁴¹ Since the "capping arene" ligand was selected to protect the Rh complex against oxidative degradation or suppression of catalysis in the presence of air, reaction with in situ aerobic Cu(II) regeneration was probed with 0.001 mol % complex 1, 30 psig of propylene, 240 equiv of Cu(OPiv)₂ and 480 equiv of HOPiv at 150 °C. Without regeneration of Cu(II), the maximum TOs are 120. For these experiments, air was added to the reactor after consumption of Cu(II) oxidant, and the reaction mixture was heated at 120 °C for in situ Cu(OPiv)₂ regeneration. After regeneration of Cu(II) (indicated by a color change from bronze to blue; see Supporting Information), air was removed with a propylene purge, and the mixture was again heated at 150 °C to continue oxidative propylene hydrophenylation. Both complex 1 and $[Rh(\mu -$

 $OAc)(\eta^2-C_2H_4)]_2$ were tested to provide a direct comparison of the impact of the capping arene ligand to the $[Rh(\mu-OAc)(\eta^2-C_2H_4)]_2$ catalyst precursor (Figure 3). Complex 1



Figure 3. Oxidative hydrophenylation of propylene with *in situ* Cu oxidant regeneration. Plot of turnovers versus time, reaction conditions: [Rh] = 0.001 mol % of complex 1 or $[Rh(\mu-OAc)(\eta^2-C_2H_4)]_2$ in 10 mL of benzene, 240 equiv of $Cu(OPiv)_2$, 480 equiv of HOPiv, 30 psig of propylene. The reactor is refilled with air and 50 psig of N₂ at every sampling point for regenerating Cu oxidant at 120 °C, and then all air is removed and the reactor is pressurized with 30 psig of propylene.

maintains activity through 10 air cycling procedures, achieving ~800 TOs, and complex 1 clearly outperforms $[Rh(\mu - OAc)(\eta^2-C_2H_4)]_2$ in both activity and longevity. As can be seen in Figure 2, after ~800 TOs have been reached, catalytic activity decreases; however, upon addition of pivalic acid and more benzene, catalyst activity resumes (see Supporting Information, Figure S4). Thus, the decrease in activity of 1 in Figure 2 is *not* due to catalyst degradation. Rather, it is likely due to the equilibrium between Cu(OPiv) and water with pivalic acid and Cu oxide (see brief discussion above), and the addition of pivalic acid can shift the equilibrium to permit facile air recycling to form the Cu(II) oxidant Cu(OPiv)_2.

Next, we tested the ability of complex 1 to catalyze benzene alkenylation under aerobic conditions *during catalysis* through

the combination of benzene, propylene, $Cu(OPiv)_2$, and HOPiv in the presence of air. That is, rather than recycling Cu(II) with air and then removing the air, we performed catalysis in the presence of air. It is noteworthy that these experiments used unpurified air and not purified oxygen. Figure 4A shows TOs and L:B ratios versus time for 0.001 mol % complex 1, 30 psig of propylene with 1 atm of air, 240 equiv of Cu(OPiv)₂, and 2400 equiv of HOPiv at 150 °C. In the absence of air, the maximum TOs are 120. Catalysis continues over a period of at least 2 days with no evidence of catalyst deactivation, as shown by the linear TOs versus time plot to give >1200 TOs after 48 h. The L:B ratio is ~ 7 (Figure 4B), which is reduced compared to catalysis under anaerobic conditions (L:B ratio is ~11). As catalysis progresses, the L:B ratio increased from 6:1 (4 h plot) to 8:1 (48 h plot), but this is due to the slow reaction of the branched product α methylstyrene in the presence of air (see Figure S5). The observed TOF (turnover frequency, calculated from Table 1, entry 8, and the first data point in Figure 4A) is decreased from 0.06 TOs/s for catalysis under anaerobic conditions to 0.01 TOs/s for catalysis under aerobic conditions. When the catalyst loading is reduced to 0.0001 mol % of 1 relative to benzene, greater than 13 000 TOs can be reached after 336 h with no evidence of catalyst deactivation (Figure 4C). The results suggest that complex 1 is quite stable under aerobic conditions using unpurified air at 150 °C. Since it has been reported that Rh and Ru catalysts can produce alkenyl arenes using purified oxygen as the oxidant, 65-67 complex 1 was probed using 1 atm of unpurified air as the sole oxidant in the absence of Cu(II). The catalysis is successful with >500 TOs after 240 h with a L:B ratio of ~5 (see Figure S6). Thus, complex 1 can catalyze oxidative alkenyl arene formation using only oxygen as the oxidant, but the observed TOF is decreased to 6×10^{-4} TOs/s (calculated with the 240 h time plot), and the L:B ratio is also decreased.

Increasing the Cu(II) amount (relative to complex 1) for the oxidative hydrophenylation of ethylene resulted in a decrease in the yield compared to lower Cu(II) amounts. For example, the yield drops from 90% to 56% when 2400 equiv of $Cu(OPiv)_2$ was applied compared with 240 equiv of Cu(OPiv)₂ (Table 1, entries 10 and 11). However, for oxidative hydrophenylation of propylene a corresponding decrease in yield is not observed upon increasing the Cu(II) amount. For example, the yield increased from 72% to 79% when 2400 equiv of Cu(OPiv)₂ was used compared to 240 equiv of $Cu(OPiv)_2$ (Table 2, entries 1 and 6). Based on these observations, we studied possible product inhibition by styrene and allylbenzene, separately, for the hydrophenylation of ethylene and propylene. To do so, we added different amounts of styrene or allylbenzene at the beginning of the reaction to determine the influence of the products on the rate of catalysis. Styrene inhibited the reaction substantially with percent yield decreasing by slightly more than 2-fold from 95% to 44% after 1 h when 480 equiv of styrene (relative to 1) was added at the start of the reaction (Table 3, entries 1 and 3). Conversely, we found that addition of pivalic acid mitigates the product inhibition; the percent yield increased from 44% to 58% after 1 h when 480 equiv of pivalic acid (relative to 1) is added to the reaction (Table 3, entries 3 and 5). However, the yield still decreases \sim 40% compared with the non-styrene addition trial (Table 3, entries 1 and 5). Allylbenzene exhibits less inhibition than styrene; the percent yield decreased from 72% to 57% when 480 equiv of allylbenzene is added at the beginning of



Figure 4. Hydrophenylation of propylene under aerobic conditions. (A) Plot of turnovers versus time, reaction conditions: [Rh] = 0.001 mol % 1 in 10 mL of benzene, 240 equiv of $Cu(OPiv)_2$, 2400 equiv of HOPiv, 30 psig of propylene with 1 atm of air at 150 °C. The reactor is refilled with air at every sampling point. (B) L:B ratio versus time plot; reaction conditions are the same as in A. (C) Plot of turnovers versus time; reaction conditions: 0.0001 mol % Rh, 2400 equiv of $Cu(OPiv)_2$, 48 000 equiv of HOPiv, 1 atm of air, 30 psig of propylene, at 150 °C. Fresh air was purged to the reactor every 24 h, and the reaction mixture was sampled every 48 h at every sample point. The data are from four separate experiments with standard deviations given.

Table 3. Study of Product Inhibition of Rh-Catalyzed Oxidative Hydrophenylation of Ethylene or Propylene Using Styrene and Allylbenzene^a

				products/TOs		
	amount of added vinyl arene/equiv ^b	HOPiv/ equiv	time/h	alkenyl benzene	<i>trans-</i> stilbene	L:B ratio
1			1	114(1)	1.3	
2	240		1	78(3)	5(1)	
3	480		1	53(3)	9(1)	
4	960		1	3(13)	22(4)	
5	480	480	1	69(7)	7(1)	
6		480	0.5	86(4)		11
7	480	480	0.5	68(2)		10

"Reaction conditions: 0.001 mol % complex 1 relative to benzene, 240 equiv of $Cu(OPiv)_2$, 50 psig of ethylene or 30 psig of propylene reacted at 150 °C. ^bStyrene is added for entries 1–5 and allylbenzene is added for entry 7. Loading is relative to complex 1.

the reaction (Table 3, entries 5 and 7). At this point we cannot assign the increased influence of styrene relative to allylbenzene to either steric or electronic effects. But, it might be expected that other products from hydrophenylation of propylene (α -methylstyrene, *cis*- β -methylstyrene, and *trans*- β -methylstyrene), which have less sterically accessible double bonds, will exhibit less product inhibition on the rate of catalysis.

Density functional theory (DFT) calculations were used to predict the elementary steps that could be responsible for the reactions of ethylene and propene catalyzed by complex 1.⁶⁹ The predicted free energy surfaces at experimental conditions suggest an oxidative arylation mechanism comprising benzene C–H activation, olefin insertion, β -hydride elimination, and regeneration by O₂ or Cu(II). Our predicted L:B ratio of 11:1 from the relative free energies of propene insertion transition states is consistent with the experimentally observed ratio of 11:1 (Table 2), which supports the mechanism from the DFT calculations.

At concentrations mimicking reaction conditions, displacement of ethylene from 2 by benzene is predicted from the DFT to be endergonic by 9.2 kcal/mol (Figure 5). Benzene C–H activation by a concerted metalation–deprotonation (CMD) mechanism has a DFT-predicted barrier of 30.6 kcal/mol. Alternatively, oxidative insertion of Rh(I) into a C–H bond followed by reductive elimination of pivalic acid leads to barriers that are lower for both the C–H oxidative addition step (24.4 kcal/mol) and the O–H reductive elimination (26.6 kcal/mol). Thus, despite the observation for many other reactions that the CMD pathway is favored for C–H activation,⁷⁰ the DFT calculations predict that for this system the oxidative addition/reductive elimination process is favored by 4 kcal/mol.

Liberation of HOPiv and coordination of ethylene generates a Rh(I) phenyl species (5) that can form a C–C bond via olefin insertion. The DFT-predicted transition state for ethylene insertion (TS3) lies 26.4 kcal/mol above starting complex 2 and 22.6 kcal/mol above the precursor 5. The three-coordinate Rh(I) alkyl complex 6 leads to styrene formation via a facile β -hydride elimination through TS4, although this can be inhibited by the favorable coordination of an additional ethylene to form 6'. The resulting Rh(I) hydride with styrene coordinated (7) can undergo ligand exchange with ethylene to form free styrene and complex 8. Either complex 7 or 8 can potentially react with Cu(II) to regenerate complex 2.

Minor products can result from branches off this pathway. Protonolysis of the Rh–C bond in 6 would divert the reaction to produce ethylbenzene. However, using pivalic acid or benzene as a proton source, the barriers for this reaction are predicted to be 8 or 18 kcal/mol higher, respectively, than the β -hydride elimination reaction that leads to the observed product styrene. A more competitive detour is the generation of stilbene by the insertion of styrene in 5' via TS3'. The barrier for the insertion of styrene is only 5 kcal/mol higher than the insertion of ethylene, which is consistent with the experimental observation of stilbene formation once styrene is formed by catalysis. Within the accuracy of DFT calculations we cannot distinguish whether C–H activation (specifically the reductive elimination transition state TS2 at 26.6 kcal/mol) or subsequent olefin insertion limits the rate of the overall reaction. Furthermore, the relative rates of these branches are



Figure 5. Free energies (kcal/mol) at 423 K from DFT calculations {M06, including PBF solvation (see Supporting Information)} of the proposed catalytic cycle for conversion of ethylene and benzene to styrene. Conditions: [Rh] = 0.11 mM, [HOPiv] = 0.053 M, 4.4 atm of C_2H_4 , 1 atm of O_2 , [styrene] = [ethylbenzene] = 0.1 M, in benzene.



Figure 6. Free energies (kcal/mol) at 423 K from DFT calculations of our proposed catalytic cycle for the oxidative hydroarylation of propene (conditions as in Figure 5). The inset displays isomers of the olefin insertion transition state, with the propene and phenyl units drawn as cylinders.



Figure 7. Free energies (kcal/mol) at 423 K from DFT calculations for reactions of oxidants with the rhodium hydride **8**. Conditions: $[Cu^{II}] = [Cu^{I}] = [Rh] = [^{\bullet}OOH] = 0.11 \text{ mM}$, [HOPiv] = 0.053 M, 4.4 atm of C_2H_4 , 1 atm of O_2 , in benzene. Superscripts denote spin multiplicities.

sensitive to the evolving concentrations of ethylene and styrene over the course of reaction.

Figure 6 shows the DFT results for the conversion of propene to linear and branched products. Since propene is easier to displace by benzene than ethylene, the computed C-H activation barriers are effectively reduced. The resulting phenyl complex lies about 4 kcal/mol uphill and precedes olefin insertion transition states that lead to linear or branched products. The four distinct arrangements of the C_s-symmetric ligand, propene, and phenyl group were predicted by DFT to have free energies of activation within 3 kcal/mol. Both transition states with linear regiochemistry lead to lower activation barriers (24.0 and 25.2 kcal/mol) than those leading to the branched product (26.2 and 26.8 kcal/mol). The ratio of the summed rates through the linear and branched paths predicted using transition state theory at 150 °C predicts a linear:branched ratio of 11.2:1. The lowest-energy transition state also has a higher vibrational entropy, suggesting the fragments in this arrangement are less tightly packed. The

calculated L:B ratio of 11, which is consistent with the value (11:1) observed from experimental observations (see Table 2), derives from a factor of ~2 from the entropic difference and a factor of ~5 from the enthalpy differences. The activation energies for β -hydride elimination transition states producing branched or linear olefin are more than 10 kcal/mol lower than the olefin insertion barriers. Therefore, the selectivity determined in the insertion step is not expected to be obscured by β -hydride elimination or product dissociation.

As a first step toward understanding the regeneration of 1 by O_2 and Cu(II), intermediates that might result from the reaction of these with the most exergonic, and likely reducing, state in Figure 5 were considered (Figure 7). One feasible route involves the Cu(II)/Cu(I) couple, represented computationally by $Cu(OPiv)_2/Cu(OPiv)(C_6H_6)$. The hydride complex 8 undergoes an exergonic single-electron oxidation by $Cu(OPiv)_2$ via a net carboxyl group transfer. Reductive elimination of pivalic acid to form the Rh(0) complex 10 is also exergonic. A second oxidation to regenerate 2 is highly

exergonic. Direct complexation of O2 to 8 is unlikely: no complex forms on the triplet surface and the singlet 11 is highly exergonic. A role for the capping arene in activating O₂ was considered, but a singlet Rh(III) complex 12 with O₂ bridging the Rh(III) and an arene carbon lies 26 kcal/mol uphill. Dissociation of ethylene from 8 to create a vacancy is also unlikely ($\Delta G = 27.7$ kcal/mol, 13). The transition state for an associative substitution of ³O₂ for ethylene was found (TS5), which could be the entry to rearrangements that exergonically produce rhodium peroxide 18. The activation barrier ($\Delta G^{\ddagger} = 25.5 \text{ kcal/mol}$) is high but comparable to those earlier in the mechanism. Slightly more favorable is a direct hydrogen atom abstraction by ${}^{3}O_{2}$ (TS6, $\Delta G^{\ddagger} = 22.2$ kcal/ mol).⁷¹⁻⁷⁵ However, a radical chain mechanism for converting the hydride is perhaps more likely than the direct involvement of O_2 . For example, reaction of 8 with a hydroperoxy radical (generated photochemically or via decomposition of a peroxide intermediate) yields the Rh(II) complex 14. The weakened Rh–H bond can easily be broken by ${}^{3}O_{2}$ to yield 18, effecting a net insertion of O2 into the RhI-H bond. Alternatively, the Rh(I) superoxide complex 19 is able to abstract a hydrogen atom from 8 exergonically to yield the Rh(0) 10, which regenerates 19 spontaneously via reaction with O₂.⁷⁶ A full mechanistic study including ligands that do not facilitate aerobic oxidation is beyond the scope of this paper, but these DFT calculations indicate that both anaerobic and aerobic pathways are viable.

CONCLUSIONS

To our knowledge, there are no previous examples of catalytic conversion of benzene and propylene to linear alkylbenzene with high selectivity for anti-Markovnikov products under aerobic conditions. We have reported that a "capping arene"-supported Rh(I) complex (5-FP)Rh(TFA)(η^2 -C₂H₄) serves as a catalyst precursor under anaerobic or aerobic conditions. These results represent the following hallmarks: (1) the Rh catalyst is quite stable in air at 150 °C, (2) the catalysis can use air as the direct oxidant without any Cu(II) salts, (3) the Rh catalyst shows a remarkable longevity that can reach a significant turnover number (>13 000) without obvious catalyst deactivation at 150 °C for at least 2 weeks of reaction, and (4) the catalyst can achieve a linear to branched ratio up to 18:1, which is to our knowledge the highest ratio for conversion of hydrocarbon substrates.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques and/or in a glovebox. Glovebox purity was maintained by periodic nitrogen purges and was monitored by an oxygen analyzer $(O_2 < 15 \text{ ppm for all reactions})$. Unless otherwise noted (e.g., for aerobic reactions), dry, oxygen-free solvents were employed throughout and stored over molecular sieves. Benzene was dried by passage through columns of activated alumina. Pentane was dried over sodium benzophenone ketyl. GC/MS was performed using a Shimadzu GCMS-QP2010 Plus system with a 30 m \times 0.25 mm SHRXI-5MS column with a 0.25 μ m film thickness using electron impact (EI) ionization. GC/FID was performed using a Shimadzu GC-2014 system with a 30 m × 90.25 mm SHRXI-5MS/HP5 column with a 0.25 μ m film thickness. ¹H NMR spectra were recorded on a Varian Inova or Bruker Avance III 600 MHz spectrometer, and ¹³C NMR spectra were recorded on a Varian Inova 600 MHz spectrometer (operating frequency 150 MHz). ¹⁹F NMR spectra were recorded on a Varian Inova 600 MHz spectrometer (operating frequency 150 MHz). All ¹H and ¹³C spectra are referenced against residual proton signals (¹H NMR) or ¹³C resonances (¹³C NMR) of the deuterated solvents. ¹⁹F spectra are referenced with hexafluor-obenzene (used as an external standard).

Ethylbenzene, cumene, styrene, phenylacetate, phenyl pivalate, cumene, allylbenzene, α -methylstyrene, trans- β -methylstyrene, cis- β methylstyrene, and biphenyl production was quantified using linear regression analysis of gas chromatograms of standard samples of an authentic product. A plot of peak area ratios versus molar ratios gave a regression line using hexamethylbenzene as the internal standard. For the GC/FID instrument, the slope and correlation coefficient of the regression lines were 1.72 and 0.99 (ethylbenzene), 1.67 and 0.99 (styrene), 0.87 and 0.99 (trans-stilbene), 1.67 and 0.99 (phenylacetate), 1.22 and 0.99 (phenyl pivalate), 1.99 and 0.99 (cumene), 1.40 and 0.99 (allylbenzene), 1.23 and 0.99 (α -methylstyrene), 1.47 and 0.99 (cis- β -methylstyrene), 1.38 and 0.99 (trans- β -methylstyrene), and 0.96 and 0.99 (biphenyl), respectively.

Propylene and ethylene were purchased in gas cylinders from GTS-Welco and used as received. $[Rh(\eta^2-C_2H_4)_2(\mu-TFA)]_2$ and 1,2-bis(*N*-7-azaindoly)benzene were prepared according to literature procedures.^{52,68} All other reagents were purchased from commercial sources and used as received.

Synthesis of $(5-FP)Rh(TFA)(\eta^2-C_2H_4)$ (1). A THF solution (10 mL) of 1,2-bis(N-7-azaindolyl)benzene (0.0810 g, 2.61×10^{-4} mol) was added to a THF solution (10 mL) of $[Rh(\eta^2-C_2H_4)_2(\mu-TFA)]_2$ $(0.0800 \text{ g}, 1.47 \times 10^{-4} \text{ mol})$ dropwise and stirred for 48 h. The reaction mixture was dried under vacuum. The resulting solid was dissolved in minimal THF (2 mL), and pentane (30 mL) was added to the solution to give a yellow precipitate. The solid was collected by filtration, washed with pentane $(3 \times 10 \text{ mL})$, and dried under vacuum to afford the analytically pure 1 (0.110 g, yield = 76%). X-ray quality crystals of 1 were grown by the vapor diffusion method using THF and n-pentane. Note: see Supporting Information for ligand labeling scheme. ¹H NMR (CD₂Cl₂, 600 MHz): δ = 9.27 (dd, ³J_{HH} = 5.3 Hz, 1.4 Hz, 1H, 5 or 5'), 8.37 (d, ${}^{3}J_{HH} = 5.5$ Hz, 1H, 5 or 5'), 7.91 (td, ${}^{3}J_{\rm HH}$ = 7.7 Hz, 1.5 Hz, 1H, 7 or 7′), 7.86 (dd, ${}^{3}J_{\rm HH}$ = 7.9 Hz, 1.6 Hz, 1H, 6 or 6'), 7.77-7.81 (m, 2H, 1H of 6 or 6' and 1H of 7 or 7'), 7.58 (dd, ${}^{3}J_{HH}$ = 7.8 Hz, 1.3 Hz, 1H, 3 or 3'), 7.45 (dd, ${}^{3}J_{HH}$ = 7.9, 1.4 Hz, 1H, 3 or 3'), 7.31 (d, ${}^{3}J_{HH} = 3.6$ Hz, 1H, 1 or 1'), 7.23 (d, ${}^{3}J_{HH} = 3.5$ Hz, 1H, 1 or 1'), 7.08 (dd, ${}^{3}J_{HH} = 7.9$ Hz, 5.3 Hz, 1H, 4 or 4'), 6.73 (dd, ${}^{3}J_{HH}$ = 7.8 Hz, 5.5 Hz, 1H, 4 or 4'), 6.48 (d, ${}^{3}J_{HH}$ = 3.6 Hz, 1H, 2 or 2'), 6.46 (d, ${}^{3}J_{HH} = 3.6$ Hz, 1H, 2 or 2'), 2.75 (br, 2H, r11, 2 of 2), 0.40 (d,) $f_{\rm HH}$ = 5.0 fr2, 11, 2 of 2), 2.75 (df, 21), ethylene-*H*), and 2.54 (br, 2H, ethylene-*H*) ppm. ¹⁹F NMR (CD₂Cl₂, 600 MHz): δ = -74.0 (s, TFA) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 150 MHz): δ = 161.9 (q, OC(O)CF₃, ²J_{CF} = 34 Hz, 151.9 (s, Ar–C), 150.4 (s, Ar–C), 148.8 (s, Ar–C), 146.2 (s, Ar–C), 131.2 (s, Ar–C), 134.8 (s, Ar-C), 131.9 (s, Ar-C), 131.1 (s, Ar-C), 131.0 (s, Ar-C), 130.6 (s, Ar-C), 130.5 (s, Ar-C), 130.4 (s, Ar-C), 130.0 (s, Ar-C), 128.8 (s, Ar-C), 121.8 (s, Ar-C), 121.1 (s, Ar-C), 117.4 (s, Ar-C), 116.6 (s, Ar-C), 103.0 (s, ethylene-C), 102.7 (s, ethylene-C) ppm. Peak of $OC(O)CF_3$ is overlapped with some Ar-C peaks. Anal. Calcd for C₂₄H₁₈F₃N₄O₂Rh: C: 52.00; H: 3.27; N: 10.11. Found: C: 51.21; H: 3.26; N: 10.00.

Catalytic Oxidative Hydrophenylation of Ethylene. A representative catalytic reaction is described (Table 1, entry 9). A stock solution containing 1 (0.0156 g, 0.0280 mmol, 0.001 mol % of rhodium catalyst), hexamethylbenzene (0.0911 g, 0.561 mmol), and benzene (250 mL) was prepared in a volumetric flask. Thick-walled glass Fisher-Porter reactors were charged with stock solution (10 mL), pivalic acid (0.0550 g, 0.539 mmol), and Cu(OPiv)₂ (0.0716 g, 0.269 mmol). The vessels were sealed, pressurized with ethylene (50 psig), and subsequently stirred and heated to 150 °C. The color of the reaction mixture is deep blue at the beginning of the reaction and turns colorless when all Cu oxidant is consumed. The reaction was sampled when the solution turned colorless. The reactors were cooled to room temperature, and aliquots of the reaction mixture (<200 μ L) were analyzed by GC/FID using relative peak areas versus the internal standard (hexamethylbenzene).

Catalytic Oxidative Hydrophenylation of Propylene. A representative catalytic reaction is described (Table 2, entry 1). A

stock solution containing 1 (0.0156 g, 0.0280 mmol, 0.001 mol % of rhodium catalyst), hexamethylbenzene (0.0911 g, 0.561 mmol), and benzene (250 mL) was prepared in a volumetric flask. Thick-walled glass Fisher-Porter reactors were charged with stock solution (10 mL), pivalic acid (0.0550 g, 0.539 mmol), and Cu(OPiv)₂ (0.0716 g, 0.269 mmol). The vessels were sealed, pressurized with propylene (30 psig), and subsequently stirred and heated to 150 °C. The color of the reaction mixture is deep blue at the beginning of the reaction and turns colorless when all Cu oxidant is consumed. The reaction was sampled when the solution turned colorless. The reactors were cooled to room temperature, and aliquots of the reaction (<200 μ L) mixture were analyzed by GC/FID using relative peak areas versus the internal standard (hexamethylbenzene).

Catalytic Oxidative Hydrophenylation of Propylene with Cu(II) Oxidant Using in Situ Regeneration. A representative catalytic reaction is described (using 1 as the catalyst). A stock solution containing 1 (0.0156 g, 0.0280 mmol, 0.001 mol % of rhodium catalyst), hexamethylbenzene (0.0911 g, 0.561 mmol), and benzene (250 mL) was prepared in a volumetric flask. Thick-walled glass Fisher-Porter reactors were charged with stock solution (10 mL), pivalic acid (0.0550 g, 0.539 mmol), and Cu(OPiv)₂ (0.0716 g, 0.269 mmol). The vessels were sealed, pressurized with propylene (30 psig), and subsequently stirred and heated to 150 °C. The color of the reaction mixture is deep blue at the beginning of the reaction and turns colorless when all Cu oxidant is consumed. The reaction was sampled when the solution turned colorless. The reactors were cooled to room temperature, and aliquots of the reaction mixture (<200 μ L) were analyzed by GC/FID using relative peak areas versus the internal standard (hexamethylbenzene). After the sampling, 1 atm of fresh air was purged into the reactor. Then the reactor was pressurized with 50 psig of N2. The reactor was heated to 120 °C for 15 min for in situ Cu(II) oxidant regeneration. After the regeneration, the reactors were cooled to room temperature and purged and pressurized with propylene (30 psig). The vessels were subsequently stirred and heated to 150 °C for the reaction.

Air in Situ Catalytic Oxidative Hydrophenylation of Propylene. A representative catalytic reaction is described (Figure 4A). A stock solution containing 1 (0.0156 g, 0.0280 mmol, 0.001 mol % of rhodium catalyst), hexamethylbenzene (0.455 g, 2.24 mmol), and benzene (250 mL) was prepared in a volumetric flask. Thick-walled glass Fisher-Porter reactors were charged with stock solution (1 mL) and benzene (9 mL), pivalic acid (0.550 g, 5.38 mmol), and Cu(OPiv)₂ (0.0716 g, 0.269 mmol). The vessels were sealed and purged with 1 atm of air, pressurized with propylene (30 psig), and subsequently stirred and heated to 150 °C. After every 24 h, the reactors were cooled to room temperature first and to 0 °C with an ice bath. Then the reactor was purged with air (1 atm), pressurized with propylene (30 psig), and reheated. The reaction mixture was sampled every 48 h. Aliquots of the reaction (<200 μ L) mixture were analyzed by GC/FID using relative peak areas versus the internal standard (hexamethylbenzene). Figure S7 shows the L:B ratio as a function of reaction time. The increase in L:B is due to the consumption of branched products during the reaction (see Supporting Information).

Catalytic Oxidative Hydrophenylation of Propylene Using Air as Oxidant. A stock solution containing 1 (0.0156 g, 0.0280 mmol, 0.001 mol % of rhodium catalyst), hexamethylbenzene (0.0911 g, 0.561 mmol), and benzene (250 mL) was prepared in a volumetric flask. Thick-walled glass Fisher-Porter reactors were charged with stock solution (10 mL) and pivalic acid (0.5500 g, 5.39 mmol). The vessels were sealed and purged with 1 atm of air, pressurized with propylene (30 psig), and subsequently stirred and heated to 150 °C. The reaction was sampled every 48 h. At each time point, the reactors were cooled to room temperature, sampled, purged with air (1 atm), pressurized with propylene (30 psig), and reheated. Aliquots of the reaction mixture (<200 μ L) were analyzed by GC/FID using relative peak areas versus the internal standard (hexamethylbenzene).

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b07728.

Detailed information about the X-ray structure determination and computational modeling (PDF) X-ray crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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