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Article

# Rhodium-Catalyzed Alkenylation of Toluene Using 1-Pentene: **Regioselectivity To Generate Precursors for Bicyclic Compounds**

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Supporting Information

ABSTRACT: Rhodium catalysts for arene alkenylation reported by our group (e.g., Science 2015, 348, 421; J. Am. Chem. Soc. 2017, 139, 5474; J. Am. Chem. Soc. 2018, 140, 17007) have demonstrated selectivity for 1-aryl alkenes over y-aryl alkenes (y > 1). This selectivity is notable because 1-aryl alkenes or 1-aryl alkanes cannot be generated using acid-based Friedel-Crafts arene alkylation or acidic zeolite catalysts. Herein, we report the extension of Rh arene alkenylation catalysis to generate 1-tolyl-1-pentenes, which are potential precursors for bicyclic



compounds. The olefin concentration, copper(II) oxidant identity and concentration, reaction temperature, and rhodium concentration for the alkenylation of toluene with 1-pentene have been optimized using  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$  as the catalyst precursor. The rhodium-based catalysis achieves up to 12(1):1 anti-Markovnikov selectivity for 1-tolyl-1-pentenes over 2-tolyl-2-pentenes and is selective for alkenylation in the meta and para positions.

## INTRODUCTION

Alkyl and alkenyl arenes are produced on a large scale and used as precursors for, inter alia, detergents, plastics, and elastomers.<sup>1-4</sup> One industrial method for alkyl arene synthesis from arenes and alkenes uses Friedel-Crafts alkylation catalysis with Lewis and Brønsted acids (e.g., HF and AlCl<sub>3</sub>).<sup>1,5</sup> Zeolites<sup>2</sup> can also catalyze arene alkylation and offer the advantage of recyclability.<sup>6</sup> However, because zeolite catalysts also operate through an acid-catalyzed mechanism, many features of Friedel-Crafts catalysis are also observed for zeolite-catalyzed arene alkylation. For example, for arene alkylation using  $\alpha$ -olefins, acid catalysts do not produce 1-aryl alkanes. In addition, carbonium intermediates from  $\alpha$ -olefins can lead to products from oligomerization. This is a result of the formation of carbocationic intermediates upon electrophilic addition to the olefin that results in preferential reactivity at the more substituted carbon to give the Markovnikov product (Scheme 1). Thus, for arene alkylation with long-chain  $\alpha$ -olefins, y-aryl alkanes (where  $\gamma > 1$ ) are produced. In industry, y-aryl alkanes (where y > 1) with linear alkane moieties are known as linear alkylbenzenes (LABs).<sup>7</sup> LABs are primarily comprised of 2- and 3-phenyl alkanes and do not include 1-phenyl alkanes. To differentiate LABs from 1-phenyl alkanes, we have termed the latter super linear alkyl benzenes (SLABs). Additionally, the regioselectivity of acid-based arene alkylation is dictated by the donor properties of the substituent on the arene ring. For electron-donating substituents, ortho/ para selectivity is observed while electron-poor arenes are generally unreactive or undergo slow reaction.

Transition metal-mediated olefin hydroarylation and oxidative arene alkenylation reactions, which often operate by a non-

acid based pathway that involves olefin insertion into metalaryl bonds and metal-mediated arene C-H activation, offer the potential for different selectivity compared with the traditional acid-based catalysis.<sup>8,9</sup> For example, as discussed above, acidcatalyzed alkylation using  $\alpha$ -olefins forms branched products (i.e., *y*-aryl alkanes with  $y \ge 2$ ) selectively due to the formation of a carbocationic intermediate upon proton addition to the olefin. In contrast, SLABs can be generated from transition metal mediated processes that involve olefin insertion into metal-aryl bonds (Scheme 2).<sup>10</sup> Despite the opportunity to produce SLABs, the selective generation of linear alkyl arenes or alkenyl variants from unactivated hydrocarbon substrates has been a challenge.<sup>10–17</sup>

Our group has studied ruthenium<sup>9,18-26</sup> and platinum<sup>27-32</sup> catalysts for olefin hydroarylation, but selectivity for the anti-Markovnikov SLAB products when using  $\alpha$ -olefins was either modest or the catalysts were selective for the branched Markovnikov products. A ruthenium catalyst from our group achieved 1.6:1 linear:branched (L:B) ratio for propylbenzene:cumene from benzene and propylene,18 as did iridium catalysts studied by the Periana and Goddard groups.<sup>14,15</sup> Goldberg and co-workers obtained a L:B ratio of up to ~1.4:1 for the production of hexylbenzene using 1-hexene and benzene with a Pt pre-catalyst,<sup>17,33</sup> and the Hartwig group reported a 19:1 L:B ratio for the generation of octylbenzene from 1-octene and benzene using stoichiometric amounts of a Ni complex.<sup>13</sup>

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<sup>a</sup>The generation of a carbocationic intermediate dictates the selective formation of cumene, the branched Markovnikov product.

Scheme 2. Comparison of Products That Have Been Observed Using Transition Metal (TM) Catalyzed and Acid-Catalyzed Arene Alkenylation/Alkylation Methods Using Benzene and Propylene



Recently, our group reported Rh-catalyzed arene alkenylation utilizing the Rh(I) catalyst precursor (FDAB)Rh(TFA)- $(\eta^2$ -C<sub>2</sub>H<sub>4</sub>) (<sup>FI</sup>DAB = N,N'-bis(pentafluorophenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene) with  $CuX_2$  {X = acetate (OAc), trifluoroacetate (TFA), pivalate (OPiv) or 2-ethyl hexanoate (OHex)} as in situ oxidant.<sup>11</sup> Using (<sup>FI</sup>DAB)Rh(TFA)( $\eta^2$ - $C_2H_4$ ) as a catalyst precursor results in the conversion of benzene, ethylene, and CuX<sub>2</sub> to styrene, CuX and HX with yields of  $\geq$ 95% with high selectivity for styrene.<sup>11</sup> Given the success of  $(^{Fl}DAB)Rh(TFA)(\eta^2-C_2H_4)$  for arene alkenylation,<sup>11,34</sup> the catalysis was extended to  $\alpha$ -olefins in order to study L:B selectivity.<sup>10</sup> Herein, 1-aryl alkanes are considered to be linear, and *y*-aryl alkanes (where y > 1) are considered to be branched (traditional linear alkylbenzenes, LABs, are y-aryl alkanes where  $y \ge 2$ ). With the rhodium precursor [Rh( $\eta^2$ - $C_2H_4)_2(\mu$ -OAc)]<sub>2</sub>, products that give 1-aryl alkanes upon hydrogenation are favored (Table 1).<sup>10,35</sup> The lowest observed L:B ratio in our previous study was ~8:1. Additionally, for monosubstituted arenes the rhodium catalysis favors the

production of *meta-* and *para-*substituted alkenyl arenes, whereas acid-based catalysis typically favors the production of *ortho-* and *para-*substituted alkenyl arenes. Thus, the arene regioselectivity for the Rh-catalyzed process is likely due to steric effects rather than electronic effects.

Although there is precedent for 1-tolyl-1-pentenes and 2-tolyl-2-pentenes serving as intermediates to form bicyclic dimethylnaphthalenes,  $^{38-40}$  acid-catalyzed arene alkylation reactions do not selectively produce 1-tolyl-1-pentenes and 2-tolyl-2-pentenes. Despite its dimensional stability, resistance to heat, and barrier to gas permeability relative to the current polyester market leader polyethylene terephthalate,  $^{41-43}$  the production of polyethylenenaphthalate (PEN) polymer has been limited since the methods for 2,6-dimethylnaphthalene (2,6-DMN) production typically require multiple steps and harsh reaction conditions (see Scheme 3 for one example of a route to 2,6-DMN).  $^{41,44}$  Thus, the development of a more economical method to produce 2,6-DMN is highly desirable as it is a precursor for PEN polymer.  $^{42}$ 

We speculated that rhodium-catalyzed alkenylation of toluene with 1-pentene could provide a strategy to selectively generate 1-tolyl-1-pentenes (Schemes 4 and 5) using readily available starting materials such as toluene and 1-pentene. Thus, this rhodium-based catalysis could be advantageous in terms of selectivity relative to acid-based catalysis, which favor the formation of the 2-tolyl-2-pentanes and 3-tolyl-2-pentanes (Scheme 6). As 2,6-DMN can be generated from isomerization of other regioisomers of dimethylnaphthalene, *meta*, *para*, and *ortho* isomers are not specified in Scheme 5. Herein, we report on our results from rhodium-catalyzed toluene alkenylation with 1-pentene to selectively generate 1-tolyl-1-pentenes that are potential precursors for 2,6-DMN.

Table 1. Examples of Arene Alkenylation Using  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$  and  $Cu(OAc)_2$  versus  $AlCl_3^a$ 

| Catalyst  | Arene   | Arene a-Olefin             |           | L:B            | TON    | Products  |
|---|---------|----------------------------|-----------|----------------|--------|---|
| AICI <sub>3</sub> <sup>[b]</sup>  | Benzene | Propylene                  | n/a       | 100% branched  | 95     | $\langle \rangle$   |
| [Rh(η²-C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> (μ-OAc)] <sub>2</sub> | Benzene | Propylene                  | n/a       | 8:1            | 80(4)  | $\bigcirc \bigcirc$   |
| AICI <sub>3</sub> <sup>[c]</sup>  | Benzene | Isobutylene                | n/a       | 100% branched  | NR     | $\checkmark \!$ |
| [Rh(η²-C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> (μ-OAc)] <sub>2</sub> | Benzene | Isobutylene <sup>[e]</sup> | n/a       | 100% linear    | 100(2) |   |
| AICI <sub>3</sub> <sup>[d]</sup>  | Toluene | Propylene                  | 3:1:2.6   | > 98% branched | I NR   | $\langle \langle \rangle$   |
| [Rh(η²-C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> (μ-OAc)] <sub>2</sub> | Toluene | Propylene                  | 1:8.9:9.3 | 9.4:1          | 86(17) | $\bigcirc \bigcirc$   |

<sup>*a*</sup>L:B ratios with  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$  were determined after hydrogenation of the unsaturated products. NR = not reported. Conditions using  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$ : 0.01 mol % or Rh relative to arene, 25 psi gaseous olefin or 2000 equiv of olefin, 150 °C, 48 h, 240 equiv Cu(OAc)\_2 relative to Rh. Hydrogenation was performed using 5% Pt/C under hydrogen atmosphere. <sup>b</sup>Data and conditions from ref 14. <sup>c</sup>Data and conditions from ref 36. <sup>d</sup>Data and conditions from ref 37. <sup>c</sup>72 h. Reprinted (adapted) with permission from *J. Am. Chem. Soc.* 2017, *139*, 5474–5480.<sup>10</sup> Copyright 2017 American Chemical Society.

Scheme 3. Overview of an Industrial Route for the Synthesis of 2,6-Dimethylnaphthalene from o-Xylene and Butadiene<sup>a</sup>



 ${}^{a}$ K catalyst = calcined CaO stirred with potassium metal at 150 °C. Adapted from refs 41, 44, 45. 2,6-DMN can also be produced through diisopropylation of naphthalene using zeolite catalysts.<sup>41</sup>

Scheme 4. Envisioned Process for a Possible Route to 2,6-DMN from Toluene and 1-Pentene Using a Rh Catalyst with a  $CuX_2$  Oxidant<sup>a</sup>



<sup>a</sup>A hydrogenation step is included for clarity (vide infra).

Scheme 5. Proposed Catalytic Cycle for Transition Metal-Catalyzed Toluene Alkenylation with 1-Pentene To Give Tolylpentenes<sup>4</sup>



<sup>*a*</sup>Linear versus branched selectivity is influenced by the olefin insertion step (Tol = tolyl).

Scheme 6. Comparison of Tolylpentane Products from Acid- and Rh-Based Functionalization and Implications for 2,6-DMN Production<sup>a</sup>



<sup>a</sup>Products from Rh catalysis are shown following a hydrogenation step. *Meta, para,* and *ortho* isomers are not shown, as 2,6-dimethylnaphthalene can be produced from isomerization.

#### Scheme 7. Examples of Possible Products and Side Products from the Rh-Catalyzed Toluene Alkenylation Reaction







<sup>*a*</sup>Conditions: 0.01 mol % Rh {Rh source =  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$ } relative to toluene, 10 equiv of cyclooctane relative to Rh, toluene, 240 equiv Cu(OPiv)\_2 relative to Rh, 250–2000 equiv 1-pentene relative to Rh, 150 °C, 1–13 h. Hydrogenation was achieved using 10% Pd/C under hydrogen atmosphere. Yields represent the total percent yield of tolylpentanes based on the amount of the copper(II) oxidant. Percent yields are the average of at least three experiments with standard deviations given in parentheses. ND = not detected. <sup>*b*</sup>Decane was not fully hydrogenated in one of the three trials; thus, data for decane formation are from two experiments.

#### Scheme 8. Examples of Possible Tolylpentenes Funneling to 1- or 2-Tolylpentanes on Hydrogenation



#### RESULTS AND DISCUSSION

Previous results using the rhodium catalyst precursor [Rh( $\eta^2$ - $(C_2H_4)_2(\mu$ -OAc)]\_2 indicated that toluene and 1-pentene were reactive toward the generation of linear alkenyl arenes via oxidative alkenylation with other coupling partners (e.g., benzene and 1-pentene, toluene and propylene).<sup>10</sup> However, due to the complexity of the resultant product mixture with toluene and 1-pentene (vide infra), the alkenylation of toluene with 1-pentene was not pursued in this previous study. Some possible products from the Rh-catalyzed toluene alkenylation with 1-pentene are shown in Scheme 7 and include ortho/ meta/para regioisomers, different products from alkenylation at the 1-, 2-, or 3-position of pentene (isomerization of 1pentene to 2-pentene provides a potential pathway for the formation of arylation at the 3-position of pentene), cis/trans isomers for all alkenyl products, C10 compounds resulting from 1-pentene coupling, bis-aryl products resulting from toluene

coupling, and pentenyl or tolyl pivalates from reaction with  $Cu(OPiv)_2$ . Since our preliminary results indicated that tolylpentenes likely could be generated with both *meta/para* and anti-Markovnikov selectivity using the rhodium catalyst precursor  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$  and  $Cu(OPiv)_2$  as the oxidant, we sought to elucidate the details of toluene/1-pentene alkenylation. The desired products for the oxidative alkenylation of toluene with 1-pentene are 1-tolyl-1-pentenes and 2-tolyl-2-pentenes, since they can be readily ring closed to yield 2,6-DMN.<sup>38–40</sup> Given the potential complexity of product analysis, to simplify quantification we hydrogenated the product mixtures to give tolylpentanes prior to analysis by GC–MS.

Using  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$  as a pre-catalyst, toluene and 1-pentene are converted to pentenyltoluenes with Cu(II) oxidants in neat toluene at 150 °C (Table 2). The production of 3-tolyl-2-pentenes is not observed under the reaction Scheme 9. Possible Explanation of the Influence of 1-Pentene Concentration on the Ratio of 1-Tolyl-1-pentene to 2-Tolyl-2-pentene (i.e., L:B Ratio)<sup>a</sup>



<sup>a</sup>Higher 1-pentene concentrations might inhibit olefin isomerization that would generate 2-tolyl-2-pentene from 1-tolyl-1-pentene.

conditions reported herein. When using  $(5-FP)Rh(TFA)(\eta^2 C_2H_4$ ) (5-FP = 1,2-bis(N-7-azaindolyl)benzene) as pre-catalyst (see below) only trace amounts of 3-tolyl-2-pentenes are observed. Therefore, after hydrogenation the observed toluene alkenylation products include ortho, meta, and para isomers of 1-tolylpentanes and 2-tolylpentanes (Scheme 8). High L:B ratios (linear:branched ratios) are calculated as the ratio of all ortho, meta, and para isomers of 1-tolyl-1-pentenes (i.e., linear) to all 2-tolyl-2-pentenes (i.e., branched) after hydrogenation. The L:B ratios are typically >7:1 with higher ratios of ~15:1 under certain conditions (Table 2). After hydrogenation,  $C_{10}$ products, which are likely formed via 1-pentene coupling reactions, are observed as decane. Cyclooctane, which was found to be inert under the reaction conditions (see Supporting Information Table S1), was used as an internal standard for the catalytic reactions.

The effects of the concentration of 1-pentene, concentration of Cu(II) oxidant, identity of Cu(II) oxidant, reaction temperature, and rhodium concentration have been examined. The amount of 1-pentene for the toluene alkenylation reaction was varied from 250 to 2000 equiv (relative to Rh), with 0.01 mol % Rh and 240 equiv of Cu(OPiv)<sub>2</sub> at 150 °C. The L:B ratio (i.e., the ratio of 1-tolyl-1-pentenes to 2-tolyl-2-pentenes) increases from 7.2(7):1 using 250 equiv of 1-pentene to 15(1):1 using 2000 equiv of 1-pentene. We propose that the higher olefin concentrations might enable more rapid dissociation of pentenyltoluenes from the Rh center, thus reducing the extent of isomerization and in turn, the amount of branched products (Scheme 9). In addition, 2-tolyl-2-pentenes can potentially form from 2-pentene, which is formed from isomerization of 1-pentene. Further, although the L:B ratio varies with olefin concentration, the yields of tolylpentanes, ~65% based on  $Cu(OPiv)_2$  as the limiting reagent, are consistent as the 1-pentene concentration is varied with the exception of the reaction with 2000 equiv of 1-pentene where the percent yield dropped to 47(4)%. Using 1-pentene amounts  $\geq$ 500 equiv (relative to Rh), several C<sub>10</sub> products that likely result from 1-pentene coupling are observed. To simplify quantification of 1-pentene coupling products, these

C<sub>10</sub> products were converted to decane by hydrogenation (see Table 2). Following hydrogenation, 4-methylnonane and pentyl pivalate were also observed by GC–MS in minor amounts but were not quantified. Control reactions in the absence of the rhodium catalyst precursor  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$  did not result in the production of decane, indicating that the Rh complex is likely involved in the generation of C<sub>10</sub> products. The preference for formation of the linear 1-tolylpentanes, similar to the preference for *n*-pentylbenzenes over 2-pentylbenzenes in the initial report for the alkenylation of benzene with 1-pentene, indicates that isomerization of 1-pentene to 2-pentene is slow under the reaction conditions or that the catalyst reacts more slowly with 2-pentene than 1-pentene.<sup>10</sup>

In addition to the selectivity for 1-tolyl-1-pentene, 2-tolyl-2pentene, and 3-tolyl-2-pentene, we elucidated the ortho, meta, and para regioselectivity. The generation of meta and para products is favored, accounting for ~60-67% and ~29-34%, respectively, of the tolylpentene products with ortho products accounting for <5% of the total (Figure 1). Thus, the meta/ para ratio for the Rh catalyzed toluene alkenylation with 1pentene is  $\sim 2:1$ , which demonstrates nearly identical selectivity for C-H activation of the meta and para positions of toluene after adjustment for the statistical ratio of meta and para hydrogen atoms. We presume that the ortho position is sterically protected by the methyl group, which likely raises the barrier for either access to Rh coordination of the ortho C-H bond or Rh-mediated breaking of the ortho C-H bond. Similar selectivity has been observed previously for organometallic C-H activation of toluene.<sup>10,33,46,47</sup>

To examine the effect of varying the amount of Cu(II) oxidant, 120–360 equiv of Cu(OPiv)<sub>2</sub> (relative to Rh) were used for toluene alkenylation with 1000 equiv of 1-pentene (relative to Rh). The L:B ratios are similar for each condition, ranging from ~12:1 to 14:1. The yield of tolylpentanes, based on Cu(II), is statistically identical for each reaction, which demonstrates that tolylpentane generation increases proportionately as a function of Cu(OPiv)<sub>2</sub> (Table 3). Therefore, under the conditions studied conversions of 1-pentene are

#### **Organometallics**



**Figure 1.** Tolylpentane product distribution as a function of 1pentene amount (relative to Rh). Error bars denote standard deviations based on at least three experiments. Conditions: 0.01 mol % Rh {Rh source =  $[Rh(\eta^2-C_2H_4)_2(\mu-OAC)]_2$ } relative to toluene, 10 equiv of cyclooctane relative to Rh, toluene, 240 equiv Cu(OPiv)<sub>2</sub> relative to Rh, 250–2000 equiv 1-pentene relative to Rh, 150 °C, 1–13 h. Hydrogenation was achieved using 10% Pd/C under hydrogen atmosphere.

apparently limited only by the amount of Cu(II). This finding is consistent our previous study regarding benzene alkenylation, in which we demonstrated that the decomposition of the Rh catalyst  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$  at 150 °C could be suppressed through the addition of soluble Cu(II) oxidants such as Cu(OPiv)<sub>2</sub>.<sup>35</sup> Under conditions with soluble oxidants, no evidence for the formation of elemental Rh is obtained. Similar to the conditions described above, the production of *meta-* and *para-*pentenyltoluenes is favored (Figure 2). Arene alkenylation is not observed in the absence of Rh using Cu(OPiv)<sub>2</sub> under the reaction conditions shown in Table 3.

In order to determine if another soluble copper(II) oxidant source could improve the L:B ratio or the yield of tolylpentanes,  $Cu(OHex)_2$  and  $Cu(Ole)_2$  (OHex = 2-ethylhexanoate, Ole = oleate) were tested for toluene alkenylation under identical reaction conditions shown in Table 3. The L:B ratio varies as a function of the copper(II) oxidant, from 11.8(4):1 with  $Cu(OPiv)_2$  to 7.4(5):1 with  $Cu(OHex)_2$  to 14.7(4):1 with  $Cu(Ole)_2$ . The yields of tolylpentanes are similar for  $Cu(OPiv)_2$  and  $Cu(OHex)_2$ , approximately 70%, but are significantly lower with  $Cu(Ole)_2$  (Table 4). The



**Figure 2.** Tolylpentane product distribution as a function of  $Cu(OPiv)_2$  amount. Error bars denote standard deviations based on three experiments. Conditions: 0.01 mol % Rh {Rh source =  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$ } relative to toluene, 10 equiv cyclooctane relative to Rh, toluene, 120–360 equiv Cu(OPiv)\_2 relative to Rh, 1000 equiv 1-pentene relative to Rh, 150 °C, 1–2 h. Hydrogenation was achieved using 10% Pd/C under hydrogen atmosphere.

preference for meta- and para-tolylpentanes does not vary with identity of copper(II) oxidant (Figure S14). The exact reason for the variation in the L:B ratio as a function of the identity of the Cu(II) oxidant is uncertain, but the carboxylate (i.e., OPiv, OHex, or Ole) of the Cu(II) oxidant is likely coordinated to Rh during all steps of catalysis, and thus it is not surprising that the identity of the carboxylation influences the selectivity of olefin insertion. These results suggest that the L:B selectivity might be more influenced by the Rh coordination sphere than the regioselectivity for C-H activation of monosubstituted arenes. CuCl<sub>2</sub> was also examined as a potential oxidant for the toluene alkenylation reaction, but only trace functionalization was observed under the reaction conditions shown in Table 4 (see Supporting Information, Figure S15). We speculate that the carboxylate ligand, which originates from the Cu(II) oxidant, is necessary for toluene C-H activation. Further, using CuCl<sub>2</sub> the selectivity is for branched products with ortho and para selectivity, which indicates a Friedel-Crafts type reaction. It seems likely that HCl is generated in situ from the CuCl<sub>2</sub>, and the HCl/CuCl<sub>2</sub> mixture results in some arene alkylation. From 120 to 180 °C, the most pronounced L:B ratio observed is ~19:1 (Table 5). Yields of tolylpentanes are similar across this temperature range as is the production of decane (Table 5). As indicated above, the formation of meta-

Table 3. Variation of Copper(II) Oxidant Amount on Tolylpentane and Decane Production<sup>a</sup>

|                    | +                   | 0.01 mol% Rh<br>20-360 eq. Cu(OPiv) <sub>2</sub><br>150 °C, 1-2 h | H <sub>2</sub><br>Pd/C +   | + decane              |
|--------------------|---------------------|---|----------------------------|-----------------------|
| equiv $Cu(OPiv)_2$ | <i>m</i> : <i>p</i> | L:B   | % yield tolylpentanes {TO} | equiv decane produced |
| 120                | 1.7:1               | 14(2):1   | 65(5)% {39(3)}             | 6.6(6)                |
| 240                | 1.9:1               | 11.8(4):1   | 64(4)% {77(5)}             | 7.81(5)               |
| 360                | 1.9:1               | 14.2(4):1   | 65(3)% {117(5)}            | 13(2)                 |

<sup>*a*</sup>Conditions: 0.01 mol % Rh {Rh source =  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$ } relative to toluene, 10 equiv of cyclooctane relative to Rh, toluene, 120–360 equiv Cu(OPiv)<sub>2</sub> relative to Rh, 1000 equiv 1-pentene relative to Rh, 150 °C, 1–2 h. Hydrogenation was achieved using 10% Pd/C under hydrogen atmosphere. % Yield represents the total % yield of tolylpentanes based on the amount of the copper(II) oxidant. Percent yields are the average of at least three experiments with standard deviations given in parentheses.

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# Table 4. Effect of Copper(II) Identity on Tolylpentane and Decane Production<sup>a</sup>



<sup>*a*</sup>Conditions: 0.01 mol % Rh {Rh source =  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$ } relative to toluene, 10 equiv of cyclooctane relative to Rh, toluene, 240 equiv CuX<sub>2</sub> relative to Rh, 1000 equiv 1-pentene relative to Rh, 150 °C, 2 h. Hydrogenation was achieved using 10% Pd/C under hydrogen atmosphere. % Yield represents the total % yield of tolylpentanes based on the amount of the copper(II) oxidant. Percent yields are the average of at least three experiments with standard deviations given in parentheses.





"Conditions: 0.01 mol % Rh {Rh source =  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$ } relative to toluene, 10 equiv of cyclooctane relative to Rh, toluene, 120 equiv Cu(OPiv)\_2 relative to Rh, 1000 equiv 1-pentene relative to Rh, 120–180 °C, 30–60 min. Hydrogenation was achieved using 10% Pd/C under hydrogen atmosphere. % Yield represents the total % yield of tolylpentanes based on the amount of the copper(II) oxidant. Percent yields are the average of at least three experiments with standard deviations given in parentheses.



|          | + 500 eq. | 0.001-0.01 mol% Rh<br>240 eq. Cu(OPiv) <sub>2</sub><br>150 °C, 3-30 h | H <sub>2</sub> + +         | + decane              |
|----------|-----------|---|----------------------------|-----------------------|
| mol % Rh | m:p       | L:B   | % yield tolylpentanes {TO} | equiv decane produced |
| 0.001    | 1.8:1     | 12(1):1   | 77(3)% {93(3)}             | <1                    |
| 0.005    | 1.8:1     | 15.4(7):1   | 84(3)% {101(4)}            | 2.9(4)                |
| 0.01     | 1.8:1     | 10(1):1   | 72(5)% {87(6)}             | 2.6(7)                |

<sup>*a*</sup>Conditions: 0.001–0.01 mol % Rh {Rh source =  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$ } relative to toluene, 10 equiv of cyclooctane relative to Rh, toluene, 240 equiv Cu(OPiv)<sub>2</sub> relative to Rh, 500 equiv 1-pentene relative to Rh, 150 °C, 3–30 h. Hydrogenation was achieved using 10% Pd/C under hydrogen atmosphere. % Yield represents the total percent yield of tolylpentanes based on the amount of the copper(II) oxidant. Percent yields are the average of at least three experiments with standard deviations given in parentheses.

#### Table 7. Effect of Rh Sources and Added HOPiv on Tolylpentane and Decane Production<sup>a</sup>

| + 500                              | 0.005 mol% F<br>240 eq. Cu(OF<br>0 or 2400 eq. H<br>150 °C, 6-12 | Rh<br>iv) <sub>2</sub><br>OPiv<br>h | +         | +                          | detected*             |
|------------------------------------|--|-------------------------------------|-----------|----------------------------|-----------------------|
| Rh source                          | HOPiv (equiv)  | m:p                                 | L:B       | % yield tolylpentanes {TO} | equiv decane produced |
| $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$ | 0  | 1.8:1                               | 15.4(7):1 | 84(3)% {101(4)}            | 2.9(4)                |
| $(5-FP)Rh(TFA)(\eta^2-C_2H_4)$     | 0  | 1.7:1                               | 17(1):1   | 79(2)% {95(2)}             | 2.3(5)                |
| $(5-FP)Rh(TFA)(\eta^2-C_2H_4)$     | 2400   | 2.5:1                               | 18(1):1   | 76(9)% {91(11)}            | 5(1)                  |

"Conditions: 0.005 mol % Rh {Rh source =  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$  or  $(5-FP)Rh(TFA)(\eta^2-C_2H_4)$ } relative to toluene, 10 equiv of cyclooctane relative to Rh, toluene, 240 equiv Cu(OPiv)<sub>2</sub> relative to Rh, 500 equiv 1-pentene relative to Rh, 0 or 2400 equiv HOPiv relative to Rh, 150 °C, 3– 30 h. Hydrogenation was achieved using 10% Pd/C under hydrogen atmosphere. % Yield represents the total percent yield of tolylpentanes based on the amount of the copper(II) oxidant. Percent yields are the average of at least three experiments with standard deviations given in parentheses. \*3-Tolyl-3-pentane was detected in trace amount for all trials with  $(5-FP)Rh(TFA)(\eta^2-C_2H_4)$ , but was not quantified.



<sup>*a*</sup>Conditions: 0.005 mol % Rh {Rh source =  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$  or (5-FP)Rh(TFA)(\eta^2-C\_2H\_4)} relative to toluene, 10 equiv of cyclooctane relative to Rh, toluene, 240 equiv Cu(OPiv)<sub>2</sub> relative to Rh, 500 equiv 1-pentene relative to Rh, 2400 equiv HOPiv relative to Rh, air (1 atm), 150 °C, 24 h. Hydrogenation was achieved using 10% Pd/C under hydrogen atmosphere. % Yield represents the total percent yield of tolylpentanes based on the amount of the copper(II) oxidant. Percent yields are the average of at least three experiments with standard deviations given in parentheses.

#### Table 9. Study of Product Inhibition for Aerobic Toluene Alkenylation<sup>a</sup>



<sup>*a*</sup>Conditions: 0.005 mol % Rh {Rh source =  $(5\text{-FP})\text{Rh}(\text{TFA})(\eta^2\text{-}C_2\text{H}_4)$ } relative to toluene, 10 equiv of cyclooctane relative to Rh, toluene, 240 equiv Cu(OPiv)<sub>2</sub> relative to Rh, 500 equiv 1-pentene relative to Rh, 2400 equiv HOPiv relative to Rh, 0 or 160 equiv added tolylpentenes, air (1 atm), 150 °C, 24 h. Hydrogenation was achieved using 10% Pd/C under hydrogen atmosphere. <sup>*b*</sup>Using *meta*-tolyl-1-pentene. <sup>*c*</sup>Using *para*-tolyl-1-pentene. <sup>*c*</sup>Using *para*-tolyl-1-pentene. % Yield represents the total percent yield of tolylpentanes based on the amount of the copper(II) oxidant. Percent yields are the average of at least three experiments with standard deviations given in parentheses.

and *para*-tolylpentanes is favored at each temperature (Figure \$16).

To elucidate the influence of the rhodium concentration on the yield and selectivity of the toluene alkenylation reaction, we examined the use of a solution with 0.001 mol % of Rh relative to toluene. With 0.001 mol % of Rh, the L:B ratio, 12(1):1, is statistically identical to the L:B ratio (10(1):1) with the higher Rh concentration of 0.01 mol % (Table 6). Also, the production of C<sub>10</sub> products is minimized when using the lower concentration of Rh. The use of 0.005 mol % Rh results in a slightly higher L:B ratio of 15.4(7):1 with >80% yield of tolylpentanes relative to the Cu(II) oxidant. Under each reaction condition, the generation of *meta-* and *para*tolylpentanes is favored (Figure S17).

Previously, we reported the use of the complex (5-FP)Rh(TFA)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) as an air-stable Rh(I) catalyst for benzene alkenylation.<sup>12</sup> Whereas under previously reported conditions [Rh( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>( $\mu$ -OAc)]<sub>2</sub> is not an effective catalyst for arene alkenylation under aerobic conditions, (5-FP)Rh-(TFA)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) was demonstrated to efficiently catalyze arene alkenylation under aerobic conditions, enabling in situ Cu(II) regeneration.

Similar to  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$ ,  $(5-FP)Rh(TFA)(\eta^2-C_2H_4)$  catalyzes the synthesis of tolylpentanes from toluene and pentane (Table 7). Both catalysts were tested under inert atmosphere to obtain an initial direct comparison. Yields of tolylpentanes were approximately 80% with each catalyst, with L:B ratios of up to 18:1 with  $(5-FP)Rh(TFA)(\eta^2-C_2H_4)$  (Table 7). The addition of HOPiv did not inhibit the synthesis of tolylpentanes, which is significant as the presence of added acid is proposed to enable more efficient recycling of the Cu(II) oxidant by minimizing the formation of Cu oxides from Cu(OPiv) and  $H_2O$ .<sup>12</sup> Under all reaction conditions, the formation of *meta-* and *para-*tolylpentanes was favored (Figure S18). The ratio of L:B products does not change with time (see Supporting Information, Table S2).

We also tested the ability of  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$  and  $(5-FP)Rh(TFA)(\eta^2-C_2H_4)$  to catalyze the toluene alkenylation reaction under aerobic conditions. Aerobic catalysis was performed in the presence of air and excess HOPiv in order to regenerate the Cu(II) oxidant in situ. Excess carboxylic acid has been shown to stabilize Cu(I) and promote its aerobic regeneration to Cu(II) by preventing reaction with water to generate insoluble and less easily oxidized Cu(I) hydroxide.<sup>35</sup> The 93(8)% yield of tolylpentenes using  $(5-FP)Rh(TFA)(\eta^2 C_2H_4$ ) after 24 h is statistically identical to the 84(6)% observed using  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$  (Table 8). The L:B ratio under aerobic conditions is lower than typical L:B ratios observed under anaerobic conditions. Similar to the anaerobic conditions, aerobic catalysis with  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$ and  $(5-FP)Rh(TFA)(\eta^2-C_2H_4)$  exhibits selectivity toward meta- and para-tolylpentanes (Figure S19).

Under aerobic conditions we anticipated an increase in percent yield of pentenyltoluenes relative to that observed under anaerobic conditions. However, the increase in yield under aerobic conditions (93(8)%) was statistically insignif-

Scheme 10. Isolation of Tolylpentenes from Representative Catalytic Reaction<sup>a</sup>



<sup>*a*</sup>Conditions: 0.01 mol % Rh {Rh source =  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$ } relative to toluene, 10 equiv of cyclooctane relative to Rh, toluene, 360 equiv Cu(OPiv)<sub>2</sub> relative to Rh, 1000 equiv 1-pentene relative to Rh, 150 °C, 2 h.

icant compared to anaerobic conditions (76(9)%) (Tables 7 and 8). We have previously reported that the hydrophenylation of ethylene catalyzed by  $(5-FP)Rh(TFA)(\eta^2-C_2H_4)$  is inhibited by the styrene product.<sup>12</sup> In order to study potential product inhibition for the aerobic toluene alkenylation, we performed aerobic catalysis using  $(5-FP)Rh(TFA)(\eta^2-C_2H_4)$ with the addition of 160 equiv of meta-tolyl-1-pentene at the beginning of the reaction under the reaction conditions shown in Table 8. While the addition of the tolylpentene does not affect the L:B ratio or ortho/meta/para selectivity (Figure S20), a significant inhibition of the rate of catalysis was observed. The yield of tolylpentenes decreased from 93% without added tolyl-1-pentene to 47% in the presence of 160 equiv of meta-tolyl-1-pentene and 39% in the presence of 160 equiv of para-tolyl-1-pentene (Table 9). Thus, the limited efficiency for the aerobic toluene alkenylation (i.e., less than 100% yield relative to Cu(II) oxidant) is likely related to product inhibition. Addressing this issue would likely require a continuous product distillation or a biphasic reaction analogue.

We have also demonstrated isolation of tolylpentene products from a representative toluene alkenylation reaction. Using the conditions in Table 3 with 360 equiv of  $Cu(OPiv)_2$ , after workup (see Figure S13), 88 mg of tolylpentenes were isolated, a 32% yield based on  $Cu(OPiv)_2$  (Scheme 10). This shows that precursors to bicyclic compounds such as 2,6-DMN can be obtained from the rhodium-catalyzed alkenylation of toluene with 1-pentene.

# CONCLUSIONS

Oxidative alkenylation of toluene with 1-pentene to generate 1tolyl-1-pentenes and 2-tolyl-2-pentenes has been achieved using the rhodium catalyst precursor  $[Rh(\eta-C_2H_4)_2(\mu-OAc)]_2$ . 1-Tolyl-1-pentenes, possible precursors to the industrially relevant bicyclic compound 2,6-dimethylnaphthalene, are the major products of the arene alkenylation reaction. In contrast, 3-tolyl-2-pentenes, the branched products that do not undergo the ring closure reaction to form dimethylnaphthalenes, are not observed. The arene alkylation reaction gives high L:B ratios  $(\sim 15:1)$  with a variety of olefin, oxidant, and rhodium concentrations and operates over a range of temperatures (120-180 °C). With the air-stable capping arene ligated Rh pre-catalyst,  $(5-FP)Rh(TFA)(\eta^2-C_2H_4)$ , similarly high yields of tolylpentanes and an optimal L:B ratio of 18:1 are observed, indicating the potential for in situ regeneration of the Cu(II) oxidant. Catalytic toluene pentylation using the Rh catalysts provides high yields based on the Cu(II) oxidant; however, product inhibition under current conditions likely inhibits access to high turnovers.

The selectivity for *meta-* and *para-*tolylpentane products using Rh catalysis further demonstrates the potential utility of transition metal mediated arene alkenylation and alkylation relative to acid-based catalytic alkylation. The selectivity of products using acid-based catalysis is dictated by the electronic properties of the arene substituent. However, since the rhodium-mediated arene alkenylation reactions do not likely operate through electrophilic aromatic substitution, it becomes possible to access unique regioselectivity for arene C–H activation and functionalization that is catalyst directed rather than substrate directed. While acid-based catalysis favors either *ortho/para* selectivity or *meta* selectivity depending on the substituents on the arene, the Rh-catalyzed arene alkenylation consistently favors *meta/para* selectivity. Thus, the Rh catalyzed arene alkenylation reactions offer access to products with new substitution patterns.

#### EXPERIMENTAL SECTION

General Considerations. All alkenylation reactions were set up under inert atmosphere in a glovebox. The purity of the glovebox atmosphere was maintained by nitrogen purges and was monitored using an oxygen analyzer  $(O_2 < 15$  ppm for all reactions). Alkenylation and hydrogenation reactions were performed in custom-built glass Fischer-Porter reactors (see Supporting Information). Toluene was distilled over calcium hydride prior to use and was stored over molecular sieves.  $Cu(OPiv)_2$  and  $[Rh(\eta-C_2H_4)_2(\mu OAc)]_2$  were synthesized according to literature procedures.<sup>48,49</sup> 1-Tolylpentanes (ortho-, meta-, and para-) were independently synthesized according to an adapted literature procedure and were used as authentic standards for quantification (see Supporting Information).<sup>50</sup> The complex  $(5-FP)Rh(TFA)(\eta^2-C_2H_4)$  [5-FP = 1,2-bis(N-7-azaindolyl)benzene] was synthesized according to a literature procedure.<sup>12</sup>  $Cu(Ole)_2$  (Ole = oleate) was synthesized according to an adapted literature procedure (see Supporting Information).<sup>51</sup> All other chemicals were purchased from commercial sources and used as received. Hydrogen was purchased from GTS-Welco and used as received.

GC-MS was performed using a Shimadzu GCMS-QP2010 Plus instrument with a 30 m  $\times$  0.25 mm SHRXI-5MS column with a 0.25  $\mu$ m thickness. Electron impact (EI) ionization was used. Products were quantified using a linear regression analysis of gas chromatograms relative to standard samples. Plots of peak areas versus molar ratios gave regression lines using cyclooctane as the internal standard for tolylpentane and decane formation (see Supporting Information). For the 1-tolyl-1-pentane products, the slope and correlation coefficient of the regression lines were 1.34 and 0.998 (1-m-tolyl-1pentane), 1.85 and 0.997 (1-p-tolyl-1-pentane) and 1.84 and 0.998 (1-o-tolyl-1-pentane), respectively. For decane, the slope and correlation coefficient were 2.08 and 0.998, respectively. The production of 2-tolyl-2-pentenes was quantified using the slope and correlation coefficient for a fit of cumene:n-propylbenzene, which enabled an approximation of the ratio of 1-tolyl-1-pentenes to 2-tolyl-2-pentenes. The slope and correlation coefficient of the regression line were 1.24 and 0.98 for cumene:n-propylbenzene, respectively.

**Catalytic Alkenylation of Toluene with 1-Pentene.** In a representative catalytic alkenylation reaction, a glass Fischer–Porter reactor was charged with a stir bar, 10 mL of a 0.01 mol % Rh stock solution {Rh source =  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$ , cyclooctane (63  $\mu$ L, 10 equiv relative to Rh), and toluene (50 mL)}, 1-pentene and CuX<sub>2</sub> oxidant (X = OPiv, OHex, or Ole). The reactor was sealed, charged with 50 psi of N<sub>2</sub> and heated and stirred in an oil bath. The reactor

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was removed from the oil bath when all of the copper(II) oxidant was consumed, as indicated by a color change from blue to brown (see Supporting Information).<sup>11</sup> After allowing the reactor to cool to room temperature, the reaction was analyzed by GC–MS and then hydrogenated.

**General Hydrogenation Procedure.** To hydrogenate the product mixture, a 0.1 mL aliquot was removed and added to a glass Fischer–Porter reactor charged with a stir bar, 8 mg of 10% Pd/C and 4 mL of ethanol. The reactor was sealed, and the headspace was evacuated prior to pressurization with 100 psi of  $H_2$ . The reaction was stirred at room temperature overnight. After venting the reactor, GC–MS was used to analyze the resulting product mixture.

Pentenyltoluene Isolation Procedure. Following a standard procedure for toluene alkenylation (see above), the reactor was allowed to cool to room temperature. Next, 40 mL of EtOAc, 10 mL of 10% aqueous NaOH solution and 50 mL of DI water were added to the reaction mixture. The layers were separated, and the aqueous layer was extracted with  $3 \times 40$  mL of EtOAc. The organic fractions were combined and washed with  $3 \times 40$  mL of DI water, dried over MgSO4 and filtered. The filtrate was concentrated in vacuo and purified using column chromatography with cyclohexane/EtOAc as the eluent and silica as the solid phase. The eluent was collected and concentrated under vacuum. The yellow product was further purified on a plug of alumina using cyclohexane as the eluent and purified by additional column chromatography using a silica column and eluting with pentane. The pentenyltoluene mixture was characterized by GC-MS following concentration in vacuo, to give 88 mg of pentenyltoluenes, a 32% isolated yield based on Cu(OPiv)2.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.9b00535.

Experimental procedures; <sup>1</sup>H NMR spectra; calibration curves for quantification; representative gas chromato-grams (PDF)

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#### Notes

The authors declare no competing financial interest.

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