

# Catalytic Synthesis of "Super" Linear Alkenyl Arenes Using an Easily Prepared Rh(I) Catalyst

Michael S. Webster-Gardiner,<sup>†</sup> Junqi Chen,<sup>†</sup> Benjamin A. Vaughan,<sup>†</sup> Bradley A. McKeown,<sup>†</sup> William Schinski,<sup>§</sup> and T. Brent Gunnoe<sup>\*,†</sup>

<sup>†</sup>Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, United States

**S** Supporting Information

**ABSTRACT:** Linear alkyl benzenes (LAB) are global chemicals that are produced by acid-catalyzed reactions that involve the formation of carbocationic intermediates. One outcome of the acid-based catalysis is that 1-phenylalkanes cannot be produced. Herein, it is reported that  $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$  catalyzes production of 1phenyl substituted alkene products via oxidative arene vinylation. Since C==C bonds can be used for many chemical transformations, the formation of unsaturated products provides a potential advantage over current processes that produce saturated alkyl arenes.



Conditions that provide up to a 10:1 linear:branched ratio have been achieved, and catalytic turnovers >1470 have been demonstrated. In addition, electron-deficient and electron-rich substituted benzenes are successfully alkylated. The Rh catalysis provides *ortho:meta:para* selectivity that is opposite to traditional acid-based catalysis.

## INTRODUCTION

Alkyl arenes are used in a wide range of products including plastics, detergents, fuels, and fine chemicals and as a liquid scintillator. Since the development of a commercially viable route to produce alkyl benzenesulfonates on a large scale in the 1940s, they have formed the basis of the detergent industry.<sup>1-3</sup> Initial synthetic routes to make alkyl benzenes produced highly branched alkyl groups, and, thus, the products were called branched alkyl benzenes (BAB). The highly branched alkyl chain of BAB rendered them resistant to biodegradation and resulted in pollution of lakes and streams.<sup>4,5</sup> Linear alkyl benzenes (LAB), which, in contrast to their moniker, are primarily composed 2- and 3-phenyl alkanes,<sup>2</sup> are more readily biodegraded than BAB, and constitute the majority of alkyl benzenesulfonates produced today.<sup>4</sup> Currently, LAB are produced from benzene and  $\alpha$ -olefins using acid-based catalysts, typically either a solid acid catalyst, HF or AlCl<sub>3</sub> in combination with a Brønsted acid (Scheme 1).<sup>1,6,7</sup> These acidbased catalytic processes generate carbocationic intermediates and, as a result, are not able to produce truly linear 1phenylalkanes, which we label as "super" linear alkyl benzenes (SLAB) to differentiate them from LAB that do not contain 1phenylalkanes. Even when utilizing shape- and size-selective zeolite catalysts, to our knowledge, the generation of SLAB is not possible.<sup>8</sup> Thus, similar to other alkyl arenes, SLAB are a potentially useful class of compounds. The discussion of anti-Markovnikov products here is specific to nonheterofunctionalized olefins, as Michael acceptors are readily functionalized in the position that is  $\beta$  to the electron-withdrawing group. Much as the development of a route to BAB and then LAB led to new commercial products, a route for the production of SLAB could provide the foundation for valuable new materials. For example,

Scheme 1. Current Route for the Synthesis of LAB and Proposed Route for the Synthesis of Straight-Chain Vinyl/ Allyl and Alkyl Benzenes (SLAB)



SLAB achieve the linearity of the alkyl chain typically found in natural soaps and detergent precursors such as stearic acid and lauric acid.<sup>9</sup> In addition, straight-chain vinyl and allyl anisole derivatives are used in the flavor and fragrance industries.<sup>10</sup> Also, it is anticipated that SLAB will have enhanced stability against dealkylation degradation compared to LAB and BAB. Further, 1-phenylalkanes have increased detersive power at low concentrations.<sup>11</sup> Currently, the preparation of SLAB involves a Friedel–Crafts acylation followed by a Clemmensen reduction, which is not viable for large-scale processes.<sup>2</sup>

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An alternative to the acid-based catalytic synthesis of alkyl arenes is the utilization of a transition-metal-mediated catalytic reaction that operates via C-H activation of the arene and olefin insertion into metal-aryl bonds.<sup>12,13</sup> For this proposed process, the linear to branched (L:B) ratio of alkyl (or unsaturated) arene product depends on the regioselectivity of olefin insertion (i.e., 2,1- versus 1,2-insertion) and, potentially, the relative rates of product formation following insertion (i.e., Curtin-Hammett conditions). This mode of control over the position of the phenyl group in the alkyl chain is not possible with acid-based methods. The intermediate following olefin insertion into the metal-aryl bond can undergo an arene C-H activation reaction to release a saturated alkyl arene, or, perhaps more desirably, it can undergo a  $\beta$ -hydride elimination reaction and net dissociation of the olefin to produce a "straight-chain" vinyl or allyl arene.

To our knowledge, a catalyst that converts simple arenes from petrochemical feedstocks (e.g., benzene or toluene) and simple  $\alpha$ -olefins (*e.g.*, propylene, 1-hexene and longer chain  $\alpha$ olefins) to straight-chain alkyl or vinyl/allyl arenes with high selectivity has not been reported. Such selectivity has been limited to heterofunctionalized aromatics and/or heterofunctionalized olefins with the regioselectivity often being directed by the use of electrophilic Michael acceptors.<sup>14</sup> Figure 1 shows



**Figure 1.** Selected catalysts that have been reported to catalyze the hydrophenylation of propylene with observed selectivities and TON. Linear:branched (L:B) refers to ratio of *n*-propylbenzene to cumene.<sup>15-21</sup>

selected examples of previously reported transition-metal catalysts for propylene hydrophenylation with observed npropylbenzene (anti-Markovnikov product) to cumene (Markovnikov product) ratios and turnover numbers (TON).<sup>15-21</sup> To date, the highest L:B ratio is 1.6:1, barely selective for linear product. Notably, Goldman, Schrock, and co-workers have developed alkyl group cross-metathesis reactions that convert alkyl benzenes and alkanes to n-alkyl benzenes.<sup>22</sup> Hartwig and co-workers reported a nickel complex that generates octylbenzene with a L:B ratio of 19:1; however, the Nimediated process is stoichiometric in nickel.<sup>23</sup> Wang and coworkers showed that  $[Rh(\mu-Cl)(COD)_2]_2$  (cod =1,5-cyclooctadiene) and an equivalent of acid produce linear selectivity when using Michael acceptors as the olefin; however, with neohexene this catalytic process favors the branched Markovnikov product.<sup>24'</sup> Milstein and co-workers showed that Ru complexes with oxygen and carbon monoxide can produce alkenyl arenes.<sup>25</sup> Further, Ackermann and co-workers showed that Ru carboxylates could generate linear products for arenes that contain heterodirecting groups.<sup>26</sup>

Recently, we reported that (<sup>FI</sup>DAB)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; TFA = trifluoroacetate] catalyzes the conversion of benzene and ethylene directly to styrene using Cu(II) salts as the *in situ* oxidant in a process similar to the commercialized Wacker–Hoechst process for ethylene oxidation.<sup>27,28</sup> Scheme 2





shows a likely catalytic cycle for this process. Although in this paper the reoxidation of Cu(I) to Cu(II) has not been demonstrated, separation of Cu(I) and reoxidation are known for the Wacker process. Herein, we report that  $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$  (1) serves as a catalyst precursor to convert arenes and  $\alpha$ -olefins to vinyl and allyl arenes, which upon hydrogenation yield straight-chain alkyl benzenes (SLAB) in ratios as high as 10:1 with a turnover (TO) > 1470 including extension of the catalysis to both electron-rich and electron-poor arenes (toluene and anisole are used as examples of electron-rich arenes, and chlorobenzene is used as a representative electron-deficient arene).

### RESULTS AND DISCUSSION

Heating a 10 mL of benzene solution of complex 1 (0.001 mol % relative to benzene) to 150 °C under 25 psi of propylene with  $Cu(OAc)_2$  (240 equiv relative to 1) over 48 h affords functionalized benzene products with a L:B ratio of 8:1

(Scheme 3 and Figure S1). Unless stated otherwise, complex 1 mol % is given relative to benzene, and Cu(II) equivalents are

Scheme 3. Oxidative Coupling of Benzene and Propylene to cis- $\beta$ -Methylstyrene, Allylbenzene, trans- $\beta$ -Methylstyrene, and  $\alpha$ -Methylstyrene



relative to **1**. The L:B ratio for the products is determined based on straight-chain products that would result from hydrogenations (i.e., allylbenzene, *cis-β*-methylstyrene, and *trans-β*methylstryene) compared to branched products from hydrogenations (i.e.,  $\alpha$ -methylstyrene). The TOs of alkenyl benzenes

 $\overline{\text{Al}}\overline{\text{Cl}_3}^{[e]}$ 

1

1

1

1

AlCl<sub>3</sub><sup>[g]</sup>

benzene

benzene

benzene

benzene

benzene

benzene

1-hexene

1-pentene [f]

2-pentene

neohexene [f]

isobutylene [f]

isobutylene

at 48 h were 73(7). Since 2 equiv of Cu(II) are used per equiv of vinyl or allyl arene product, the maximum yield is 50% of the amount of Cu(II). Thus, 73(7) TOs using 240 equiv of Cu(OAc)<sub>2</sub> corresponds to ~60% yield. Aliquots of the reaction mixture were analyzed by GC/FID using relative peak areas versus an internal standard (hexamethylbenzene). Detection limits for the instruments were equivalent to ~1 TO of product.

For the reaction of benzene and propylene catalyzed by 1, four products were observed (TOs after 48 h are given for each): allylbenzene: 31(2), *cis-β*-methylstyrene: 5(1), *trans-β*methystryene: 28(4), and  $\alpha$ -methylstyrene: 9(1). The 1.1:1 ratio of allylbenzene to  $\beta$ -methystryene could suggest that there is negligible difference between  $\beta$ -hydride elimination from the terminal CH<sub>3</sub> group or the benzylic position of the putative {Rh-C(CH<sub>3</sub>)HCH<sub>2</sub>Ph} intermediate. In contrast to Pt(II) catalysts for olefin hydroarylation,<sup>16</sup> these Rh-catalyzed reactions do not give difunctionalized products.

Using CuCl<sub>2</sub> or CuO at 150 or 180 °C over 48 h afforded no vinyl or allyl benzene products. In contrast, use of 240 equiv of

Catalyst	Arene	Coupling Partner	o:m:p	L:B	TON	Product
AlCl <sub>3</sub> <sup>[b]</sup>	toluene	propylene	3:1:2.6	>98% B	n.r.	
1	toluene	propylene	1:8.9:9.3	9.4:1	86(17)	
AlCl <sub>3</sub> <sup>[c]</sup>	chlorobenzene	2-chloropropane	6.4:1:5.1	100% B	n.r.	ÇI ÇI
1	chlorobenzene	propylene	1:11:7	10:1	116(3)	
AlCl <sub>3</sub> <sup>[d]</sup>	anisole	2-chloropropane	62:4:34	100% B	n.r.	OMe OMe
1	anisole	propylene	1:2.4:6.4	7.8:1	92(7)	
$AlCl_3^{[e]}$	benzene	propylene	n/a	100% B	95	
1	benzene	propylene	n/a	8:1	80(4)	$1 \rightarrow \Upsilon$

Table 1. Comparison of Arene A	Ikylation Using AlC	l <sub>3</sub> as the Primary Catal	lyst versus [Rh(µ-OA	lc)(ŋ	$[^{2}-C_{7}H_{4})_{7}]_{7}(1)$
	, a				2 T/212 \ /

n/a

n/a

n/a

n/a

n/a

n/a

100% B

8:1

1:3.4

100% L

100% L

100% B

67

122(10)

97(10)

30(8)

100(2)

n.r.

R = propyl or butyl

<sup>&</sup>lt;sup>*a*</sup>L:B ratios and total TO of alkylated products determined after hydrogenation of unsaturated products. Unless otherwise noted, conditions are 0.01 mol % 1 relative to arene, 25 psig gaseous olefin or 2000 equiv of olefin, 150 °C, 48 h, 240 equiv Cu(OAc) <sub>2</sub> relative to 1. Hydrogenation was achieved through 5%Pt on carbon under hydrogen atmosphere. n.r. = not reported. <sup>*b*</sup>Data and conditions are from ref 31. <sup>*c*</sup>Data and conditions are from ref 32.

Cu(OPiv)<sub>2</sub> (OPiv = pivalate) gave 72(3) TO after 12 h with a L:B ratio of 6:1. The total TO using Cu(OPiv)<sub>2</sub> (~100 TO, ~ 83% yield) is improved relative to Cu(OAc)<sub>2</sub> (~80 TO). These experiments revealed the potential importance of having a carboxylate group to achieve catalysis, as only Cu(II) salts with carboxylate groups are effective (see Figure S2). Transition-metal carboxylates have been implicated in efficient arene C–H activation, and thus we tentatively conclude that the apparent necessity of Cu(II) carboxylates, which are likely integral for arene C–H activation.<sup>29</sup> Furthermore, the effect of oxidant loading was investigated and revealed that increasing the oxidant:catalyst ratio increases rate of catalysis in a manner that is approximately first-order in oxidant, revealing higher TO with increasing Cu(II) amounts (Figure S3).

The effect of temperature was examined (Figure S1). At temperatures lower than 150 °C, a negligible amount of catalytic activity is observed. The catalyst is stable and demonstrates increased catalytic activity at temperatures higher than 150 °C, however, undesired side reactions become accessible. For example, small quantities of biphenyl (11(1) TO) and phenyl acetate (8(1) TO) are produced at 180 °C, in addition to 84(12) TO of vinylbenzenes. The generation of phenyl acetate is a side reaction mediated by the Cu oxidant, as it is also observed when benzene and  $Cu(OAc)_2$  are heated at 180 °C in the absence of olefin and Rh catalyst.<sup>30</sup> We probed the impact of starting concentration of 1 on TO (Figure S4). Performing catalysis over a concentration range from 0.01 to 0.001 mol % 1 (relative to benzene) revealed very little difference in TO versus time plots, and similar L:B selectivities were observed. The reaction appears to only be limited by the amount of oxidant. Cu(OPiv)<sub>2</sub> was investigated as the oxidant due to its solubility in benzene, and thus experimental stirring challenges are relieved. For example, catalysis using 0.001 mol % of 1 with 2400 equiv of  $Cu(OPiv)_2$  led to 1148(133) TO of alkylated products after 48 h, which corresponds to a 96% yield based on the limiting oxidant (Figure S5). The addition of more oxidant (1200 equiv to the reaction), before complete consumption of the initial oxidant, resulted in continued catalytic activity with a total of 1474(3) TO obtained after 96 h for an overall 82% yield. Catalyst decomposition appears to occur after consumption of oxidant.

We probed catalysis using other olefins and arenes (Table 1) using a standard set of conditions {10 mL of benzene, 0.01 mol % 1 (relative to benzene), 2000 equiv of olefin (relative to 1) or 25 psig for gaseous olefins, and 240 equiv of  $Cu(OAc)_2$ (relative to 1)}. The production of vinyl and allyl species was observed for all olefins except neohexene, for which allyl arene formation is not possible. Reported TOs in Table 1 are based on analysis of hydrogenated products after the completion of catalytic reactions. For neohexene, only the 100% linear product (3,3-dimethylbutyl)benzene was observed [30(8) TO after 72 h]. With isobutylene, the vinyl and allyl anti-Markovnikov products were produced with 100% selectivity and hydrogenated to give isobutylbenzene [100(2) TO after 72 h]. Hydrogenated samples from catalysis with 1-pentene gave 100% yield relative to oxidant and an  $\sim$ 8:1 ratio of linear (*n*pentylbenzene, 110(10) TO) to branched (2-pentylbenzene, 12(3) TO) products after 72 h. It is important to note that the reaction of 1-pentene can yield 1-pentyl or 2-pentyl products, while reaction with 2-pentene can generate 2-pentyl or 3-pentyl products. Therefore, the observation of minimal (<2 TO) 3pentylbenzene production indicates that isomerization of 1pentene to 2-pentene is slow, that reaction with 2-pentene is likely selective for the 2-pentyl product, and/or that the catalyst reacts more rapidly with 1-pentene than 2-pentene. Interestingly, utilizing the internal olefin 2-pentene produces 22(4) TO of *n*-pentylbenzene, 48(6) TO of 2-pentylbenzene with 27(5) TO of 3-pentylbenzene after hydrogenation. Starting with 2-pentene, the amount of 1-pentene is likely low since it is thermodynamically disfavored. Thus, the formation of *n*-pentylbenzene starting from 2-pentene suggests that reaction of the catalyst with 1-pentene is likely more rapid than reaction with 2-pentene.

In the absence of copper oxidant, complex 1 catalyzes rapid isomerization of 1-pentene to 2-pentene as conversion of 1pentene to 2-pentene achieved equilibrium after at least 48 h (see Table S1). In contrast, in the presence of  $Cu(OAc)_2$  $Cu(OTFA)_2$ , or  $Cu(OPiv)_2$ , the rate of isomerization of 1pentene to 2-pentene by 1 is much slower. For example, without added Cu(OAc)<sub>2</sub> after 72 h, only 12% 1-pentene remains, whereas with 240 equiv of  $Cu(OAc)_2$  (relative to 1), 78% remains as 1-pentene after 72 h. The different rate of 1pentene isomerization in the presence (slower) and absence (faster) of Cu(OAc)<sub>2</sub> suggests the possibility that a Rh-H intermediate could play a key role in the olefin isomerization.  $Cu(OAc)_2$  might rapidly react with the Rh-H intermediate, which would compete with its ability to isomerize 1-pentene. It is interesting to note that catalysis with benzene and 2-pentene produces 22 TO of n-pentylbenzene, but 1-pentene likely remains approximately 1% of the total pentene throughout catalysis. Thus, 1 appears to react more rapidly with 1-pentene than 2-pentene.

The efficacy and selectivity of acid-based arene alkylation varies dramatically with arene substrate, and selectivity is typically dictated by directing group effects. But, catalysis using 1 appears to be broadly applicable to different types of arenes with selectivity appearing to be catalyst driven. Table 1 shows the results using AlCl<sub>3</sub> and complex 1 for several arenes and olefins (note: the selectivities in Table 1 are determined after hydrogenation using 5% Pt on carbon to yield saturated alkyl substituents). For AlCl<sub>3</sub>-catalyzed alkylation, electron-deficient arenes react substantially slower, often not at all. For example, the rate of chlorobenzene alkylation (AlCl<sub>3</sub> with propylene in nitromethane at 25 °C) is approximately 10 times slower relative to benzene with a product distribution of ortho:meta:para (o:m:p) of ~11:1:8. $^{6,31,32}$  In contrast, using AlCl<sub>3</sub>, electron-rich arenes react faster relative to benzene.<sup>33</sup> Using AlCl<sub>3</sub> as a catalyst, toluene alkylation with propylene (AlCl<sub>3</sub> in nitromethane at 25 °C) produces an unselective o:m:p ratio of 3:1:2.6.31 Using standard conditions with 1, catalysis with chlorobenzene gave 116(3) TO (97% yield) of alkyl chlorobenzene with a L:B ratio of 10:1 and o:m:p ratio of 1:11:7. Toluene and anisole were investigated as representative electron-rich arenes to evaluate catalytic activity. The reaction of toluene and propylene gave 86(17) TO (72% yield) of alkyl toluene, L:B ratio of 9.4:1, and an o:m:p ratio of 1:8.9:9.3. Anisole gave a 92(7) TO (77% yield) of alkyl anisole, L:B of 7.8:1, and an o:m:p ratio of 1:2.4:6.4. Catalysis using 1 reveals an unusually high selectivity toward meta products, which could provide routes to new or difficult to access compounds. Further, the anisole results are particularly intriguing because the para products are estragole (allyl) and anethole (vinyl), which are common materials in the flavors and fragrance industries.<sup>10</sup>

For all the aromatic substrates evaluated, catalysis using 1 provides alternative selectivity to traditional acid-based methods. The arene electronics have a negligible impact on TO and the rate of reaction. Table 1 shows comparisons between acid-based catalysis (AlCl<sub>3</sub>) and the results using Rh precatalyst 1. The *o:m:p* ratios highlight the differences between rhodium-mediated catalysis and acid-based catalysis. For rhodium-mediated catalysis using 1, the relative TO is comparable to benzene reactivity, and the o:m:p ratio favors meta and para functionalization, regardless of benzene functionality, presumably based on the regioselectivity of Rhmediated C-H activation.<sup>34</sup> In addition, the rhodium precatalyst 1 generates the vinyl and allyl products for each product in an approximate 1:1 ratio. In contrast, AlCl<sub>3</sub>, a typical Friedel-Crafts catalyst, generates only saturated products and is highly selective in all cases for branched products.

To our knowledge, there are no previous examples of catalytic conversion of simple arenes and  $\alpha$ -olefins, such as propylene, 1-pentene, 1-hexene, etc., to alkyl or vinyl/allyl products with high selectivity for anti-Markovnikov products. Herein, we have reported that a simple Rh(I) catalyst precursor, easily generated from commercially available materials,<sup>37,38</sup> achieves such transformations. Such catalysis opens the door to a range of previously inaccessible products using common petrochemicals. Furthermore, the catalytic process is effective for benzene substituted with electron-donating or -withdrawing groups with *ortho/meta/para* selectivity that is unique from acid-based catalysis. The range of arene and olefin scope allows for the generation of previously synthetically challenging materials using air-recyclable Cu(II) oxidants.

# EXPERIMENTAL SECTION

**General Considerations.** All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk or high-vacuum techniques and/or in a glovebox. Glovebox purity was maintained by periodic nitrogen purges and was monitored by an oxygen analyzer (O<sub>2</sub> < 15 ppm for all 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-SMS column with 0.25  $\mu$ m film thickness using electron impact (EI) ionization. GC/FID was performed using a Shimadzu GC-2014 system with a 30 m  $\times$  90.25 mm HP5 column with 0.25  $\mu$ m film thickness.

Phenyl acetate, 3-pentylbenzene, 2-pentylbenzene, n-pentylbenzene, cumene, *n*-propylbenzene,  $\alpha$ -methylstyrene, *trans-\beta*-methylstyrene, and biphenyl production was quantified using linear regression analysis of gas chromatograms of standard samples of authentic product. A plot of peak area ratios versus molar ratios gave a regression line. For the GC/FID instrument, the slope and correlation coefficient of the regression lines were 2.51 and 0.97 (phenyl acetate), 1.78 and 0.98 (3-pentylbenzene), 1.82 and 0.98 (2-pentylbenzene), 2.09 and 0.98 (n-pentylbenzene), 0.68 and 0.99 (cumene), 0.73 and 0.99 (npropylbenzene), 0.74 and 0.99 ( $\alpha$ -methylstyrene), 0.72 and 0.99 (trans- $\beta$ -methylstyrene), 1.55 and 0.98 (biphenyl), 2.78 and 0.99 (1pentene), 2.9 and 0.99 (2-pentene), respectively. Quantification of allyl benzene was estimated using the slope and correlation coefficient of the regression lines for cumene. Quantification of  $cis-\beta$ -methylstyrene was estimated using the slope and correlation coefficient of the regression lines for *trans-\beta*-methylstyrene. For the GC/MS instrument, the slope and correlation coefficient of the regression lines were 0.63 and 0.99 (4-ethylanisole), 0.56 and 0.99 (4-ethylchlorobenzene), 0.29 and 0.99 (3-ethylchlorobenzene), 0.55 and 0.99 (n-propylbenzene), and 0.55 and 0.99 (n-pentylbenzene). Quantification of 2-propylanisole, 3-propylanisole, 4-propylanisole, and 4-isopropylanisole was estimated using the slope and correlation coefficient of the regression lines for 4-ethylanisole. Quantification of 2-propylchlorobenzene, 3propylchlorobenzene, 4-propylchlorobenzene, 3-isopropylchlorobenzene, and 4-isopropylchlorobenzene was estimated using the slope and correlation coefficient of the regression lines for 3-ethylchlorobenzene and 4-ethylchlorobenzene. Quantification of 2-propyltoluene, 3propyltoluene, 4-propyltoluene, 3-isopropyltoluene, 4-isopropyltoluene, and isobutyl benzene was estimated using the slope and correlation coefficient of the regression lines for cumene. Quantification of 3,3-dimethylbutylbenzene was estimated using the slope and correlation coefficient of the regression lines for *n*-pentylbenzene. Identification of peaks due to linear versus branched products was determined by studying the mass fragmentation patterns. Branched products have substantially larger peak 15 m/z units less than the molecular ion peak relative to linear products. Linear products reveal loss of alkyl chain up to the benzylic position.

Propylene and isobutylene were purchased in gas cylinders from GTS-Welco and used as received. All other reagents were purchased from commercial sources and used as received.  $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$  (1) was prepared according to literature procedures.<sup>38</sup>

**Catalytic Oxidative Hydrophenylation of Propylene.** A representative catalytic reaction is described. A stock solution containing **1** (0.005 g, 0.012 mmol, 0.001 mol % of rhodium), hexamethylbenzene (0.075 g, 0.45 mmol), and benzene (200 mL) was prepared in a volumetric flask. Glass Fisher-Porter reactors were charged with stock solution (10 mL) and Cu(OAc)<sub>2</sub> (0.050 g, 0.28 mmol). The vessels were sealed, pressurized with propylene (25 psig), and subsequently stirred and heated to 150 °C. The reaction was sampled every 4 h for the first 12 h, then at the 24 h time point, and then every 24 h subsequently. At each time point, the reactors were cooled to room temperature, sampled, recharged with propylene, and reheated. Aliquots of the reaction (<200  $\mu$ L) mixture were analyzed by GC/FID using relative peak areas versus the internal standard (hexamethylbenzene).

**Hydrogenation General Procedure.** To a glass Fischer-Porter reactor, an aliquot of reaction sample was mixed in a 1:1 v:v mix with absolute ethanol, and approximately 50 mg of 5% Pt on carbon, and a stir bar were added. The reactor was then pressurized with hydrogen and released ( $3 \times 70$  psi) before being placed under 150 psig of hydrogen while stirring for 17 h. The reaction was then degassed, and the mixture was analyzed by GC/MS or GC/FID.

Olefin Identity Experiments. A stock solution containing 1 (0.01 mol % relative to benzene), hexamethylbenzene (20 equiv relative to 1), and benzene (200 mL) was prepared in a volumetric flask. When using liquid olefins, 2000 equiv (relative to 1) of olefin was added to the stock solution. Glass Fisher-Porter reactors were charged with stock solution (10 mL) and oxidant (240 equiv relative to 1). The vessels were sealed, charged with olefin or N2 (25 psig), and subsequently stirred and heated to 150 °C. The reaction was sampled after 24 h, 48 h, and 72 h. At each time point, the reactors were cooled to room temperature, sampled, recharged with gaseous olefin or N<sub>2</sub>, and reheated. Aliquots of the reaction (<200  $\mu$ L) mixture were analyzed by GC/MS using relative peak areas versus the internal standard (hexamethylbenzene). Using neohexene, 30(8) TO of 100% linear product (3,3-dimethylbutyl)benzene and 27(6) TO of the olefin coupled product 2,2,4,6,6-pentamethylheptane were observed after 72 h.

**Oxidant Loading Experiments.** A stock solution containing 1 (0.001 mol % relative to benzene), hexamethylbenzene (20 equiv relative to Rh), and benzene (200 mL) was prepared in a volumetric flask. Glass Fisher-Porter reactors were charged with stock solution (10 mL) and  $Cu(OAc)_2$  (60, 120, or 240 equiv relative to 1). The vessels were sealed, charged with propylene (25 psig), and subsequently stirred and heated to 150 °C. The reaction was sampled every 4 h for the first 12 h, then at the 24 h time point, and then every 24 h subsequently. At each time point, the reactors were cooled to room temperature, sampled, recharged with propylene, and reheated. Aliquots of the reaction (<100  $\mu$ L) mixture were analyzed by GC/FID

using relative peak areas versus the internal standard (hexamethylbenzene).

**Temperature Variation Experiments.** A stock solution containing 1 (0.001 mol % relative to benzene), hexamethylbenzene (20 equiv relative to Rh), and benzene (200 mL) was prepared in a volumetric flask. Glass Fisher-Porter reactors were charged with stock solution (10 mL) and Cu(OAc)<sub>2</sub> (240 equiv relative to 1). The vessels were sealed, charged with propylene (25 psig), and subsequently stirred and heated to 120, 150, or 180 °C. The reaction was sampled every 4 h for the first 12 h, then at the 24 h time point, and then every 24 h after that. At each time point, the reactors were cooled to room temperature, sampled, recharged with propylene, and reheated. Aliquots of the reaction (<100  $\mu$ L) mixture were analyzed by GC/FID using relative peak areas versus an internal standard (hexamethylbenzene).

**Rhodium Loading Experiments.** Three stock solutions containing 1 (0.001 mol % relative to benzene, 0.005 mol % relative to benzene, or 0.01 mol % relative to benzene), hexamethylbenzene (20 equiv relative to Rh), and benzene (200 mL) were prepared in volumetric flasks. Glass Fisher-Porter reactors were charged with stock solution (10 mL) and Cu(OAc)<sub>2</sub> (240 equiv relative to 1). The vessels were sealed, charged with propylene (25 psig), and subsequently stirred and heated to 150 °C. The reaction was sampled every 4 h for the first 12 h, then at the 24 h time point, and then every 24 h subsequently. At each time point, the reactors were cooled to room temperature, sampled, recharged with propylene, and reheated. Aliquots of the reaction (<100  $\mu$ L) mixture were analyzed by GC/ FID using relative peak areas versus an internal standard (hexamethylbenzene).

**High-Turnover Experiment.** A stock solution containing 1 (0.001 mol % relative to benzene), hexamethylbenzene (20 equiv relative to 1), and benzene (200 mL) was prepared in a volumetric flask. Glass Fisher-Porter reactors were charged with stock solution (10 mL) and  $Cu(OPiv)_2$  (2400 equiv relative to 1). The vessels were sealed, charged with propylene (50 psig), and subsequently stirred and heated to 150 °C. The reaction was sampled at 12 h, 24 h, 48 h, 72 h and 96 h. At each time point, the reactors were cooled to room temperature, sampled, recharged with propylene, and reheated. Aliquots of the reaction (<200  $\mu$ L) mixture were analyzed by GC/FID using relative peak areas versus the internal standard (hexamethylbenzene). After the 48 h sampling, an additional 1200 equiv Cu(OPiv)<sub>2</sub> was added.

Arene Identity Experiments. A stock solution containing 1 (0.01 mol % relative to arene), hexamethylbenzene (20 equiv relative to Rh), and arene (100 mL) was prepared in a volumetric flask. Glass Fisher-Porter reactors were charged with stock solution (10 mL) and oxidant (240 equiv relative to 1). The vessels were sealed, charged with propylene (25 psig), and subsequently stirred and heated to 150 °C. The reaction was sampled after 24 h, 48 h, and 72 h. At each time point, the reactors were cooled to room temperature, sampled, recharged with propylene, and reheated. Aliquots of the reaction (<100  $\mu$ L) mixture were analyzed by GC/MS using relative peak areas versus the internal standard (hexamethylbenzene).

**Isomerization of 1-Pentene.** A stock solution containing 1 (0.01 mol % relative to benzene), hexamethylbenzene (20 equiv relative to 1), and benzene (200 mL) was prepared in a volumetric flask. Either 1-pentene or 2-pentene (2000 equiv relative to 1) was added to the stock solution. Glass Fisher-Porter reactors were charged with stock solution (10 mL), and, if required, Cu(OAc)<sub>2</sub> (240 equiv relative to 1) was added. An initial sample (100  $\mu$ L) was taken before heating (t = 0 h) and analyzed by GC/FID to determine the ratio of 1-pentene and 2-pentene. The vessels were sealed, stirred, and heated to 150 °C. The reaction was sampled at 48 h and 72 h. At each time point, the reactors were cooled to room temperature, sampled at 0 °C and reheated. Aliquots of the reaction (<100  $\mu$ L) mixture were analyzed by GC/FID using relative peak areas versus the internal standard (hexamethylbenzene). The total concentration of pentenes decreases over time due to the high volatility.

# ASSOCIATED CONTENT

# Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b01165.

Effect of temperature, copper oxidant identity, oxidant concentration, rhodium loading, high-TO experiment, isomerization, representative mass spectrum (PDF)

## AUTHOR INFORMATION

#### **Corresponding Author**

\*tbg7h@virginia.edu

#### **ORCID**

Benjamin A. Vaughan: 0000-0001-9607-5696 T. Brent Gunnoe: 0000-0001-5714-3887

#### Notes

The authors declare no competing financial interest. <sup>§</sup>Retired. Consulting scientist, San Rafael, CA 94903.

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#### REFERENCES

 Kocal, J. A.; Vora, B. V.; Imai, T. Appl. Catal., A 2001, 221, 295.
Olah, G. A.; Molnár, Á. Hydrocarbon chemistry; Wiley & Sons: New York, 1995.

(3) Tadros, T. In *Kirk-Othmer Encyclopedia of Chemical Technology*; John Wiley & Sons, Inc.: Hoboken, NJ, 2000.

(4) Kosswig, K. In Ullmann's Encyclopedia of Industrial Chemistry; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000.

(5) de Almeida, J. L. G.; Dufaux, M.; Taarit, Y. B.; Naccache, C. J. Am. Oil Chem. Soc. 1994, 71, 675.

(6) Röper, M.; Gehrer, E.; Narbeshuber, T.; Siegel, W. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000.

(7) Perego, C.; Ingallina, P. Green Chem. 2004, 6, 274.

(8) Cao, Y.; Kessas, R.; Naccache, C.; Ben Taarit, Y. Appl. Catal., A 1999, 184, 231.

(9) Schumann, K.; Siekmann, K. In Ullmann's Encyclopedia of Industrial Chemistry; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000.

(10) Fahlbusch, K.-G.; Hammerschmidt, F.-J.; Panten, J.; Pickenhagen, W.; Schatkowski, D.; Bauer, K.; Garbe, D.; Surburg, H. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000.

(11) Baumgartner, F. N. Ind. Eng. Chem. 1954, 46, 1349.

(12) Andreatta, J. R.; McKeown, B. A.; Gunnoe, T. B. J. Organomet. Chem. 2011, 696, 305.

(13) Foley, N. A.; Lee, J. P.; Ke, Z.; Gunnoe, T. B.; Cundari, T. R. Acc. Chem. Res. 2009, 42, 585.

(14) Ritleng, V.; Sirlin, C.; Pfeffer, M. Chem. Rev. 2002, 102, 1731.

(15) McKeown, B. A.; Prince, B. M.; Ramiro, Z.; Gunnoe, T. B.; Cundari, T. R. ACS Catal. 2014, 4, 1607.

(16) McKeown, B. A.; Foley, N. A.; Lee, J. P.; Gunnoe, T. B. Organometallics **2008**, 27, 4031.

(17) Clement, M. L.; Grice, K. A.; Luedtke, A. T.; Kaminsky, W.; Goldberg, K. I. Chem. - Eur. J. 2014, 20, 17287.

(18) Lail, M.; Arrowood, B. N.; Gunnoe, T. B. J. Am. Chem. Soc. 2003, 125, 7506.

(19) Matsumoto, T.; Taube, D. J.; Periana, R. A.; Taube, H.; Yoshida, H. J. Am. Chem. Soc. **2000**, 122, 7414.

(20) Oxgaard, J.; Muller, R. P.; Goddard, W. A., III; Periana, R. A. J. Am. Chem. Soc. 2004, 126, 352.

(21) Periana, R. A.; Liu, X. Y.; Bhalla, G. Chem. Commun. 2002, 24, 3000.

(22) (a) Dobereiner, G. E.; Yuan, J.; Schrock, R. R.; Goldman, A. S.;

Hackenberg, J. D. J. Am. Chem. Soc. 2013, 135, 12572. (b) Ahuja, R.; Punji, B.; Findlater, M.; Supplee, C.; Schinski, W.; Brookhart, M.;

Goldman, A. S. Nat. Chem. 2011, 3, 167.

(23) Bair, J. S.; Schramm, Y.; Sergeev, A. G.; Clot, E.; Eisenstein, O.; Hartwig, J. F. J. Am. Chem. Soc. **2014**, *136*, 13098.

- (24) Zheng, L.; Wang, J. Chem. Eur. J. 2012, 18, 9699.
- (25) Weissman, H.; Song, X.; Milstein, D. J. Am. Chem. Soc. 2001, 123, 337.

(26) Schinkel, M.; Marek, I.; Ackermann, L. Angew. Chem., Int. Ed. 2013, 52, 3977.

(27) Vaughan, B. A.; Webster-Gardiner, M. S.; Cundari, T. R.; Gunnoe, T. B. Science 2015, 348, 421.

(28) Eckert, M.; Fleischmann, G.; Jira, R.; Bolt, H. M.; Golka, K. In Ullmann's Encyclopedia of Industrial Chemistry; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000.

(29) Li, L.; Brennessel, W. W.; Jones, W. D. Organometallics 2009, 28, 3492.

(30) Webster-Gardiner, M. S.; Piszel, P. E.; Fu, R.; McKeown, B. A.; Nielsen, R. J.; Goddard, W. A., III; Gunnoe, T. B. *J. Mol. Catal. A: Chem.* **2017**, 426, 381.

(31) Olah, G. A.; Flood, S. H.; Kuhn, S. J.; Moffatt, M. E.; Overchuck, N. A. J. Am. Chem. Soc. **1964**, 86, 1046.

(32) Olah, G. A.; Flood, S. H.; Moffatt, M. E. J. Am. Chem. Soc. 1964, 86, 1060.

(33) Germain, J. E. Catalytic conversion of hydrocarbons; Academic Press: London, 1969.

(34) Jones, W. D. Inorg. Chem. 2005, 44, 4475.

(35) Kovacic, P.; Hiller, J. J. J. Org. Chem. 1965, 30, 1581.

(36) Olah, G. A.; Olah, J. A.; Ohyama, T. J. Am. Chem. Soc. 1984, 106, 5284.

(37) Cramer, R.; McCleverty, J. A.; Bray, J. In *Inorganic Syntheses*; John Wiley & Sons, Inc.: New York, 2007; p 86.

(38) Werner, H.; Poelsma, S.; Schneider, M. E.; Windmüller, B.; Barth, D. Chem. Ber. **1996**, *129*, 647.