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# Oxidative Hydrophenylation of Ethylene Using a Cationic Ru(II) Catalyst: Styrene Production with Ethylene as the Oxidant

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Professor Bergman's contributions to chemistry are wide ranging and impactful, and the authors wish to congratulate him for the well-deserved recognition of the 2017 Wolf Prize in Chemistry.

**Abstract:** The complex [(MeOTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt) (NCMe) Ph][BAr'<sub>4</sub>] (MeOTMM = 4,4',4''-(methoxymethanetriyl)-tris (1benzyl-1H-1,2,3-triazole), BAr'<sub>4</sub> = tetrakis[3,5-bis (trifluoromethyl)phenyl]borate) is used to catalyze the hydrophenylation of ethylene to produce styrene and ethylbenzene. The selectivity of styrene versus ethylbenzene varies as a function of ethylene pressure, and replacing the MeOTTM ligand with tris(1-phenyl-1H-1,2,3-triazol-4-yl)methanol reduces the selectivity toward styrene. For styrene production ethylene serves as the oxidant to produce ethane, as determined by both <sup>1</sup>H NMR spectroscopy and GC-MS. The Ru(III/II) potentials of  $[(MeOTTM)Ru[P(OCH_2)_3CEt](NCMe)Ph][BAr'_4]$ (0.86 V) and  $[(HC(pz^5)_3)Ru[P(OCH_2)_3CEt](NCMe)Ph][BAr'_4]$ (0.82 V)  $(HC(pz^5)_3 = tris(5-methyl-pyrazolyl)methane)$  are nearly identical. Since catalytic conversion of ethylene and benzene by  $[(HC(pz^5)_3)Ru[P(OCH_2)_3CEt](NCMe)Ph][BAr'_4]$  is known to selectively produce ethylbenzene, the formation of styrene using  $[(MeOTTM)Ru[P(OCH_2)_3CEt](NCMe)Ph][BAr'_4]$  is attributed to the substituents on the triazole rings of the MeOTTM ligand.

Keywords: Ruthenium · C-H Activation · Olefin Hydroarylation · Ethylbenzene · Styrene

### 1. Introduction

Styrene is one of the major building blocks of the plastics industry.<sup>[1]</sup> Currently, styrene is produced from benzene ethylation, trans-alkylation, and dehydrogenation of ethylbenzene.<sup>[2]</sup> Ethylbenzene is produced either by traditional Friedel-Crafts alkylation catalyzed by a Lewis acid (e.g., AlCl<sub>3</sub>) in the presence of a Brønsted acid (such as HCl or HF) or by using a zeolite catalyst.<sup>[3–6]</sup> Acid-catalyzed alkylation is generally faster for alkyl-substituted arenes, which often gives rise to the undesired polyalkylation of benzene. Thus, in order to optimize yield of ethylbenzene, energy consuming distillation and then transalkylation of benzene and polyethylbenzenes are performed. Herein, we disclose new Ru(II) catalysts that convert benzene and two equivalents of ethylene to styrene and ethane in a process that offers possible benefits over existing routes to styrene or other vinyl or alkenyl arenes.

Transition metal catalyzed olefin hydroarylation or oxidative olefin hydroarylation that does not generate carbocation intermediates offers a strategy for the alkylation or alkenylation of arenes, respectively, that is complementary to current processes.<sup>[7-26]</sup> Along these lines, our groups have been studying a series of neutral ruthenium(II) catalysts with the general formula TpRu(L)(NCMe)Ph (Tp=hydridotris(pyrazolyl)borate; L=CO, PMe<sub>3</sub>, P(pyr)<sub>3</sub>,  $_{P(OCH_2)_2(OCCH_3)}$ , P(OCH<sub>2</sub>)<sub>3</sub>CEt; pyr=*N*-pyrrolyl) for catalytic ethylene hydrophenylation.<sup>[21,27-33]</sup> In those studies, we demonstrated that more strongly donating ligands "L" result in an increase in the activation barrier for ethylene insertion into Ru–Ph bonds,<sup>[27,29,32]</sup> and, as a result, ethylene C–H activation, ultimately to form thermally stable and catalytically inactive  $\eta^3$ -methylallyl complexes,<sup>[25,27,29,32]</sup> competes with ethylene insertion. Hence, the most electron-poor complex among the series TpRu (L)(NCMe)Ph, with L=CO, proved to be the longest-lived catalyst. Accordingly, more electron-poor Ru(II) complexes

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have been pursued in efforts to further improve catalytic activity.

One strategy to access more electron-deficient Ru(II) catalyst precursors has been to prepare cationic variants of TpRu(L)(NCMe)Ph complexes (Scheme 1). Replacement of Tp with a tetra(pyrazolyl)alkane resulted in intramolecular C–H activation of a pyrazolyl ring.<sup>[34]</sup> Thus, the cationic Ru(II) complex was synthesized using  $HC(pz^5)_3$  ( $HC(pz^5)_3$ =tris(5-methyl-pyrazolyl)methane) in which the pyrazolyl 5-positions are protected by incorporation of methyl substituents. Under optimized conditions, the cationic Ru(II) complex [( $HC(pz^5)_3$ ) Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(NCMe)Ph][BAr'<sub>4</sub>] successfully increased the TON (turnover numbers) of the ethylene hydrophenylation reaction by over 30-fold compared to TpRu(P(OCH<sub>2</sub>)<sub>3</sub> CEt)(NCMe)Ph.<sup>[27,35]</sup>



**Scheme 1.** Changes in performance and selectivity based upon the tridentate ligand coordinated to the  $Ru(P(OCH_2)_3CEt)(NCMe)Ph$  fragment (BAr'<sub>4</sub> = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, Bn = benzyl).

With the success of  $[(HC(pz^5)_3)Ru(P(OCH_2)_3CEt)(NCMe)]$ Ph][BAr'<sub>4</sub>] for catalytic hydrophenylation of ethylene, we have been seeking to explore related motifs that provide reduced electron density at Ru. Tris(triazolyl)methanol ligands have a similar coordination mode as Tp and HC(pz<sup>5</sup>)<sub>3</sub>.<sup>[36-38]</sup> It was anticipated that tris(triazolyl)methanol ligands would have reduced donor ability compared to Tp and  $HC(pz^{5})_{3}$ . Thus, we sought to prepare a Ru(II) catalyst precursor supported by a tris(triazolyl)methanol ligand to test for ethylene hydrophenylation. Since we have obtained data to directly compare catalytic ethylene hydrophenylation using TpRu(P(OCH<sub>2</sub>)<sub>3</sub> CEt)(NCMe)Ph and  $[(HC(pz^5)_3)Ru(P(OCH_2)_3CEt)(NCMe)Ph]$ [BAr'<sub>4</sub>],<sup>[35]</sup> we sought to prepare variations of this motif with tris(triazolyl)methanol in place of Tp and HC(pz<sup>5</sup>)<sub>3</sub>. Herein, we report on the synthesis and studies of catalytic ethylene hydrophenylation, including the surprising result of selective styrene production in which ethylene serves as oxidant (see Ru(II) catalyst on right in Scheme 1).

#### 2. Results and Discussion

The ruthenium precursor ( $\eta^6$ -p-cymene)Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(Ph) Br (1) and the proligand MeOTMM {4,4',4''-(methoxymethanetriyl)tris(1-benzyl-1H-1,2,3-triazole)} were prepared according to literature procedures.<sup>[27,35–36]</sup> An acetonitrile solution of complex 1 was heated for 3.5 hours at 70 °C to yield the putative complex (NCMe)<sub>3</sub>Ru[P(OCH<sub>2</sub>)<sub>3</sub>CEt](Ph)Br (2).<sup>[35]</sup> Complex 2 was then reacted with MeOTTM to produce [(MeOTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(NCMe)Ph]Br (3) in 76% isolated yield. A metathesis reaction of 3 with NaBAr'<sub>4</sub> in THF gives the Ru(II) complex [(MeOTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub> CEt)(NCMe)Ph][BAr'<sub>4</sub>] (4) in 95% isolated yield (Scheme 2).



**Scheme 2.** Synthesis of  $[(MeOTTM)Ru[P(OCH_2)_3CEt](NCMe)Ph]$ [BAr'<sub>4</sub>] (4) (MeOTMM = 4,4',4''-(methoxymethanetriyl)-tris(1-benzyl-1H-1,2,3-triazole), Bn = benzyl).

Cyclic voltammetry of complex **4** shows a reversible Ru(III/II) oxidation at 0.86 V (vs. NHE), which is a +0.04 V shift compared to the previously reported complex,  $[(HC(pz^5)_3 Ru(P(OCH_2)_3)CEt)(NCMe)Ph][BAr'_4].^{[35]}$  Chart 1 shows a series of Ru(II) complexes with P(OCH\_2)\_3CEt, NCMe and Ph ligands coordinated by different tridentate ligands and Ru(III/II) potentials.<sup>[27,29,35]</sup> Surprisingly, the exchange of HC(pz<sup>5</sup>)<sub>3</sub> with MeOTTM has negligible impact on the Ru(III/II) redox potential. Therefore, we anticipated that complex **4** might display catalytic activity and selectivity for ethylene hydrophenylation similar to  $[(HC(pz^5)_3Ru(P(OCH_2)_3)CEt)(NCMe) Ph][BAr'_4].^{[35]}$ 



**Chart 1.** Comparison of Ru(III/II) potentials (vs. NHE) for a series of Ru(II) complexes.

The use of complex **4** as a catalyst for ethylene hydrophenylation was investigated at different temperatures (Table 1). The catalytic reactions produce substantial quantities of both ethylbenzene and styrene. Heating 10 mL benzene solutions of complex **4** (0.001 mol% relative to benzene) at different temperatures (90 °C, 120 °C, 150 °C and 180 °C) affords up to 57 TON with a mixture of styrene and ethylbenzene after 4 hours (three experiments were performed at each temperature). The data show that higher temperatures facilitate the catalytic reaction. However, catalyst decomposition is also accelerated at elevated temperatures. The optimal temperature was determined to be 150 °C, which provided a

**Table 1.** TON for catalytic hydrophenylation of ethylene using  $[(MeOTTM)Ru(P(OCH_2)_3CEt)(NCMe)Ph][BAr'_4]$  (4).



<sup>a</sup> Conditions: 0.001 mol% of complex **4** dissolved in 10 mL of benzene with decane as an internal standard and 40 psig of ethylene. <sup>b</sup> TON were determined by GC-FID after 4 hours and are the average of three separate experiments. Standard deviations are given in parentheses.

styrene TON of 53. At all temperatures, styrene is favored over ethylbenzene with styrene/ethylbenzene ratios ranging from 6.9 to 70. At 150 °C, we explored ethylene hydrophenylation under different ethylene pressures (Table 2). The results indicate that the selectivity for styrene increases with increasing ethylene pressure, and 100% selectivity toward styrene was observed under 75 psig of ethylene.

Table 2. TON of styrene and ethylbenzene and % styrene under different ethylene pressures.  $^{\rm a}$ 



<sup>a</sup> Conditions: 0.001 mol% of complex 4 dissolved in 10 mL benzene with decane as an internal standard at 150 °C.<sup>b</sup> TON were determined by GC-FID after 4 hours and are the average of three separate experiments. Standard deviations are given in parentheses.

Since the cationic Ru(II) complex  $[(HC(pz^5)_3)Ru( P(OCH_2)_3CEt)(NCMe)Ph][BAr'_4]$  is selective for ethylbenzene production and is electronically similar to complex 4 (i.e., similar Ru(III/II) potentials),<sup>[35]</sup> we considered that the formation of styrene using 4 might be a result of the steric influence of the benzyl groups at the triazolyl 4-position.<sup>[36]</sup> Thus, we sought to change the identity of the 4-position substituent to determine the influence of ancillary ligand sterics on selectivity. We prepared the complex [(PhTTM)  $Ru(P(OCH_2)_3CEt)(NCMe)Ph]Br$  (5) (PhTTM = tris(1-phenyl-1H-1,2,3-triazol-4-yl)methanol) as shown in Scheme 3. Cyclic voltammetry data show that the electron densities change of complex 4 (0.86 V vs NHE) and complex 5 (0.85 V vs NHE) are nearly identical, which suggests negligible differences in the electron donor ability of the MeOTTM and PhTTM ligands coordinated to Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(NCMe)Ph.

We probed ethylene hydrophenylation with 5 as a catalyst precursor at variable ethylene pressures (Figure 1). The results



Scheme 3. Synthesis of [(PhTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(NCMe)Ph]Br (5).



**Figure 1.** Percent styrene formation as a function of ethylene pressure using catalyst precursors  $[(MeOTTM)Ru(P(OCH_2)_3 CEt)(NCMe)Ph]Br$  (3) and  $[(PhTTM)Ru(P(OCH_2)_3CEt)(NCMe)Ph]Br$  (5) (Conditions: 0.001 mol% of complex 3 or 5 dissolved in 10 mL benzene with decane as an internal standard at 150 °C).

show that the cationic ruthenium catalyst **5** is less selective for styrene production than complex **4**. Although the steric A values, which are indicative of the steric bulk of the substituent based on impact on substituted cyclohexane confirmations,<sup>[39]</sup> show that the steric bulk of a phenyl group (A=3) is larger than that of a benzyl group (A=1.81),<sup>[40]</sup> the differences in the two-dimensional phenyl versus three-dimensional benzyl render any evaluation of relative steric influence challenging. At a minimum, the selectivity differences **3** and **5** indicate that the steric profile of the triazole substituent plays a role.

We recently reported that Rh catalyst precursors efficiently catalyze oxidative olefin hydroarylation with Cu(II) oxidants to form alkenyl arene.<sup>[41–43]</sup> Thus, we attempted to improve catalysis using **4** by adding external oxidants. However, when  $O_2$  or Cu(II) salts were added to catalytic reaction using **4**, no improvement in catalysis was observed (Table 3).

Under anaerobic conditions and in the absence of an external oxidant {e.g., Cu(II)}, we assumed that ethylene is serving as the oxidant for styrene production with the

 Table 3. The effect of external oxidants on the oxidative ethylene hydrophenylation catalyzed by complex 4.



<sup>a</sup> Reactions were performed with 0.001 mol% complex 4 dissolved in 10 mL benzene with decane as an internal standard at 150 °C with 40 psig of ethylene. <sup>b</sup> 10 equivalents of copper(II) salt relative to complex 4 were used for entries 2 and 3, 15 psig of air was used in entry 4. <sup>c</sup> TON were determined by GC-FID after 4 hours and are the average of three experiments. Standard deviations are given in parenthesis.

formation of one equivalent of ethane per equivalent of styrene. The production of ethane was confirmed by heating the solution of complex **4** in  $C_6D_6$  with 25 psig ethylene pressure at 70 °C for 40 hours. Monitoring by <sup>1</sup>H NMR spectroscopy reveled styrene production as well as a singlet at 0.88 ppm, which is consistent with ethane- $d_1$ . Additionally, ethane- $d_1$  was detected in the head space of the reactor by GC-MS. Thus, the overall reaction for styrene formation is likely conversion of benzene and two equivalents of ethylene to styrene and ethane.

A proposed catalytic cycle is shown in Scheme 4. Initial exchange of coordinated NCMe with ethylene forms [(MeOTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)Ph][BAr'<sub>4</sub>]. Then ethylene inserts into the Ru-Ph bond and results in the formation of a phenethyl intermediate.<sup>[8]</sup> The complex  $[(MeOTTM)Ru(P(OCH_2)_3CEt)(\eta^2-styrene)(H)]^+$ can be formed via β-hydride elimination from [(MeOTTM)Ru(- $P(OCH_2)_3CEt)(CH_2CH_2Ph)$ <sup>+</sup>. Net ligand exchange of styrene and ethylene completes the process for styrene formation. Ethylene then inserts into the Ru-H bond of [(MeOTTM)  $Ru(P(OCH_2)_3CEt)(\eta^2-C_2H_4)(H)]^+$  to form a Ru-ethyl complex. Finally, the coordination and C-H activation of benzene liberates ethane and regenerates the Ru-Ph moiety.

One likely key step in olefin hydroarylation catalyzed by 4 and 5 is the dissociation of the coordinated acetonitrile to create a coordination site for ethylene. We expected that the cationic nature of complexes 4 and 5 might slow the rate of



**Scheme 4.** Proposed catalytic cycle for oxidative ethylene hydrophenylation using [(MeOTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(Ph)(NCMe)][BAr'<sub>4</sub>] (4) ([Ru]=[(MeOTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)]<sup>+</sup>).

NCMe dissociation compared to the charge neutral complex TpRu(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(NCMe)Ph. The rate of exchange between coordinate NCMe and free NCMe- $d_3$  was determined using <sup>1</sup>H NMR spectroscopy by heating acetonitrile- $d_3$ solutions of complex **4** at 70, 75, 90, and 105 °C (Scheme 5). Values for  $k_{obs}$  of  $1.53(2) \times 10^{-5} \text{ s}^{-1}$  (70 °C),  $2.8(3) \times 10^{-5} \text{ s}^{-1}$ (75 °C),  $2.1(2) \times 10^{-4} \text{ s}^{-1}$  (90 °C) and  $1.0(1) \times 10^{-3} \text{ s}^{-1}$  (105 °C), were determined by monitoring the reactions using <sup>1</sup>H NMR spectroscopy. As anticipated, at 70 °C the exchange rate for **4** is slower by ~2 fold compared to the charge neutral complex TpRu(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(NCMe)Ph ( $k_{obs} = 3.2(2) \times 10^{-5} \text{ s}^{-1}$  at  $70 ^{\circ}\text{C}$ .<sup>[29]</sup>

We probed for a possible kinetic isotope effect (KIE) comparing the rates of catalysis using  $C_6H_6$  and  $C_6D_6$  (Scheme 6). For hydrophenylation of ethylene using  $C_6H_6$  and



Scheme 5. Degenerate NCMe/NCMe- $d_3$  exchange for [(MeOTTM) Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(NCMe)Ph][BAr'<sub>4</sub>] (4).

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Scheme 6. Kinetic isotope effect experiment using [(MeOTTM)  $Ru(P(OCH_2)_3CEt)(Ph)(NCMe)$ ][BAr'<sub>4</sub>] (4).

 $C_6D_6$ , the previously reported complexes TpRu(CO)(NCMe) Ph and  $[(HC(pz^5)_3)Ru(P(OCH_2)_3CEt)(NCMe)Ph][BAr'_4]$  exhibit KIEs of 2.1(1) and 2.11(5), respectively.<sup>[29,35]</sup> We probed catalysis (0.001 mol% of **4** in benzene at 150°C and 40 psig ethylene) in a 1:1 molar ratio of  $C_6H_6$  to  $C_6D_6$ . Presumably, this leads to the formation of both  $[(MeOTTM)Ru(P(OCH_2)_3)]$ CEt)(CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)][BAr'<sub>4</sub>] and [(MeOTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub>) CEt ( $CH_2CH_2C_6D_5$ ) [BAr'<sub>4</sub>] as intermediates, which would result in the production of per-protio styrene and styrene- $d_5$ .<sup>[41]</sup> The ratio of styrene and styrene- $d_5$  provides a determination of the KIE for catalytic styrene formation. After 1 hour, a  $k_{\rm H}/k_{\rm D}$ of 3.2(6) was determined by examining the ratio of perprotiostyrene (m/z = 104) to styrene- $d_5$  (m/z = 109) (Scheme 6). In addition, benzene H/D exchange is observed when heating up 4 in benzene- $d_6$  solution, indicating that the stoichiometric C<sub>6</sub>D<sub>6</sub> activation occurs. This observation supports the possibility that the cleavage of the C-H bond of benzene precedes or is the rate-determining step in the catalytic cycle.

In an effort to gain more insight into the proposed mechanism of this transformation, density functional theory (DFT) calculations were employed. Complex **5** was employed as the model system as it eliminates the multiple possible confirmations associated with the benzyl substituents of the MeOTMM analog in complex **3**. Examining the proposed mechanism given in Scheme 4, the species were optimized using the Gaussian09 software package<sup>[44]</sup> in the gas phase using the B3LYP functional<sup>[45–46]</sup> and LANL2dz basis set for Ru and 6-31G(d,p) basis set on all other atoms. Single point energies of the optimized geometries were performed using the SMD solvation model<sup>[47]</sup> with GD3BJ empirical dispersion,<sup>[48]</sup> and thermal frequency corrections at 423.15 K were employed to calculate Gibbs energy values.

Calculations were referenced to the starting precatalyst **5** as the zero point in Gibbs energy (Scheme 7). Loss of acetonitrile is calculated to be moderately endergonic by 12.1 kcal/mol, and binding of ethylene is slightly stabilizing compared to the 5-coordinate intermediate at 10.6 kcal/mol. The transition state for ethylene insertion into the Ph ligand is calculated to be 31.6 kcal/mol, about 21 kcal/mol above the precursor [(PhTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub>)CEt]( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)Ph][BAr'<sub>4</sub>].



Scheme 7. Calculated free energies (in kcal/mol) for oxidative ethylene hydrophenylation to form styrene using 5 { $[Ru] = (PhTTM)Ru(P(OCH_2)_3 CEt)$ }.

This insertion results in an phenethyl ligand that possesses an agostic C-H bond interaction that is calculated to be 17.0 kcal/mol relative to the precatalyst 5. A  $\beta$ -hydride elimination step is calculated to have a very low barrier at only 0.8 kcal/mol above the phenethyl intermediate with an overall free energy of 17.8 kcal/mol above 5. The resulting Ru-styrene/hydride intermediate is calculated to be endergonic from the precatalyst 5 by 9.0 kcal/mol. Loss of styrene to yield the coordinatively unsaturated hydride species is 9.7 kcal/mol or approximately energetically equivalent to the styrene hydride. Ethylene binding to the hydride is calculated to be slightly more favorable, having an energy of 6.6 kcal/mol relative to the precatalyst. The transition state for ethylene insertion into the hydride is also quite low with a free energy of 15.0 kcal/mol, which results in an agostic stabilized ethyl intermediate with an energy of 12.3 kcal/mol. The largest calculated barrier in the system is the transition state for a  $\sigma$ bond metathesis C-H activation in which benzene is exchanged for the ethyl ligand and has an energy of 37.0 kcal/ mol relative to the precatalyst. An off-cycle intermediate is the binding of NCMe to the 5-coordinate hydride, which is calculated to be the likely resting state of the system with an energy of -4.5 kcal/mol relative the starting precatalyst.

The calculations indicate that the proposed mechanism shown in Scheme 4 is plausible with the highest barrier resulting from C–H activation of benzene to release ethane, which is consistent with the observed kinetic isotope effect  $(k_{\rm H}/k_{\rm D})$  of 3.2(6) (see above). Two possible explanations for the styrene selectivity (versus ethylbenzene) arise from the calculations. First, the  $\sigma$ -bond metathesis C–H activation of benzene with the phenethyl unit (the transition state that would likely be responsible for ethylbenzene formation) is calculated to be 3.6 kcal/mol higher in energy (40.5 kcal/mol) than the same benzene C-H activation by the Ru-ethyl fragment (36.9 kcal/mol). If one envisions a Curtin-Hammett scenario, then all of the olefin insertion steps are reversible and the product selectivity would be controlled by the relative energy barriers for benzene C-H activation (Scheme 8). That is, the overall calculated free energy of activation (using 5 as the benchmark) for ethylbenzene formation is 40.5 kcal/mol while that for styrene formation is 36.9 kcal/mol. Another possible product controlling feature could be relative binding of styrene versus ethylene to the 5-coordinate hydride intermediate  $[(PhTTM)Ru(P(OCH_2)_3CEt)(H)]^+$ . Calculations predict the ethylene binding is favored over styrene coordination by 3.4 kcal/mol, again indicating a preference for styrene formation. In this explanation, it is the rapid equilibrium between  $[(PhTTM)Ru(P(OCH_2)_3CEt)(H)(\eta^2-styrene)]^+$  and [(PhTTM) $Ru(P(OCH_2)_3CEt)(H)(\eta^2-C_2H_4)]^+$ , which the calculations predict favors the ethylene complex, and the relative rates of ethylbenzene formation from the styrene complex and styrene and ethane formation from ethylene complex that dictates the ethylbenzene/styrene ratio. The calculated free energy of activation from [(PhTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(H)( $\eta^2$ -styrene)]<sup>+</sup> to the benzene C-H activation transition state that produces ethylbenzene is 31.5 kcal/mol, while the calculated free energy of activation from  $[(PhTTM)Ru(P(OCH_2)_3CEt)(H)(\eta^2-C_2H_4)]^+$ to the benzene C-H activation transition state that produces styrene/ethane is 30.3 kcal/mol. It is this more complete assessment that provides a rationalization for increased styrene



**Scheme 8.** The lower free energy of the transition state for C–H activation by the Ru-ethyl complexes (right) than that of the Ruphenethyl complex (left) favors styrene production over ethylbenzene  $\{[Ru] = (PhTTM)Ru(P(OCH_2)_3CEt)\}$ .

production at higher ethylene pressures since these conditions should increase the ratio of [(PhTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub> CEt)(H)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)]<sup>+</sup> to [(PhTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(H)( $\eta^2$ -styrene)]<sup>+</sup>.

#### 3. Summary and Conclusions

The new cationic Ru(II) complexes supported by tris(triazolyl) methanol ligand [(MeOTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(NCMe)Ph]<sup>+</sup> and [(PhTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(NCMe)Ph]<sup>+</sup> catalyze oxidative ethylene hydrophenylation to produce styrene. In contrast, similar Ru(II) catalysts with trispyrazolylborate (Tp) or trispyrazolylmethane ligands are highly selective for ethylbenzene production.<sup>[29,35]</sup> The complex [(MeOTTM)Ru(-P(OCH<sub>2</sub>)<sub>3</sub>CEt)(NCMe)Ph][BAr'<sub>4</sub>] produces 53 TON of styrene under 40 psig of ethylene at 150 °C, and the selectivity toward styrene production increases when higher ethylene pressures are used. The work reported herein is unique in its direct use of ethylene, a reactant, as the oxidant for this process whereas previously disclosed work by our group and that of Milstein and co-workers utilized copper(II) salts<sup>[41-43]</sup> or  $O_2^{[22]}$  as oxidant. The reduced ethylene, to form ethane, can in principle be easily recycled to ethylene. Determination of reversible Ru(III/II) potentials using cyclic voltammetry indicate minor differences in electron-density at Ru for [(HC(pz<sup>5</sup>)<sub>3</sub>Ru(- $P(OCH_2)_3)CEt)(NCMe)Ph]^+$ , [(MeOTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub>  $(\text{CEt})(\text{NCMe})\text{Ph}]^+$  and  $[(\text{PhTTM})\text{Ru}(\text{P}(\text{OCH}_2)_3\text{CEt})(\text{NCMe})]$  Ph]<sup>+</sup>. Thus, the change in selectivity for styrene versus ethylbenzene is likely a result of steric profile of the ligands. That is, the benzyl and phenyl substituents on the MeOTTM and PhTTM ligands biases the catalysis toward styrene production. DFT calculations provide an explanation: the equilibrium between [(PhTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(H)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)]<sup>+</sup> to [(PhTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(H)( $\eta^2$ -styrene)]<sup>+</sup> favors the ethylene complex, which ultimately leads to styrene formation. Furthermore, assessment under Curtin-Hammett conditions is consistent with favorable styrene production (see above). Since ethylene is produced directly from ethane, this new process for styrene production without an added external oxidant is promising as outlined in Scheme 9.



Scheme 9. Vision for a new process for styrene production.

### **Experimental Section**

General Considerations: Unless otherwise noted, all synthetic procedures were performed under anaerobic conditions in a nitrogenfilled glovebox or by using standard Schlenk techniques. Glovebox purity was maintained by periodic nitrogen purges and was monitored by an oxygen analyzer ( $O_2 < 15$  ppm for all reactions). Tetrahydrofuran and diethyl ether were dried by distillation from sodium/ benzophenone, respectively. Benzene, methylene chloride, and hexanes were purified by passage through a column of activated alumina. Benzene- $d_6$ , acetone- $d_6$ , CD<sub>3</sub>CN, and THF- $d_8$  were used as received and stored under a N2 atmosphere over 4 Å molecular sieves. <sup>1</sup>H NMR spectra were recorded on a Varian 600, Varian 500 MHz or a Bruker 600~MHz or 800 MHz spectrometer, and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Varian 600 MHz (operating frequency 125 MHz), Bruker 600 MHz (operating frequency = 150 MHz) or a Bruker 800 MHz (operating frequency = 201 MHz). All <sup>1</sup>H and <sup>13</sup>C spectra are referenced against residual proton signals (<sup>1</sup>H NMR) or <sup>13</sup>C resonances (<sup>13</sup>C NMR) of the deuterated solvents. <sup>31</sup>P{<sup>1</sup>H} NMR spectra were obtained on a Varian 500 MHz (operating frequency = 201 MHz) or Varian 600 MHz (operating frequency = 243 MHz) spectrometer and referenced against an external standard of  $H_3PO_4$  ( $\delta = 0$ ). GC/MS was performed using a Shimadzu GCMS-OP2010 Plus system with a  $30 \text{ m} \times 0.25 \text{ mm}$  RTx-Qbond column with 8 µm thickness using electron impact 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. Styrene 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 system, the slope and correlation coefficient of the regression line were 1.34 and 0.99, respectively. FID response factors for other products were determined in a similar fashion, using authentic standards of products. All other reagents were used as received from commercial sources. The preparation, isolation and characterization of  $[(\eta^6-p-cymene)Ru(Br)(\mu-Br)]_2$ , NaBAr'<sub>4</sub> (sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate), Ph2Mg[THF]2, MeOTTM {4,4',4"-(methoxymethanetriyl)-tris(1-benzyl-1H-1,2,3-

triazole)}, PhTTM {4,4,4"-(hydroxymethanetriyl)-tris(1-phenyl-1H-1,2,3-triazole)}, ( $\eta^6$ -*p*-cymene)Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(Br)Ph were performed according to literature procedures.<sup>[27,35-36,49-50]</sup> Elemental analyses were performed by Atlantic Microlab, Inc.

[(MeOTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(NCMe)Ph]Br (3): The complex ( $\eta^6$ p-cymene)Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(Br)Ph (1) (0.55 g, 1.0 mmol) was dissolved in NCMe (20 mL), added to a pressure tube, and heated for 3.5 h at 70 °C. The reaction was allowed to cool to room temperature. The mixture was filtered through Celite, and the filtrate was concentrated to dryness yielding the putative complex (NCMe)<sub>2</sub>Ru(-P(OCH<sub>2</sub>)<sub>3</sub>CEt)(Br)Ph.<sup>[35]</sup> The resulting solid was taken up in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and added to a 50 mL thick-wall glass pressure tube with MeOTTM (0.57 g, 1.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The solution was heated to 70 °C for 15 h after which it was cooled to room temperature and filtered through Celite. The volatiles were removed from the filtrate under reduced pressure. Benzene was added, and the mixture was stirred for 10 min. The solution was filtered through Celite, and the filtrate was discarded. The remaining white solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered through Celite. The filtrate was concentrated to 2 mL, and hexanes were added to induce precipitation. The colorless precipitate was collected on a fine porosity frit. The solid was washed with pentane and dried in vacuo to yield a tan solid (73%). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) & 8.38 (s, 1H, triazole-H), 8.36 (s, 1H, triazole-H), 8.21 (s, 1H, triazole-H), 7.38-7.29 (m, 15H, phenyl form benzyl), 6.91 (d,  ${}^{3}J_{HH} = 7$  Hz, 2H, phenyl *ortho-H*), 6.83-6.76 (m, 3H, phenyl meta and para-H), 5.65 (m, 1H, -CH<sub>2</sub>-), 5.59-5.54 (m, 2H, -CH<sub>2</sub>-), 5.53 (s, 1H, -CH2-), 5.50 (s, 1H, -CH2-), 5.46 (s, 1H, -CH2-), 4.19-4.11 (m, 6H, P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub>), 4.07 (s, 3H, -OCH<sub>3</sub>), 2.30 (s, 3H, NCMe), 1.20 (q,  ${}^{3}J_{HH} = 8$  Hz, 2H, P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub>), 0.83 (t,  ${}^{3}J_{HH} =$ 8 Hz, 3H, P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub>).<sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 134.7. Anal. Calcd for C43H46O4N10PBrRu: C, 52.18; H, 4.80; N, 14.49. Found: C, 52.43; H, 4.92; N, 14.51.

[(MeOTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(NCMe)Ph][BAr'<sub>4</sub>] (4): The Ru(II) complex (MeOTTM)Ru(P(OCH<sub>2</sub>)<sub>2</sub>CEt)(NCMe)Ph]Br (0.978 g. 0.300 mmol) was suspended in THF (10 mL) in a round bottom flask to form a heterogeneous mixture. NaBAr'<sub>4</sub> (0.270, 0.303 mmol) in THF (5 mL) was slowly added, resulting in a colorless homogenous solution. The reaction was stirred at room temperature for 2.5 h during which time it turned from colorless to grey. The solution was filtered through Celite, and the filtrate was concentrated to dryness. The resulting solid was reconstituted in Et<sub>2</sub>O and filtered through Celite. The filtrate was concentrated to drvness to vield a golden solid. The golden solid was reconstituted in benzene and filtered through Celite. The filtrate was concentrated to dryness to yield a golden foam solid (53%). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.74 (br s, 8H, BAr'<sub>4</sub>, ortho-H), 7.64 (s, 1H, triazole-H), 7.63 (s, 1H, triazole-H), 7.59 (s, 1H, triazole-H), 7.57 (br s, 4H, BAr'<sub>4</sub>, para-H), 7.38-7.31 (m, 6H, phenyl), 7.24-7.23 (m, 4H, phenyl), 6.95-6.94 (m, 2H, phenyl ortho-H), 6.87-6.83 (m, 3H, phenyl *meta* and *para-H*), 5.63 (d,  ${}^{2}J_{HH} = 15$  Hz, 2H,  $-CH_{2}$ -), 5.56 (d,  ${}^{2}J_{HH} = 15$  Hz, 2H,  $-CH_{2}$ -), 5.51 (d,  ${}^{2}J_{HH} = 14$  Hz, 2H,  $-CH_{2}$ -), 5.43 (m, 5H), 4.21 (m, 6H, P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub>), 3.86 (s, 3H, -OCH<sub>3</sub>), 2.33 (s, 3H, NCMe), 1.21 (q, 2H,  ${}^{3}J_{HH} = 8$  Hz, P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub>), 0.84 (t, 3H,  ${}^{3}J_{HH} = 8$  Hz, P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub>).  ${}^{13}$ C NMR (151 MHz,  $CD_2Cl_2$ )  $\delta$  166.8 (d,  ${}^2J_{CP} = 17$  Hz, ipso of phenyl), 162.8, 162.5, 162.2, 161.8 (four line pattern,  ${}^{1}J_{CB} = 50$  Hz, BAr'<sub>4</sub>), 145.8, 145.8, 145.6, 142.4, 134.0, 133.8, 129.9-129.6 (m) (each a s, phenyl groups of benzyl substituents), 135.4 (s, BAr'<sub>4</sub>), 128.9 (d,  ${}^{2}J_{CP} = 7$  Hz), 126.1, 125.8, 124.3 (each a s,triazole-H), 121.1-120.9 (m, -CH<sub>2</sub>-), 118.1 (s, NCCH<sub>3</sub>)., 74.6 (d,  ${}^{2}J_{CP} = 7$  Hz, P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub>), 56.3-56.1(m), 55.6( $-OCH_3$ ), 35.8(d,  ${}^{3}J_{CP} = 31 \text{ Hz}$ , P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub>), 24.1 (s,  $P(OCH_2)_3CCH_2CH_3)$ , 7.5 (s,  $P(OCH_2)_3CCH_2CH_3)$ , 4.9 (s,  $NCCH_3$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 134.6. <sup>19</sup>F NMR (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -62.9. CV (NCMe): E<sub>1/2</sub>=0.86 V. Anal. Calcd for  $C_{75}H_{58}BO_4N_{10}PF_{24}Ru;$  C, 51.12; H, 3.22; N, 7.95. Found: C, 50.88; H, 3.46; N, 8.17.

[(PhTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(NCMe)Ph]Br (5): Following the above procedure for **3** and using PhTTM, **5** was obtained as a white powder (44% yield). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.86 (s, 1H, *triazole-H*), 8.75 (s, 1H, *triazole-H*), 8.64 (s, 1H, *triazole-H*), 7.83–7.39 (m, 15H, phenyl from benzyl), 7.26 (d, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 2H, phenyl *ortho-H*), 6.82 (t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 2H, phenyl *meta-H*), 6.75 (t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, 1H, phenyl *para-H*), 4.27 (dt, <sup>2</sup>J<sub>HH</sub> = 6.3, 2.8 Hz, 6H, P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub>), 2.32 (s, 3H, NCMe), 1.21 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 2H, P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub>), 0.82 (t, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 3H, P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub>). 0.82 (t, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 3H, P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub>). 0.81 (Hz, CD<sub>2</sub>Cl<sub>2</sub>) δ 134.6. Anal. Calcd for C<sub>39</sub>H<sub>38</sub>O<sub>4</sub>N<sub>10</sub>PBrRu: C, 50.76; H, 4.15; N, 15.18. Found: C, 51.82; H, 4.15; N, 16.26.

**Catalytic Oxidative Hydrophenylation of Ethylene:** A representative catalytic reaction is described. A stock solution containing **4** (0.040 g, 0.023 mmol), decane (88  $\mu$ L, 0.46 mmol), and benzene (200 mL) was prepared in a volumetric flask. Thick-walled Fisher-Porter reactors were charged with stock solution (10 mL). The vessels were sealed, pressurized with ethylene (40 psig), and subsequently stirred and heated to 150 °C. The reaction was sampled every 1 h for the first 2 h, then every 2 h. At each time point, the reactors were cooled to room temperature, sampled, recharged with ethylene (40 psig), and heated. Aliquots of the reaction mixture were analyzed by GC/FID using relative peak areas versus the internal standard.

**Temperature Variation Experiments:** A stock solution containing 4 (0.001 mol% relative to benzene), decane (20 equiv. relative to 4), and benzene (200 mL) was prepared in a volumetric flask. Thick-walled Fisher-Porter reactors were charged with stock solution (10 mL). The vessels were sealed, charged with ethylene (40 psig), and subsequently stirred and heated to 90, 120, 150, or  $180^{\circ}$ C (3 reactors per temperature). The reaction was sampled every 1 h for the first 2 h, then every subsequent 2 h. At each time point, the reactors were cooled to room temperature, sampled under N<sub>2</sub>, recharged with ethylene pressure, and reheated. Aliquots of the reaction mixture were analyzed by GC/FID using relative peak areas versus an internal standard.

Ethylene Pressure Experiments: A stock solution containing 4 (0.001 mol% relative to benzene), decane (20 equiv. relative to 4), and benzene (200 mL) was prepared in a volumetric flask. Thick-walled Fisher-Porter reactors were charged with stock solution (10 mL). The vessels were sealed, charged with ethylene (15, 25, 40, 50, or 75 psig, 3 reactors at each pressure), and subsequently stirred and heated to  $150 \,^{\circ}$ C. The reaction was sampled every 1 h for 6 h. At each time point, the reactors were cooled to room temperature, sampled, recharged with ethylene pressure, and reheated. Aliquots of the reaction mixture were analyzed by GC/FID using relative peak areas versus the internal standard (decane).

Degenerate NCCH<sub>3</sub>/NCCD<sub>3</sub> Exchange for [(MeOTTM)Ru(-P(OCH<sub>2</sub>)<sub>3</sub>CEt)(NCMe)Ph][BAr'<sub>4</sub>]: In a 1 mL volumetric flask [(MeOTTM)Ru(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(NCMe)Ph][BAr'<sub>4</sub>] (0.054 g) was dissolved in CD<sub>3</sub>CN. A small crystal of hexamethylbenzene was added as an internal standard. The solution was divided between three J. Young NMR tubes (300  $\mu$ L per tube). <sup>1</sup>H NMR spectra were taken every 15 minutes. Each spectrum required 2 minutes to complete. Eight scans were acquired for each spectrum. The delay time was set to 12.8 s, and the acquisition time was set to 2.2 s. The exchange reaction was repeated at 70 °C, 90 °C and 110 °C only the tubes were reheated in a temperature-controlled oil bath. <sup>1</sup>H NMR spectra using a 12.8 s pulse delay time were acquired periodically. All reactions were monitored through at least three half-lives.

Kinetic Isotope Effect Experiments: A stock solution containing 4 (0.001 mol% relative to benzene) and a 1:1 molar mixture of C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>D<sub>6</sub> (30 mL) was prepared in a volumetric flask. Thick-walled Fisher-Porter reactors were charged with stock solution (10 mL). The vessels were sealed, charged with ethylene (40 psig), and subsequently stirred and heated to 150 °C. The reaction was sampled at 1, 2, and 4 h. At each time point, the reactors were cooled to room temperature, sampled, recharged with ethylene, and reheated. Aliquots of the reaction mixture were analyzed by GC/MS. KIE was determined by examining the ratio of styrene (m/z = 104) to styrene- $d_5$  (m/z = 109) in the mass spectrum, accounting for the initial isotopic distribution and natural abundance. No change in the isotopic distribution for benzene was observed over the course of the reaction, and the observed isotopic distribution of product was consistent with the initial distribution. No  $d_{6-8}$  products were observed, except those predicted by the natural abundance of deuterium in ethylene.

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### **FULL PAPER**



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Oxidative Hydrophenylation of Ethylene Using a Cationic Ru(II) Catalyst: Styrene Production with Ethylene as the Oxidant