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## Communication

Studies of the decomposition of the ethylene hydrophenylation catalyst  $\text{TpRu}(\text{CO})(\text{NCMe})\text{Ph}$ Evan E. Joslin <sup>a,1</sup>, Bradley A. McKeown <sup>a</sup>, Thomas R. Cundari <sup>b</sup>, T. Brent Gunnoe <sup>a,\*</sup><sup>a</sup> Department of Chemistry, University of Virginia, Charlottesville, VA 22904, USA<sup>b</sup> Center for Advanced Scientific Computing and Modeling (CASCaM), University of North Texas, Denton, TX 76203, USA

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## ABSTRACT

$\text{TpRu}(\text{CO})(\text{NCMe})\text{Ph}$  is a catalyst for the conversion of benzene and ethylene to ethylbenzene. Previously, the formation of ethylbenzene has been shown to occur through a pathway that involves ethylene coordination to Ru, insertion of ethylene into the Ru–phenyl bond and Ru–mediated benzene C–H activation. The effect of ethylene pressure and catalyst concentration (between 0.2 and 0.01 mol % based on benzene) on the decomposition of  $\text{TpRu}(\text{CO})(\text{NCMe})\text{Ph}$  was examined. Studies have shown that there are two competing catalyst deactivation pathways. At higher concentrations of  $\text{TpRu}(\text{CO})(\text{NCMe})\text{Ph}$ , the dominant deactivation pathway is likely initiated by a binuclear reaction of two Ru complexes that leads to formation of unidentified paramagnetic species. Kinetic studies reveal that this pathway for catalyst decomposition occurs with a second-order rate of  $0.007 (1) \text{ M}^{-1} \text{ s}^{-1}$ . At lower Ru concentrations, ethylene C–H activation to form the allyl complex  $\text{TpRu}(\text{CO})(\eta^3\text{-C}_4\text{H}_7)$  is the predominant deactivation pathway. The effect of ethylene pressure on catalyst decomposition was also examined. At higher ethylene pressure nearly quantitative formation of  $\text{TpRu}(\text{CO})(\eta^3\text{-C}_4\text{H}_7)$  was observed.

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## 1. Introduction

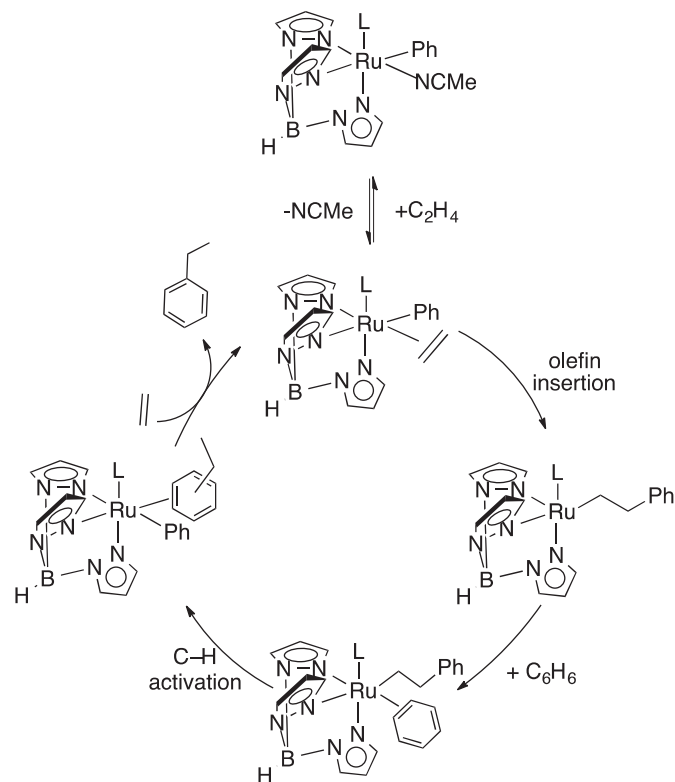
Alkyl arenes traditionally have been synthesized using acid-based catalysts such as Friedel–Crafts catalysts (*i.e.*, a Lewis acid with a Brønsted acid) or using zeolites [1–6]. The use of transition metal catalysts that mediate the same overall process but through a different pathway that involves metal-mediated olefin insertion into metal–aryl bonds and C–H activation provides possible benefits [7–11]. Examples of olefin hydroarylation using simple hydrocarbons, such as benzene and ethylene, are relatively rare [8,12–22]. Our group and others have made progress developing catalysts based on Ir [12,13,23], Pt [14,18–20,24,25], Rh [17,26], and Ru [7,16,27–33] to convert arenes and olefins to alkyl or alkenyl arenes.

Our group has studied ruthenium based catalysts for olefin hydroarylation using  $\text{TpRu}(\text{L})(\text{NCMe})\text{Ph}$  (Tp = hydridotris(pyrazolyl) borate; L = CO,  $\text{PMe}_3$ ,  $\text{P}(\text{OCH}_2)_3\text{CEt}$ , and 2,6,7-trioxa-1-phosphabicyclo [1,2,2]heptane) complexes [7,27–31]. Through

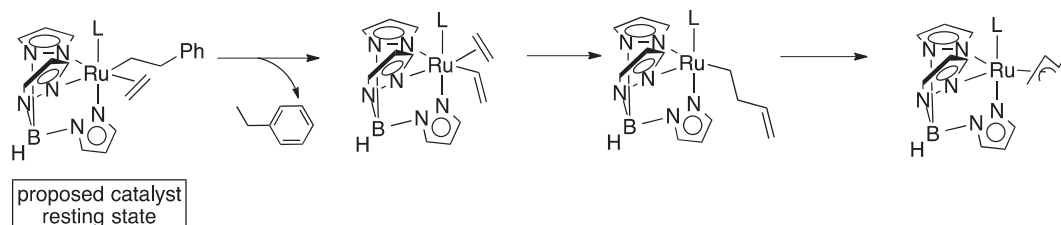
experimental and computational studies, using the hydrophenylation of ethylene to produce ethylbenzene as a model reaction, we have determined that the mechanism for transition metal catalyzed olefin hydroarylation includes two fundamental steps: ethylene insertion into a Ru–Ph bond and benzene C–H activation (Scheme 1) [7]. An important conclusion from our studies of the  $\text{TpRu}(\text{L})(\text{NCMe})\text{Ph}$  series is that the ancillary ligand (L) has a significant influence on catalytic performance. For instance, as the ancillary ligand becomes more strongly donating and the Ru(II) center more electron rich (as determined by cyclic voltammetry), the activation barrier for ethylene insertion into the Ru–Ph bond increases. As a result, the rate of ethylene insertion into the Ru–Ph bond is decreased for complexes with more donating L ligands, and ethylene C–H bond activation becomes competitive with catalytic turnover. The net result is that for  $\text{TpRu}(\text{L})(\text{NCMe})\text{Ph}$  complexes with L =  $\text{PMe}_3$ ,  $\text{P}(\text{OCH}_2)_3\text{CEt}$ , or 2,6,7-trioxa-1-phosphabicyclo [1,2,2]heptane catalyst deactivation occurs rapidly with the formation of  $\text{TpRu}(\text{L})(\eta^3\text{-C}_4\text{H}_7)$  complexes (Scheme 2) [7,27–29]. This was also observed to be the mechanism of catalyst deactivation for the cationic Ru(II) catalyst precursor  $[(\text{HC}(\text{pz}^5)_3)\text{Ru}(\text{P}(\text{OCH}_2)_3\text{CEt})(\text{NCMe})\text{Ph}][\text{BAR}'_4]$  [ $\text{HC}(\text{pz}^5)_3$  = tris(5-methyl-pyrazolyl)methane;  $\text{BAR}'_4$  = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate] [16].

\* Corresponding author.

E-mail address: [tbg7h@virginia.edu](mailto:tbg7h@virginia.edu) (T.B. Gunnoe).<sup>1</sup> Present Address: Department of Chemistry, University of the South: Seawee, Seawee, TN 37383, USA.



**Scheme 1.** Proposed catalytic cycle for olefin hydroarylation with  $\text{TpRu(L)(NCMe)Ph}$  complexes.



**Scheme 2.** Formation of  $\eta^3$ -methyl allyl through ethylene C–H activation by  $\text{TpRu}$  complexes.

Thus, we have demonstrated that incorporation of the strongly  $\pi$ -acidic ligand CO (i.e., catalyst precursor  $\text{TpRu(CO)(NCMe)Ph}$ ) gives rise to the longest-lived and most active catalyst among the  $\text{TpRu(L)(NCMe)Ph}$  series [7,27–32]. Using 0.025 mol % (relative to benzene) of  $\text{TpRu(CO)(NCMe)Ph}$  at 90 °C and with 0.1 MPa of ethylene, 415 turnovers (TOs) of ethylbenzene were achieved before catalyst deactivation [27]. In contrast, under 0.2 MPa of ethylene in benzene at 90 °C, 0.1 mol % of  $\text{TpRu(CO)(NCMe)Ph}$  (relative to benzene) catalyzes the formation of ethylbenzene with only approximately 75 TOs of ethylbenzene [31]. Unlike the phosphine and phosphite catalysts, formation of an  $\eta^3$ -allyl  $\text{Ru(II)}$  decomposition product was not observed. However, in the absence of benzene,  $\text{TpRu(CO)(NCMe)Ph}$  and ethylene (1.7 MPa) in THF (70 °C) were demonstrated to convert to  $\text{TpRu(CO)(}\eta^3\text{-C}_4\text{H}_7\text{)}$  in nearly quantitative yield [29]. Instead, studies suggest that the deactivation product is a paramagnetic (NMR silent) multinuclear Ru species that could not be definitively characterized [30]. Given the performance of  $\text{TpRu(CO)(NCMe)Ph}$  and the apparent departure in pathway for catalyst deactivation, we more closely studied the decomposition of  $\text{TpRu(CO)(NCMe)Ph}$  during catalytic ethylene hydrophenylation. We have found two competing pathways for

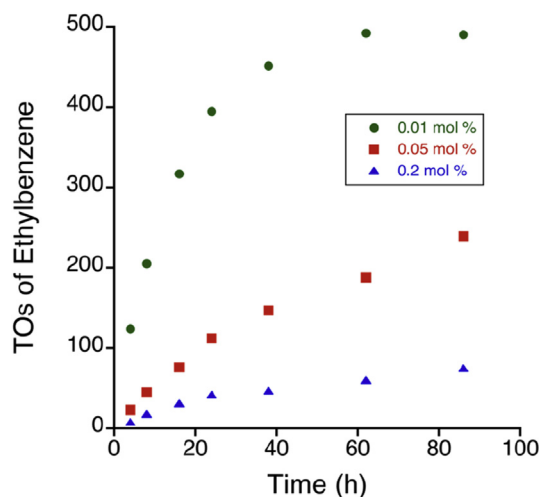
catalyst deactivation that are dependent on the reaction conditions.

## 2. Results and discussion

### 2.1. Study of $\text{TpRu(CO)(NCMe)Ph}$ concentration

To further investigate the disparity between the catalytic results for  $\text{TpRu(CO)(NCMe)Ph}$  using 0.1 and 0.025 mol % catalyst loadings, a systematic screening of catalyst loading (0.2–0.01 mol % relative to benzene) was performed. Data are shown in Fig. 1. Using a catalyst loading of 0.2 mol %  $\text{TpRu(CO)(NCMe)Ph}$ , under 0.1 MPa of ethylene at 90 °C catalytic ethylene hydrophenylation results in only 90 TOs of ethylbenzene. Ethylbenzene production increases by more than 5-fold when the catalyst loading is decreased to 0.01 mol % to give 490 TOs.

For the reactions shown in Fig. 1, we probed for the formation of the allyl complex  $\text{TpRu(CO)(}\eta^3\text{-C}_4\text{H}_7\text{)}$ . After cessation of catalyst activity using 0.2 mol %  $\text{TpRu(CO)(NCMe)Ph}$ , analysis of the non-volatiles of the reaction by  $^1\text{H}$  NMR spectroscopy revealed isolation of  $\text{TpRu(CO)(}\eta^3\text{-C}_4\text{H}_7\text{)}$  in 12% yield based on HMDS (hexamethyldisiloxane) as an internal standard. The yield of  $\text{TpRu(CO)(}\eta^3\text{-C}_4\text{H}_7\text{)}$  increases with decreased starting catalyst loading (Table 1). This suggests that a competition exists between deactivation pathways to form the previously proposed NMR silent paramagnetic multinuclear Ru species and  $\text{TpRu(CO)(}\eta^3\text{-C}_4\text{H}_7\text{)}$  (Scheme 3) [30]. As the starting catalyst concentration is decreased, the deactivation pathway to form  $\text{TpRu(CO)(}\eta^3\text{-C}_4\text{H}_7\text{)}$  becomes increasingly competitive.



**Fig. 1.** Comparison of catalytic hydrophenylation of ethylene by  $\text{TpRu(CO)Ph(NCMe)}$  at 0.1 MPa ethylene and 90 °C at Ru mol % loadings of 0.01, 0.05, and 0.2 mol % (relative to benzene).

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