Transition Metal Catalyzed Hydroarylation of Multiple Bonds: Exploration of Second Generation Ruthenium Catalysts and Extension to Copper Systems

Professor T. Brent Gunnoe
North Carolina State University
Department of Chemistry, Campus Box 8204
Raleigh, NC 27695-8204

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P.I.: T. Brent Gunnoe, North Carolina State University, Department of Chemistry, Campus Box 8204, Raleigh, NC 27695-8204; Email: brent_gunnoe@ncsu.edu; phone: (919) 513-3704

Graduate Students (2007-2008 only): Bradley McKeown, Nicholas Foley, John Lee (will defend Ph. D. thesis in June, hired by Eastman Chemical Company)

Undergraduate Students (2007-2008 only): George Davis

Abstract Text: Catalysts provide foundational technology for the development of new materials and can enhance the efficiency of routes to known materials. New catalyst technologies offer the possibility of reducing energy and raw material consumption as well as enabling chemical processes with a lower environmental impact. The rising demand and expense of fossil resources has strained national and global economies and has increased the importance of accessing more efficient catalytic processes for the conversion of hydrocarbons to useful products. The goals of the research are to develop and understand single-site homogeneous catalysts for the conversion of readily available hydrocarbons into useful materials. A detailed understanding of these catalytic reactions could lead to the development of catalysts with improved activity, longevity and selectivity. Such transformations could reduce the environmental impact of hydrocarbon functionalization, conserve energy and valuable fossil resources and provide new technologies for the production of liquid fuels.

This project is a collaborative effort that incorporates both experimental and computational studies to understand the details of transition metal catalyzed C-H activation and C-C bond forming reactions with olefins. Accomplishments of the current funding period include: (1) We have completed and published studies of C-H activation and catalytic olefin hydroarylation by TpRu{P(pyr)3}(NMe)R (pyr = N-pyrryl) complexes.1 While these systems efficiently initiate stoichiometric benzene C-H activation, catalytic olefin hydroarylation is hindered by inhibition of olefin coordination, which is a result of the steric bulk of the P(pyr)3 ligand. (2) We have extended our studies of catalytic olefin hydroarylation by TpRu(L)(NMe)Ph systems to L = P(OCH2)2CEt. Thus, we have now completed detailed mechanistic studies of four systems with L = CO, PMe3, P(pyr)3 and P(OCH2)2CEt, which has provided a comprehensive understanding of the impact of steric and electronic parameters of "L" on the catalytic hydroarylation of olefins. (3) We have completed and published a detailed mechanistic study of stoichiometric aromatic C-H activation by TpRu(L)(NMe)Ph (L = CO or PMe2).2 These efforts have probed the impact of functionality para to the site of C-H activation for benzene substrates and have allowed us to develop a detailed model of the transition state for the C-H activation process. These results have led us to conclude that the C-H bond cleavage occurs by a σ-bond metathesis process in which the C-H transfer is best viewed as an intramolecular proton transfer. (4) We have completed studies of Ru complexes possessing the N-heterocyclic carbene IMes (IMes = 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene).3 One of these systems is a unique four-coordinate Ru(II) complex that catalyzes the oxidative hydrophenylation of ethylene (in low yields) to produce styrene and ethane (utilizing ethylene as the hydrogen acceptor) as well as the hydrogenation of olefins, aldehydes and ketones. These results provide a map for the preparation of catalysts that are selective for oxidative olefin hydroarylation. (5) The ability of TpRu(PMe3)(NMe)R systems to activate sp3 C-H bonds has been demonstrated including extension to subsequent C-C bond forming steps.4 These results open the door to the development of catalysts for the functionalization of more inert C-H bonds. (6) We have discovered that Pt(II) complexes supported by simple nitrogen-based ligands serve as catalysts for the hydroarylation of olefins.5 Given the extensive studies of Pt-based catalytic C-H activation, we believe these results will provide an entry point into an array of possible catalysts for hydrocarbon functionalization. We are especially intrigued by the possibility of extending catalysis to alkane substrates. Within the past funding cycle, four manuscripts have been published that acknowledge DOE funding with one manuscript submitted and one manuscript in the final stages of preparation for submission. In the past year, the grant has supported the research of three graduate students (one of these students has accepted a position at
Eastman Chemical Company), two former students previously supported by this grant are employed by BASF Corporation and the Environmental Protection Agency, a former postdoctoral researcher is currently employed as an Assistant Professor at Rollins College, and two former undergraduate students supported by this grant are enrolled in medical school at UNC Chapel Hill and the Ph. D. program in Textiles Chemistry at NCSU. These projects have been performed in collaboration with Professor Tom Cundari at the University of North Texas.
Progress Report

I. Results

Introduction: Previous studies revealed that TpRu(CO)(NCMe)R {R = CH₃, CH₂CH₂Ph, Ph, 2-thienyl or 2-furyl; Tp = hydridotris(pyrazolyl)borate} complexes serve as catalyst precursors for the addition of aromatic C-H bonds across C=C bonds. The products of these reactions are alkylationaromatic compounds, and the reactions that incorporate α-olefins are moderately selective for linear over branched products. Detailed mechanistic studies reveal that the transformations do not proceed via traditional Friedel-Crafts mechanisms. Rather, the Ru(II) metal center serves to directly mediate both C-H activation and C-C bond forming steps (Scheme 1). In our preliminary studies we established the mechanism of the catalytic hydroarylation transformations, determined the scope of reactivity accessible with TpRu(CO)(NCMe)R including range of olefins and aromatic substrates, studied insertion reactions of unsaturated substrates that possess heteroatomic functionality with TpRu(L)(NCMe)Ph (L = CO), and studied the impact of single-electron oxidation on the reactivity of TpRu(L)(NCMe)R systems. In the past two years of funding, we have extended our studies to catalyst synthesis of TpRu(L)(NCMe)R {L = PMe₃, P(N-pyrrolyl)₃, P(OCH₂)₂Et, P(OMe)₃ or PF₃} systems, demonstrated that TpRu(L)R systems can activate sp³ C-H bonds followed by C-C and C-N bond formation, studied the details of aromatic C-H activation by TpRu(L)(NCMe)Me using Hammett correlations, worked toward the synthesis of EpRu(L)(Cl)R (Ep = tris(pyrazolyl)ethane, L = neutral, 2-electron donor ligands) complexes, prepared and studied the reactivity of new Ru(II) complexes with N-heterocyclic carbene ligands, pursued catalysis with substrates that possess C-heteroatom multiple bonds using TpRu(PMe₃)(NCMe)R, extended our efforts on catalyst development to Cu(I) and Cu(II) alkyl and phenyl systems, prepared a precursor to be anchored to a mesoporous solid support (in collaboration with Professor Victor Lin, Iowa State University), and extended studies to new d⁸ systems including Pt(II) and Rh(I).

Hammett Correlation for Aromatic C-H Activation by TpRu(L)(NCMe)Me: In order to probe the nature of the C-H activation step by TpRu(L)(NCMe)R systems (L = CO or PMe₃), we studied the reaction rates (theoretically) for the conversion of TpRu(L)(η²-C₆H₅X)Me to TpRu(L)(p-C₆H₄X) and CH₄ where X was varied among Br, Cl, CN, F, H, NH₃, NO₂, and OMe. For both systems linear Hammett correlations were calculated with positive ρ values of 2.6 for L = CO and 3.2 for L = PMe₃ (e.g., see Figure 1). Given the relatively small ρ values, the calculated kinetic data indicate that an electrophilic aromatic substitution mechanism is unlikely; however, these data are consistent with a model of the transition state in which coordination of the C-H bond imparts acidic character and, hence, increases the negative charge in the aromatic ring. While experimental studies could not replicate the entire range of calculated Hammett plots, observed
reactivity trends are consistent with the calculations that suggest activation barriers to overall metal-mediated arene C-H bond cleavage are reduced by the presence of electron-withdrawing groups in the position para to the site of activation. For example, TpRu(PMe$_3$)(NCMe)R only reacts with 2-substituted meta-xylyl compounds when the functionality is strongly electron-withdrawing (eq 1). Chart 1 shows a model of the transition state for Ru(II)-mediated C-H activation based on these experiments. Coordination of the C-H bond imparts acidic character and results in an intramolecular proton transfer in which Ru back-donates electron density to stabilize the activated protic hydrogen. Thus, in the transition state Ru is best considered in the +4 oxidation state. In addition, enhancing Ru-based electron density should increase the strength of the Ru-H bond in the transition state, which would reduce the Δ$\Gamma$ for aromatic C-H activation.

Impact of Ancillary Ligand "L" on TpRu(L)(NCMe)R Catalyzed Addition of C-H Bonds across C=C Bonds: In an effort to explore the impact of steric and electronic properties of the catalyst system on various steps in the olefin hydroarylation cycle, we have extended our studies to TpRu(L)(NCMe)R {L = P(pyr)$_3$, (pyr = N-pyrrolyl), PMe$_3$, P(OCH$_2$)$_3$CEt and P(OMe)$_3$} systems (Scheme 2 and Figure 2). In particular, we are interested in the impact of the electron-donating ability of L on the activation barrier to metal-mediated C-H bond cleavage and olefin insertion as well as the ability of L to control the regioselectivity of olefin insertion based on steric profile (and, hence, control of linear to branched ratios of alkyl aromatic products). For example, we have found that TpRu(PMe$_3$)(NCMe)Me initiates C-H activation (stoichiometric) of benzene to produce methane and TpRu(PMe$_3$)(NCMe)Ph in a reaction that is 2 to 3 times more rapid than corresponding reactions with TpRu(CO)(NCMe)Me.$^2$ Despite the more facile C-H activation of benzene by the PMe$_3$ system (compared to the CO complex), catalytic hydroarylation of ethylene using TpRu(PMe$_3$)(NCMe)Ph is less efficient than catalysis using TpRu(CO)(NCMe)Ph. Detailed studies have revealed the complications. Substitution of PMe$_3$ for CO both decreases the activation barrier for aromatic C-H activation and increases the activation barrier for olefin insertion. Importantly, experimental and computational studies indicate that the activation barrier for olefin insertion is more dramatically influenced (~ 6-7 kcal/mol) by the ancillary ligand L than is the activation barrier for C-H activation (~ 1 kcal/mol). The result is that for the PMe$_3$ system, ethylene C-H activation leads to the formation of a stable η$^3$-allyl complex, which competes with the catalytic olefin hydroarylation cycle. Therefore, in the absence of substantial changes in the ligand framework or metal identity/oxidation state, increasing catalyst efficacy can likely only be achieved when L is not strongly donating or by altering the pyrazolyl ligand to compensate for a strongly donating ligand L. Increasing catalyst longevity might be achieved by moving toward systems that do not possess the CO co-ligand, which can promote catalyst decomposition via the formation of CO-bridged multi-nuclear complexes. Without altering the
TpRu(L)(NCMe)R motif, such catalysts would incorporate ligands with overall donor ability similar to CO \{e.g., PF$_3$ or P(pyr)$_3$\} or combine an overall cationic metal system with more strongly donating ancillary ligands. Thus, in the past year we pursued studies of TpRu{P(pyr)$_3$}(NCMe)R and TpRu{P(OCH$_2$)$_3$CEt}R systems as well as the preparation of TpRu(PF$_3$)(NCMe)R. Cyclic voltammetry has been utilized to determine relative electron densities of TpRu(L)(NCMe)R complexes. Table 1 shows Ru(III/II) (vs. NHE) of a series of systems as a function of ligand L. Note that the P(OCH$_2$)$_3$CEt and P(pyr)$_3$ complexes are intermediate between the previously studied CO and PMe$_3$ systems.

Table 1. Ru(III/II) redox potentials (V vs. NHE) of TpRu(L)(NCMe)Ph systems.

<table>
<thead>
<tr>
<th>L</th>
<th>Ru(III/II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMe$_3$</td>
<td>0.29</td>
</tr>
<tr>
<td>P(OCH$_2$)$_3$CEt</td>
<td>0.54</td>
</tr>
<tr>
<td>P(pyr)$_3$</td>
<td>0.82</td>
</tr>
<tr>
<td>CO</td>
<td>1.03</td>
</tr>
</tbody>
</table>

Scheme 3. Inter- and intramolecular C-H activation by TpRu{P(pyr)$_3$}(NCMe)R.

Despite the observation of benzene C-H activation, attempted catalytic hydrophenylation of ethylene using TpRu{P(pyr)$_3$}(NCMe)Ph results in the production of ethylbenzene with low turnover numbers. Combined experimental and computational studies reveal that the difference in catalytic activity of TpRu{P(pyr)$_3$}(NCMe)Ph (less active catalyst) and TpRu(CO)(NCMe)Ph (more active catalyst) is a result of the different propensity toward coordination of ethylene. For the former, ethylene coordination is inhibited by the steric bulk of the P(pyr)$_3$ ligand as indicated by experimental and computational studies.$^1$ These studies suggest that the combined steric bulk of Tp and P(pyr)$_3$ are too substantial and underpin a key factor for any future catalyst development for TpM(L)R and related systems: L will likely be required to have a cone angle < 145° in order to access active catalysts.

As a result of studies with the P(pyr)$_3$ system, we sought a less donating ligand than PMe$_3$ that possesses a cone angle < 145°. Initially, we prepared TpRu{P(OMe)$_3$}(NCMe)R; however, cyclometallation of the phosphite ligand was problematic. At the suggestion of Professor John Verkade (Iowa State University), we prepared TpRu{P(OCH$_2$)$_3$CEt}(NCMe)Ph since the bicyclic phosphite ligand is constrained against cyclometallation. Comparison of the rate of stoichiometric benzene C-H(D) activation for TpRu(L)(NCMe)Ph systems \{L = CO, PMe$_3$ and P(OCH$_2$)$_3$CEt\} reveals that increased donating ability of L results in an increase in the rate of overall benzene C-H activation.$^{13}$ Despite the fact that there are a number of factors that contribute to the $k_{obs}$ values for overall benzene C-H activation as well as the Ru(III/II) potentials, a plot of $k_{obs}$ versus Ru(III/II) potential gives a linear correlation with an $R^2$ of 0.97 (Figure 3). Although the data set is limited, this trend is consistent with the proposal that increased metal...
electron density facilitates the overall rate of benzene C-H activation (see above), and the linear relationship suggests that $d^6/d^5$ redox potentials might be used as a predictor for the overall rate of aromatic C-H activation by TpRu(L)(NMe3)R catalysts and, potentially, for closely related $d^6$ complexes of Ru(II) and other transition metal systems.

Studies of catalytic hydrophenylation of ethylene by TpRu{P(OCH2)2CEt}(NCMe)Ph are consistent with our conclusions from comparison of catalysis by TpRu(PMe3)(NCMe)Ph and TpRu(CO)(NCMe)Ph. Previously, we demonstrated that the increased electron density of TpRu(PMe3)(NCMe)Ph {cf. TpRu(CO)(NCMe)Ph} results in a substantial inhibition to olefin insertion (for the PMe3 system) and a corresponding increase in the rate of ethylene C-H activation (vs. rate of ethylene hydrophenylation). Given that the Ru(III/II) potential of TpRu{P(OCH2)2CEt}(NCMe)Ph (0.54 V) is intermediate that of the PMe3 system (0.29 V) and the CO system (1.03 V), we anticipated that ethylene hydrophenylation would be observed with the phosphite system but that eventually ethylene C-H activation and ultimate formation of TpRu{P(OCH2)2CEt}(η6-C6H6Me) would disrupt catalysis.

Heating TpRu{P(OCH2)2CEt}(NCMe)Ph in benzene under ethylene pressure results in the catalytic production of ethylbenzene. Testing the reactivity from 10 psi to 1000 psi of ethylene and temperatures from 60 °C to 105 °C revealed the optimal conditions for catalysis. Representative TONs after 28 hours are shown in Figure 4. A maximum activity of approximately 10 TONs was achieved at 90 °C and 10 psi of ethylene. Catalytic trials carried out at 60 °C (not shown in Figure 4) gave less than 2 TONs after 28 hours. Increasing the temperature to 105 °C results in an initial increase in the rate of ethylbenzene production, but overall nearly the same TONs after 28 hours as reactions at lower temperatures. Figure 5 shows the general rates of catalysis for TpRu{P(OCH2)2CEt}(NCMe)Ph in benzene at 25 psi of ethylene at 75 °C, 90 °C and 105 °C. All reactions at these conditions yield a total of approximately 8 TONs of ethylbenzene. For reactions at temperatures greater than 90 °C, catalysis is halted after approximately 28 hours of reaction. Increasing the pressure of ethylene decreases the rate of ethylbenzene formation (Figure 4), suggesting that the rate of catalysis is inversely dependent upon olefin concentration. The same trend has been observed for catalytic olefin hydroarylation by TpRu(CO)(NCMe)Ph.

**N-Heterocyclic Carbene Ruthenium Systems:** The TpRu systems provide catalysts for "non-oxidative" olefin hydroarylation. We have begun to work toward systems that can afford oxidative hydroarylation of olefins in which the oxidant that sequesters the two hydrogen atoms is the olefin. Such processes could be useful for the preparation of unsaturated vinylarenes. For example, styrene is currently produced on a large scale by initial reaction of benzene and ethylene under harsh conditions to prepare ethylbenzene, which is dehydrogenated in low yield (again, under harsh conditions). The direct conversion of benzene and two equivalents of ethylene to styrene and ethane (which can be recycled to produce ethylene) would provide a more direct route; however, such reactions require a different class of catalysts (from those that we have been studying) that, in addition to olefin hydroarylation, are capable of catalytic olefin hydrogenation. We have been targeting N-heterocyclic carbene (NHC) complexes of low-
coordinate Ru(II) systems, believing that such complexes should undergo facile \(\beta\)-hydride elimination and, due to coordinative unsaturation, exhibit a greater propensity toward subsequent olefin substitution. Enhancement of \(\beta\)-hydride elimination and olefin substitution should facilitate oxidative olefin hydroarylation.

The reaction of previously reported \([\text{Ru(CO)}_2\text{Cl}]_2\) with the NHC ligand IMes (IMes = 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene) in toluene followed by methanol allows isolation of the five-coordinate Ru(II) complex \(\text{trans-(IMes)}_2\text{Ru(CO)}\)\(\text{(H)}\)\(\text{Cl}\). Reaction of \(\text{trans-(IMes)}_2\text{Ru(CO)}\)\(\text{(H)}\)\(\text{Cl}\) with \(\text{NaBAR}^{'\text{r}}\) yields the four-coordinate complex \([\text{IMes}^2\text{Ru(H)}\text{(CO)}][\text{BAR}^{'\text{r}}]\) (eq 2). Attempts to grow crystals of \([\text{IMes}^2\text{Ru(H)}\text{(CO)}][\text{BAR}^{'\text{r}}]\) resulted in the formation of \([\text{IMes}^2\text{Ru(H)}\text{(CO)}\text{(N}_2\text{)}][\text{BAR}^{'\text{r}}]\). This dinitrogen complex can be observed by spectroscopy at low temperatures or under high pressures of nitrogen. Evidence that \([\text{IMes}^2\text{Ru(H)}\text{(CO)}][\text{BAR}^{'\text{r}}]\) is a four-coordinate Ru(II) complex is derived from: a) CO stretching frequency increases from 1886 cm\(^{-1}\) to 1933 cm\(^{-1}\) upon chloride removal from \([\text{IMes}^2\text{Ru(H)}\text{(CO)}\text{(Cl)}]\); b) NMR spectroscopy of \([\text{IMes}^2\text{Ru(H)}\text{(CO)}][\text{BAR}^{'\text{r}}]\) is consistent with the proposed structure; c) reaction of \([\text{IMes}^2\text{Ru(H)}\text{(CO)}][\text{BAR}^{'\text{r}}]\) with \([\text{Bu}_4\text{N}]\text{Cl}\) quantitatively produces \([\text{IMes}^2\text{Ru(CO)}\text{(H)}\text{(Cl)}]\); d) reaction with \(\text{D}_2\) produces \([\text{IMes}^2\text{Ru(D)}\text{(CO)}][\text{BAR}^{'\text{r}}]\) within minutes at room temperature; and e) reaction of \([\text{IMes}^2\text{Ru(H)}\text{(CO)}][\text{BAR}^{'\text{r}}]\) with excess \(\text{t-BuNC}\) produces \([\text{IMes}^2\text{Ru(H)}\text{(CO)}\text{(t-BuNC)}][\text{BAR}^{'\text{r}}]\) (Figure 6). \([\text{IMes}^2\text{Ru(H)}\text{(CO)}][\text{BAR}^{'\text{r}}]\) is a unique four-coordinate and 14-electron system. The following key features have been elucidated from combined experimental and computational studies: a) No evidence of stabilizing C-H agostic interactions has been observed, which would make \([\text{IMes}^2\text{Ru(H)}\text{(CO)}][\text{BAR}^{'\text{r}}]\) a unique "true" 14-electron Ru(II) system. b) The two known 14-electron Ru(II) systems (no C-H agostic interactions) are paramagnetic due to square planar geometries.\(^{14, 15}\) \([\text{IMes}^2\text{Ru(H)}\text{(CO)}][\text{BAR}^{'\text{r}}]\) is diamagnetic, and we attribute this electronic feature to a see-saw type structure (based on DFT calculations), which may suggest that it is inherently stable for four-coordinate Ru(II) systems to adopt such geometries in the absence of ligand constraints that "force" square planar coordination environments. c) \([\text{IMes}^2\text{Ru(H)}\text{(CO)}][\text{BAR}^{'\text{r}}]\) efficiently catalyzes the hydrogenation of a range of substrates (Tables 2 and 3). d) The reaction of \([\text{IMes}^2\text{Ru(H)}\text{(CO)}][\text{BAR}^{'\text{r}}]\) with \(\text{D}_2\) results in H/D exchange with hydride ligand and the methyl groups of the IMes aryl groups. Hence, this complex can initiate C-H activation. e) \([\text{IMes}^2\text{Ru(H)}\text{(CO)}][\text{BAR}^{'\text{r}}]\) catalyzes the oxidative hydrophenylation of ethylene to give styrene. Although the turnover numbers are low (only a few catalytic turnovers are

Table 2. Ru-catalyzed hydrogenation of olefins. Unless noted otherwise, reactions performed in \(\text{C}_2\text{D}_4\), at \(60 ^\circ\text{C}\), \(30 \text{ psi H}_2\) and \(5 \text{ mol}\%\) of catalyst relative to olefin concentration.
observed under optimal conditions), these reactions are unique examples of the olefin serving as the oxidant to sequester hydrogenation.

**Study of Copper Complexes:** We have initiated preliminary studies focused on the utilization of well-defined copper alkyl and aryl complexes for aromatic C-H activation and, ultimately, catalytic conversion of aromatic C-H bonds to C-C bonds using inexpensive Cu reagents. Our interest is to utilize electrophilic Cu systems to mediate olefin insertion processes as well as C-H activation events that resemble electrophilic aromatic substitution. Initial efforts have been focused on fundamental reactivity of (NHC)Cu(Me) systems. At the Cu(I) oxidation state, (NHC)Cu(R) systems decompose in benzene at elevated temperatures to form a range of hydrocarbons including methane, ethane and ethylene. We found no evidence for aromatic C-H activation, which is consistent with calculations that predict the $\Delta G^\ddagger$ for benzene C-H activation by (NHC)Cu(Me) is a substantial 47 kcal/mol. In contrast, DFT calculations suggest that analogous benzene C-H activation by the cationic Cu(II) system $[(\text{NHC})\text{Cu(Me)}]^+$ is only 13 kcal/mol! Thus, we studied the fundamental reactivity of $[(\text{NHC})\text{Cu(Me)}]^+$ systems. At the Cu(II) oxidation state, these systems rapidly undergo reductive elimination of R-R via bimolecular and non-radical pathways. We have found that the addition of pyridine retards the rate of reductive R-R coupling, suggesting that three-coordinate Cu(II) systems might provide access more stable systems. In the past year, we have worked toward the preparation of three-coordinate Cu(II) systems that will serve as precursors to Cu(II) aryl complexes. The preparation of such complexes has been challenging; however, recently we have had preliminary success with a chelating heterocyclic carbene as outlined in Scheme 4.

**Studies of Pt(II) Systems:** Pt(II) complexes have been among the most widely studied systems for the activation of C-H bonds. Given the robust nature of many Pt systems utilized for C-H activation, we felt such complexes might prove amenable for catalytic olefin hydroarylation. In addition, the four-coordinate $d^8$ structure provides a contrast to the octahedral $d^6$ systems previously studied in our group and by Periana et al. 1,2,6-8,20,21

![Scheme 4](image)

**Table 3.** Ru-catalyzed hydrogenation of carbonyl groups. All reactions performed in C$_6$D$_6$ at 60 °C, 30 psi H$_2$ and 5 mol % of catalyst relative to carbonyl concentration.

<table>
<thead>
<tr>
<th>entry</th>
<th>substrate</th>
<th>catalyst (5 mol %)</th>
<th>Time (hrs)</th>
<th>% conversion</th>
<th>TOF$^*$</th>
<th>product</th>
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</thead>
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<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>48</td>
<td>5</td>
<td>0.058</td>
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</tr>
<tr>
<td>2</td>
<td>3</td>
<td>3</td>
<td>17</td>
<td>100</td>
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<td>3</td>
<td>5</td>
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<td>100</td>
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<td>4</td>
<td>2</td>
<td>4</td>
<td>84</td>
<td>100$^*$</td>
<td>0.7</td>
<td></td>
</tr>
</tbody>
</table>

$^*$ % conversions were determined by $^1$H NMR spectroscopy. TOF=10$^{-3}$. $^\dagger$ % conversion to 3-ethyl-benzylalcohol. $^\ddagger$ TOF for two equivalents of H$_2$.

We chose as an entry point to Pt catalyzed olefin hydroarylation the ($^{11}$bpy)Pt(Ph)$_2$ ($^{11}$bpy = 4,4'-di-tert-butyl-2,2'-bipyridine) system due to the potential for enhanced solubility from the tert-butyl substituents. Heating a 0.1 mol % benzene solution of complex 1 with HBAr'$_4$ ($Ar' = 3,5-(CF$_3$)$_2$C$_6$H$_3$; one equivalent relative to complex ($^{11}$bpy)Pt(Ph)$_2$) to 120 °C under 25 psi of ethylene results in ~ 12 TOs (turnovers) of ethylbenzene after 16 hours (eq 3). Control experiments using HBAr'$_4$ in the absence of ($^{11}$bpy)Pt(Ph)$_2$ and ($^{11}$bpy)Pt(Ph)$_2$ in the absence of HBAr'$_4$ revealed minimal TOs of ethylbenzene.

The absence of catalysis in control reactions using only ($^{11}$bpy)Pt(Ph)$_2$ suggests that the catalysis observed starting with ($^{11}$bpy)Pt(Ph)$_2$ and HBAr'$_4$ results from protonation of a phenyl ligand to generate the coordinatively unsaturated cation [(bpy)Pt(Ph)]$^+$ (with Bar'$_4$ counterion). However, the poor solubility of HBAr'$_4$ in benzene likely precludes quantitative entry of Pt into the catalytic cycle. Thus, we sought to isolate cationic Pt(II) precursors that would provide better defined catalysis. Reacting
with NaBAR'₄ in THF yields [(tBu-bpy)Pt(Ph)(THF)][BAR'₄]•2THF (eq 4). Fully soluble in benzene, [(tBu-bpy)Pt(Ph)(THF)][BAR'₄] was used over a range of temperatures (90 °C – 140 °C) under ethylene pressure to test for ethylbenzene production (Table 4) with maximal ethylbenzene production of 66 TOs after 16 hours at 100 °C and 15 psi of ethylene. Increasing the temperature of the reactions accelerated ethylbenzene production but also lead to rapid catalyst decomposition. Increasing the concentration of ethylene suppresses the production of alkylated products, an effect that we are studying. In addition to ethylbenzene, approximately 25-30% of ethylbenzene produced was converted to diethylbenzene, a result that we attribute to relatively high activation barriers to dissociation of ethylbenzene (see below).

Table 5 shows a slightly expanded substrate scope for olefin hydroarylation by [(tBu-bpy)Pt(Ph)(THF)][BAR'₄]. The hydroarylation of ethylene using ethylbenzene gives 1,2-, 1,3- and 1,4-diethylbenzene with relative selectivity of 1:126:113 ortho:para:meta (statistically corrected). Extension of ethylene hydroarylation to furan results in the regioselective production of 2-ethylfuran with 76 TOs after 16 hours. To investigate reactivity for α-olefins propylene was tested for hydrophenylation. After 4 hours at 100 °C, a total of 33.5 turnovers of propylene was detected with a cumene to n-propylbenzene ratio of 25.0:8.5. The production of linear propylbenzene provides strong evidence that these reactions are not proceeding by Friedel-Crafts mechanisms.

**EpRu(L)(Cl)R:** For systems of the type TpRu(L)(NCMe)R, the use of strongly donating ligands for "L" disrupts catalytic olefin hydroarylation due to increased activation barriers for olefin insertion. In order to incorporate donating phosphine and phosphite ligands into Ru(II) catalysts, we plan to formally replace Tp with Ep {Ep = tris(pyrazolyl)ethane}.

Table 4. Hydrophenylation of ethylene catalyzed by [(tBu-bpy)Pt(Ph)(THF)][BAR'₄] under various conditions.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Ethylene</th>
<th>Diethyl benzenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp (°C)</td>
<td>C₂H₅ (psi)</td>
<td>1,2-</td>
</tr>
<tr>
<td>90</td>
<td>15</td>
<td>7.2 (20.3)</td>
</tr>
<tr>
<td>100</td>
<td>15</td>
<td>27.9 (65.9)</td>
</tr>
<tr>
<td>100</td>
<td>30</td>
<td>7.9 (20.8)</td>
</tr>
<tr>
<td>100</td>
<td>45</td>
<td>5.0 (13.1)</td>
</tr>
<tr>
<td>100</td>
<td>60</td>
<td>0.6 (0.9)</td>
</tr>
<tr>
<td>120</td>
<td>15</td>
<td>38.6 (40.5)</td>
</tr>
<tr>
<td>140</td>
<td>15</td>
<td>35.8 (29.6)</td>
</tr>
</tbody>
</table>

0.1 % catalyst in benzene with 0.1 % hexamethylbenzene as internal standard. Setup in an N₂ atmosphere, purged and pressurized with ethylene to desired amount and then brought to a total pressure of 120 psi with N₂. **Turnovers relative to catalyst loading after 4 hours (turnovers after 16 hours).**

Table 5. Hydroarylation of olefins catalyzed by [(tBu-bpy)Pt(Ph)(THF)][BAR'₄].

<table>
<thead>
<tr>
<th>Olefin</th>
<th>Aromatic</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylene</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 (0.2)</td>
<td>11.3 (34.6)</td>
<td>6.3 (17.7)</td>
</tr>
<tr>
<td>propylene</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 (10.1)</td>
<td>29.3 (76.2)</td>
<td>7.1 (17.7)</td>
</tr>
</tbody>
</table>

All reactions run with 0.1 % hexamethylbenzene as internal standard, charged with atmospheric olefin pressure and then pressurized to a total pressure of 120 psi with N₂. **0.1 % catalyst.** **0.05% catalyst.** **Turnovers relative to catalyst loading after 4 hours (turnovers after 16 hours).**
Activation of sp³ C-H Bonds: Until recently, our studies of catalytic C-H activation by TpRu(L)(NCMe)R systems have been focused on aromatic C-H bonds. Extension of C-H functionalization to sp³ C-H bonds would extend the potential utility of these transformations. Thus, we probed the ability of TpRu(PMe₃)(NCMe)Me to activate a variety of substrates with sp³ hybridized C-H bonds. Heating TpRu(PMe₃)(NCMe)Me at 60 °C in CH₃CN results in C-H activation of acetonitrile to release methane and produce TpRu(PMe₃)(NCMe)(CH₂CN) (eq 5 and Figure 5). Reactions with CD₃CN in sealed NMR tubes reveal the formation of CH₃D (1:1:1 triplet at ~0.15 ppm). The rate of acetonitrile activation at 70 °C (in NCCD₃) under pseudo-first order conditions is \( k_{\text{obs}} = 1.82(3) \times 10^{-5} \text{s}^{-1} \). Based on studies of benzene C-H activation (see above), the rate determining step for the conversion of TpRu(PMe₃)(NCMe)Me to TpRu(PMe₃)(NCMe)CH₂CN is expected to be the C-H activation event. Consistent with this hypothesis, a primary kinetic isotope effect of \( k_H/k_D = 2.0(2) \) was obtained for this reaction. The approximately two-fold faster rate of C-H vs. C-D activation is similar to the previously reported KIE for benzene C-H/D activation by \( 1 \) {\( k_H/k_D = 2.7(1) \)}.

Even though the nitrile ligand of TpRu(PMe₃)(NCMe)(CH₂CN) is labile, attempts to observe benzene C-H(D) activation upon placing TpRu(PMe₃)(NCMe)(CH₂CN) in C₆D₆ at 60 °C resulted in decomposition to multiple undetermined complexes after 20 hours and no observation of the previously reported TpRu(PMe₃)(NCMe)Ph-\( d_5 \) complex or H/D exchange between benzene and the cyanomethyl ligand, which is consistent with Jones et al.’s report that the presence of a cyano group may provide ground state stabilization relative to alkyl ligands. Furthermore, attempts at degenerate C-H(D) activation of NCCD₃ by TpRu(PMe₃)(NCMe)(CH₂CN) to yield TpRu(PMe₃)(NCCD₃)(CD₂CN) resulted in no observable reaction by \( ^1 \text{H} \) NMR after 15 hours at 100 °C. These results suggest that replacing the methyl ligand of TpRu(PMe₃)(NCMe)Me with the less basic cyanomethyl ligand increases the \( \Delta G^\ddagger \) for C-H activation.

Heating TpRu(PMe₃)(NCMe)Me in nitromethane for 3 hours results in the formation of TpRu(PMe₃){κ²-O,N,N(O)(C(H)(NO₂))} in 64% isolated yield and the stoichiometric formation of propionamide (Scheme 6). The formation of TpRu(PMe₃){κ²-O,N,N(O)(C(H)(NO₂))} likely proceeds via initial dissociative loss of the NCMe ligand, coordination and metal-mediated C-H activation of nitromethane to release methane.
and form unsaturated \{\text{TpRu}(\text{PMe}_3)(\text{CH}_2\text{NO}_2)\}, followed by reaction with additional \text{MeNO}_2 to produce \text{TpRu}(\text{PMe}_3)(\kappa^2-O,N:O(C(H)(\text{NO}_2)}) and propionamide (Scheme 6).

Heating \text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Me} at 80 °C for 24 hours in acetone in the presence of 5 equivalents of NCM results in the formation of \text{TpRu}(\text{PMe}_3)(\kappa^2-O,N:O(C(H)(\text{CMe}))\text{Me})\text{NH}_2. Based on in situ NMR studies, we have proposed that the most likely pathway for this reaction involves initial C-H activation of coordinated acetone to release methane and produce the unsaturated complex \{\text{TpRu}(\text{PMe}_3)(\text{CH}_2\text{C(O)CH}_3)\}, which likely coordinates NCM to form \text{TpRu}(\text{PMe}_3)(\text{NCMe})(\text{CH}_2\text{C(O)CH}_3) (Scheme 7). The addition of one equivalent of pyridinium chloride to a solution of \text{TpRu}(\text{PMe}_3)(\text{NCMe})(\text{CH}_2\text{C(O)CH}_3) in NCCD$_3$ immediately produces a new complex by $^1$H NMR spectroscopy, which is presumed to be \text{TpRu}(\text{PMe}_3)(\text{Cl})(\kappa^1-N:O(C(Me)C(H)C(Me))\text{NH}_2).

Heating the reaction at 60 °C results in the formation of free acetylacetanilide (verified by $^1$H NMR spectroscopy and GC/MS) in 86% yield, free pyridine, \text{TpRu}(\text{PMe}_3)(\text{NCCD}_3)\text{Cl}, and a second complex, which is assigned as \text{TpRu}(\text{PMe}_3)(\text{pyridine})\text{Cl} (Scheme 7). The overall transformation from \text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Me} and acetone is a metal-mediated aldol-type reaction between acetone and acetonitrile.

\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Me} initiates C-H activation of aromatic C-H bonds, olefin C-H bonds as well as sp$^3$ C-H bonds of acetonitrile, acetone and nitromethane. There are likely two key events in the overall C-H activation reactions: (1) coordination of the substrate being activated via ligand exchange with NCM and (2) the C-H bond scission step. More specifically, the failure of 1 to cleanly activate cyclohexane and THF could be due to the inability to sufficiently coordinate these compounds (in competition with NCM) and/or inherently high activation barriers for the C-H activation step for substrates that do not possess electron-withdrawing groups (e.g., nitro, cyano or acyl). To assess the source of the substrate selectivity, we performed a density functional theory study for several representative substrates (Scheme 8).

Scheme 8 depicts the results of calculations beginning with \text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Me}. In addressing the source of substrate selectivity for C-H activation (i.e., coordination vs. activation energy for the discrete C-H activation step), we have focused on two sets of data: 1) the calculated $\Delta H$ values for substrate coordination via displacement of NCM and 2) the calculated $\Delta H^\ddagger$ values from the C-H adducts to the transition state for C-H activation. The computational results suggest that ground and transition state factors contribute to substrate selectivity by \text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Me}. The values for the discrete C-H activation step indicate that the more acidic C-H bonds of MeNO$_2$, MeCN and acetone possess a lower $\Delta H^\ddagger$ than cyclohexane and THF. Also, calculated $\Delta H$ for competitive coordination of cyclohexane and
THF (vs. NCMe) reveal a bias, which is more pronounced for cyclohexane than for THF, against coordination of these substrates relative to MeNO\textsubscript{2}, acetone and MeCN.

The decreased $\Delta H^\ddagger$ for C-H bond scission for relatively acidic C-H bonds fits into an emerging picture of C-H activation by TpRu(L)R fragments as an intramolecular proton transfer (IPT) (see above). Consistent with these models, previous computational studies suggest that the basicity of the ligand receiving the activation hydrogen greatly impacts the extent to which Ru interacts with the activated proton in the transition state. For example, we have recently disclosed that when the ligand receiving the activated hydrogen atom possesses a lone pair (e.g., hydroxo or amido ligands), the calculated Ru-H distance in the transition state is increased relative to when X = Me. In this model, it is anticipated that increasing the acidity of C-H or increasing the basicity of the receiving ligand X should facilitate the Ru-mediated C-H activation, and vice versa. For TpRu(PMe\textsubscript{3})(NCMe)X, when X = Me the C-H(D) activation of acetonitrile proceeds smoothly at 60 °C (eq 5); however, for X = CH\textsubscript{2}CN, which is less basic than Me, no evidence of degenerate C-H(D) activation of NCCD\textsubscript{3} could be found up to 100 °C.

II. Objectives for the Next Year

A. Continuation of Work toward TpRu(PF\textsubscript{3})(NCMe)R and [EpRu(L)R]\textsuperscript{+} Systems: As delineated above, our combined experimental and computational studies of TpRu(L)(NCMe)R systems have revealed a substantial level of information about the impact of steric and electron properties of "L" on catalytic olefin hydroarylation. These studies suggest that poorly donating ligands with modest steric bulk will be optimal for catalysis. For octahedral d\textsuperscript{6} complexes with tris(pyrazolyl) ligands (Xp), our studies suggest that complexes of the type (Xp)M(L')(L')R (L' = labile ligand or halide) should contain L with cone angle $< 145^\circ$ and d\textsuperscript{6}/d\textsuperscript{5} redox potentials of $\sim 1$ V (vs. NHE). Thus, the complexes TpRu(PF\textsubscript{3})(NCMe)R, [EpRu(PMe\textsubscript{3})R]\textsuperscript{+} and [EpRu{P(OCH\textsubscript{2})\textsubscript{3}CET\textsubscript{3}]}\textsuperscript{+} are likely to be ideally suited for regioselective olefin hydroarylation. In the past year we pursed the synthesis of the Ep systems; however, poor solubility of synthetic precursors thwarted our efforts. In the next year, we will attempt to use [EpRu(COD)Cl][BAR\textsubscript{4}], which has greatly enhanced solubility properties, as an entry point into the desired catalysts (see Scheme 5 for an example). Should we be unable to access Ep system suitable for catalysis, our strategy will switch to triazacyclononane ligands. For TpRu(PF\textsubscript{3})(NCMe)R, we have accessed TpRu(PPh\textsubscript{3})(PF\textsubscript{3})Cl (Figure 8), which ideally is two steps from a testable catalyst precursor (Scheme 9). Although we have not yet found conditions suitable to convert TpRu(PPh\textsubscript{3})(PF\textsubscript{3})Cl to
TpRu(PF₃)(NCMe)R systems, we will continue to test variable reaction conditions and substrates. In addition, we have demonstrated that TpRu[PO(CH₂)₃]₂CEt(NCMe)Ph serves as an ethylene hydrophenylation catalyst; however, the electron-density of this complex renders ethylene C-H activation competitive with catalysis. The asymmetric bicyclic phosphite shown in Chart 2 has enhanced π-acidity {cf. P(OCH₂)₃CEt}, which is likely due to reduced overlap with the phosphine p-orbital in the P-O/C σ* orbital. We will make the TpRu(L)(NCMe)R analogs with this phosphite and test catalysis.

**B. Study of Ru(II) Systems with N-Heterocyclic Carbene Ligands:** The four-coordinate Ru(II) system [(IMes)₂Ru(H)Cl][BAR′₄] catalyzes the oxidative hydroarylation of ethylene (with limited turnover), initiates rapid intramolecular C-H activation and serves as an efficient catalyst for hydrogenation; however, the combined steric bulk of two NHC ligands serves to inhibit intermolecular C-H activation chemistry. Thus, we are working toward complexes that incorporate a single heterocyclic carbene group. Our strategy is to utilize a ligand with a carbene fragment and chelating moiety, and the initial entry will be the preparation of the system shown in Chart 3. Using this complex as a catalyst precursor, we will probe the catalytic hydroarylation of a range of substrates.

**C. Preparation and Study of Cu(I) Systems:** Having delineated the fundamental reactivity of (NHC)Cu(R) complexes at the Cu(I) and Cu(II) oxidation states, we have been pursuing the isolation and reactivity of stabilized Cu(II) systems. These efforts are prompted by DFT calculations suggesting that the ΔG for benzene C-H activation by [(SIPr)Cu(Me)]⁻ is reduced by a ~34 kcal/mol upon oxidation from Cu(I) (n = 0) to Cu(II) (n = 1). The inhibition of decomposition of putative [(NHC)Cu(R)]⁺ systems upon addition of coordinating Lewis base (e.g., pyridine) suggests that the Cu(II) alkyl/aryl systems are stabilized by three-coordinate systems. Keeping with the theme of NHC ligands, recently we have targeted the preparation of the Cu(I) complex with a chelating NHC/aryloxide ligand shown in Scheme 4. In the next year, we will work to isolate this and related systems, prepare corresponding hydrocarbyl complexes, and study the ability of these systems to initiate aromatic C-H activation.

**D. Extension of Chemistry to Pt(II), Rh(I) and Fe(II) Systems:** In the past two months, we have begun to extend our studies of catalytic olefin hydroarylation beyond Ru(II) systems. For example, our studies of TpRu(II) complexes provide a foundation on which to build efforts with octahedral d⁶ systems and new metals. Based on these efforts, we suggest that TpM(L)Ar (Ar = aryl; M = d⁶ transition metal) systems should be feasible catalysts for olefin hydroarylation if L has a small steric profile (e.g., we will target ligands with a cone angle < 145 º) and if the d⁶/d⁵ redox potential is in the range of ~1 V (vs. NHE). In the next year of funding, we will prepare TpFe(L)(L')R systems (L = PMe₃, NHC, P(OCH₂)₃CEt, RNC, etc.; L' = labile ligand) and study the ability to catalyze C-H functionalization via olefin hydroarylation (Chart 4). Extension of such reactions to Fe would represent a substantial achievement since examples of Fe-mediated C-H activation are rare and Fe is a relatively inexpensive metal.

In an effort to broaden our understanding of olefin hydroarylation outside the octahedral d⁶ landscape, we recently have begun working on...
catalysis with Pt(II) and Rh(I) $d^8$ complexes (see above for preliminary results with Pt). It is anticipated that such systems will exhibit features distinct from the octahedral/$d^9$ complexes. We have already demonstrated that cationic Pt(II) complexes can catalyze the hydroarylation of olefins, and in the next year these studies will be extended to a range of Pt(II) complexes including new cationic systems and charge neutral complexes. For example, catalytic hydrophenylation of ethylene by $[\text{tBu}^bpy\text{Pt(Ph)(THF)}][\text{BAR}']$ produces more diethylbenzene than should be observed based on comparison of the relative rates of ethylene hydroarylation with benzene vs. ethylbenzene. One possible explanation is that after formation of ethylbenzene within the Pt coordination sphere a second C-H activation competes with dissociation of ethylbenzene. Interestingly, catalytic hydrophenylation of ethylene by a closely related Pt(II) complex anchored by S-donor ligands (not discussed herein) shows almost no formation of ethylbenzene. Thus, we plan to study such transformations with a range of well-defined Pt complexes that are supported by S-donor ligands. Finally, we have also extended our studies to Rh(I) complexes, which complement our efforts with Pt(II) systems, and will continue this pursuit in the next year.

**E. Hydroalkylation of Olefins:** Pt(II) complexes have been amongst the most widely studied systems for alkane C-H activation and functionalization. Having demonstrated that a cationic Pt(II) complex can catalyze the hydroarylation of olefins, we will pursue extension of such reactions to the hydroalkylation of olefins. Of particular interest is the incorporation of methane into catalytic cycles that afford liquid hydrocarbon products.
References


State of Unexpended Funds: We do not anticipate any unexpended funds at the end of the budget period.

Current Support (no proposals are currently pending):
17. "Development of Catalytic Reactions using Well-Defined Monomeric Cu(I) Complexes with Non-Dative Heteroatomic Ligands: Fundamental Exploration of Scope and Mechanism of C-X (X = N, O or S) Bond Forming Reactions" American Chemical Society Petroleum Research Fund, $45,000 total costs (6/1/07 – 5/31/08)

16. "Transition Metal Catalyzed Hydroarylation of Multiple Bonds: Exploration of Second Generation Ruthenium Catalysts and Extension to Copper Systems" Office of Basic Energy Sciences, U. S. Department of Energy, $420,000 total costs (9/15/06 – 9/14/09); DE-FG02-03ER15490

15. "Research Experience for Undergraduate at the North Carolina State University Department of Chemistry" National Science Foundation, one of twelve participants with Prof. Lin He as PI and Prof. Paul Maggard as co-PI, $229,988 total costs

14. "Beckman Scholars Program" Arnold and Mabel Beckman Foundation, selected as participant from internal (on-campus) competition (10 total participants selected), Professor Larry Blanton PPI, $105,600

13. "Ru and Cu Amido Complexes: Aryl Coupling, C-H Activation and C-N Multiple Bond Metathesis Reactions" National Science Foundation CAREER Award, $480,000 total costs (1/1/03 – 4/30/08); CHE 0238167

Publications for Current Funding Year (May 2007 – April 2008)

Joint funding by DOE (including other DOE grants) and other Federal or Non-Federal Sources:


Funding by other Federal or Non-Federal Sources (2007 – 2008):


All Publications Resulting from DOE Grant DE-FG02-03ER15490 (2003 – 2008):

Book chapter

Publications


Recent Awards, Notes and Honors for PI:
Publication in Angew. Chem. Int. Ed. (DOE funding) selected as "Hot Paper" 2008
Invited Speaker at International Conference on Organometallic Chemistry 2008
Manuscript in Organometallics noted as the 15th most accessed article for 2007 2007
Speaker at NSF Inorganic Workshop 2007
LeRoy and Elva Martin Award for Teaching Excellence 2006-2007
Elected Sigma Xi Treasurer (NCSU Chapter) 2006 – 2007
Elected Sigma Xi Secretary (NCSU Chapter) 2005 – 2006
Alfred P. Sloan Research Fellowship 2004 – 2006

RECENT INVITED RESEARCH LECTURES (*Denotes scheduled seminar)
54. Georgia Institute of Technology* November 2008
53. Rutgers University* October 2008
52. International Conference on Organometallic Chemistry (Rennes, France)* July 2008
51. University of California at Berkeley February 2008
50. Iowa State University November 2007
49. Brandeis University October 2007
<table>
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<th>Event Description</th>
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<tr>
<td>48. National Science Foundation Workshop on Inorganic Chemistry</td>
<td>June 2007</td>
</tr>
<tr>
<td>47. Western Carolina University</td>
<td>March 2007</td>
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<td>46. University of Southern California</td>
<td>February 2007</td>
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<td>45. Oklahoma State University</td>
<td>October 2006</td>
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<td>44. University of North Texas</td>
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<td>43. Dept. of Energy/Basic Energy Sciences Catalysis Program Meeting</td>
<td>May 2006</td>
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<td>42. Texas A &amp; M University</td>
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<td>39. East Carolina University</td>
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<td>38. Pacifichem Conference (Symposium on C-H Activation)</td>
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