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Reactivity of Ruthenium(II) and Copper(I) Complexes that Possess Anionic Heteroatomic Ligands: Synthetic Exploitation of Nucleophilicity and Basicity of Amido, Hydroxo, Alkoxo, and Aryloxo Ligands for the Activation of Substrates that Possess Polar Bonds as well as Nonpolar C–H and H–H Bonds

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Keywords: Nondative heteroatomic ligands / Ruthenium / Copper / C–H Activation

The preparation and reactivity of late transition-metal complexes in low oxidation states with nondative-heteroatomic ligands (e.g., amido, hydroxo, alkoxo, and aryloxo ligands) are described. For such complexes the disruption of ligand-to-metal π-donation because of a filled dπ manifold can enhance the nucleophilic and/or basic reactivity at the nondative-heteroatomic ligand relative to transition-metal complexes in high oxidation states. The chemistry of five- and six-coordinate Ru complexes with amido, hydroxo, methoxo, and aryloxo ligands is described including Brønsted acid/base reactions, coordination, and activation of polar substrates toward N–C bond forming reactions and metal-mediated activation of dihydrogen and C–H bonds. The impact of ancillary ligands and Ru oxidation states (Ru^{II} versus Ru^{III}) are discussed. In addition, the preparation and reactivity of well-defined monomeric two- and three-coordinate Cu complexes with amido, alkoxo, hydroxo, and aryloxo ligands are presented including examples of reactions to probe fundamental reactivity patterns as well as catalytic addition of N–H and O–H bonds across C=C bonds of olefins.

Introduction

Nondative-heteroatomic fragments are a common class of ligand that formally bear anionic, dianionic, or trianionic charge. Such ligands based on nitrogen, oxygen, or sulfur, including amido, alk-/aryl-/hydr-oxo, alkyl-/aryl-/hydro-sulfido, oxide, sulfide, imido, and nitrido, have been utilized as nonreactive ancillary supports for reactive transition-metal systems as well as for *active participation* in "group transfer" and other catalytic processes. Prominent examples of the latter include olefin epoxidation and aziridination, olefin dihydroxylation, and polymerization sequences.[1–9] As part of our efforts to understand and develop the reactivity of late transition-metal complexes in low oxidation states with formally anionic heteroatomic ligands, our group has been studying the synthesis and reactivity of Ru^{II} and Cu^{I} systems. Herein, the scope of complexes accessed and their reactivity are reviewed with a focus on the development of new stoichiometric and catalytic reactions that are based on the nucleophilic/basic character of the nondative ligands.

Bonding between a transition metal and an anionic heteroatomic ligand results from a metal–ligand σ bond and one ligand–metal π-interaction. Thus, when the metal center possesses one or more empty orbitals of π-symmetry metal–ligand multiple bonds result.[10] On the basis of metal–X (X = OR, NR_2 or SR ligand) bond polarity it is anticipated that nondative-heteroatomic ligands should exhibit inherent nucleophilicity and basicity; however, ligand-to-metal π-donation can serve to delocalize electron density from the heteroatomic ligand to the metal center. As a result, the electron density centered on the heteroat-

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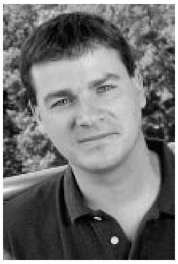
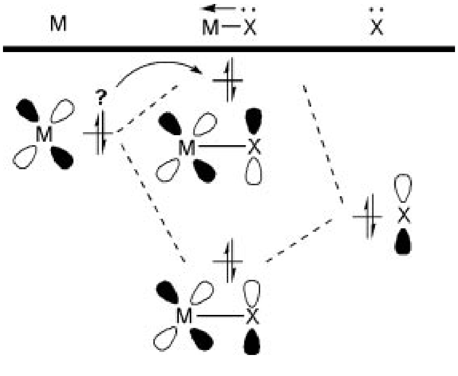


T. Brent Gunnoe was born in Charleston, West Virginia, USA in 1971. He received his B. A. in chemistry from West Virginia University in 1993 where he worked on early transition-metal aryloxo chemistry with Dr. Jeffrey Petersen. Under the supervision of Dr. Joseph L. Templeton, he received a PhD in 1997 from the University of North Carolina at Chapel Hill with research efforts focused on chiral group VI organometallic complexes. After working with Dr. W. Dean Harman as a postdoctoral researcher at the University of Virginia on the development of metal-mediated dearomatization sequences based on chiral Re^{I} *systems, he began as Assistant Professor at North Carolina State University in 1999. His current title is Associate Professor of Chemistry with research interests that include organometallic and inorganic chemistry especially applied to homogeneous catalysis.*

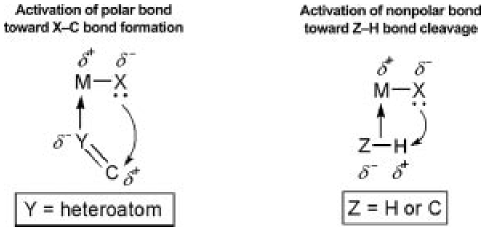
omic ligand can be attenuated and, in some cases, the heteroatomic ligand is rendered relatively inert. Schrock-type carbene complexes supported by alkoxo and imido ligands represent classic examples of unreactive anionic heteroatomic ligands. For these complexes, the formally anionic and dianionic heteroatomic ligands are reaction inert relative to the carbene moiety.[11] High oxidation states for metal centers tend to facilitate the ligand-to-metal π-bonding and, hence, serve to decrease the impact of M–X bond polarity and ligand-centered electron density and, consequently, to decrease nucleophilic and/or basic reactivity at the heteroatomic ligand. The lack of reaction of $TpOs^{IV}(Cl)_2NHPh$ with HCl (a thermodynamic effect) serves as a striking example that potentially illustrates the effect on reactivity of reduced charge density at the anionic heteroatomic ligand (due to increased ligand-to-metal π-donation).[12]

The majority of anionic heteroatomic ligands of early or middle transition elements are coordinated to relatively high oxidation state systems. In contrast, late(r) transition metals, which are more predisposed toward low oxidation states, often have high d-electron counts that disrupt ligand-to-metal π-bonding (Scheme 1). Until relatively recently, examples of anionic heteroatomic ligands coordinated to late transition-metal systems in low oxidation states were scant compared with high oxidation state complexes of the early and middle transition elements.[13–15] Recent efforts have substantially increased the number of late transition-metal complexes and revealed a wealth of interesting reactivity.[15–22] Careful studies of thermodynamic trends and reactivity indicate that the bond dissociation energies (BDEs) between heteroatom-based ligands and late transition-metal centers can be substantial, and recent bonding models suggest that these M–L bonds are relatively strong; however, the disruption of metal-to-ligand π-bonding can afford enhanced reactivity by decreasing electron delocalization from the ligand to the metal.[17]



Scheme 1. M–X (M = transition metal, X = NR_2, OR, SR, etc.) multiple bonding occurs if dπ orbital(s) is vacant. Filled dπ manifold results in no net π-bond.

Our group has been interested in understanding and exploiting the reactivity of late transition-metal systems with highly nucleophilic/basic heteroatom-based ligands including amido and alk-/aryl-/hydroxo ligands coordinated to Ru^{II} and Cu^{I}.[23–38] From the perspective of catalyst development, the positioning of a nucleophilic/basic heteroatomic ligand adjacent to a Lewis acidic metal center provides opportunities for the coordination and activation of external organic substrates toward controlled bond-breaking and bond-forming reactions (Scheme 2). From a fundamental perspective, we have been studying the impact of metal identity, ancillary ligand identity, and the heteroatomic ligand identity and substituents on reactivity. Herein, we summarize results over the past five years and comment on future prospects.

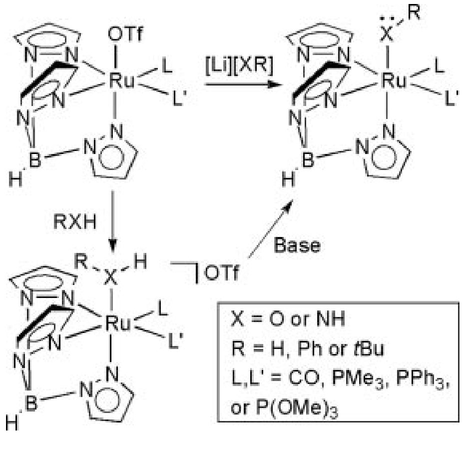


Scheme 2. Potential use of Lewis acidic metal centers with the basic anionic ligand "X" (X = NR_2, OR, SR, etc.) to activate substrates with polar and nonpolar bonds.

Octahedral $TpRu^{II}$ Systems

Preparation and Characterization

We have used the monoanionic hydridotris(pyrazolyl)borate (Tp) ligand[39] as a foundation to build octahedral Ru complexes with anionic heteroatom-based ligands.[24,26,31–36] Our strategy has been to utilize the template $[TpRu(L)(L')X]^{n+}$ (L, L′ = neutral, two-electron donor ligands, X = anionic heteroatomic ligand; n = 0 or 1) to access systems with variable ancillary ligands (L/L′), heteroatomic ligands (X), and oxidation states. Two strategies have been used for syntheses: (1) coordination of amine or alcohols followed by deprotonation and (2) metathesis of the anionic heteroatomic moiety with Ru–halide or Ru–triflate linkages (Scheme 3).



Scheme 3. Two general routes used for the preparation of TpRu(L)(L′)NHR and TpRu(L)(L′)OR systems.

For the Ru^{II} oxidation state, the hydroxo and parent amido complexes exhibit upfield chemical shifts between –1 and –4 ppm for the N–H/O–H resonances (^{1}H NMR spectroscopy), which is indicative of electron-rich nondative-heteroatomic ligands (a hallmark of the disruption of ligand-to-metal π-donation for amido and hydroxo ligands). Upfield chemical shifts have been observed for related Ru^{II} systems.[26,31,34] For the anilido complexes [TpRu(L)(L′)-NHPh], variable-temperature ^{1}H NMR spectroscopy provides a convenient means to determine the Gibbs free energy of activation for rotation around the $Ru–N_{amido}$ and the $C_{ipso}–N_{amido}$ bonds (Scheme 4).[33] Although the data set is limited there is an inverse correlation between the magnitudes of these two rotational barriers, a result that is consistent with anticipated Ru–N multiple-bond character in response to metal-electron density. That is, the presence of strongly electron-donating and poorly π-acidic ancillary L/L′ reduces anilido-to-Ru multiple bonding (via three-center, four-electron interactions), which most likely increases the extent of anilido-to-phenyl π* back-bonding and hence increases the $N_{amido}–C_{ipso}$ multiple-bond character. Using this rationale, an inverse correlation between $Ru–N_{amido}$ and $C_{ipso}–N_{amido}$ bond lengths is anticipated. In fact, comparing structural data for the series of octahedral Ru^{II}–anilido complexes [TpRu(CO)(PPh_3)NHPh],[35] [TpRu{P-$(OMe)_3\}_2$NHPh],[33] [(η^6-C_6Me_6)Ru(Ph)(PMe_3)NHPh],[40] and [$(PMe_3)_4$Ru(H)NHPh][41] reveals such a trend (Figure 1). In addition, the equilibrium constants for a series of reactions of [TpRu$(PMe_3)_2$NHPh] with *p*-substituted anilines (NH_2Ar) to form [TpRu$(PMe_3)_2$(NHAr)] (Ar = *p*-substituted phenyl) and aniline afforded a Hammett plot (using σ_p^-) with $\rho = 4.1$, which is consistent with the delocalization of electron density from the amido ligand to the aryl substituent.[31] This ρ value is similar to the value of 3.4 obtained for Cp*Ni(PEt_3)(NHPh)/NH_2Ar reactions.[42] In contrast, a study of equilibria for four-coordinate Re^{III}–aryloxo complexes revealed a correlation with Hammett σ parameters with a much smaller ρ value of 0.7.[43]

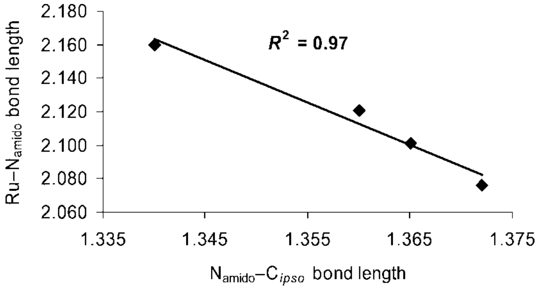
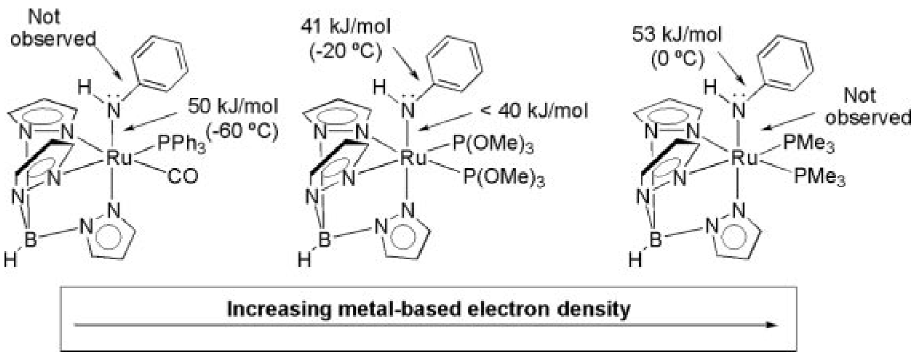


Figure 1. Plot of $Ru–N_{amido}$ and $N_{amido}–C_{ipso}$ bond lengths (Å), which illustrates an inverse relationship for the series of Ru–anilido complexes [TpRu(CO)(PPh_3)NHPh],[35] [TpRu{P$(OMe)_3\}_2$-NHPh],[33] [(η^6-C_6Me_6)Ru(Ph)(PMe_3)NHPh],[40] and [$(PMe_3)_4$Ru-(H)NHPh].[41]

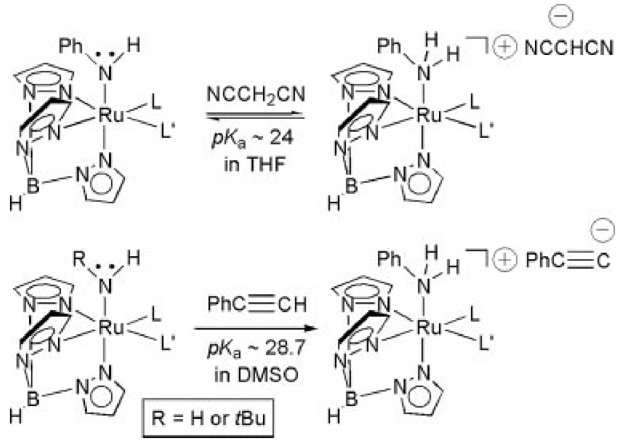
Acid–Base Reactions

The coordination of anionic heteroatomic ligands to late transition-metal complexes in low oxidation states can impart substantial basicity/nucleophilicity to the ligand, a feature that has been attributed to polar metal–ligand bonds and the disruption of ligand-to-metal π-donation. For example, Bergman et al. have demonstrated that *trans*-[$(DMPE)_2$Ru(H)NH_2] {DMPE = 1,2-bis(dimethylphosphanyl)ethane} forms an acid–base equilibrium upon reaction with triphenylmethane ($pK_a \approx 31.5$ in THF) to form *trans*-[$(DMPE)_2$Ru(H)NH_3][Ph_3C],[44] and related octahedral Ru^{II} and Fe^{II} parent amido complexes exhibit analogous reactivity.[45,46] Similarly, [TpRu(L)(L′)NHR] (R = Ph, H or *t*Bu) complexes react with weakly acidic C–H bonds. For example, the anilido complexes [TpRu(L)(L′)NHPh] form acid–base equilibria with malononitrile ($pK_a \approx 24$ in THF),[47] which is the least acidic substrate that we have found to react at room temperature with the anilido complexes (Scheme 5).[33] For [TpRu(L)(L′)NHR] (R = H or *t*Bu), the combination with phenylacetylene ($pK_a \approx 28.7$ in DMSO)[48] results in the formation of ion pairs [TpRu(L)(L′)NH_2R][PhC_2] at room temperature (Scheme 5).[31] Thus, the formal substitution of H or *t*Bu for phenyl as the amido substituent likely increases basicity by several orders of magnitude. For [TpRu$(PMe_3)_2$-(NH_2*t*Bu)][PhC_2], heating to 80 °C cleanly forms free *t*BuNH_2 and [TpRu$(PMe_3)_2$(C≡CPh)].

Although no reaction is observed at room temperature, heating solutions of [TpRu(L)(L′)NHPh] and phenylacetylene to 80 °C forms free aniline and [TpRu(L)(L′)(C≡CPh)]; however, detailed mechanistic studies have revealed that these transformations do not likely proceed through the formation of ion pairs [TpRu(L)(L′)(NH_2Ph)][PhC_2] (as do the parent amido and *t*Bu-amido systems, see above).[31] Rather, small and undetectable quantities of [TpRu(L)(L′)-

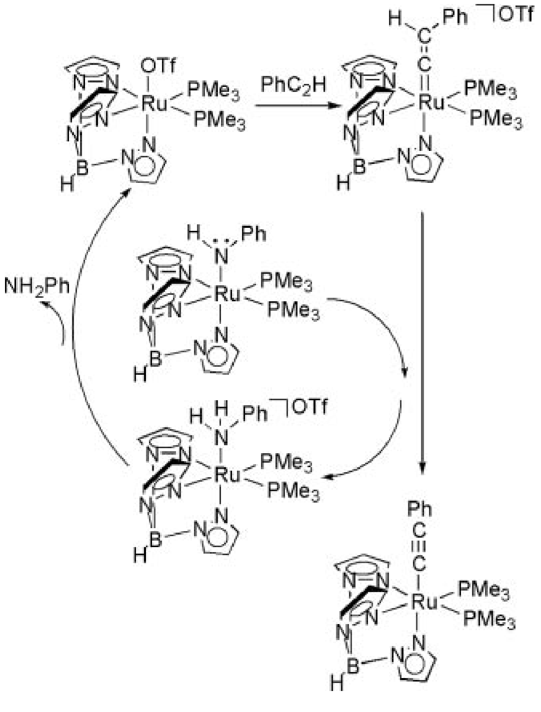


Scheme 4. Impact of ancillary ligands on Ru–N and $N_{amido}–C_{ipso}$ bond rotational barriers.



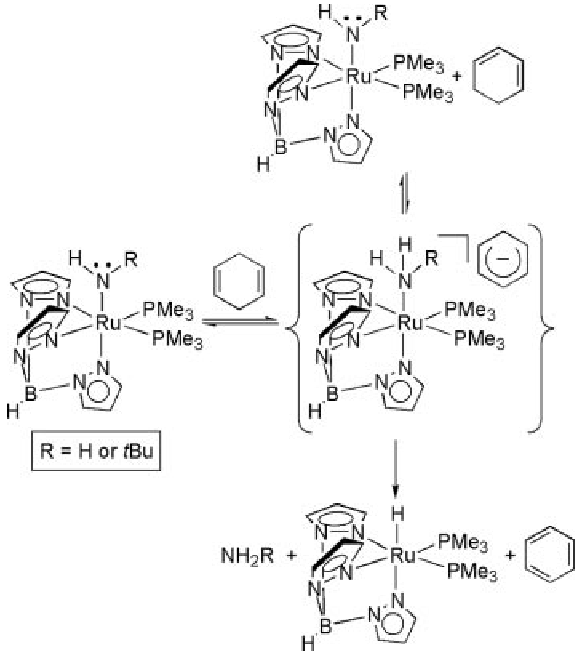
Scheme 5. Acid/base equilibria observed for [TpRu(L)(L′)NHR] (R = H, *t*Bu or Ph) systems upon treatment with malononitrile or phenylacetylene.

OTf] likely catalyze the reaction as shown in Scheme 6. For the PMe_3 system, late in the reaction the putative vinylidene intermediate is trapped by free aniline to form the Fischer carbene complex $[Tp(PMe_3)_2Ru{=}C(CH_2Ph)(NHPh)]$, a reaction that is confirmed by independent conversion of $[Tp(PMe_3)_2Ru{=}C{=}C(H)Ph]$ and aniline to $[Tp(PMe_3)_2Ru{=}C(CH_2Ph)(NHPh)]$.



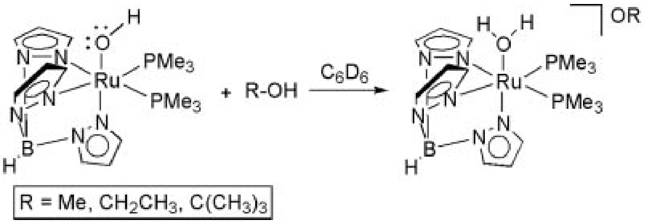
Scheme 6. Proposed pathway for the conversion of $[TpRu(PMe_3)_2NHPh]$ and phenylacetylene to $[TpRu(PMe_3)_2C{\equiv}CPh]$, which is catalyzed by $[TpRu(PMe_3)_2OTf]$.

At 80 °C, $[TpRu(PMe_3)_2NHR]$ (R = H or *t*Bu) complexes react with 1,4-cyclohexadiene to ultimately form benzene, free amine, and $[TpRu(PMe_3)_2H]$ with a 1:1 molar ratio of benzene and Ru–hydride.[31] Preceding the formation of benzene and Ru–hydride, the isomerization of 1,4-cyclohexadiene to 1,3-hexadiene is observed (k_{obs} = 2.0×10^{-5} s^{-1} at 80 °C). The addition of free PMe_3 does not influence the rate of isomerization of the 1,4-cyclohexadiene. We have proposed that these reactions occur by the acid–base pathway shown in Scheme 7. Although hydrogen atom abstraction pathways are also possible and have been observed for late transition-metal complexes with heteroatomic ligands in which the metal centers are in relatively high oxidation states,[49–57] the failure of $[TpRu(PMe_3)_2NHPh]$, which is much less basic than the parent or *t*Bu-amido complexes, to react with 1,4-cyclohexadiene is consistent with the proposed acid–base pathway. Furthermore, initial hydrogen atom abstraction would form a cyclohexadienyl radical and $[TpRu^I(PMe_3)_2NH_2R]$, which is a 19-electron Ru^I complex that is likely to be a high-energy species. For $[TpRu(PMe_3)_2NHR]$ systems, the Ru(II/I) potential is negative of –2.0 V (vs. NHE), which supports the suggestion that access to $[TpRu^I(PMe_3)_2NH_2R]$ is most likely a high-energy process. In comparison, an octahedral Fe^{III}–methoxo complex that converts 1,4-cyclohexadiene to benzene by a proposed hydrogen atom abstraction pathway exhibits an Fe(III/II) potential of 0.73 V.[52,53]

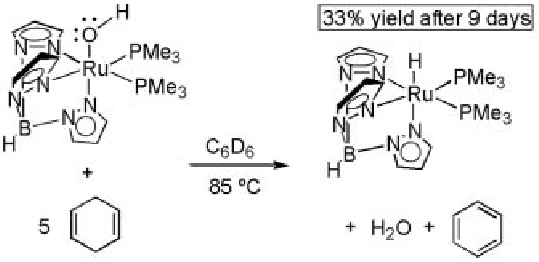


Scheme 7. Proposed pathway for isomerization of 1,4-cyclohexadiene to 1,3-cyclohexadiene by $[TpRu(PMe_3)_2NHR]$ and ultimate conversion to benzene, $[TpRu(PMe_3)_2H]$, and amine.

We have recently extended our studies of octahedral Ru^{II} complexes to $[TpRu(PMe_3)_2OH]$.[24,26,36] Similar to the amido complexes, the Ru^{II}–hydroxo complex is basic. For example, reactions with MeOH, EtOH, or *t*BuOH result in the formation of species whose NMR spectra are consistent with the ion pairs $[TpRu(PMe_3)_2OH_2][OR]$ [R = Me, Et, or *t*Bu; Equation (1)].[36] In contrast to the parent amido complexes, $[TpRu(PMe_3)_2OH]$ does not react with phenylacetylene at room temperature; however, at an elevated temperature (80 °C) $[TpRu(PMe_3)_2OH]$ and phenylacetylene are converted to water and $[TpRu(PMe_3)_2(C{\equiv}CPh)]$. Similar to the amido complexes, at 85 °C $[TpRu(PMe_3)_2OH]$ and 1,4-cyclohexadiene are converted to benzene, water, and $[TpRu(PMe_3)_2H]$ with a 1:1 molar ratio of benzene to Ru–H [Equation (2)]. Consistent with an acid–base pathway (see Scheme 7) and the reduced basicity of the hydroxo complex relative to the parent and *t*Bu-amido complexes, the reaction of $[TpRu(PMe_3)_2OH]$ and 1,4-cyclohexadiene is only 33% complete after 9 days at 85 °C. In comparison, $[TpRu(PMe_3)_2NH_2]$ and 1,4-cyclohexadiene produce benzene and $[TpRu(PMe_3)_2H]$ in about 50% conversion after 3 days at 75 °C.

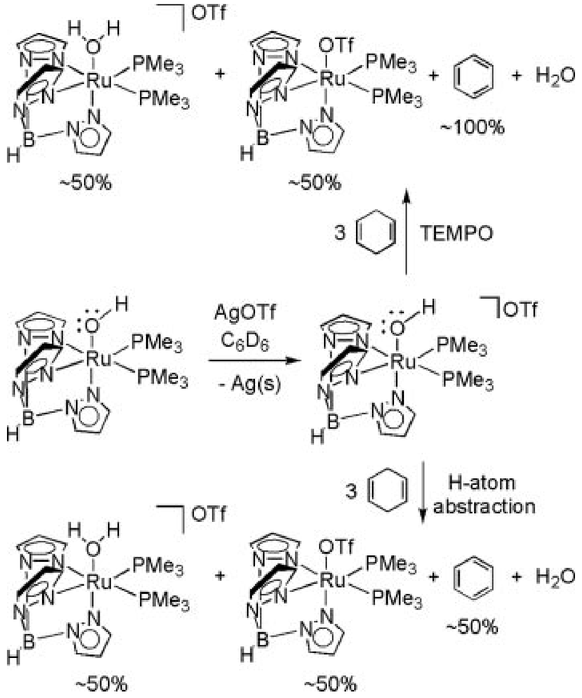


(1)



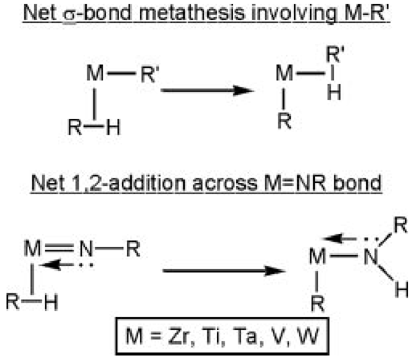
(2)

Single-electron oxidation of $[TpRu(PMe_3)_2OH]$ yields the paramagnetic and NMR spectroscopic silent Ru^{III} system $[TpRu(PMe_3)_2OH]^+$.[36] For the cationic Ru^{III}–hydroxo complex, Evans NMR spectroscopic experiments reveal $\mu_{eff} = 1.78\ \mu_B$ (room temperature), which is consistent with a single unpaired electron and close to the spin-only value of $1.73\ \mu_B$. Similar to the Ru^{II}–hydroxo complex $[TpRu(PMe_3)_2OH]$, the Ru^{III} system $[TpRu(PMe_3)_2OH]^+$ converts 1,4-cyclohexadiene to benzene; however, experimental evidence points to a pathway that involves net hydrogen atom abstraction rather than even-electron acid–base chemistry (Scheme 8). In the absence of an external radical trap, $[TpRu(PMe_3)_2OH]^+$ most likely reacts with 1,4-cyclohexadiene to produce $[TpRu(PMe_3)_2(OH_2)]^+$ and a cyclohexadienyl radical, the latter is probably consumed rapidly by a second equivalent $[TpRu(PMe_3)_2OH]^+$ to form benzene and a second equivalent of $[TpRu(PMe_3)_2(OH_2)]^+$. The observed stoichiometry of products (2:1 molar ratio of $[TpRu(PMe_3)_2(OH_2)]^+$ and benzene) is consistent with the proposed mechanism. When the radical trap TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidinyloxy) is added the cyclohexadienyl radical is trapped by TEMPO to give benzene and hence a 1:1 ratio of $[TpRu(PMe_3)_2(OH_2)]^+$ and benzene in the products. $[TpRu(PMe_3)_2OH]^+$ reacts with substrates that possess C–H bonds with bond dissociation energies up to ca. 335 kJ/mol. Using the approximate pK_a of $[TpRu(PMe_3)_2(OH_2)]^+$ and the Ru(III/II) potential of $[TpRu(PMe_3)_2OH]$ a thermodynamic cycle has been used to estimate the O–H BDE of $[TpRu(PMe_3)_2OH_2]^+$ to be between 343 and 356 kJ/mol, which is consistent with the experimental reactivity of the $[TpRu^{III}(PMe_3)_2OH]^+$ complex. Furthermore, DFT calculations of the model $[(Tab)Ru(PH_3)_2(OH_2)]^+$ [Tab = tris(azo)borate] reveal that the O–H BDE is 351 kJ/mol.



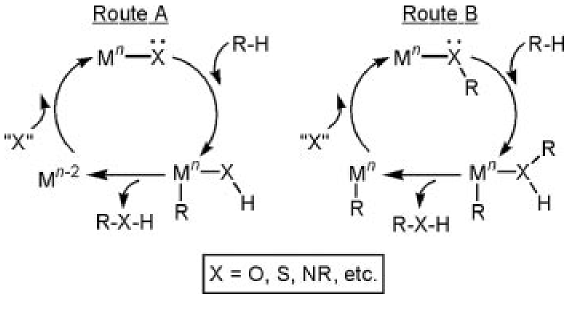
Scheme 8. The conversion of 1,4-cyclohexadiene to benzene by $[TpRu(PMe_3)_2OH]^+$ most likely proceeds by hydrogen-atom abstraction.

From a synthetic perspective, our interest in anionic heteroatomic ligands coordinated to late transition metals is derived predominantly from the positioning of a basic/nucleophilic moiety adjacent to a Lewis acidic metal center (Scheme 2). Hence, opportunities exist to coordinate substrates to the Lewis acidic metal and to activate them toward reactions with the heteroatomic ligands. For example, metal-mediated C–H activation by σ-bond metathesis pathways involve the conversion of M–R and R′–H to M–R′ and R–H via a transition state in which net H^+ is transferred to a basic alkyl or aryl ligand "R" (Scheme 9). We have considered that related reactions of late transition metals with nondative-heteroatomic ligands might provide facile and controlled C–H activation/functionalization. In this case, the net C–H activation might be best viewed as an intramolecular proton transfer to the basic heteroatomic ligand. In related examples, the net 1,2-additions of dihydrogen across Ru amido ligands have been implicated in enantioselective ketone hydrogenation as well as Rh and Ir catalysts.[58–62] Morris et al. have demonstrated that the reaction of a Ru^{II} amido complex with dihydrogen yields a complex in which the H–H bond is intermediate between protic-hydridic and dihydrogen,[63] dihydrogen adds across an Ir^{III}–amido bond,[64] and the chelating amido ligand of $\{Ru(Cl)(PPh_3)[N(SiMe_2CH_2PPh_2)_2]\}$ deprotonates dihydrogen to yield $\{Ru(Cl)(H)(PPh_3)[NH(SiMe_2CH_2PPh_2)_2]\}$.[65] In addition, early transition-metal imido complexes have been demonstrated to activate C–H bonds for 1,2-addition across the M = NR moiety to yield amido and alkyl or aryl ligands (Scheme 9).[66–74] Studies have demonstrated that key factors in the imido-based C–H activation include coordination of the C–H bond to the metal center and the polar nature of the metal–imido bond.[75–77] We have been pursuing the utilization of Ru^{II} systems for the activation of nonpolar bonds such as dihydrogen and carbon–hydrogen bonds.



Scheme 9. Net 1,2-addition of C–H bonds across early transition-metal imido fragments has been observed.

Several strategies exist for oxygen or nitrogen functionalization of C–H bonds via metal-mediated activation, and the net 1,2-addition of C–H bonds across metal heteroatom bonds is a potentially viable step in catalytic sequences. For example, Scheme 10 depicts two possible catalytic cycles for C–H functionalization involving the 1,2-addition of C–H bonds across M–X bonds (X = amido, imido, oxide, alkoxo, etc.). Route A illustrates C–H functionalization with three key steps: (1) 1,2-addition of a C–H bond across a metal–oxide or metal–imido bond, (2) O–C or N–C reductive elimination, and (3) formal oxidation of the metal to reform the oxide or imido complex. Although the 1,2-addition of C–H bonds across M–X bonds has been demonstrated for early transition-metal–imido complexes (see above),[66–77] the product forming reductive elimination from electropositive early transition metals is likely to be substantially unfavorable. In contrast, N–C and O–C reductive elimination reactions have been successfully incorporated into catalytic cycles involving late transition-metal systems (e.g., catalytic arylamine or aryl ether preparation).[78–82] Thus, *catalytic cycles* by Route A are potentially more viable with late transition-metal systems; however, the 1,2-addition of C–H bonds across late transition-metal–oxide or –imido bonds remains, to the best of our knowledge, unknown.

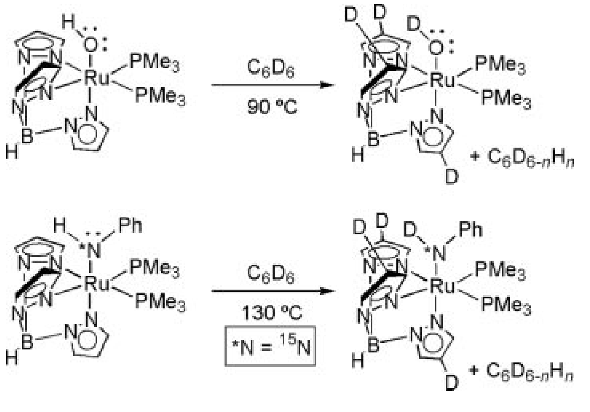


Scheme 10. Two possible routes to incorporate the net 1,2-addition of C–H bonds across transition-metal–heteroatom bonds (e.g., imido, oxide, amido, alkoxo, etc. ligands) into catalytic cycles.

Route B (Scheme 10) illustrates an alternative catalytic cycle with three key steps: (1) the 1,2-addition of a C–H bond occurs across a metal–amido or metal–alkoxo (or aryloxo) bond, (2) dissociation of the alcohol or amine, and (3) net oxygen atom or nitrene insertion into the newly formed M–R or M–Ar bond.[83] To the best of our knowledge, prior to our work and efforts by Periana et al., evidence for the 1,2-addition of C–H bonds across the bonds of late transition metals and amido, alkoxo, and related ligands was unknown.[24,26,84] Macgregor et al. have suggested a related pathway for a C–H cyclometalation by Pd–acetate and Ir complexes.[85,86] Addition of a C–H bond across a Pt–Cl bond has been proposed as a possibility in the Shilov reaction.[87] Establishing the viability of these potential catalytic cycles requires an understanding of the metal-mediated C–H activation by late transition-metal amido, alkoxo, and related systems.

In addition to the C–H activation step, oxo or nitrogen functionalization of the M–R or M–Ar bond is a substantial challenge to the development of catalytic cycles shown in Route B. For example, insertions of metal–oxo ligands into metal–alkyl (or aryl) bonds are extremely rare, especially under nonphotolytic conditions.[88,89] However, Periana et al. have recently reported kinetically facile conversions of a Re^{VII}–methyl ligand and external oxidants to a Re–OMe linkage, and they have proposed that the key to the relatively low activation barriers is a mechanism that does not involve a rhenium–oxo ligand but rather resembles the classic organic Baeyer–Villiger reaction.[83] *Thus, both of the reaction steps for catalytic oxy functionalization of C–H bonds by Route B in* Scheme 10 *have been observed to be kinetically accessible under reasonably mild reaction conditions using late transition-metal systems.* With a better understanding of both reactions, it might be possible to merge the two steps with a single catalyst.

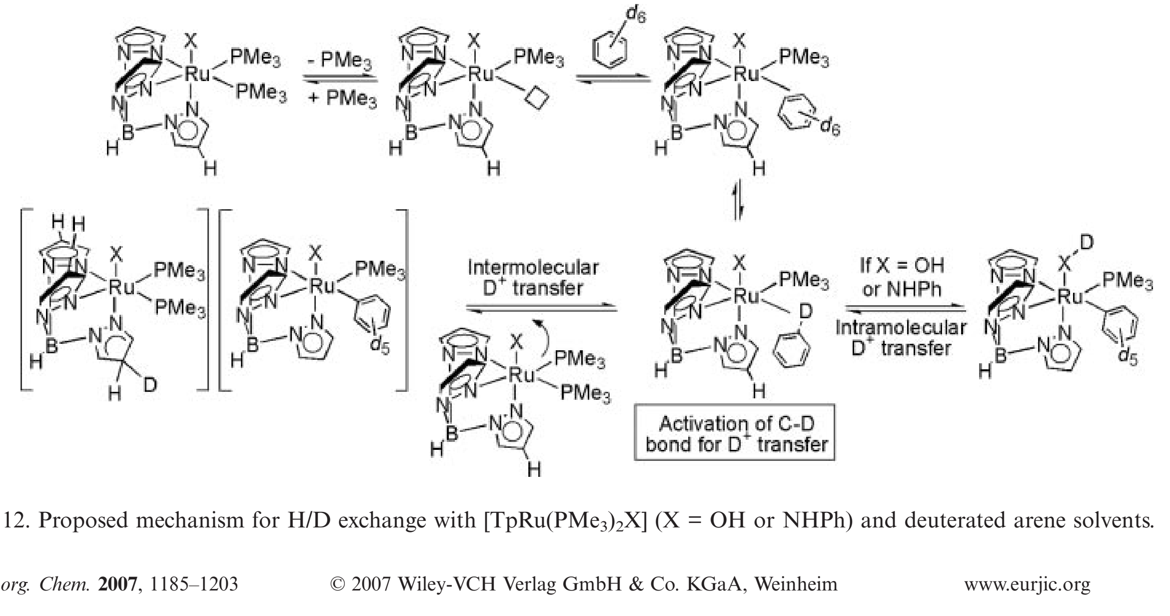
$[TpRu(PMe_3)_2OH]$ and $[TpRu(PMe_3)_2NHPh]$ provide kinetic access to aromatic C–H activation sequences that involve the net 1,2-addition of C–H(D) bonds across the Ru–OH and Ru–NHPh bonds.[24,26] For example, heating these systems in C_6D_6 results in H/D exchange between the deuterated benzene and the hydroxo and anilido ligands, which has been observed by both ^1H and ^2H NMR spectroscopy. In addition to the incorporation of deuterium at the heteroatomic ligand, highly regioselective H/D exchange is observed at the Tp 4-position (Scheme 11). On the basis of several experimental results including detailed kinetic studies and complementary computational studies,[24] the mechanism in Scheme 12 has been proposed. Initial dissociation of PMe_3 provides a pathway to coordinate and activate the aromatic substrate (benzene in Scheme 12). Activation of the aromatic C–H(D) bond imparts acidic character, which results in the transfer of the "protic" hydrogen to the basic hydroxo or anilido site (intramolecular transfer) or transfer to the most basic pyrazolyl position (the 4-position, intermolecular transfer). The proposed mechanism suggests that the C–H(D) activations are thermally disfavored, and consistent with this notion heating $[TpRu(PMe_3)_2Ph]$ and aniline in C_6D_6 initially results in the conversion to benzene and $[TpRu(PMe_3)_2NHPh]$. In closely related work, Periana et al. have directly observed the conversion of an octahedral Ir^{III}–methoxo complex, which is isoelectronic to the $[TpRu(PMe_3)_2X]$ systems, and benzene to the corresponding Ir^{III}–phenyl and methanol.[84]



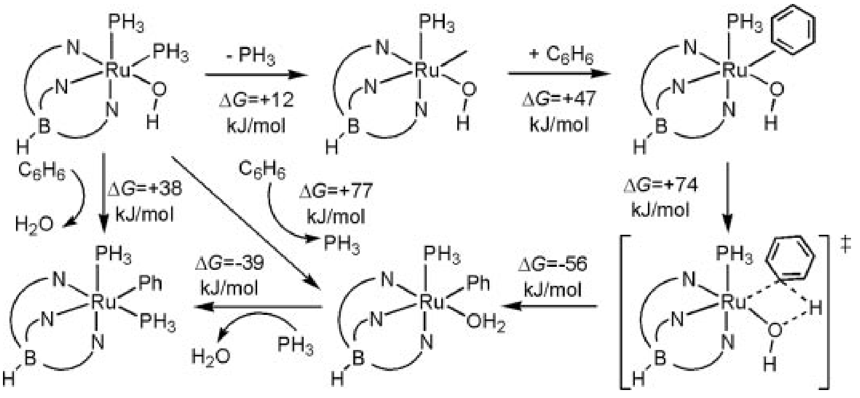
Scheme 11. Observed H/D exchange from heating $[TpRu(PMe_3)_2X]$ (X = OH or NHPh) in C_6D_6 (N* = isotopically labeled ^{15}N).

DFT calculations performed by Cundari et al. using the Tp model "Tab" [Tab = tris(azo)borate] and PH_3 reveal the energetics for the conversion of $[(Tab)Ru(PH_3)_2OH]$ and benzene to $[(Tab)Ru(PH_3)_2Ph]$ and H_2O (Scheme 13). Consistent with the experimental evidence suggesting that the 1,2-additions of the benzene C–H(D) bonds are thermally disfavored, the conversion of $[(Tab)Ru(PH_3)_2OH]$ and benzene to $[(Tab)Ru(PH_3)(OH_2)Ph]$ and free PH_3 is calculated to be endergonic by 77 kJ/mol, and conversion to $[(Tab)Ru(PH_3)_2Ph]$ and free H_2O is calculated to be endergonic by 38 kJ/mol relative to starting materials. Similar to calculations for C–H activation by isoelectronic [TpRu(L)R] (R = alkyl) systems,[90,91] the calculated pathway for benzene C–H activation by $[(Tab)Ru(PH_3)OH]$ does not involve oxidative addition but rather more closely resembles a σ-bond metathesis reaction that is typically observed with d^0 metal systems (i.e., the C–H and O–H bonds are simultaneously broken and formed). The intramolecular C–H activations with Ru–X (X = OH or NHPh) are perhaps best considered as intramolecular deprotonations (see below).

While examples of C–H activation by late transition-metal complexes that involve the overall conversion of M–R + R′H to M–R′ and RH or oxidative addition of C–H bonds are relatively common,[90–110] related examples involving M–X + R–H to M–R + X–H (X = amido, alkoxo, etc.) are rare. Thus, an important fundamental aspect of the latter transformations is the relative predilection toward C–H activation for systems that possess nondative-heteroatomic ligands. *That is, what features of the metal center and ligand "X" decrease the activation barrier for the C–H activation?* Part of our efforts with late transition-metal nondative-heteroatomic complexes is directed toward elucidating such features. For example, *our preliminary results and calculations suggest that the net 1,2-addition of C–H bonds across M–X (X = anionic heteroatomic ligand) may be more facile than related reactions involving M–R bonds, which may be explained by considering the C–H activation as an intramolecular proton transfer that is facilitated by the lone pair on the hydroxo and related ligands* (Scheme 14). For example, Scheme 15 depicts benzene C–H activation by $[TpRu(PMe_3)X]$ (X = OH, NHPh, or Me) fragments. The activated benzene C–H bond can either produce a net transfer of H^+ to the pyrazolyl ring of another Ru system (k_{inter} in Scheme 15) or the intramolecular transfer of H^+ to X (k_{intra}) in Scheme 15. For X = OH and NHPh, k_{intra} is more rapid than k_{inter}; however, for X = Me, k_{inter} is more rapid that k_{intra}, ***results which are consistent with the presence of a lone pair on ligand X facilitating the intramolecular transfer of a proton from the activated benzene C–H(D) bond***. The

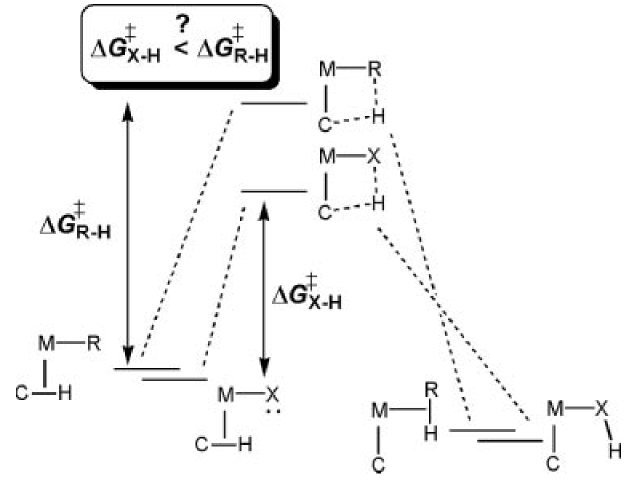


Scheme 12. Proposed mechanism for H/D exchange with $[TpRu(PMe_3)_2X]$ (X = OH or NHPh) and deuterated arene solvents.



Scheme 13. Calculated energetics for benzene C–H activation using a model complex [(Tab)Ru(PH_3)$_2$OH].

k_{inter} for X = Me is an estimate based on an approximate half-life acquired in an NMR tube reaction of [TpRu(PMe_3)$_2$Me] in C_6D_6 to produce [TpRu(PMe_3)$_2$(Ph-d_5)] and CH_3D at 130 °C.



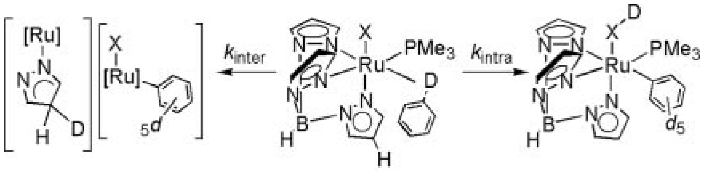
Scheme 14. For late transition-metal systems in low oxidation states the net 1,2-addition of C–H bonds across M–X (X = anionic heteroatomic ligand such as hydroxo, amido, etc.) may possess inherently lower activation barriers than analogous reactions of M–R (R = alkyl or aryl) bonds.

Clearly, more work is needed to substantiate (or disprove) this possibility as well as to understand the influence of the metal oxidation state, metal identity, identity of the nondative-heteroatomic ligand, identity of substituents on the nondative ligand, and the donating ability of the ancillary ligands. We are currently studying such details both experimentally and computationally. However, these preliminary experimental and computational results suggest that 1,2-additions of C–H bonds across M–X (X = anionic heteroatomic ligand) bonds with late transition metals in low oxidation states might be viable reactions for catalytic C–H functionalization.

Five- and Six-Coordinate (PCP)Ru^{II} Systems

Preparation and Characterization of (PCP)Ru^{II} Systems

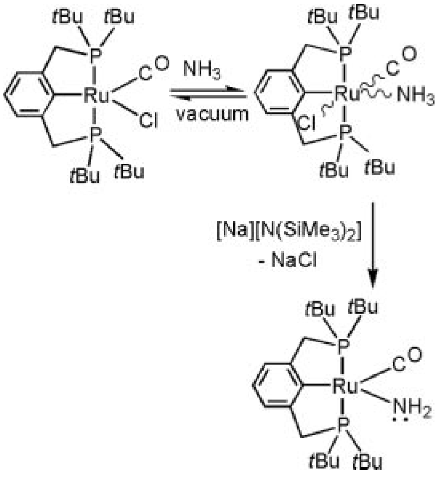
In order to access coordinatively unsaturated Ru^{II} amido complexes we employed the sterically bulky PCP ligand 2,6-(CH_2P-$t$$Bu_2$)$_2$$C_6H_3$, which is strongly donating and coordinates in a meridonal fashion.[111] The addition of ammonia to the previously reported complex [(PCP)Ru(CO)Cl] results in reversible coordination of the amine to form [(PCP)Ru(CO)(NH_3)Cl], and reactions of the Ru^{II}–amine complex with strong bases produce the parent amido complex [(PCP)Ru(CO)NH_2] (Scheme 16).[29] In contrast to the octahedral 18-electron [TpRu(L)(L′)NH_2] parent amido complexes (see above), the resonance arising from the amido protons appears downfield at δ = 4.36 ppm. The



X	k_{intra}	k_{inter}	k_{intra}/k_{inter}
OH[a]	2.4×10^{-4}[b]	5.2×10^{-6}	46
NHPh[c]	1.4×10^{-5}	5.6×10^{-6}	2.5
Me[c]	1.1×10^{-6}	1.1×10^{-5}	0.1

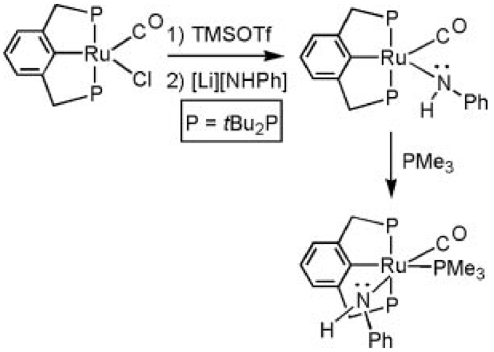
Scheme 15. Comparison of rates of inter- versus intramolecular transfer of the proton (D^+) from the activated benzene C–D bond for a series of complexes [TpRu(PMe_3)(C_6D_6)X] (X = OH, NHPh or Me) {[a] Data at 90 °C, [b] calculated at 90 °C from the value acquired at 80 °C (assuming constant $\Delta G^‡$), [c] Data at 130 °C}.

downfield chemical shift most likely reflects amido-to-Ru π-donation as a result of the metal's coordinative and electronic unsaturation.

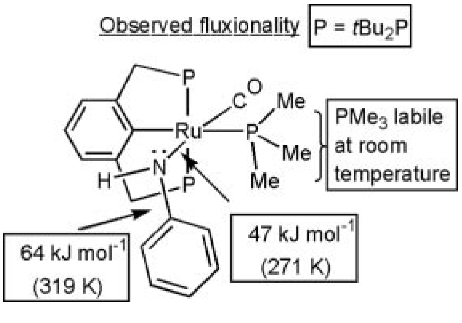


Scheme 16. Preparation of five-coordinate [(PCP)Ru(CO)NH_2].

The anilido complex [(PCP)Ru(CO)NHPh] has been prepared via transformation of [(PCP)Ru(CO)Cl] and TMSOTf to [(PCP)Ru(CO)OTf] followed by reaction with [Li][NHPh].[27,28] The addition of PMe_3 to [(PCP)Ru(CO)-NHPh] allows the isolation of the octahedral complex [(PCP)Ru(CO)(PMe_3)NHPh] (Scheme 17). Variable-temperature ^1H and ^{31}P NMR spectroscopy of [(PCP)Ru(CO)(PMe_3)NHPh] reveals three fluxional processes including facile dissociation of PMe_3 and hindered rotation about the Ru–$N_{anilido}$ ($\Delta G^{\ddagger}$ = 47 kJ/mol at 271 K) and $N_{anilido}$–C_{ipso} ($\Delta G^{\ddagger}$ = 64 kJ/mol at 319 K) bonds (Scheme 18).



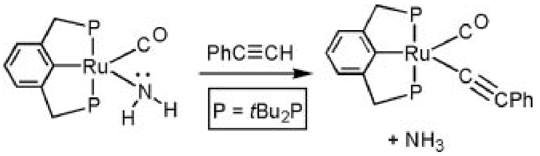
Scheme 17. Preparation of [(PCP)Ru(CO)NHPh] and [(PCP)Ru(CO)(PMe_3)NHPh].



Scheme 18. Fluxional processes observed for [(PCP)Ru(CO)-(PMe_3)NHPh] using variable-temperature NMR spectroscopy.

Reactivity of (PCP)Ru^{II} Systems

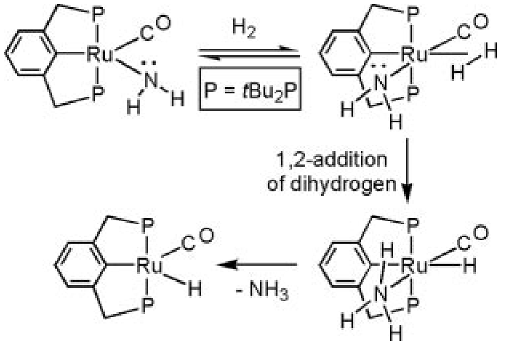
The (PCP)Ru^{II} amido complexes undergo reactions similar to the TpRu^{II} amido complexes, but also afford access to transformations not observed with the Tp systems. For example, similar to the TpRu parent amido complexes, [(PCP)Ru(CO)NH_2] reacts with phenylacetylene to produce free ammonia and [(PCP)Ru(CO)(C≡CPh)]; however, in contrast to the Tp systems, the putative intermediate(s) [(PCP)Ru(CO)NH_3][PhC_2] or [(PCP)Ru(CO)(NH_3)-(C≡CPh)] are not observed (even at –78 °C) as they apparently undergo rapid conversion to the five-coordinate acetylide complex [(PCP)Ru(CO)(C≡CPh)] (Scheme 19).



Scheme 19. Reaction of [(PCP)Ru(CO)NH_2] and phenylacetylene to produce [(PCP)Ru(CO)C≡CPh] and free ammonia.

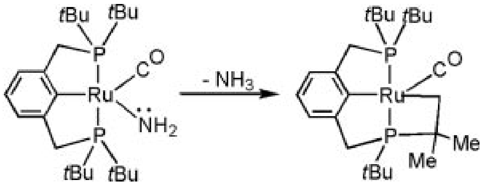
The failure of the TpRu parent amido complexes to react with dihydrogen is potentially attributable to the lack of an open coordination site to bind and activate the dihydrogen. Consistent with this notion, the five-coordinate complex [(PCP)Ru(CO)NH_2] rapidly reacts with dihydrogen at room temperature to produce [(PCP)Ru(CO)H], and mechanistic studies suggest the pathway displayed in Scheme 20.[29] In related chemistry, Morris et al. demonstrated that the reaction of a Ru^{II} amido complex with dihydrogen yields a complex in which the H–H bond is intermediate between protic-hydridic and dihydrogen bonding.[63] Fryzuk et al. have reported the 1,2-addition across a Ru–amido bond in which the amido is part of a chelated PNP ligand.[65] Rauchfuss has recently reported the addition of dihydrogen across an Ir^{III}–amido bond.[64] Also, the 1,2-addition of dihydrogen across Ru–amido linkages has been implicated for asymmetric hydrogenation reactions.[58,59] The conversion of [(PCP)Ru(CO)NH_2] and dihydrogen to [(PCP)Ru(CO)H] and ammonia suggests that nonpolar bonds can be activated with late transition metals in low oxidation states that possess anionic heteroatomic ligands.

Despite the facile activation of dihydrogen by [(PCP)-Ru(CO)NH_2], this system does not mediate the 1,2-addition of C–H bonds of benzene or methane across the Ru–NH_2 bond. Rather, intramolecular C–H activation of a *t*Bu group of the PCP ligand kinetically competes with intermolecular C–H activation (Scheme 21). Fryzuk et al. have recently reported a related intramolecular cyclometalation of a triphenylphosphane ligand that involves the conversion of an amido moiety to amine coordinated to Ru^{II}.[112] The intramolecular C–H activation occurs for [(PCP)Ru(CO)X] (X = NH_2 or Me) with the rate of reaction approximately



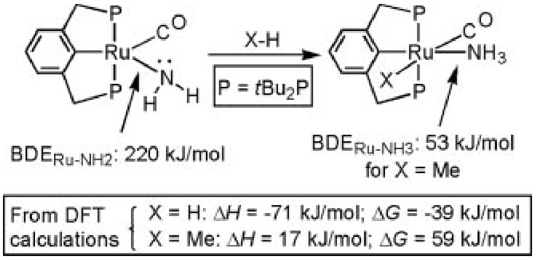
Scheme 20. Proposed pathway for the conversion of [(PCP)Ru(CO)NH_2] and dihydrogen to free ammonia and [(PCP)Ru(CO)H].

five times faster for the methyl complex at 50 °C. Eyring plots for both complexes over a temperature range of 30 °C revealed identical $\Delta H^{\ddagger}$ values of 75(4) kJ/mol with a $\Delta S^{\ddagger}$ value of –23(4) eu for [(PCP)Ru(CO)NH_2] and –18(4) eu for [(PCP)Ru(CO)Me]. Thus, the difference in the reaction rate for intramolecular 1,2-addition of C–H bonds across Ru^{II}–X (X = NH_2 or Me) bonds for these systems is predominantly due to a more ordered transition state for X = NH_2 than X = Me. Interestingly, the comparative rates of intramolecular C–H activation for the PCP systems with X = NH_2 or Me are in contrast to the more rapid 1,2-addition of benzene C–D bonds by [TpRu(PMe_3)$_2$OH] versus [TpRu(PMe_3)$_2$Me] (see above).



Scheme 21. Intramolecular C–H activation via 1,2-addition of the C–H bond across the Ru–NH_2 bond.

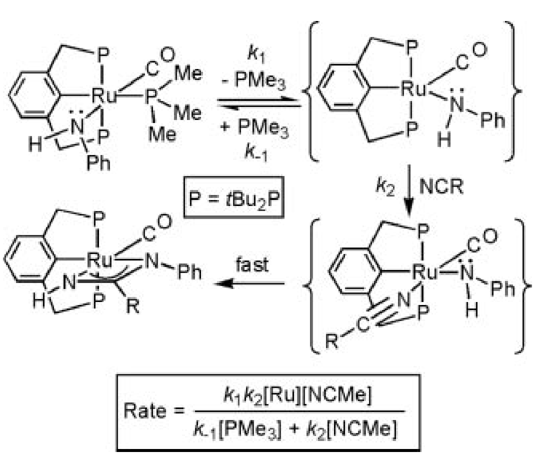
Consistent with experimental observations, DFT calculations {B3LYP/SBK(d)} by Cundari et al. suggest that the conversion of [(PCP′)Ru(CO)NH_2] (PCP′ = model PCP ligand with *t*Bu groups replaced with hydrogen) and dihydrogen to [(PCP′)Ru(CO)(NH_3)H] is exothermic (ΔH = –71 kJ/mol) and exergonic (ΔG = –39 kJ/mol; Scheme 22). In contrast, the 1,2-addition of a C–H bond of methane to [(PCP′)Ru(CO)NH_2] to form [(PCP′)Ru(CO)(NH_3)Me] is calculated to be both endothermic (ΔH = +17 kJ/mol) and endergonic (ΔG = +59 kJ/mol). While the calculated endergonic nature of the methane conversion is not entirely unexpected (due to consumption of gaseous methane), the endothermic nature is perhaps more difficult to rationalize. For example, the enthalpic change from the cleavage of a C–H bond of methane in combination with Ru–C_{Me} and N–H bond formation is calculated to be ca. 134 kJ/mol; however, calculations also reveal that the conversion of the Ru–NH_2 moiety to the dative Ru←NH_3 bond comes at the expense of approximately 167 kJ/mol (Scheme 22)! Thus, in addition to intramolecular competition with the *t*Bu groups, the calculations reveal that the desired intermolecular C–H activation is thermally disfavored, and these results are consistent with both calculations and experimental observations for [TpRuL_2X] (X = amido or hydroxo) systems (see above). These results suggest that *direct observation* of the 1,2-addition of C–H bonds across the bonds of late transition-metal–heteroatomic ligands requires a more favorable change in M–X BDE. Interestingly, Periana et al. have reported that benzene C–H activation by an Ir^{III}–methoxo complex, which is isoelectronic to our Ru^{II} systems, to form methanol and an Ir–phenyl complex is thermally favored.[84]



Scheme 22. Calculations for 1,2-addition of H–H and C–H (methane) across the Ru–NH_2 bond of [(PCP)Ru(CO)NH_2].

In addition to reactivity with nonpolar H–H and C–H bonds the combination of a Lewis acidic metal center and nucleophilic amido ligand of [(PCP)Ru(CO)NHPh] can be utilized to coordinate and activate polar bonds.[27,28] These transformations are of potential relevance to transition-metal-catalyzed polymerization of heterofunctionalized monomers such as carbodiimides, carbon dioxide, lactams, lactones, lactides, isocyanates, epoxides, and aziridines,[6,8,9,113–124] catalytic hydration of nitriles,[125] catalytic transamidation and transesterification,[126–135] and related transformations.

[(PCP)Ru(CO)(PMe_3)NHPh] reacts with nitriles to form the amidinate complexes. Detailed kinetic studies for the reaction with NCMe are consistent with the rate law from the mechanism shown in Scheme 23, which involves dissociation of PMe_3, coordination of acetonitrile, and intramolecular C–N bond formation. For reactions with 10 equiv. of



Scheme 23. Proposed pathway for the conversion of [(PCP)Ru(CO)(PMe_3)NHPh] and nitriles to amidinate complexes, and the corresponding rate law.

acetonitrile and 10 to 25 equiv. of PMe_3, the rate of conversion of complex **1** and acetonitrile to the amidinate complex **2** is inverse first order in concentration of PMe_3, which is consistent with the term in the denominator "$k_{-1}[PMe_3]$" dominating the term "$k_2[NCMe]$" *under the specific conditions of these experiments* with k_{obs} under pseudo-first-order conditions being equal to $k_1k_2[NCMe]/k_{-1}[PMe_3]$. A plot of k_{obs} versus the concentration of NCMe for reactions with 10 equiv. of PMe_3 and between 10 and 50 equiv. of NCMe reveals a first-order dependence on the concentration of NCMe at low concentrations of NCMe while saturation kinetics are apparent at higher concentrations. Thus, in agreement with the observation of an inverse dependence of reaction rate on the concentration of PMe_3 at lower concentrations of NCMe, the term "$k_{-1}[PMe_3]$" is greater than "$k_2[NCMe]$" with the pseudo-first-order rate constant equal to $k_1k_2[NCMe]/k_2[PMe_3]$. At elevated concentrations of NCMe the term "$k_2[NCMe]$" becomes greater than "$k_{-1}[PMe_3]$" with k_{obs} independent of the concentration of NCMe. Monitoring the rate of disappearance of $[(PCP)Ru(CO)(PMe_3)NHPh]$ in the presence of 100 equiv. of acetonitrile with 10, 15, or 20 equiv. of PMe_3 reveals that k_{obs} is independent of the PMe_3 concentration and is equal to $1.29(7) \times 10^{-5}\ s^{-1}$. For reactions that are pseudo-first order in concentration of $[(PCP)Ru(CO)(PMe_3)NHPh]$, rearrangement of the rate law shown in Scheme 23 indicates that a plot of $1/k_{obs}$ versus $[PMe_3]/[NCMe]$ should be linear with the slope equal to k_{-1}/k_1k_2 and the y intercept equal to $1/k_1$ [Equation (3)]. From the plot shown in Figure 2, k_1 was estimated to be $1.8 \times 10^{-5}\ s^{-1}$, and using the value of k_1 and the slope from the plot in Figure 2, the ratio of k_{-1}/k_2 was calculated to be 3; however, small deviations in the slope can result in substantial deviations for the y intercept.

$$1/k_{obs} = \frac{k_{-1}[PMe_3]}{k_1k_2[NCR]} + \frac{1}{k_1} \tag{3}$$

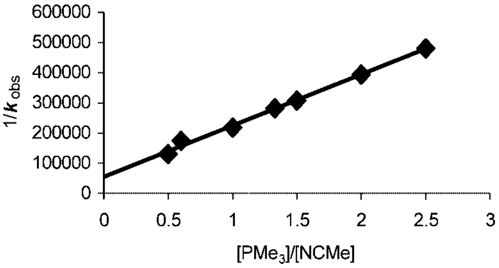
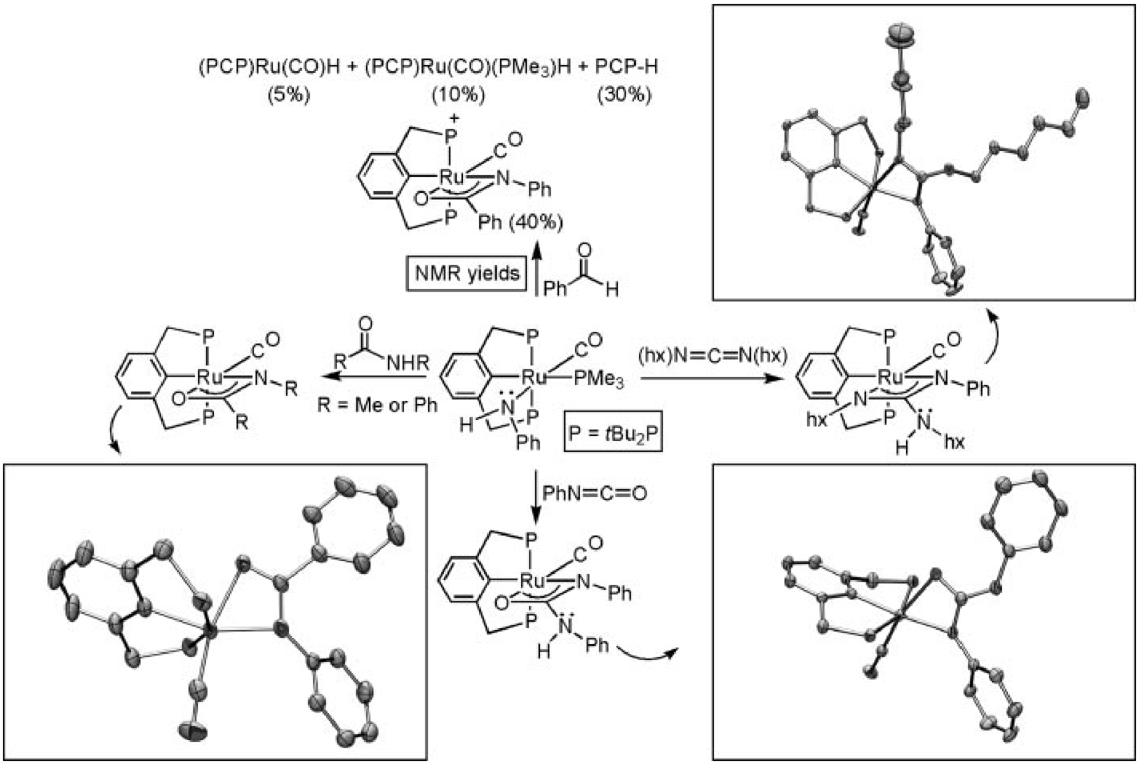


Figure 2. Plot of $1/k_{obs}$ versus $[PMe_3]/[NCMe]$ for the conversion of $[(PCP)Ru(CO)(PMe_3)NHPh]$ and NCMe to the amidinate complex ($R^2 = 0.99$).

$[(PCP)Ru(CO)(PMe_3)NHPh]$ also reacts with carboxamides, isocyanates, carbodiimides, benzaldehyde, and water (Scheme 24). The reactions with carbodiimides, isocyanates, and benzaldehyde follow similar pathways to the reaction of $[(PCP)Ru(CO)(PMe_3)NHPh]$ with nitriles to form κ^2-ligands, which most likely result from intramolecular C–N bond formation. Thus, coordination of polar substrates with Lewis basic sites by the Ru^{II} fragment activates the



Scheme 24. Reactions of $[(PCP)Ru(CO)(PMe_3)NHPh]$ including ORTEPs (30% probability) of three products (with hydrogen atoms and tBu groups omitted).

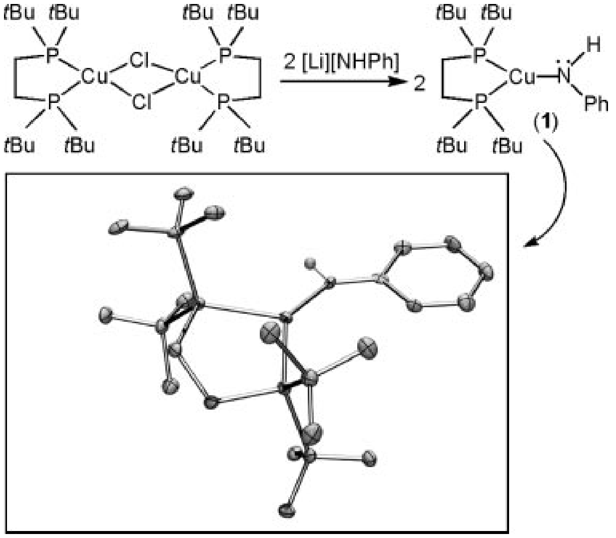
unsaturated molecules toward intramolecular nucleophilic addition by the amido ligand. For benzaldehyde, the amidate complex is isolated in only 40% yield because of side reactions that produce [(PCP)Ru(CO)H] (5%), [(PCP)Ru(CO)(PMe_3)H] (10%), and free PCPH (30%).

Two- and Three-Coordinate Cu^I Systems

Preparation and Characterization of Cu^I Systems

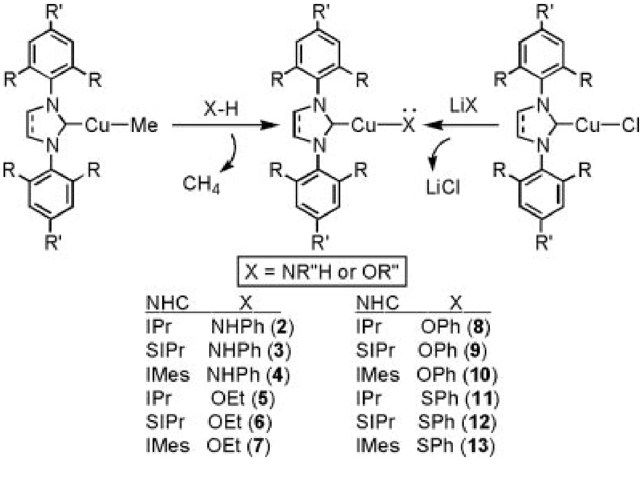
Copper has played an important role in the development of metal-mediated organic synthesis. However, despite the prevalence of anionic heteroatomic ligands with early and middle transition metals, increasing evidence for the highly reactive nature of late transition-metal complexes with anionic heteroatomic ligands and the possibility that Cu–imido complexes are intermediates in Cu-catalyzed olefin aziridination,[3,136–140] the isolation and full characterization of *monomeric* Cu amido complexes was, to the best of our knowledge, unknown prior to our efforts. Multinuclear systems with bridging-amido ligands have been reported,[141–146] including an example of a nonbridging amido that is part of a chelated ligand.[147] In addition, reports of monomeric Cu–alkoxo and Cu–aryloxo complexes are relatively scant.[148–154] Thus, we sought ligand platforms and synthetic routes that would allow the isolation of well-defined *monomeric* Cu^I systems with amido, alkoxo, and related ligands. Sterically bulky ancillary ligands have been incorporated in an effort to inhibit the formation of dimeric or multinuclear Cu systems bridged by the heteroatomic ligands.

Chloride/amido metathesis between [(dtbpe)Cu(μ-Cl)]$_2$ {dtbpe = 1,2-bis(di-*tert*-butylphosphanyl)ethane} and [Li][NHPh] allows the isolation of monomeric [(dtbpe)Cu(NHPh)] (**1**) (Scheme 25).[30] The bulky dtbpe most likely prevents the dimerization of **1** via bridging-anilido ligands, and the strongly donating nature probably prevents reduction of Cu^I to Cu^0 by the lithium amide salt (as is observed for Cu^I systems with more weakly donating aryl–phosphane ligands). The Cu–N$_{amido}$ bond length {1.890(6) Å} of **1** is shorter than that of the corresponding aniline complex [(dtbpe)Cu(NH_2Ph)][OTf] by ca. 0.12 Å. Recently, Johnson et al. have reported a multinuclear Cu$_9$ system that possesses Cu–amido linkages.[147] The three-coordinate d^{10} Cu^I complex **1** has a vacant p orbital of π-symmetry with respect to the Cu–N$_{amido}$ bond, and the amido ligand is oriented for overlap with the Cu-based p orbital. For example, the P–Cu–N–C$_{ipso}$ torsion angle is about 13°, while a torsion angle of 0° would provide an orientation optimized for π-overlap (see Figure 4 below). This amido orientation is approximately perpendicular to that observed by Hillhouse and Mindiola for the closely related d^9 Ni^I complex (dtbpe)Ni{NH(2,6-CHMe$_2$)C$_6$H$_3$}.[155] The phenyl substituent of **1** is also oriented for π-overlap with the amido lone pair (see Figure 4 below).



Scheme 25. Preparation of the monomeric Cu^I–anilido complex [(dtbpe)Cu(NHPh)] (**1**) and its ORTEP diagram (30%).

Similar to the preparation of Cu–methyl complexes by Sadighi et al,[156] we have employed NHC (NHC = N-heterocyclic carbene) ligands to stabilize monomeric two-coordinate Cu^I systems with anionic heteroatomic ligands.[23,25,38] The NHC ligand has been varied between IMes {1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene}, IPr {1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene}, and SIPr {1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene}. Complexes with amido, alkoxo, and aryloxo ligands can be prepared upon reaction of amines or alcohols with [(NHC)Cu(R)] (R = Me or Et) complexes or via metathesis using [(NHC)Cu(Cl)] and lithium salts of the anionic heteroatomic ligand (Scheme 26). For the conversion of [(IPr)Cu(Me)] and aniline to methane and [(IPr)Cu(NHPh)] (**2**) studies suggest that the reaction involves the initial coordination of aniline followed by protonation of the methyl ligand.[25]



Scheme 26. Two routes for the preparation of [(NHC)Cu(X)] complexes (X = NHPh, OEt or OPh).

Several of these complexes have been characterized by single-crystal X-ray diffraction. In all cases the structures reveal approximately linear two-coordinate monomeric systems (Figure 3). We have structurally characterized three Cu–NHPh complexes: [(dtbpe)Cu(NHPh)], [(IPr)-Cu(NHPh)], and [(SIPr)Cu(NHPh)]. In all three systems, the plane of the anilido–phenyl group is approximately coplanar with the H–N–C$_{phenyl}$ plane, which optimizes delocalization of the amido lone pair into the phenyl π* system (Figure 4). Consistent with the amido-to-phenyl electron delocalization, the N$_{amido}$–C$_{phenyl}$ bond lengths {1.351(4) Å to 1.359(3) Å} are shorter than a typical N–C single bond (1.47 Å) and shorter than the corresponding N–C bond of the aniline complex [(dtbpe)Cu(NH$_2$Ph)][PF$_6$], which is 1.444(4) Å.[23,30]

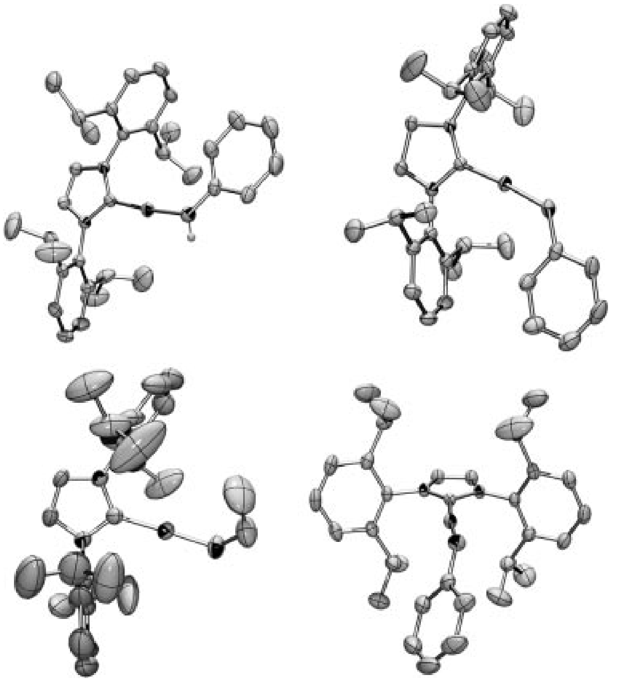


Figure 3. ORTEPs (30%) of representative examples of [(NHC)-Cu(X)] (X = nondative heteroatomic ligand) complexes including [(IPr)Cu(NHPh)] (**2**), [(SIPr)Cu(NHPh)] (**3**), [(IPr)Cu(OEt)] (**5**), and [(IPr)Cu(OPh)] (**8**) (presented from left to right and top to bottom).

Consistent with the solid-state structures that suggest a negligible Cu–N$_{amido}$ π-interaction for the Cu^{I} anilido complexes **1**–**4**, the calculated Kohn–Sham (KS) HOMO of these systems has little Cu character, and that which is present is Cu 3d (p$_{amido}$–d$_{Cu}$ π*) rather than 4p (Figure 5).[23] However, the KS HOMOs possess a substantial contribution from the phenyl π-system.

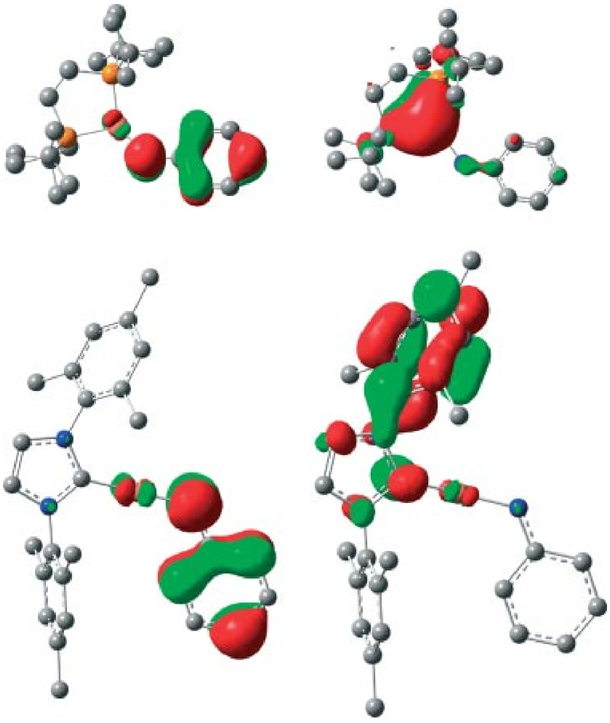


Figure 5. Highest occupied (left) and lowest unoccupied (right) Kohn–Sham orbitals for [(dtbpe)Cu(NHPh)] (**1**) (top pair) and [(IMes)Cu(NHPh)] (**4**) (bottom pair). Orbitals for other NHC Cu^{I}–anilido complexes are similar.

Reactivity of Cu^{I} Systems

As a straight-forward probe of nucleophilic reactivity, the rates of net S$_N$2 reactions of Ru^{II}– and Cu^{I}–anilido complexes with bromoethane to produce the corresponding metal–bromide and ethyl aniline were compared.[23] The complexes [TpRu(PMe$_3$)$_2$NHPh], [(dtbpe)Cu(NHPh)] (**1**), [(IPr)Cu(NHPh)] (**2**), [(SIPr)Cu(NHPh)] (**3**), and [(IMes)-Cu(NHPh)] (**4**) all react with bromoethane with the rate of reaction for Ru being considerably slower than Cu (Scheme 27 and Table 1). Using $\Delta G^{\ddagger}$ values calculated at variable temperatures and calculating rate constants at 298 K, which assumes a constant $\Delta G^{\ddagger}$, reveals that the reactions with the Cu complexes are 55000 to 250000 times more rapid than for the TpRu system. These results suggest

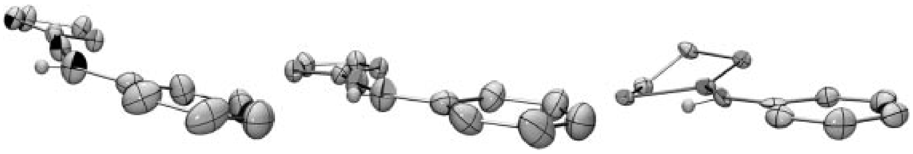
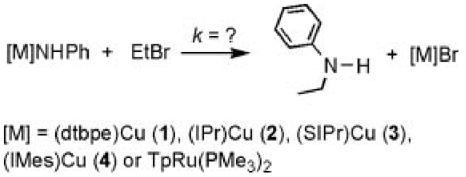


Figure 4. Depiction of the orientation of phenyl substituents of anilido ligands of [(SIPr)Cu(NHPh)] (**3**) (left), [(IPr)Cu(NHPh)] (**2**) (middle), and [(dtbpe)Cu(NHPh)] (**1**) (right) with most atoms removed.

that the $L_nCu–X$ (X = anionic heteroatomic ligand) are highly reactive and indicate that they may be useful for the development of Cu-mediated catalytic organic syntheses.



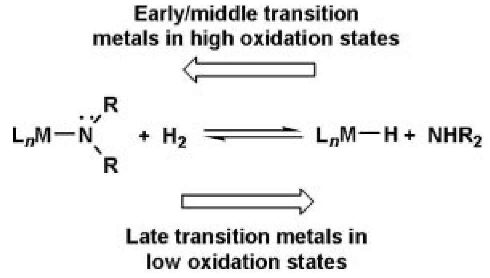
Scheme 27. Nucleophilic substitution reaction of amido complexes with bromoethane.

Table 1. Kinetic data for the reaction of bromoethane with [(IPr)Cu(NHPh)] (**2**), [(SIPr)Cu(NHPh)] (**3**), [(IMes)Cu(NHPh)] (**4**), [(dtbpe)Cu(NHPh)] (**1**), and [TpRu(PMe$_3$)$_2$(NHPh)] (see Scheme 27). All reactions were carried out at room temperature except [TpRu(PMe$_3$)$_2$NHPh], which was performed at 80 °C.

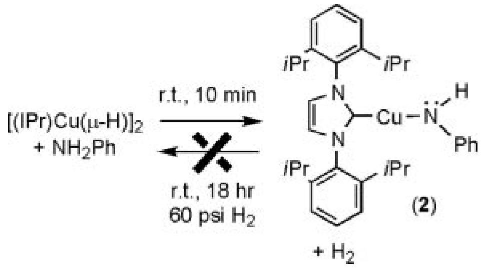
Complex	k_{obs} [s^{-1}]	$t_{1/2}$[a]	$\Delta G^{\ddagger}$[b]
[(dtbpe)Cu(NHPh)]	$5.5(2)\times10^{-4}$	21.0(6)	91
[(IMes)Cu(NHPh)]	$3.3(3)\times10^{-4}$	35(3)	92
[(IPr)Cu(NHPh)]	$2.4(2)\times10^{-4}$	49(4)	93
[(SIPr)Cu(NHPh)]	$1.1(1)\times10^{-4}$	109(8)	94
[TpRu(PMe$_3$)$_2$(NHPh)]	$8.6(3)\times10^{-6}$	22[c]	121

[a] Minutes. [b] kJ/mol. [c] Hours.

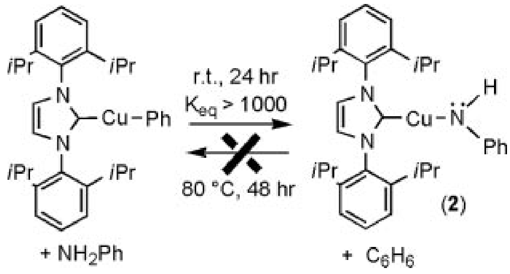
In general, the thermodynamics of reactions between transition-metal amido (and related) complexes and dihydrogen to form metal–hydride complexes and free amines appear to be dependent upon the identity of the metal center. Early and middle transition-metal systems in relatively high oxidation states tend to favor metal–amido/dihydrogen while late transition-metal systems in low oxidation states exhibit a trend toward the metal–hydride/free amine (Scheme 28 and see below for examples). This trend can be rationalized by increased metal–amido bond energies due to amido-to-metal π-donation for metal centers in relatively high oxidation states. For late transition-metal centers in low oxidation states the π-bonding is disrupted and the M–N$_{amido}$ BDE is presumably decreased relative to systems in which π-bonding is present. The [(NHC)Cu(NHPh)] systems exhibit reactivity that contrasts these general trends. For example, [(IPr)Cu(NHPh)] (**2**) does not react with dihydrogen, while [[(IPr)Cu(μ-H)]$_2$] rapidly reacts with aniline to form dihydrogen and complex **2** (Scheme 29), reactivity which is consistent with an *early* transition-metal system. Furthermore, [(IPr)Cu(Ph)] reacts with aniline to produce benzene and [(IPr)Cu(NHPh)] with an equilibrium constant > 1000 (Scheme 30).



Scheme 28. Equilibrium trends between metal–amido/dihydrogen and metal–hydride/amine based on the identity and oxidation state of the transition metal.



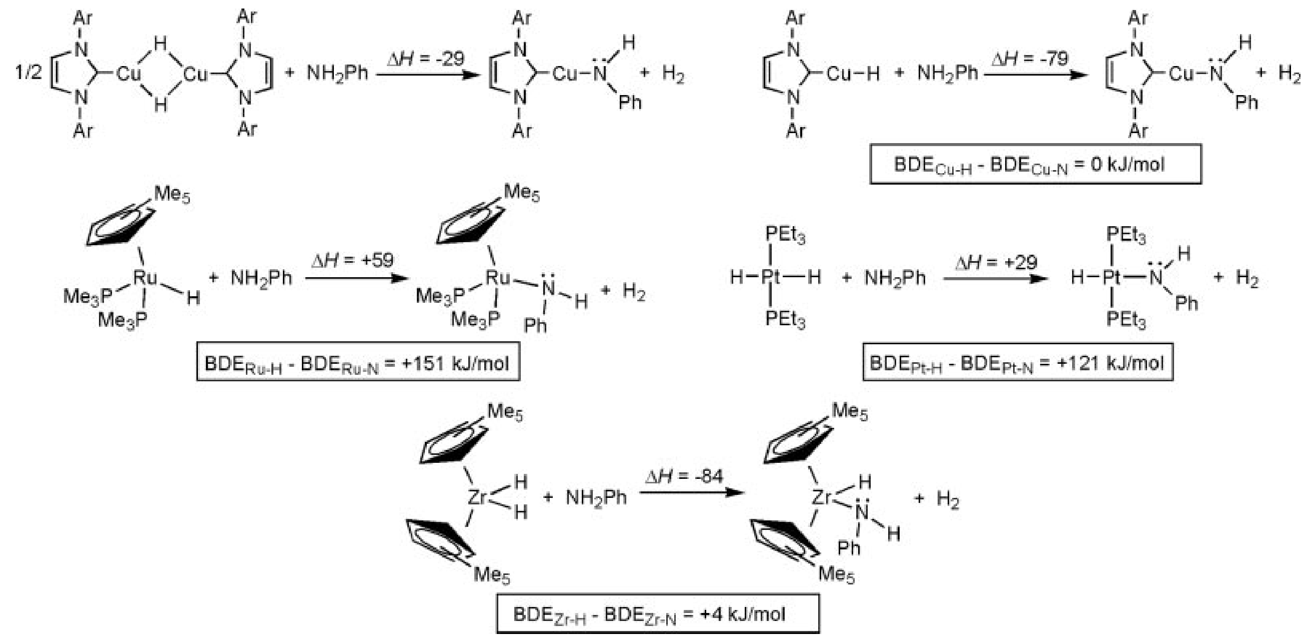
Scheme 29. Observed equilibrium for Cu–hydride/aniline and Cu–anilido/dihydrogen.



Scheme 30. Observed equilibrium for Cu–phenyl/aniline and Cu–anilido/benzene.

Examples of systems that follow the relative thermodynamics for reactions of amido complexes and dihydrogen (see paragraph above) include the conversion of [Cp*Ru(PMe$_3$)$_2$(NPh$_2$)] (Cp* = pentamethylcyclopentadienyl) and dihydrogen to free amine and Ru–hydride complexes,[157] reaction of [(PCP)Ru(CO)NH$_2$] and dihydrogen to produce free ammonia and Ru–hydride complexes,[29] release of aniline and formation of a Pt–dihydride upon combination of *trans*-[(PEt$_3$)$_2$Pt(H)NHPh] and dihydrogen,[158] and reaction of Cp*$_2$M(H)$_2$ (M = Zr or Hf) with ammonia to produce dihydrogen and the corresponding parent amido complexes.[159] In contrast to the late transition metal and low oxidation state Ru^{II} and Pt^{II} systems, complex **2** favors the Cu–amido and dihydrogen. The conversion of [(IPr)Cu(Ph)] and aniline to [(IPr)Cu(NHPh)] (**2**) and benzene also contrasts reactivity observed with another late transition-metal anilido complex. [(PCP)Ir(H)(Ph)] and free NH$_2$Ph are thermally favored over [(PCP)Ir(H)(NHPh)] and free C$_6$H$_6$ with K_{eq} = 105.[160] In contrast, the [(IPr)Cu^I] fragment demonstrates a thermodynamic propensity for the formation of a Cu–NHPh bond and free benzene, which seems to suggest a shift in the relative magnitude of M–H/M–N$_{anilido}$ and M–C$_{phenyl}$/M–N$_{anilido}$ BDEs from established norms.

Analysis of the Cu–N$_{amido}$ BDE using B3LYP/CEP-31G(d) calculations provides a rationale for the observed equilibria. For [(IPr)Cu(NHPh)], the Cu–N$_{amido}$ BDE is



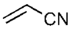
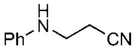
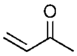
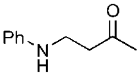
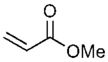
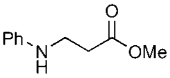
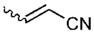
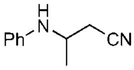
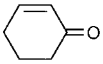
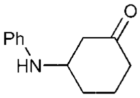
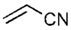
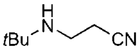
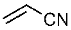
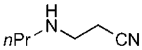
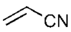
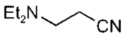
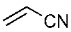
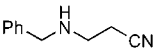
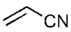
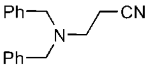
Scheme 31. DFT calculated changes in enthalpy (kJ/mol) for conversion of transition-metal–hydride complexes and aniline to transition-metal–anilido complexes and dihydrogen.

calculated to be 364 kJ/mol. In comparison, the calculated $M–N_{amido}$ BDEs of $[Cp^*_2Zr(NHPh)(H)]$ (284 kJ/mol; Cp* = pentamethylcyclopentadienyl), *trans*-$[(Et_3P)_2Pt(H)(NHPh)]$ (180 kJ/mol), and $[Cp^*Ru(PMe_3)_2NHPh]$ (146 kJ/mol) are substantially weaker (Scheme 31).[23] The difference in $M–N_{amido}$ BDE for the Zr and Pt/Ru systems is easily rationalized by, at least in part, the π-bonding component of the $Zr–N_{amido}$ bond, which is likely to be negligible for Pt^{II} and octahedral Ru^{II}. The large BDE for the $Cu–N_{amido}$ is more difficult to rationalize, and future studies will address whether this is an anomaly or a central feature of Cu^{I} systems with anionic heteroatomic ligands. *At this point it can be stated that in terms of ground-state energetics the Cu–NHPh systems appear similar to early/middle transition-metal systems in high oxidation states. In contrast, the reactivity of Cu–NHPh related systems is more reminiscent of highly nucleophilic complexes in low oxidation states.*

The hydroamination or hydroalkoxylation of electron-deficient olefins under acidic or basic conditions is known; however, such reactions typically require relatively harsh conditions, including high temperatures that are often incompatible with functional groups and do not allow the control of regio-, chemo- or stereoselectivity.[161] In contrast, transition-metal-catalyzed reactions offer the promise of more ambient conditions and greater control over product selectivity. For example, both early and late transition-metal complexes as well as lanthanide systems have been developed for olefin hydroamination, with many of these systems limited to specific substrates or more facile intramolecular reactions.[162–167]

Copper catalysts for the enantioselective conjugate addition of carbon-based nucleophiles have been reported,[168] and we have become interested in related reactions for hetero-conjugate additions. $Cu(OTf)_2$ systems have been recently reported to catalyze the hydroamination of olefins.[169] The [(NHC)Cu(X)] and [(dtbpe)Cu(X)] (X = anionic heteroatomic ligand) complexes catalyze the conjugate

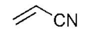
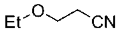
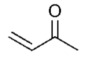
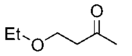
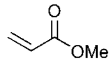
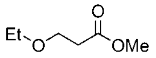
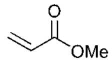
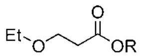
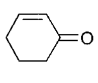
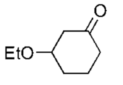
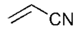
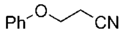
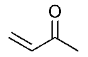
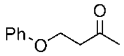
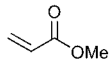
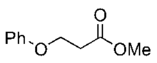
Table 2. Hydroamination of electron-deficient olefins catalyzed by [(IPr)Cu(NHPh)] (**2**) and uncatalyzed control experiments.

Olefin	Nucleophile	Time[a]	% Conv.[b]	Product	Control expt.[c]
	$PhNH_2$	12 h	>95		0
	$PhNH_2$	5 min	>95		0
	$PhNH_2$	19 h	55		0
	$PhNH_2$	40 h[d]	54		0[d]
	$PhNH_2$	3 h	85		0
	$tBuNH_2$	22 h	57		0
	$nPrNH_2$	1 h	>95		0
	Et_2NH	9 h	>95		14
	$PhCH_2NH_2$	5 min	>95		0
	$(PhCH_2)_2NH$	90 h	60		0

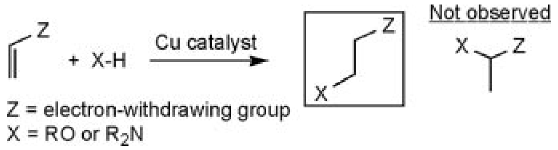
[a] All reactions performed with 5 mol-% catalyst at room temperature in C_6D_6. [b] % Conversions determined by ^1H NMR spectroscopy. [c] Control experiments reported after similar reaction times and given in % conversion. [d] Reaction conducted at 80 °C.

addition of N–H and O–H bonds across the C=C bonds of electron-deficient olefins (Table 2 and Table 3).[37] In all examples studied the reactions are regioselective for the "anti-Markovnikov" product (Scheme 32). Under conditions identical to catalysis some of the substrates undergo transformation in the absence of a Cu catalyst; however, comparison of reaction rates clearly indicates that the Cu complexes are serving as catalysts. For comparison, Table 2 and Table 3 depict results from control experiments under identical reaction conditions and times for the Cu-catalyzed transformations.

Table 3. Hydroalkoxylation and hydroaryloxylation of olefins and uncatalyzed control reactions.

[Cu]	Olefin	Nucleophile	Temp (°C)	Time[a]	% Conv.[b]	Products	Control expt.[c]
5		EtOH	r.t.	20 h	93		0%
5		EtOH	r.t.	7 h	>95		0%
5, 6		EtOH	r.t.	--	0[d]		0%
5		EtOH	r.t.	1 h	>95[e]	 R = Me, Et	0%
6		EtOH	r.t.	4.5 h	25		0%
8		PhOH	80	40 h	64		0%
8		PhOH	80	52 h	60		0%
8		PhOH	120	235 h	40[f]		0%

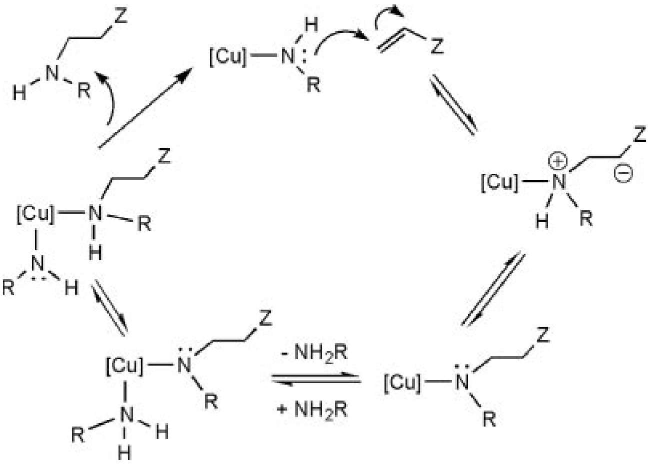
[a] All reactions performed with 5 mol-% catalyst in C_6D_6. [b] % Conversions determined by ^1H NMR spectroscopy. [c] Control experiments are reported after similar reaction times to catalyzed variants and are given in % conversion. [d] Transesterification observed. [e] Addition of *t*BuNC (1 equiv. based on EtOH) allows observation of hydroalkoxylation. [f] Approximately 10% transesterification also observed.



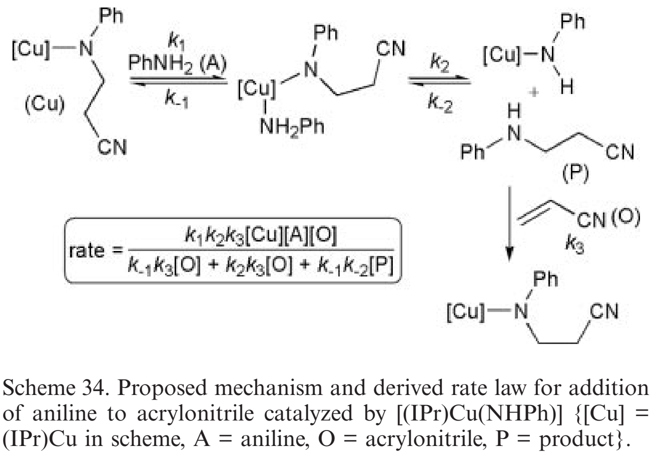
Scheme 32. Cu-catalyzed additions of N–H and O–H across C=C bonds of electron-deficient olefins are selective for the "anti-Markovnikov" products.

In general, reactions that incorporate stronger nucleophiles react more rapidly. For example, among amines and alcohols, catalysis is generally slower and less broad in scope for alcohols than for amines. Amongst a series of amines, alkylamines react more rapidly than arylamines. Table 2 shows comparative reactions for aniline and alkylamines with acrylonitrile. The exception to this generalization is the sterically bulky $tBuNH_2$, which reacts more slowly with acrylonitrile than aniline.

We have recently proposed a reaction mechanism for the copper-catalyzed hydroamination (and related reactions) of electron-deficient olefins in which initial intermolecular nucleophilic addition of the amido ligand to the olefin produces an unobserved zwitterionic intermediate.[38] Subsequent proton transfer yields a new copper amido complex and reaction with aniline (presumably via coordination to Cu) yields a free organic product and regenerates the original Cu system (Scheme 33). The hydroalkoxylation reactions are proposed to proceed through a similar mechanism with the exception that product formation likely originates from the zwitterionic intermediate or a linkage isomer Cu–alkyl complex. The relative rate of catalysis is consistent with a nucleophilic addition pathway. For example, reactivity decreases in the order N(H)*n*Pr > N(H)Ph > OEt > OPh for reactions with acrylonitrile. It is also possible that olefin coordination precedes N–C or O–C bond formation; however, this pathway seems unlikely as it does not necessarily account for the observed anti-Markovnikov regioselectivity. Furthermore, the addition of coordinating *t*BuNC slightly accelerates the rate of catalysis for the addition of aniline to acrylonitrile. If olefin coordination precedes N–C bond formation, competition for coordination between acrylonitrile and the isocyanide would be anticipated to re-



Scheme 33. Proposed catalytic cycle for Cu–amido catalytic hydroamination reactions.



$$\text{rate} = \frac{k_1k_2k_3[\text{Cu}][\text{A}][\text{O}]}{k_{-1}k_3[\text{O}] + k_2k_3[\text{O}] + k_{-1}k_{-2}[\text{P}]}$$

Scheme 34. Proposed mechanism and derived rate law for addition of aniline to acrylonitrile catalyzed by [(IPr)Cu(NHPh)] {[Cu] = (IPr)Cu in scheme, A = aniline, O = acrylonitrile, P = product}.

duce the rate of catalysis. In addition, reaction of [(IPr)Cu(NHPh)] and acrylonitrile produces [(IPr)CuN(Ph)(CH_2CH_2CN)]. Finally, kinetic studies (using initial rates) for the addition of aniline to acrylonitrile reveal that the catalysis is first order in Cu catalyst and aniline, 0.7 order in acrylonitrile, and inhibited by the presence of organic product. These results are consistent with the proposed mechanism and derived rate law shown in Scheme 34 in which the rate-determining step is the reaction with acrylonitrile.[37]

Summary and Future Outlook

Work presented herein and reported by others have demonstrated that anionic heteroatomic ligands coordinated to metal centers in low oxidation states results in highly reactive heteroatomic ligands. Such substrates are potentially useful for catalytic polymerizations as well as transformations of small molecules. Using well-defined Ru^{II} and Cu^{I} systems, we have demonstrated controlled stoichiometric and catalytic N–C bond formation using polar substrates, N–C and O–C bond formation using olefins as well as metal-mediated activation of dihydrogen and carbon–hydrogen bonds. Mechanistic studies indicate that, in some cases, the combination of a Lewis acidic metal center and nucleophilic/basic heteroatomic ligand form the foundation of these transformations.

Future efforts will be directed toward continued development of catalysts using these, and related, complexes. For example, we are presently pursuing strategies to extend the scope and selectivity of Cu-catalyzed hydroamination and hydroalkoxylation reactions as well as to develop other methods of N–C and O–C bond formation using these reactive Cu systems. Furthermore, efforts toward using the 1,2-addition of C–H bonds across metal–heteroatom bonds as a key step for C–H functionalization sequences are continuing. In terms of the reactivity of anionic heteroatomic ligands, future work will be directed toward an increased understanding of the impact of ancillary ligands, metal identity, and metal oxidation state on accessible reactions.

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[1] K. A. Jørgensen, *Chem. Rev.* **1989**, *89*, 431.
[2] J. P. Collman, X. Zhang, V. J. Lee, E. S. Uffelman, J. I. Brauman, *Science* **1993**, *261*, 1404.
[3] P. Müller, C. Fruit, *Chem. Rev.* **2003**, *103*, 2905.
[4] H. C. Kolb, M. S. VanNieuwenhze, K. B. Sharpless, *Chem. Rev.* **1994**, *94*, 2483.
[5] Q.-H. Xia, H.-Q. Ge, C.-P. Ye, Z.-M. Liu, K.-X. Su, *Chem. Rev.* **2005**, *105*, 1603.
[6] K. Shibayama, S. W. Seidel, B. M. Novak, *Macromolecules* **1997**, *30*, 3159.
[7] H.-Z. Tang, Y. Lu, G. Tian, M. D. Capracotta, B. M. Novak, *J. Am. Chem. Soc.* **2004**, *126*, 3722.
[8] J. Cheng, T. J. Deming, *J. Am. Chem. Soc.* **2001**, *123*, 9457.
[9] D. R. Moore, M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2003**, *125*, 11911.
[10] W. A. Nugent, J. M. Mayer, *Metal-Ligand Multiple Bonds*, John Wiley & Sons, New York, **1988**.
[11] R. R. Schrock, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2003**, *42*, 4592.
[12] J. D. Soper, B. K. Bennett, S. Lovell, J. M. Mayer, *Inorg. Chem.* **2001**, *40*, 1888.
[13] J. M. Mayer, *Comments Inorg. Chem.* **1988**, *8*, 125.
[14] K. G. Caulton, *New J. Chem.* **1994**, *18*, 25.
[15] R. G. Bergman, *Polyhedron* **1995**, *14*, 3227.
[16] J. R. Fulton, A. W. Holland, D. J. Fox, R. G. Bergman, *Acc. Chem. Res.* **2002**, *35*, 44.
[17] P. L. Holland, R. A. Andersen, R. G. Bergman, *Comments Inorg. Chem.* **1999**, *21*, 115.
[18] H. E. Bryndza, W. Tam, *Chem. Rev.* **1988**, *88*, 1163.
[19] M. D. Fryzuk, C. D. Montgomery, *Coord. Chem. Rev.* **1989**, *95*, 1.
[20] P. R. Sharp, *Comments Inorg. Chem.* **1999**, *21*, 85.
[21] P. R. Sharp, *J. Chem. Soc., Dalton Trans.* **2000**, 2647.
[22] D. M. Roundhill, *Chem. Rev.* **1992**, *92*, 1.
[23] L. A. Goj, E. D. Blue, S. A. Delp, T. B. Gunnoe, T. R. Cundari, A. W. Pierpont, J. L. Petersen, P. D. Boyle, *Inorg. Chem.* **2006**, *45*, 9032.
[24] Y. Feng, M. Lail, N. A. Foley, T. B. Gunnoe, K. A. Barakat, T. R. Cundari, J. L. Petersen, *J. Am. Chem. Soc.* **2006**, *128*, 7982.
[25] L. A. Goj, E. D. Blue, C. Munro-Leighton, T. B. Gunnoe, J. L. Petersen, *Inorg. Chem.* **2005**, *44*, 8647.
[26] Y. Feng, M. Lail, K. A. Barakat, T. R. Cundari, T. B. Gunnoe, J. L. Petersen, *J. Am. Chem. Soc.* **2005**, *127*, 14174.
[27] J. Zhang, T. B. Gunnoe, J. L. Petersen, *Inorg. Chem.* **2005**, *44*, 2895.
[28] J. Zhang, T. B. Gunnoe, P. D. Boyle, *Organometallics* **2004**, *23*, 3094.
[29] D. Conner, K. N. Jayaprakash, T. R. Cundari, T. B. Gunnoe, *Organometallics* **2004**, *23*, 2724.
[30] E. D. Blue, A. Davis, D. Conner, T. B. Gunnoe, P. D. Boyle, P. S. White, *J. Am. Chem. Soc.* **2003**, *125*, 9435.
[31] D. Conner, K. N. Jayaprakash, M. B. Wells, S. Manzer, T. B. Gunnoe, P. D. Boyle, *Inorg. Chem.* **2003**, *42*, 4759.
[32] D. Conner, K. N. Jayaprakash, T. B. Gunnoe, P. D. Boyle, *Organometallics* **2002**, *21*, 5265.
[33] D. Conner, K. N. Jayaprakash, T. B. Gunnoe, P. D. Boyle, *Inorg. Chem.* **2002**, *41*, 3042.
[34] K. N. Jayaprakash, D. Conner, T. B. Gunnoe, *Organometallics* **2001**, *20*, 5254.
[35] K. N. Jayaprakash, T. B. Gunnoe, P. D. Boyle, *Inorg. Chem.* **2001**, *40*, 6481.
[36] Y. Feng, T. B. Gunnoe, T. V. Grimes, T. R. Cundari, *Organometallics* **2006**, *25*, 5456.
[37] C. Munro-Leighton, S. A. Delp, E. D. Blue, T. B. Gunnoe, *Organometallics* **2007**, ASAP.
[38] C. Munro-Leighton, E. D. Blue, T. B. Gunnoe, *J. Am. Chem. Soc.* **2006**, *128*, 1446.
[39] S. Trofimenko, *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, **1999**.
[40] J. M. Boncella, T. M. Eve, B. Rickman, K. A. Abboud, *Polyhedron* **1998**, *17*, 725.
[41] J. F. Hartwig, R. A. Andersen, R. G. Bergman, *Organometallics* **1991**, *10*, 1875.
[42] P. L. Holland, R. A. Andersen, R. G. Bergman, J. Huang, S. P. Nolan, *J. Am. Chem. Soc.* **1997**, *119*, 12800.

[43] T. K. G. Erikson, J. C. Bryan, J. M. Mayer, *Organometallics* **1988**, *7*, 1930.

[44] J. R. Fulton, S. Sklenak, M. W. Bouwkamp, R. G. Bergman, *J. Am. Chem. Soc.* **2002**, *124*, 4722.

[45] A. W. Holland, R. G. Bergman, *J. Am. Chem. Soc.* **2002**, *124*, 14684.

[46] D. J. Fox, R. G. Bergman, *Organometallics* **2004**, *23*, 1656.

[47] K. Abdur-Rashid, T. P. Fong, B. Greaves, D. G. Gusev, J. G. Hinman, S. E. Landau, A. J. Lough, R. J. Morris, *J. Am. Chem. Soc.* **2000**, *122*, 9155.

[48] F. G. Bordwell, *Acc. Chem. Res.* **1988**, *21*, 456.

[49] J. M. Mayer, *Acc. Chem. Res.* **1998**, *31*, 441.

[50] J. R. Bryant, J. E. Taves, J. M. Mayer, *Inorg. Chem.* **2002**, *41*, 2769.

[51] A. S. Larsen, K. Wang, M. A. Lockwood, G. L. Rice, T.-J. Won, S. Lovell, M. Sadílek, F. Turecek, J. M. Mayer, *J. Am. Chem. Soc.* **2002**, *124*, 10112.

[52] C. R. Goldsmith, R. T. Jonas, T. D. P. Stack, *J. Am. Chem. Soc.* **2002**, *124*, 83.

[53] R. T. Jonas, T. D. P. Stack, *J. Am. Chem. Soc.* **1997**, *119*, 8566.

[54] M. J. Baldwin, V. L. Pecoraro, *J. Am. Chem. Soc.* **1996**, *118*, 11325.

[55] M. Taki, S. Itoh, S. Fukuzumi, *J. Am. Chem. Soc.* **2001**, *123*, 6203.

[56] S. Ogo, S. Wada, Y. Watanabe, M. Iwase, A. Wada, M. Harata, K. Jitsukawa, H. Masuda, H. Einaga, *Angew. Chem. Int. Ed.* **1998**, *37*, 2102.

[57] H. V. Obias, Y. Lin, N. N. Murthy, E. Pidcock, E. I. Solomon, M. Ralle, N. J. Blackburn, Y.-M. Neuhold, A. D. Zuberbühler, K. D. Karlin, *J. Am. Chem. Soc.* **1998**, *120*, 12960.

[58] C. A. Sandoval, T. Ohkuma, K. Muñiz, R. Noyori, *J. Am. Chem. Soc.* **2003**, *125*, 13490.

[59] K. Murata, H. Konishi, M. Ito, T. Ikariya, *Organometallics* **2002**, *21*, 253.

[60] R. Guo, R. H. Morris, D. Song, *J. Am. Chem. Soc.* **2005**, *127*, 516.

[61] S. E. Clapham, A. Hadzovic, R. H. Morris, *Coord. Chem. Rev.* **2004**, *248*, 2201.

[62] K. Abdur-Rashid, S. E. Clapham, A. Hadzovic, J. N. Harvey, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **2002**, *124*, 15104.

[63] K. Abdur-Rashid, M. Faatz, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **2001**, *123*, 7473.

[64] Z. M. Heiden, T. B. Rauchfuss, *J. Am. Chem. Soc.* **2006**, *128*, 13048.

[65] M. D. Fryzuk, C. D. Montgomery, S. J. Rettig, *Organometallics* **1991**, *10*, 467.

[66] P. J. Walsh, F. J. Hollander, R. G. Bergman, *J. Am. Chem. Soc.* **1988**, *110*, 8729.

[67] H. M. Hoyt, F. E. Michael, R. G. Bergman, *J. Am. Chem. Soc.* **2004**, *126*, 1018.

[68] J. L. Bennett, P. T. Wolczanski, *J. Am. Chem. Soc.* **1997**, *119*, 10696.

[69] C. C. Cummins, S. M. Baxter, P. T. Wolczanski, *J. Am. Chem. Soc.* **1988**, *110*, 8731.

[70] J. D. With, A. D. Horton, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 903.

[71] C. P. Schaller, P. T. Wolczanski, *Inorg. Chem.* **1993**, *32*, 131.

[72] C. P. Schaller, J. B. Bonanno, P. T. Wolczanski, *J. Am. Chem. Soc.* **1994**, *116*, 4133.

[73] C. P. Schaller, C. C. Cummins, P. T. Wolczanski, *J. Am. Chem. Soc.* **1996**, *118*, 591.

[74] D. F. Schafer II, P. T. Wolczanski, *J. Am. Chem. Soc.* **1998**, *120*, 4881.

[75] T. R. Cundari, *J. Am. Chem. Soc.* **1992**, *114*, 10557.

[76] T. R. Cundari, T. R. Klinckman, P. T. Wolczanski, *J. Am. Chem. Soc.* **2002**, *124*, 1481.

[77] L. M. Slaughter, P. T. Wolczanski, T. R. Klinckman, T. R. Cundari, *J. Am. Chem. Soc.* **2000**, *122*, 7953.

[78] S. L. Buchwald, A. R. Muci, in *Topics in Current Chemistry* (Ed.: N. Miyaura), vol. 219, *Cross-Coupling Reactions: A Practical Guide*, chapter *Practical Palladium Catalysts for C–N and C–O Bond Formation*, Springer, Berlin, **2002**, pp. 131–209.

[79] J. F. Hartwig, in *Modern Amination Methods* (Ed.: A. Ricci), Wiley-VCH, Weinheim, **2000**, pp. 195.

[80] J. P. Wolfe, S. Wagaw, J.-F. Marcoux, S. L. Buchwald, *Acc. Chem. Res.* **1998**, *31*, 805.

[81] S. L. Buchwald, J. P. Wolfe, M. Palucki, Massachusetts Institute of Technology, USA, US Patent 6,166,226, Dec. 26, **2000**, p. 1.

[82] J. F. Hartwig, *Angew. Chem. Int. Ed.* **1998**, *37*, 2046.

[83] B. L. Conley, S. K. Ganesh, J. M. Gonzales, W. J. Tenn, K. J. H. Young, J. Oxgaard, W. A. Goddard III, R. A. Periana, *J. Am. Chem. Soc.* **2006**, *128*, 9018.

[84] W. J. Tenn III, K. J. H. Young, G. Bhalla, J. Oxgaard, W. A. Goddard III, R. A. Periana, *J. Am. Chem. Soc.* **2005**, *127*, 14172.

[85] D. L. Davies, S. M. A. Donald, S. A. Macgregor, *J. Am. Chem. Soc.* **2005**, *127*, 13754.

[86] D. L. Davies, S. M. A. Donald, O. Al-Duaij, S. A. Macgregor, M. Pölleth, *J. Am. Chem. Soc.* **2006**, *128*, 4210.

[87] P. E. M. Siegbahn, R. H. Crabtree, *J. Am. Chem. Soc.* **1996**, *118*, 4442.

[88] S. N. Brown, J. M. Mayer, *Organometallics* **1995**, *14*, 2951.

[89] S. N. Brown, J. M. Mayer, *J. Am. Chem. Soc.* **1996**, *118*, 12119.

[90] M. Lail, C. M. Bell, D. Conner, T. R. Cundari, T. B. Gunnoe, J. L. Petersen, *Organometallics* **2004**, *23*, 5007.

[91] K. A. Pittard, J. P. Lee, T. R. Cundari, T. B. Gunnoe, J. L. Petersen, *Organometallics* **2004**, *23*, 5514.

[92] B. A. Arndtsen, R. G. Bergman, *Science* **1995**, *270*, 1970.

[93] A. G. Wong-Foy, G. Bhalla, X. Y. Liu, R. A. Periana, *J. Am. Chem. Soc.* **2003**, *125*, 14292.

[94] C. N. Iverson, C. A. G. Carter, R. T. Baker, J. D. Scollard, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2003**, *125*, 12674.

[95] D. M. Tellers, R. G. Bergman, *J. Am. Chem. Soc.* **2000**, *122*, 954.

[96] A. A. Bengali, B. A. Arndtsen, P. M. Burger, R. H. Schultz, B. H. Weiller, K. R. Kyle, C. B. Moore, R. G. Bergman, *Pure App. Chem.* **1995**, *67*, 281.

[97] R. G. Bergman, *Science* **1984**, *223*, 902.

[98] T. O. Northcutt, D. D. Wick, A. J. Vetter, W. D. Jones, *J. Am. Chem. Soc.* **2001**, *123*, 7257.

[99] W. D. Jones, F. J. Feher, *Acc. Chem. Res.* **1989**, *22*, 91.

[100] U. Fekl, K. I. Goldberg, *J. Am. Chem. Soc.* **2002**, *124*, 6804.

[101] U. Fekl, W. Kaminsky, K. I. Goldberg, *J. Am. Chem. Soc.* **2003**, *125*, 15286.

[102] D. D. Wick, K. I. Goldberg, *J. Am. Chem. Soc.* **1997**, *119*, 10235.

[103] K. I. Goldberg, A. S. Goldman, in *ACS Symposium Series*, vol. 885, American Chemical Society, Washington, DC, **2004**.

[104] K. Krogh-Jespersen, M. Czerw, K. Zhu, B. Singh, M. Kanzelberger, N. Darji, P. D. Achord, K. B. Renkema, A. S. Goldman, *J. Am. Chem. Soc.* **2002**, *124*, 10797.

[105] S. Reinartz, P. S. White, M. Brookhart, J. L. Templeton, *Organometallics* **2000**, *19*, 3854.

[106] C. N. Kostelansky, M. G. MacDonald, P. S. White, J. L. Templeton, *Organometallics* **2006**, *25*, 2993.

[107] M. Lail, B. N. Arrowood, T. B. Gunnoe, *J. Am. Chem. Soc.* **2003**, *125*, 7506.

[108] W. H. Lam, G. Jia, Z. Lin, C. P. Lau, O. Eisenstein, *Chem. Eur. J.* **2003**, *9*, 2775.

[109] T. C. Flood, K. E. Janak, M. Iimura, H. Zhen, *J. Am. Chem. Soc.* **2000**, *122*, 6783.

[110] S. M. Ng, W. H. Lam, C. C. Mak, C. W. Tsang, G. Jia, Z. Lin, C. P. Lau, *Organometallics* **2003**, *22*, 641.

[111] M. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759.

[112] M. D. Fryzuk, M. J. Petrella, B. O. Patrick, *Organometallics* **2005**, *24*, 5440.

[113] H.-Z. Tang, P. D. Boyle, B. M. Novak, *J. Am. Chem. Soc.* **2005**, *127*, 2136.

[114] T. J. Deming, B. M. Novak, *J. Am. Chem. Soc.* **1993**, *115*, 9101.
[115] T. E. Patten, B. M. Novak, *Macromolecules* **1993**, *26*, 436.
[116] L. Jia, H. Sun, J. T. Shay, A. M. Allgeier, S. D. Hanton, *J. Am. Chem. Soc.* **2002**, *124*, 7282.
[117] J. N. Cha, G. D. Stucky, D. E. Morse, T. J. Deming, *Nature* **2000**, *403*, 289.
[118] S. W. Seidel, T. J. Deming, *Macromolecules* **2003**, *36*, 969.
[119] D. J. Darensbourg, M. W. Holtcamp, *Coord. Chem. Rev.* **1996**, *153*, 155.
[120] I. C. Stewart, C. C. Lee, R. G. Bergman, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 17616.
[121] L. R. Rieth, D. R. Moore, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2002**, *124*, 15239.
[122] R. Bizzarri, F. Chiellini, R. Solaro, E. Chiellini, S. Cammas-Marion, P. Guerin, *Macromolecules* **2002**, *35*, 1215.
[123] S. Bloembergen, D. A. Holden, T. L. Bluhm, G. K. Hamer, R. H. Marchessault, *Macromolecules* **1989**, *22*, 1663.
[124] E. Chiellini, R. Solaro, *Adv. Mater.* **1996**, *8*, 305.
[125] K. L. Breno, M. D. Pluth, D. R. Tyler, *Organometallics* **2003**, *22*, 1203.
[126] J. Otera, *Chem. Rev.* **1993**, *93*, 1449.
[127] M. G. Stanton, M. R. Gagné, *J. Am. Chem. Soc.* **1997**, *119*, 5075.
[128] M. G. Stanton, M. R. Gagné, *J. Org. Chem.* **1997**, *62*, 8240.
[129] M. G. Stanton, C. B. Allen, R. M. Kissling, A. L. Lincoln, M. R. Gagné, *J. Am. Chem. Soc.* **1998**, *120*, 5981.
[130] R. M. Kissling, M. R. Gagné, *J. Org. Chem.* **2001**, *66*, 9005.
[131] W. Y. Mills, R. M. Kissling, M. R. Gagné, *Chem. Commun.* **1999**, 1713.
[132] S. E. Eldred, D. A. Stone, S. H. Gellman, S. S. Stahl, *J. Am. Chem. Soc.* **2003**, *125*, 3422.
[133] D. A. Kissounko, I. A. Guzei, S. H. Gellman, S. S. Stahl, *Organometallics* **2005**, *24*, 5208.
[134] J. M. Hoerter, K. M. Otte, S. H. Gellman, S. S. Stahl, *J. Am. Chem. Soc.* **2006**, *128*, 5177.
[135] C. Han, J. P. Lee, E. Lobkovsky, J. A. Porco Jr, *J. Am. Chem. Soc.* **2005**, *127*, 10039.
[136] D. A. Evans, M. M. Faul, M. T. Bilodeau, *J. Org. Chem.* **1991**, *56*, 6744.
[137] D. A. Evans, M. M. Faul, M. T. Bilodeau, B. A. Anderson, D. M. Barnes, *J. Am. Chem. Soc.* **1993**, *115*, 5328.
[138] Z. Li, K. R. Conser, E. N. Jacobsen, *J. Am. Chem. Soc.* **1993**, *115*, 5326.
[139] P. Brandt, M. J. Södergren, P. G. Andersson, P.-O. Norrby, *J. Am. Chem. Soc.* **2000**, *122*, 8013.
[140] Y. M. Badiei, A. Krishnaswamy, M. M. Melzer, T. H. Warren, *J. Am. Chem. Soc.* **2006**, *128*, 15056.
[141] H. Chen, M. M. Olmstead, S. C. Shoner, P. P. Power, *J. Chem. Soc., Dalton Trans.* **1992**, 451.
[142] H. Hope, P. P. Power, *Inorg. Chem.* **1984**, *23*, 936.
[143] P. P. Power, *Prog. Inorg. Chem.* **1991**, *39*, 75.
[144] S. Gambarotta, M. Bracci, C. Floriani, A. Chiesi-Villa, C. Guastini, *J. Chem. Soc., Dalton Trans.* **1987**, 1883.
[145] T. Tsuda, M. Miwa, T. Saegusa, *J. Org. Chem.* **1979**, *44*, 3734.
[146] T. Tsuda, K. Watanabe, K. Miyata, H. Yamamoto, T. Saegusa, *Inorg. Chem.* **1981**, *20*, 2728.
[147] A. L. Keen, M. Doster, H. Han, S. A. Johnson, *Chem. Commun.* **2006**, 1221.
[148] N. P. Mankad, D. S. Laitar, J. P. Sadighi, *Organometallics* **2004**, *23*, 3369.
[149] P. M. Jeffries, S. R. Wilson, G. S. Girolami, *Inorg. Chem.* **1992**, *31*, 4503.
[150] A. P. Purdy, C. F. George, J. H. Callahan, *Inorg. Chem.* **1991**, *30*, 2812.
[151] K. Osakada, T. Takizawa, M. Tanaka, T. Yamamoto, *J. Organomet. Chem.* **1994**, *473*, 359.
[152] B. A. Jazdzewski, P. L. Holland, M. Pink, J. Young Jr, D. J. E. Spencer, W. B. Tolman, *Inorg. Chem.* **2001**, *40*, 6097.
[153] N. Kitajima, K. Fujisawa, M. Tanaka, Y. Moro-oka, *J. Am. Chem. Soc.* **1992**, *114*, 9232.
[154] A. F. Stange, T. Sixt, W. Kaim, *Chem. Commun.* **1998**, 469.
[155] D. J. Mindiola, G. L. Hillhouse, *J. Am. Chem. Soc.* **2001**, *123*, 4623.
[156] N. P. Mankad, T. G. Gray, D. S. Laitar, J. P. Sadighi, *Organometallics* **2004**, *23*, 1191.
[157] H. E. Bryndza, L. K. Fong, R. A. Paciello, W. Tam, J. E. Bercaw, *J. Am. Chem. Soc.* **1987**, *109*, 1444.
[158] R. L. Cowan, W. C. Trogler, *J. Am. Chem. Soc.* **1989**, *111*, 4750.
[159] G. L. Hillhouse, J. E. Bercaw, *J. Am. Chem. Soc.* **1984**, *106*, 5472.
[160] M. Kanzelberger, X. W. Zhang, T. J. Emge, A. S. Goldman, J. Zhao, C. Incarvito, J. F. Hartwig, *J. Am. Chem. Soc.* **2003**, *125*, 13644.
[161] P. Perlmutter, *Conjugate Addition Reactions in Organic Synthesis*, vol. 9, Pergamon Press, Oxford, **1992**.
[162] J. J. Brunet, D. Neibecker, in *Catalytic Heterofunctionalization: From Hydroamination to Hydrozirconation* (Eds.: A. Togni, H. Grützmacher), Wiley-VCH, Weinheim, **2001**, pp. 91.
[163] T. E. Müller, M. Beller, *Chem. Rev.* **1998**, *98*, 675.
[164] M. Beller, J. Seayad, A. Tillack, H. Jiao, *Angew. Chem. Int. Ed.* **2004**, *43*, 3368.
[165] S. Hong, T. J. Marks, *Acc. Chem. Res.* **2004**, *37*, 673.
[166] J. F. Hartwig, *Pure Appl. Chem.* **2004**, *76*, 507.
[167] K. C. Hultzsch, *Adv. Synth. Catal.* **2005**, *347*, 367.
[168] A. Alexakis, C. Benhaim, *Eur. J. Org. Chem.* **2002**, 3221.
[169] J. G. Taylor, N. Whittall, K. K. Hii, *Org. Lett.* **2006**, *8*, 3561.

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