Transition-Metal Catalysis

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Divergent Coupling of Anilines and Enones by Integration of C–H Activation and Transfer Hydrogenation

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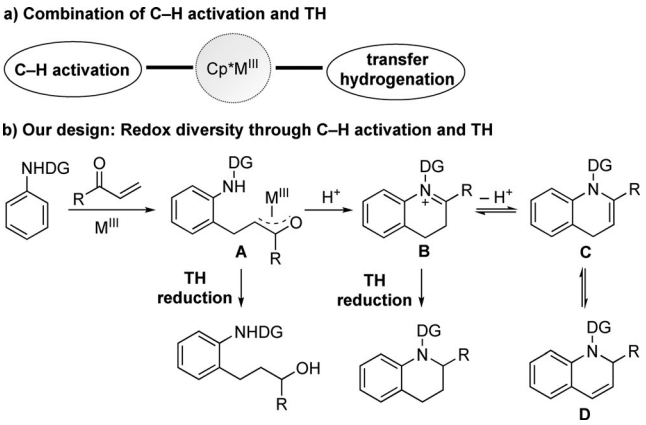
Abstract: *Cp^*Rh^{III}/Ir^{III} complexes are known to play important roles in both C–H activation and transfer hydrogenation (TH). However, these two areas evolved separately. They have been integrated in redox- and chemodivergent coupling reactions of N-pyridylanilines with enones. The iridium-catalyzed coupling with enones leads to the efficient synthesis of tetrahydroquinolines through TH from ^iPrOH. Counter-intuitively, ^iPrOH does not serve as the sole hydride source, and the major reaction pathway involves disproportionation of a dihydroquinoline intermediate, followed by the convergent and iterative reduction of quinolinium species.*

In the past decade, stable Cp^*Rh^{III}/Ir^{III} complexes have been extensively established as versatile and efficient catalysts for the direct C–H functionalization of arenes.[1] This rich and vibrant chemistry boils down to the key role of M^{III}–C species. On the other hand, M–H species constitute another class of reactive intermediates in catalysis. In particular, metal-catalyzed transfer hydrogenation and hydrogen-borrowing reactions have emerged as a convenient and powerful strategy in modern synthetic chemistry.[2] Cp^*Rh^{III}/Ir^{III} complexes are also among the repertoire of active catalysts for TH of polar π-bonds.[3] Despite the intrinsic high activity of these complexes in both systems, these two important areas essentially evolved independently,[4a,b] although H_2-evolving C–H activation has been reported sporadically.[4c–f] Ideally, these two areas could be integrated for the redox-divergent synthesis of useful products under facile catalyst control or control by the reaction conditions. Such redox-divergent coupling systems are rare.[5]

Our objective was to integrate C–H activation and TH by Cp^*M^{III} catalysis. We reasoned that systems with ketone and imine/iminium functionalities may provide handles for TH. We selected *N*-pyridylanilines and enones as coupling partners (Scheme 1). We rationalized that hydroarylation of the activated olefin (via **A**), followed by nucleophilic cyclization may give a hemiaminal[6] en route to an iminium species **B** or its dihydroquinoline conjugate base **C**, whereby both the iminium and the hydroarylation product are susceptible to reduction by TH. However, suitable hydrogen donors had to be identified and had to be compatible with the C–H activation step. Furthermore, the selectivity was to be controlled by judicious choice of the reaction parameters. We now report diverse coupling reactions of anilines and enones through C–H activation and TH.



Scheme 1. Combination of C–H activation and transfer hydrogenation. Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl, DG = directing group.

We previously reported the rhodium(III)-catalyzed oxidative annulation of *N*-pyridylaniline (PhNHPy, **1a**) with acrylates through C–H olefination–cyclization.[7] We reasoned that the tendency of intermediates to undergo β-H elimination leading to olefination should be lower with an enone because of the formation of a trihaptic metal enolate **A** that favors hydroarylation with possible subsequent cyclization (to **B** and **C**).[8,9] We initially focused on the synthesis of dihydroquinolines to explore the feasibility of the cyclization. Cyclohexane was eventually identified as the optimal solvent for the coupling of **1a** and ethyl vinyl ketone (EVK, **2a**) in the presence of an Ir^{III} catalyst and $Zn(OAc)_2$ additive. However, 1,2-dihydroquinoline **3aa** rather than the 1,4-dihydroquinoline was isolated (58% yield), most likely owing to thermodynamic stability. The yield was generally moderate for the synthesis of other dihydroquinolines bearing alkyl, aryl, and halogen groups (Scheme 2). The relatively low yield was ascribed to competitive disproportionation.[10] In fact, by switching the $Zn(OAc)_2$ additive to $Zn(OTf)_2$, the coupling of **1a** and EVK afforded tetrahydroquinoline **5aa** and the corresponding quinolinium salt **4aa**-NTf_2 as major products.

The formation of tetrahydroquinoline **5aa** by disproportionation boded well for its synthesis by reductive coupling. Tetrahydroquinolines have also been prepared in racemic form or enantioselectively by the hydrogenation of quinolines.[3b] With the same Ir^{III} catalyst and the PivOH additive, the

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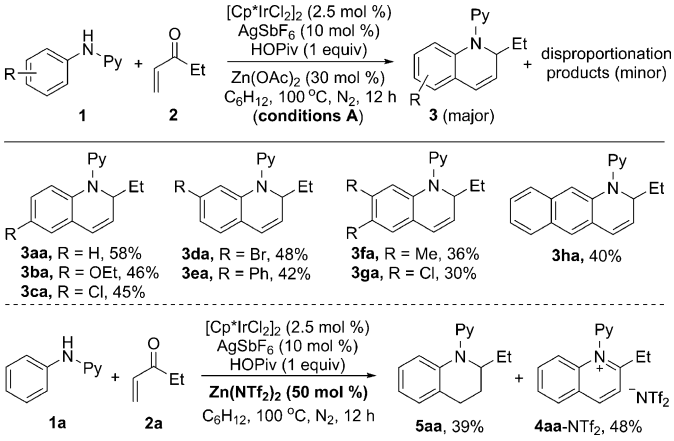
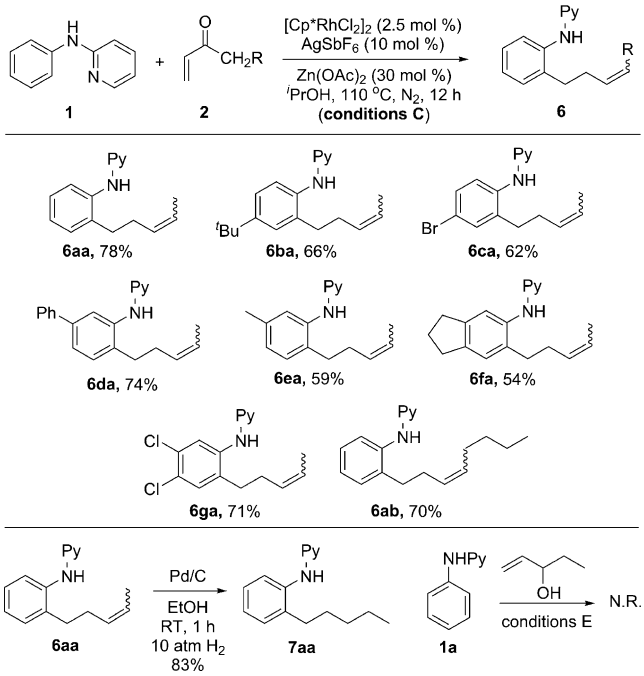


Scheme 2. Redox-neutral 1,2-dihydroquinoline synthesis (conditions A) and disproportionation. PivOH = pivalic acid, Tf = trifluoromethanesulfonyl.

reaction of **1a** and EVK afforded **5aa** as the major product through TH in isopropanol,[15] and the yield was optimal when $Ni(OAc)_2$ was introduced (Scheme 3, conditions B). Anilines bearing electron-donating and electron-withdrawing groups at different positions all coupled smoothly to afford the tetrahydroquinolines **5ba–ra** in moderate to good yields. The scope of the reaction with respect to the enone substrate was also broad, although the alkyl group in the enone had great influence on the reaction efficiency (products **5ab–af**). $PhCH_2CH_2$- (product **5ae**) and benzyl-substituted enones (product **5af**) coupled with lower yield because of competitive formation of dihydroquinoline by-products.

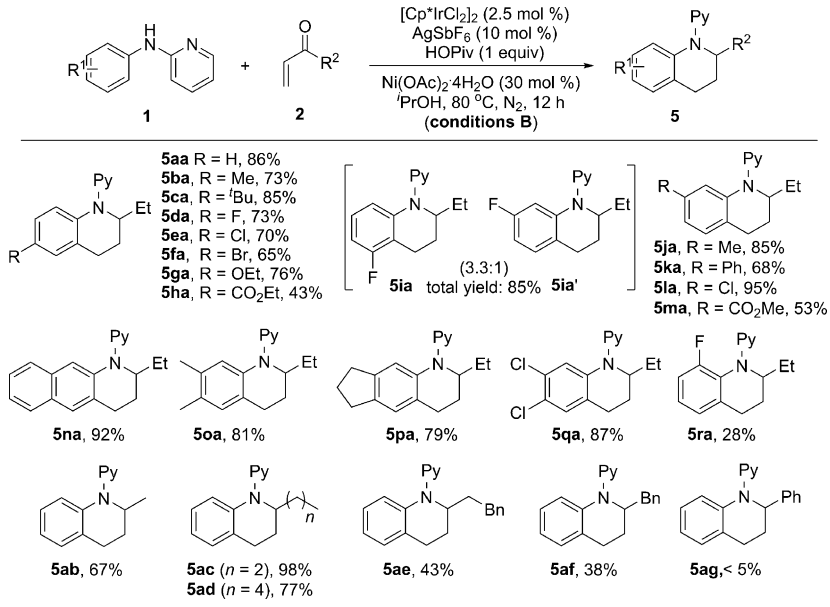
The difference between iridium and rhodium catalysts in C–H activation has been documented.[11] Furthermore, Ir^{III} catalysts are generally better players than Rh^{III} catalysts in TH, possibly owing to the higher stability and reactivity of iridium hydrides.[12] It was discovered that the Rh^{III}-catalyzed coupling of PhNHPy and EVK proceeded at elevated temperature to give a *Z*/*E* mixture of the homoallylated product **6aa** (78%) in ^{i}PrOH in the presence of a catalytic amount of $Zn(OAc)_2$ (Scheme 4). The identity of the products



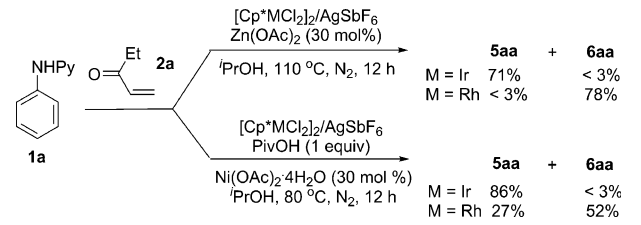
Scheme 4. Rhodium(III)-catalyzed alkylation through TH (conditions C).

in the mixture was confirmed by GC–MS and by Pd/C-catalyzed hydrogenation to give a sole product **7aa**. The reaction of different substrates occurred in moderate to good yields (products **6aa–ga**, **6ab**). The reaction probably proceeded through a sequence of hydroarylation, TH reduction by ^{i}PrOH, and dehydration of the alcohol intermediate, as evidenced by two control experiments. In a negative control experiment, no desired reaction occurred when 1-penten-3-ol was used as a coupling partner, which indicated that the reaction did not involve initial enone reduction. In a positive control, a hydroarylated compound **8aa** proved to be an intermediate for this transformation (Scheme 6). We also confirmed by control experiments that the different selectivity of our rhodium- and iridium-catalyzed reductive coupling reactions was largely controlled by the catalyst (Scheme 5).

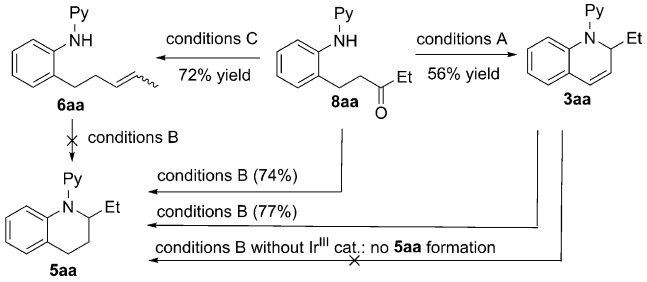
Intermediates of these coupling systems were determined (Schemes 6). Ketone **8aa** was isolated as the major product of the coupling of PhNHPy and EVK at a lower temperature under Ir^{III} catalysis (see the Supporting Information). It proved to be a common intermediate in all the coupling



Scheme 3. Reductive synthesis of tetrahydroquinolines (conditions B). Bn = benzyl.



Scheme 5. Comparison of Ir and Rh catalysts for TH reduction.



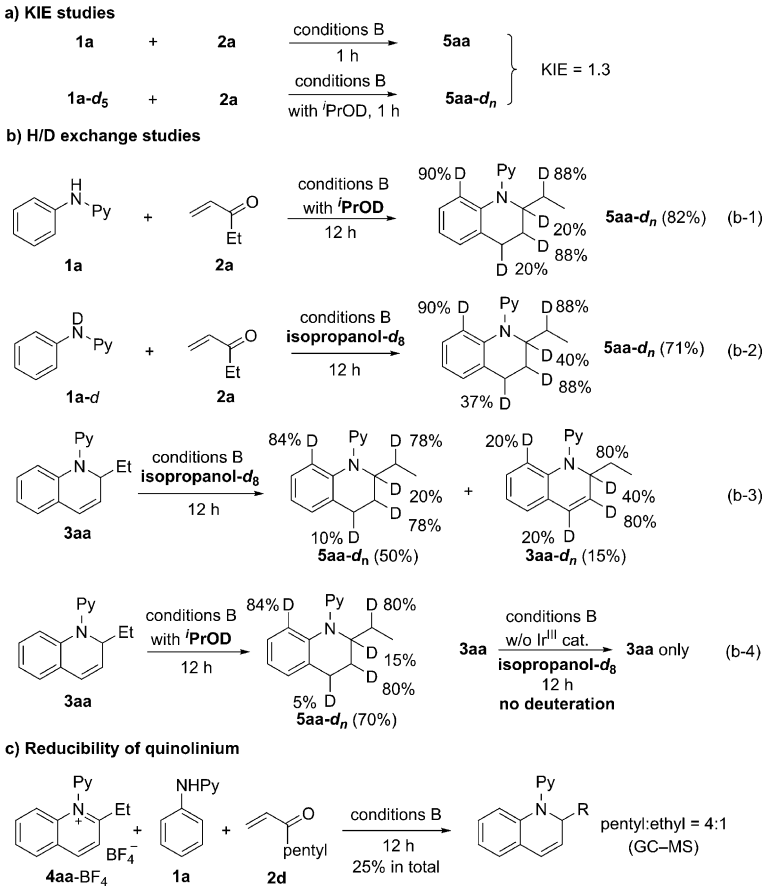
Scheme 6. Establishment of intermediates in redox-divergent coupling reactions.

systems, with the formation of **3aa**, **5aa**, and **6aa** under the corresponding conditions. Compound **3aa** was also an intermediate in the formation of **5aa** (conditions B).

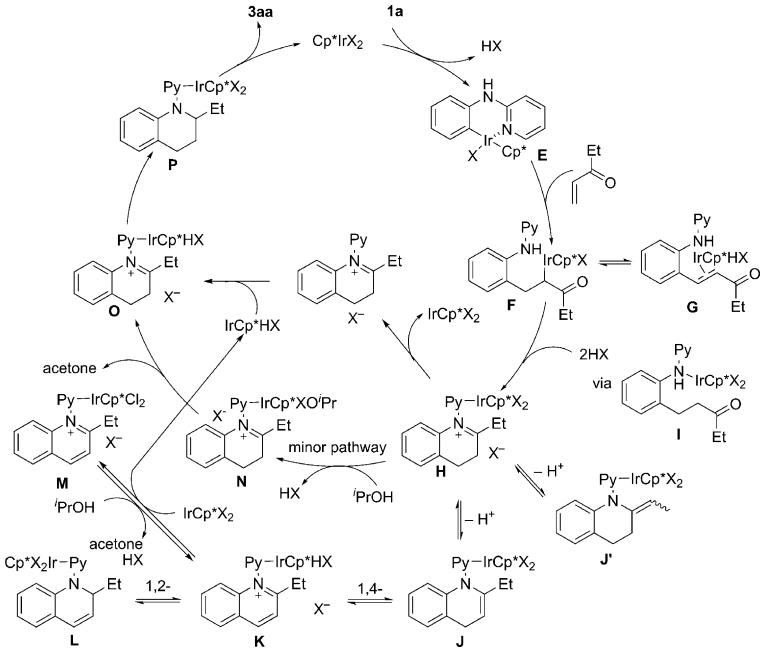
The mechanism of the iridium(III)-catalyzed reductive coupling was studied in detail. Olefin **6aa** was not an intermediate in the formation of **5aa** under conditions B (Scheme 6). This result suggests the unlikelihood of intramolecular hydroamination. To explore organometallic intermediates in this system, we prepared a six-membered iridacycle and applied it as a catalyst precursor for the coupling of **1a** and EVK, from which product **5aa** was isolated in 79% yield (see the Supporting Information), thus suggesting the relevance of C–H activation. The kinetic isotope effect was then measured from parallel experiments using **1a** and **1a-d_5**. The relatively small value of $k_H/k_D = 1.3$ indicated that C–H cleavage is not turnover-limiting (Scheme 7a).

Extensive H/D exchange studies were performed to probe the mechanism of coupling of **1a** and EVK, particularly to clarify the hydride source. H/D exchange using ^{i}PrOD as a solvent revealed 90% deuteration at the *ortho′* position of the product (Scheme 7b-1). Furthermore, equally high deuteration (88%) was detected at the C3 and the CH_2Me position, which can probably be ascribed to a rapid enamine–iminium equilibrium between a dihydroquinoline **C** (Scheme 1) and imine **B**. The observed 20% D at the C4 position may suggest reversible β-hydrogen elimination of the corresponding iridium alkyl intermediate **A** (Scheme 1) to give a Ir^{III}–H atom that is exchangeable with ^{i}PrO*D*, and the deuterium of Ir–D may end up at the C2 position through reduction of the iminium species **B**. To our great surprise, although ^{i}PrOH is a well-known hydrogen source, the C2 position was only 40% deuterated when isopropanol-d_8 was used as the solvent (Scheme 7b-2, several trials). This low level of deuteration stands in contrast to the high levels at the *ortho′* and 3-positions, thus indicating the presence of other hydride sources.[13]

The observed disproportionation and low level of C2 deuteration collectively suggest that dihydroquinoline itself serves as a major hydride source.[10a] This hypothesis is consistent with another H/D exchange reaction using dihydroquinoline **3aa** with deuterated isopropanol (Scheme 7b-3), for which a similar deuteration pattern was observed in product **5aa-d_n**, and the lower deuteration (10%) at the benzylic position agrees with the absence of any iridium–alkyl species and β-H elimination. Moreover, ^{1}H NMR analysis of the recovered starting material revealed significant H/D exchange at these four positions (see Scheme 7b-4 for control experiments). The discrepancy in the product yields in Schemes 7b-3 and 7b-4 is ascribed to the kinetic isotope effect of the isopropanol solvent/reductant (see the Supporting Information). These results strongly suggest reversible elimination of the C(2)-hydrogen of **3aa** to give a quinolinium and a Ir^{III}-H that adds back to the quinolinium at the 2- or 4-position.[14] Indeed, an Ir–H signal was detected when dihydroquinoline **3fa** was treated with [IrCp*Cl$_2$]$_2$/NaBAr^F (NaBAr^F = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate).



Scheme 7. Mechanistic studies on iridium(III)-catalyzed TH reduction.



Scheme 8. Proposed mechanism for the reductive synthesis of tetrahydroquinolines.

Our observations that the C2 deuteration is twice as high as that at the C4 position may suggest that C2 is the more reactive site, most likely owing to chelation assistance. Our observation stands in contrast to the 1,4-insertion pathway proposed by Zhou and co-workers.[14f] To probe the likelihood of the reduction of the quinolinium ion, we performed the coupling of PhNHPy and enone **2d** in the presence of an equimolar amount of quinolinium **4ac**-BF_4 (Scheme 7c). Although no exhaustive reduction was observed, two dihydroquinolines were detected (4:1 ratio). This observation, in connection with the established intermediacy of a 1,2-dihydroquinoline under reaction conditions B, verified the reducibility of the quinolinium species.

On the basis of our observations, we propose the following iridium(III)-catalyzed TH-coupling[15] mechanism (Scheme 8): C–H activation of aniline **1** gives iridacycle **E** together with HX. Coordination and insertion of an enone into the Ir–Ar bond generates an Ir^{III} alkyl complex **F** in equilibrium with hydride **G** through β-H elimination. Protonolysis of the Ir–alkyl complex and subsequent cyclization catalyzed by a Lewis acid (Zn^{II} or Ni^{II}) gives an iminium ion **H**. In the minor pathway, ligand exchange with isopropoxide is followed by β-H elimination to give an Ir^{III} hydride **O**, which then undergoes direct hydride attack to give amine **P**. The product **3aa** is released upon ligand dissociation, which completes the catalytic cycle. The major pathway involves reversible deprotonation of iminium **H** to give enamines **J**/**J′**. Intermediates **J**, **K**, and **L** form an equilibrium system through reversible and rapid 1,2- and 1,4-hydride insertion into quinolinium **K**. Shuffling of the metal fragments IrCp*HX and $IrCp^*X_2$ between **H** and **K** through ligand dissociation–association leads to disproportionation to give the oxidized form **M** and the reduced form **P**. The former undergoes reduction by ^{i}PrOH to further enter the catalytic cycle via iminium **H**. Overall, **3aa** is produced through disproportionation of a dihydroquinoline (**J**/**L**), followed by convergent and iterative reduction of the quinolinium intermediate. A similar scenario has been previously reported by Zhou and co-workers in the context of the hydrogenation of neutral quinoxalines through the disproportionation of NH dihydroquinoxalines.[16]

In summary, we have described the C–H activation of *N*-pyridylanilines and their coupling with enones both under redox control and under the control of the reaction conditions. The iridium-catalyzed reductive synthesis of tetrahydroquinolines through TH has been studied in detail. Counterintuitively, isopropanol does not serve as the sole hydride source, and the major reaction pathway most likely involves disproportionation of a dihydroquinoline intermediate, followed by convergent and iterative reduction of the quinolinium species. The rare integration of C–H activation and transfer hydrogenation may open doors to new C–H activation systems for the rapid construction of useful products.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: anilines · C–H activation · disproportionation · olefins · transfer hydrogenation

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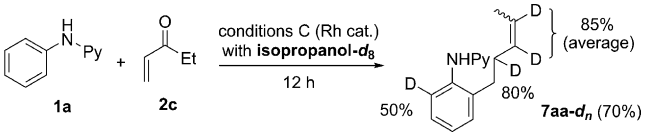
[13] In contrast, the rhodium(III)-catalyzed reductive coupling gave no complication in terms of H/D exchange: Both the allylic and the olefinic positions were highly deuterated, which is consistent with TH reduction by ^{i}PrOH.



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