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Effect of Ancillary Ligand in Cyclometalated Ru(II)–NHC-Catalyzed Transfer Hydrogenation of Unsaturated Compounds

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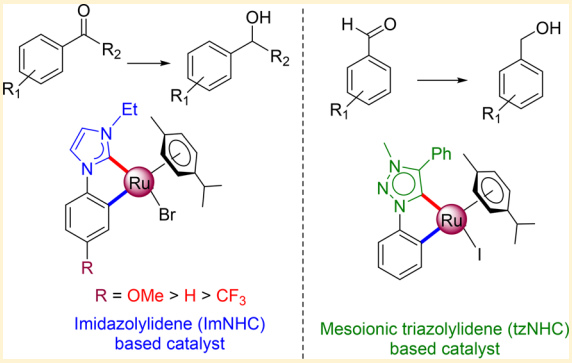
Supporting Information

ABSTRACT: In an effort to develop efficient Ru(II)–NHC-based catalyst considering their stereoelectronic effect for hydride-transfer reaction, we found that the ancillary NHC ligand can play a significant role in its catalytic performance. This effect is demonstrated by comparing the activity of two different types of orthometalated precatalysts of general formula [(*p*-cymene)(NHC)-$Ru^{II}(X)$] (NHC = an imidazolylidene-based ImNHC, compound **2a–c**, or a mesoionic triazolylidene-based tzNHC, compound **4**) in transfer hydrogenation of carbonyl substrates. The electron-rich precatalyst, **2c**, containing *p*-OMe-substituted NHC ligand performed significantly better than both unsubstituted complex **2a** and *p*-CF_3 substituted electron-poor complex **2b** in ketone reduction. Whereas bulky mesoionic triazolylidene ligand containing complex **4** was found to be superior catalyst for aldehyde reduction and the precatalyst **2a** is more suitable for the selective transfer hydrogenation of a wide range of aromatic aldimines to amines. To the best of our knowledge, this is the first systematic study on the effect of stereoelectronic tuning of ancillary orthometalated NHC ligand in Ru(II)-catalyzed transfer hydrogenations of various types of unsaturated compounds with broad substrate scope.



INTRODUCTION

Ancillary ligand plays an important role on the catalytic activity of a metal–ligand complex, and the steric and electronic profile are normally considered as important factors to tweak their properties and hence catalytic activity.[1] *N*-Heterocyclic carbene (NHC) has evolved over the last couple of decades as an important class of ligand for the synthesis of efficient homogeneous catalysts. This is mainly due to their straightforward synthesis that allows easy modifications to fine-tune their stereoelectronic properties and strong σ-donor properties.[2] Steric and electronic parameters of various NHCs have been studied extensively[3] and relatively better σ-donor properties than that of ubiquitous trivalent phosphine analogues are proposed. Given the fact that the NHC ligands serve as excellent ancillary ligands for the synthesis of a variety of homogeneous catalysts, study on the effect of steric and electronic tuning of the ancillary NHC ligands in metal complex catalyzed organic transformations would give us valuable input for the design of new efficient catalysts. Hydride transfer is a key step in many important catalytic processes such as (transfer) hydrogenation, H_2 storage/release, hydro elementation, olefin isomerization, and so on.[4] Transfer hydrogenation reaction of unsaturated compounds is usually a more convenient and less hazardous process than direct hydrogenation using dihydrogen gas and a wide range of substrates (such as carbonyl groups, imines, nitriles, C=C bonds, etc.) can be reduced which make this reaction as one of the most investigated hydrogenation reaction.[5] Therefore, transfer hydrogenation reaction was chosen as model for the hydride transfer process.

Ruthenium(II)–NHC complexes proved to be efficient catalysts in various important organic transformations[6a–e] including transfer hydrogenation reaction.[5a,6f–h] Chelating Ru(II)–NHC complexes are found to be one of the most effective class of catalysts for transfer hydrogenation reactions possibly due their enhanced stability compared to that of their monodentate analogue and ability to hinder the catalyst deactivation during the catalytic cycle.[6f–h,7] Among these chelating Ru(II) complexes, NHC ligands with pyridine pendant arms are most widely studied.[7a,d] Whereas, the related orthometalated NHC complexes with Ru–C_{aryl} bond are relatively less explored although some of them were found to be effective catalysts for this transformation.[6g,7e] Thus, further studies are required to develop this area. 1-Phenyl imidazole based NHCs have been shown to be promising ligands for the synthesis of orthometalated late-transition metal complexes with possible variations at the ligand backbone.[8] Therefore, this ligand system offers to tune the stereoelectronic parameters of the corresponding metal complexes. Detailed study of the combined steric and electronic influence of an ancillary orthometalated NHC ligand in the transition metal catalyzed transfer hydrogenation reaction has not been explored much.[6h,9] To study such effect, we have chosen a

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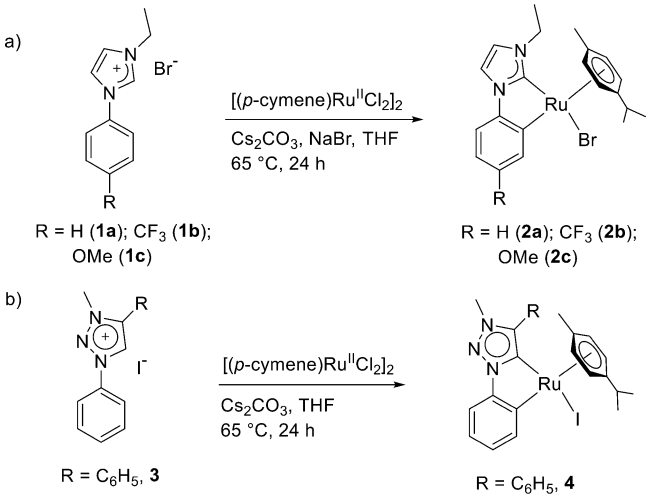
series of orthometalated ruthenium(II)−NHC complexes with varying stereoelectronic properties and described here the facile tailoring of the Ru(II)−NHC based catalyst either by introducing electron donating/accepting substituent at the *p*-position of the *N*-phenyl ring with respect to imidazolylidene moiety of the C_{NHC}^C_{phenyl}-bidentate chelating NHC ligand or by using a bulky mesoionic triazolylidene ligand. These modifications substantially alter the catalytic activity of these orthometalated ruthenium(II)−NHC complexes which was confirmed by applying them in the catalytic reduction of a library of unsaturated compounds via transfer hydrogenation strategy.

RESULTS AND DISCUSSION

Synthesis of Complexes 2a−c and 4. Reaction of imidazolium salts **1a−c** with $[(p\text{-cymene})RuCl_2]_2$ using Cs_2CO_3 as base yielded the orthometalated Ru(II) NHC complexes **2a−c** (Scheme 1a) in good yield of 60−78%. In a similar way, complex **2b-I** with the iodo instead of bromido ligand attached to ruthenium was synthesized for crystallization purpose from the corresponding imidazolium salt with iodide counterion **1b-I** (see Supporting Information). Complex **4** was synthesized following a similar procedure (Scheme 1b). Previously, chloro-substituted analogue of complex **4** was synthesized via transmetalation strategy from the corresponding in situ generated Ag(I)−NHC complex.[10] All the complexes are air- and moisture-stable in nature and readily soluble in common polar organic solvents. The complexes are fully characterized by NMR spectroscopy, mass spectrometry (ESI-MS), and X-ray crystallography for complexes **2a** and **2b-I**.

Scheme 1. Synthesis of Orthometalated Ru(II)−NHC Complexes 2a−c and 4



Formation of complexes **2a−c** is supported by the complete absence of the acidic imidazolium N−CH−N protons (10.88 ppm, **1a**; 11.05 ppm, **1b**; 10.71 ppm, **1c**) and the presence of the characteristics Ru(II)-coordinated C_{NHC} signals (Table 1; reasonably upfield-shifted C_{NHC} resonance in **2c** suggests the presence of a relatively more electron-rich C_{NHC} in **2c** than in **2a** and **2b**). These carbene resonances are significantly downfield-shifted from their nonorthometalated analogues which are observed in the range of 165−175 ppm.[11] This could be attributed to the formal replacement of a halide ion by a stronger phenylic carbon donor in **2a−c** making the ruthenium center less Lewis acidic and thus leading to downfield shift of the C_{NHC} signals.[12]

Table 1. $^{13}C\{^1H\}$ NMR Chemical Shifts of C_{NHC} in Complexes 2a−c and 4

entry	complex	C_{NHC} chemical shifts (ppm)
1	**2a**	187.00
2	**2b**	187.98
3	**2c**	185.41
4	**4**	171.40

Orthometalation of the phenyl ring is further supported by the absence of an aromatic proton along with the presence of the orthometalated carbon signals[8b,13] at 162.4−164.2 ppm. In addition, loss of symmetry of the complex as evidenced by the presence of four instead of two sets (should be observed in the absence of orthometalation) of aromatic protons in the region of 5.31−5.59 ppm for the *p*-cymene moiety also supports the orthometalation of the phenyl ring. All other proton and carbon resonances were found at the expected region.[8b,13] From the above NMR spectral data, it is clear that the ligand is coordinated to the Ru(II) center in a bidentate chelating fashion (C_{NHC}^C_{phenyl}) via neutral carbenic and anionic phenylic carbons. On the basis of the literature, we suggest that the orthometalation has occurred via ligand-assisted concerted-metalation−deprotonation (CMD) pathway which is mechanistically related to sigma-bond metathesis.[12d,14a,b] Formation of complex **4** via selective activation of only the N-substituted phenyl group was confirmed by comparing the NMR spectroscopic data with the related chloro complex.[10] ESI mass spectrometry further supports the composition of the complexes showing the presence of major intensity peaks at *m*/*z* 475.0931 (**2b**) for the $[M - Br]^+$ ion and at *m*/*z* 489.0290 (**2a**) and 519.0413 (**2c**) for $[M + H]^+$ ions in good agreement with the theoretical isotopic patterns. Finally, the X-ray crystal structure determinations for **2a** and **2b-I** (Figure 1) confirm the structure of the complexes.

Single crystals of **2a** and **2b-I** for X-ray crystallographic studies were grown from THF and hexane/pentane at ambient temperature. The crystal structures of both the complexes show that the NHC ligand is coordinated to Ru(II) center as a bidentate chelate via neutral carbenic and anionic phenylic

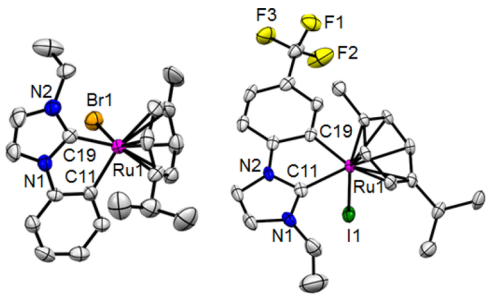


Figure 1. Molecular structures of **2a** (left) and **2b-I** (right) with displacement parameters at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) for **2a** [for **2b-I**]: Ru1−C_{aryl} = 2.065(7) [2.061(3)], Ru1−C_{NHC} = 2.010(7) [2.015(3)], Ru1−$C_{centroid}$ = 1.735 [1.745], Ru1−halide = 2.5404(9) [2.7080(3)]; C11−Ru1−C19 = 77.3(3) [76.82(13)], N1−C_{NHC}−N2 = 103.9(6) [104.2(3)], N1−C_{NHC}−Ru1 = 117.9(4) [137.7(2)], N2−C_{NHC}−Ru1 = 138.1(5) [118.1(2)].

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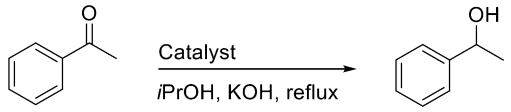
carbons forming a planar five-membered ruthenacycle (Figure 1) confirming the conclusions drawn from NMR spectroscopic analysis. The complexes feature a typical piano-stool arrangement and the pseudo-octahedral geometry around the ruthenium center is satisfied by the facially arranged planar *p*-cymene, bidentate NHC, and halide ligands. Both the complexes show similar structural parameter. The Ru−C_{NHC} bond lengths (2.011−2.015 Å) are slightly shorter than that of Ru−C_{phenyl} bonds (2.061−2.066 Å) possibly due to π-back-donation from the metal center.[7e,12d,13a] The bite angle and yaw distortion angles at the NHC/aryl ligand,[15] two important geometrical parameters for the steric profile of a chelating ligand,[9a,15] are measured to be 77.3(3)° and 10.1°/6.2°, respectively, for **2a** and 76.82(13)° and 9.8°/5.7°, respectively, for **2b-I**.

Catalytic Transfer Hydrogenation of Ketones. After having these complexes with varying electronic and steric properties, we probed the effect of ligand tuning in model transfer hydrogenation reaction of acetophenone using complexes **2a−c** and **4**. Initially, under the standard transfer hydrogenation condition (2-proponol as both solvent and hydrogen source and KOH as base) using substrate/catalyst/base ratio of 100:0.5:20, complex **2c** displayed the best activity (almost completed in 60 min; Table 2). The catalytic activity

Table 2. Reduction of Acetophenone to 1-Phenyl Ethanol Using Different Catalysts[a]



entry	catalyst	mol % (time, min)	yield[b]
1	**2a**	0.5 (60)	68
		1 (60)	93
2	**2b**	0.5 (60)	53
3	**2c**	**0.5 (60)**	**95**
		1 (30)	94
4	**4**	0.5 (60)	25

[a]General conditions: ketone (1.0 mmol), catalyst (0.005/0.01 mmol), KOH (0.2 mmol), ^{i}PrOH (5 mL), reflux temperature. [b]Determined by GC-MS using mesitylene as internal standard.

of the complex is substantially enhanced when a *p*-OMe substituent is present on the NHC ligand backbone keeping other factors unchanged (95% yield), whereas it is diminished in the presence of an electron-withdrawing *p*-CF_3 substituent (53% for **2b**) from that of unsubstituted complex **2a** (68%) (Table 2). When the catalyst loading of **2c** was reduced to 0.2 mol %, satisfyingly 90% yield was observed in 1.5 h. Catalyst **2c** performs significantly better when compared with the previous structurally related Ru(II)−NHC complexes[7e,9b,17] although the activity is less than the best performing Ru(II)−NHC complexes in this transformation.[6g,7a] Other bases (NaOH/K*t*BuO) did not show any significant change in catalytic activity.

Almost a 2-fold increase of the catalytic activity of complex **2c** relative to that of parent complex **2a** (Table 2) can possibly be attributed to the presence of an electron-rich Ru(II) center in **2c** as evidenced by $C_{NHC}\{^{13}C\}$ resonances (Table 1) and lower Ru^{II}/Ru^{III} redox potential for **2c** than those for **2a** and **2b** ($E_{1/2}$ = 101 mV (**2a**), 224.5 mV (**2b**), 72.0 mV (**2c**) vs Fc) (Figure S21).[9a,16] Presence of an electron-donating substituent at the *p*-position of the *N*-Ph ring of a NHC ligand was previously found to improve although to a lesser extent the rate of Ir(III)-catalyzed transfer hydrogenation of acetophenone.[9a,14c] This is due to the contribution of some electron density to the ruthenium center by the *p*-OMe substituent (a good π-donor) via p-π conjugation of OMe lone pair with the phenyl ring which is facilitated by the coplanar arrangement of the aryl ring with the imidazolylidene ring (Figure 1). The steric influence of the NHC ligand can be ignored here as all of them have the same ligand environment with almost similar bite and yaw angle around the ruthenium center (Figure 1). Thus, variation of the *p*-substituents at the *N*-phenyl group of the NHC ligand can be seen as an effective tool to finely tune the electronic profile and thus optimize the catalytic efficiency of orthometalated Ru(II)−NHC complexes **2a−c**. This type of findings provide useful information for the development of new efficient catalyst systems.

The mesoionic triazolylidene ligand based precatalyst, **4**, afforded lower yield of the product than that observed for the complex **2a** (Table 2) although tzNHC ligands are reported to be electron donors superior to ImNHC ligands toward transition metal ions[10,18] which are also reflected in their better performances in transition metal catalyzed organic transformations.[19] Notably, the observed $E_{1/2}$ values for the Ru^{II}/Ru^{III} process of complexes **2c** and **4** are almost same (Figure S21) which implies a similar electronic profile of the Ru(II) centers in both the complexes.

On the basis of better performance, catalyst **2c** was then applied to a variety of substrates which include aromatic, heteroaromatic, cyclic, and acyclic aliphatic ketones using the optimized conditions to evaluate the scope of the present catalytic systems and the catalytic results are shown in Table 3. Gratifyingly, the secondary alcohols were either isolated in excellent yield of 89−98% after column chromatography (entry 1−11) or GC-MS analysis showed almost quantitative yield (entry 12−16).

This catalytic system tolerates both electron-withdrawing (chloro, fluoro) and electron-donating (methyl, methoxy) substituents at the phenyl ring and the corresponding alcohols were isolated in excellent yields (entry 2−6). The electron-poor substrates undergo faster reduction compared to that of the electron-rich one as expected. This is supported by the linear correlation between the Hammett σ-constants of *p*-substituents on the phenyl ring of acetophenone and the percentage yield furnishing a positive slope (Figure S22). This observation might be correlated to the ease of hydride transfer from the in situ generated metal−hydride species (see the "Mechanistic Investigation" section) to ketones as the electron-withdrawing substituents increase the electrophilicity of the carbonyl group and thereby facilitating the process, whereas electron-donating substituents have the opposite effect.

Notably, sterically crowded substrates, e.g., (substituted) benzophenone and fluorenone, are also readily and efficiently reduced to the corresponding alcohols (entry 9−11). It is worth mentioning that benzophenone can also be reduced with lower catalyst loading of 0.1 mol % giving 84% yield of the corresponding alcohol in 3 h (entry 9). This is important as some of the NHC-based Ru(II) catalysts show very poor activity in the transfer hydrogenation of these bulky substrates.[17c,20] Aryl halide bonds are fully preserved, and no hydro-dehalogenation was observed (entries 2−4 and 10). The more challenging and less explored heteroaromatic substrates such as 4/2-acetylpyridine (entries 12 and 13) and 2-

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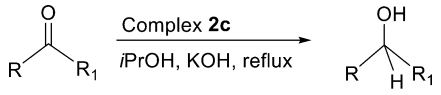
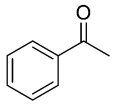
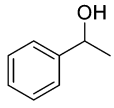
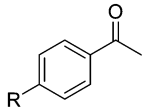
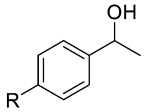
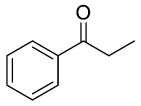
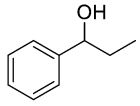
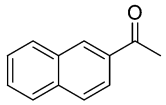
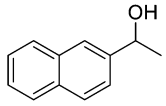
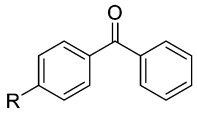
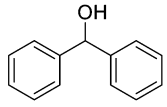
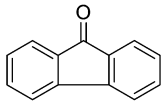
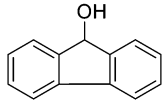
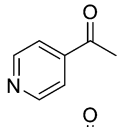
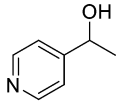
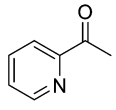
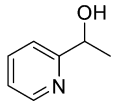
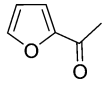
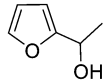
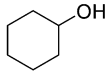
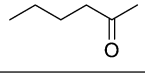
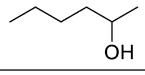
Table 3. Catalytic Transfer Hydrogenation of Various Ketones Using the Complex 2c[a]



Entry	Ketone	Alcohol	Time (min)	Yield(%)[b]
1			90	94
2 R = F			60	91
3 Cl			60	95
4 Br			90	93
5 Me			90	92
6 OMe			120	89
7			90	96
8			90	91
9 R = H			45(180[c])	98(84[d])
10 Cl			45	96
11			60	93
12			30	99[d]
13			60	97[d]
14			150	90[d]
15			30(120[c])	100[d]
16			120	99[d]

[a]General conditions: ketone (1.0 mmol), catalyst **2c** (0.005 mmol), KOH (0.2 mmol), [i]PrOH (5 mL), reflux temperature. [b]Isolated yield. [c]0.1 mol % **2c** was used. [d]Determined by GC-MS using mesitylene as internal standard, average of two runs.

acetylfuran (entry 14) also worked competently. The reduction of 4-acetylpyridine is significantly faster (completed within 30 min) when compared with that of (substituted)acetophenones. The success for 2-acetylpyridine, known to be a challenging substrate for most catalysts because of possible catalyst poisoning via chelation of the substrate as well as the produced alcohol,[21] indirectly provides support for the strong chelating nature of the NHC ligand even during the catalytic process. The catalyst also performs well for both the cyclic and acyclic aliphatic ketones. Cyclohexanone was reduced significantly faster and the reaction was completed within 30 min (entry 15). Notably, quantitative yield was also achieved in 2 h even the catalyst loading was reduced to 0.1 mol % (entry 15). However, 2-hexanone undergoes reduction relatively slowly and the reaction requires 2 h to complete (entry 16).

Catalytic Transfer Hydrogenation of Aldehydes. We further extended our study to more challenging carbonyl substrate aldehydes.[21b,22] Only few reports based on Ru(II)−

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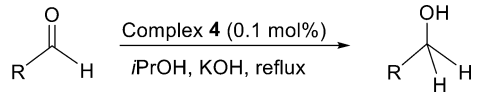
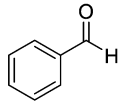
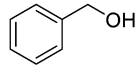
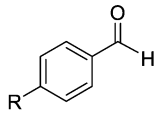
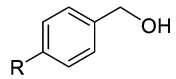
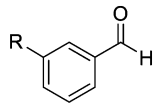
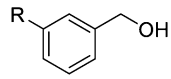
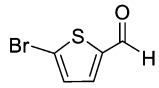
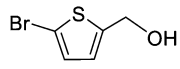
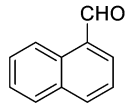
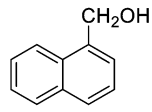
Table 4. Catalytic Transfer Hydrogenation of Various Aldehydes Using the Complex 4[a]



Entry		Aldehyde	Alcohol	Yield(%)[b]
1				95
2	R = F			81
3	Cl			93
4	Br			92
5	Me			97
6	OMe			79[c]
7	CN			70[d]
8	R = Cl			92
9	Br			88
10				78
11				65(83)[e]

[a]General conditions: aldehyde (2.0 mmol), complex **4** (0.002 mmol), KOH (0.2 mmol), [i]PrOH (5 mL), reflux temperature for 30 min. [b]Isolated yield. [c]Reaction time of 120 min. [d]25% isopropyl-4-cyanobenzoate was isolated as additional product. [e]Complex **2a** instead of **4** was used.

NHC catalytic system are available for the transfer hydrogenation of aldehyde and the catalytic efficiency was also found to be very low with limited substrate scope along with the formation of aldol condensation product (via coupling of aldehydes with acetone generated during the catalytic cycle) or acid as byproduct in some cases.[17c,20,23] To evaluate the scope of this present catalytic system, parent catalyst **2a** was initially tested for the benzaldehyde reduction. Although complete conversion of the benzaldehyde was observed within 30 min (0.1 mol % **2a** and 10 mol % KOH in refluxing *i*PrOH), benzyl alcohol was isolated in about 70% yield due to the formation of benzoic acid/benzoate as byproduct possibly generated via base-assisted Cannizaro reaction.[24] Similarly, significant amount of benzoic acid/benzoate was also formed along with benzyl alcohol for precatalysts **2b** and **2c**.

Gratifyingly, benzyl alcohol was isolated in 95% yield when we employed the bulky triazolylidene based catalyst **4** under the same reaction condition indicating insignificant proportion or absence of Cannizaro reaction. The reaction was completed within 20 min giving TOF of 2850 h^{-1}. It is noteworthy that the related triazole based cationic Ru(II) complex gave exclusively the aldol condensation product rather than benzyl alcohol at maximum conversion.[20a] Motivated by satisfying performance of complex **4**, various aldehyde substrates were screened and the primary alcohols isolated in good to excellent yield of 78−97% (Table 4; entry 1−10).

4-Substituted benzaldehydes containing both electron-withdrawing (entry 2−4) and electron-donating (entry 5−6) substituents are effectively reduced to the corresponding alcohols although 4-methoxybenzaldehyde required relatively longer time to give substantial yield (entry 6) as expected based on lower electrophilicity of its aldehyde moiety. Position of the substituent on the phenyl ring of benzaldehydes does not affect the catalytic outcome (entry 8−9). 4-Cyanobenzaldehyde is also active giving 70% of the isolated 4-cyanobenzyl alcohol; however, we also observed the formation of isopropyl-4-cyanobenzoate along with the alcohol (entry 7). This is possibly formed via condensation of 4-cyanobenzoic acid (produced as side product) with isopropanol. It is important to note that the nitrile group is unaffected during the process, thus demonstrating excellent selectivity of this catalytic system toward aldehyde over nitrile.

Next, we tried the heteroatom-containing substrate 5-bromo-2-thiophene, which also worked well, and the alcohol was isolated in decent yield of 78%. Sterically demanding substrate such as 1-napthaldehyde is not a good substrate for this catalyst system (63% yield) which might be due to steric crowding around the metal center imparted by the phenyl group at the triazole backbone. Keeping the steric factor in mind, when we applied complex **2a** with relatively less steric congestion around the metal center, the corresponding alcohol could be isolated in good yield of 83% (entry 11).

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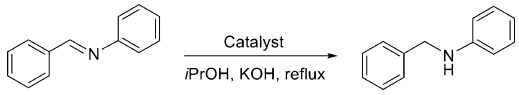
Catalytic Transfer Hydrogenation of Imine. Amines are important precursors for the synthesis of bioactive compounds, agrochemicals, fragrance materials, and industrially relevant polymers[25] and transfer hydrogenation of imines is one of the convenient method for their selective synthesis.[26] Ru(II)−NHC complexes are scarcely reported for the transfer hydrogenation of imine with broad substrate scope[7a,17e,27] possibly due to lower activity of imines than that of ketones. After having success in transfer hydrogenation of carbonyl compounds, we focused our attention toward aromatic aldimines, which are more challenging than ketimines due to their less stability as compared to ketimines.

To study the scope of our Ru(II)−NHC based system, *N*-benzylideneaniline was chosen as model substrate. It was found to be completely hydrogenated to *N*-benzylaniline in 24 h using catalyst **2a** (2 mol % loading; Table 5) although the activity is substantially less compared to ketone as expected. Similar to that observed for ketone reduction, *p*-OMe-substituted electron-rich complex **2c** performed better, whereas *p*-CF_3 substituted **2b** is less active than unsubstituted complex **2a**. An essentially quantitative reaction was observed within 10 h for **2c**, and only 73% product formation was observed in 24 h for **2b** (Table 5). Even though the performance of **2c** was found to be superior to that of **2a** in the transfer hydrogenation of *N*-benzylideneaniline, we observed considerable percentage of decomposition to the corresponding aniline and aldehyde/alcohol for some of the imines during initial screening. In accordance with its low activity in ketone reduction, complex **4** was also found to be ineffective in this transformation (Table 5). On the basis of these catalytic results, we proceeded with precatalyst **2a**, and the scope of the system was explored by applying to variety of aromatic aldimines featuring variations on both the *C*-phenyl and *N*-phenyl rings (Table 6).

Table 5. Transfer Hydrogenation of *N*-Benzylideneaniline to *N*-Benzylaniline Using Different Catalysts[a]



entry	catalyst	time (h)	yield[b]
1	**2a**	24	99
2	**2b**	24	73
3	**2c**	10	98
4	**4**	24	17

[a]General conditions: imine (0.5 mmol), catalyst (0.01 mmol), KOH (0.1 mmol), ^{i}PrOH (4 mL), reflux temperature. [b]Determined by GC-MS using mesitylene as internal standard.

Imines with various functionalization displayed the same trends as observed for the ketone substrates. Electron-donating *p*-substituents on the *C*-phenyl ring of imines slow down the reaction (entry 4−5), whereas electron-withdrawing groups substantially enhance the reaction rate (entry 2−3). The position of electron-withdrawing substituents at the *C*-phenyl ring did not have much effect on the reaction outcome (entries 2 and 3 vs 6 and 7). Notably, variations of substituents on *N*-Ph ring have minimal effect on the reaction rate (entries 2 and 11/12) and this is in sharp contrast with the *C*-Ph ring substituents that have substantially higher influences (entries 2−5 vs 10−12). α-Naphthalene-based aldimine, although sterically more crowded, was reduced faster compared to that of the β-naphthalene-based one (entries 8 and 9) possibly due to more electrophilic nature of the imine moiety in α-derivative. In contrast to aromatic aldimines, analogous aliphatic compound is a relatively poor substrate for this catalyst system, and only moderate formation of the product was achieved even after prolonged reaction time (entry 13).

Mechanistic Investigations. In order to have some insight about the reaction mechanism, various controlled experiments were carried out. The ^{1}H NMR spectra of complexes **2a** and **4** after refluxing in isopropanol for 90 min (Figures S31 and 32) did not show any loss of the *p*-cymene ligand/opening of the orthometalated ring. Although the presence of excess 1,3,5-trimethoxybenzene in the reaction mixture did not affect the yield of **2c**-catalyzed transfer hydrogenation reaction of acetophenone, the same reaction in the presence of excess *p*-cymene instead of 1,3,5-trimethoxybenzene resulted in the 20% decrease of the reaction yield. These observations indicate that the dissociation of *p*-cymene ligand might be involved in the catalytic cycle. Dissociation of *p*-cymene from the Ru(II) center during catalytic cycle has been observed previously.[16,17c,28] Addition of mercury (3 equiv with respect to substrate) does not have any effect on the reaction outcome (94% yield of isolated 1-phenyl ethanol using **2c** and 91% yield of isolated benzyl alcohol using **4** under the same reaction condition as mentioned above) which suggests the homogeneous nature of the catalytic system.[17c,29] The ^{1}H NMR spectra of reaction mixtures after reacting complexes **2a** and **4** with KOH in refluxing isopropanol showed the presence of Ru(II)−H resonances[17c,30] (−10.33 ppm, **2a** and −10.00 ppm, **4**; see the Supporting Information), which suggests that a Ru−H species is involved in the catalytic process. This is further substantiated by quantitative transformation of 4-chlorobenzaldehyde to the corresponding alcohol (within 10 min at ambient temperature) when treated with in situ generated Ru−H species from complex **2a**/**4** (see Supporting Information). On the basis of these mechanistic observations along with the related literature reports,[31] a plausible mechanism is proposed for the transfer hydrogenation of the carbonyl compounds (Scheme 2).

In the first step, reaction of precatalysts **2**/**4** with KO*i*Pr (formed via reaction of *i*PrOH with KOH under the reaction condition) would generate ruthenium(II) isopropoxide complex **A** via salt elimination. Complex **A** then undergoes β-hydride elimination[9a,17c] to form Ru(II)−H species **B** along with the elimination of acetone. In the next step, carbonyl substrate is reduced via hydride transfer (Scheme 2, **C**) followed by the elimination of the product alcohol under the regeneration of active catalyst **A**. The better activity of **2c** having the NHC ligand installed with an electron-donating substituent than that of complexes containing NHC ligands either unsubstituted (**2a**) or substituted with electron-withdrawing substituent (**2b**) may be explained by better stabilization of the positive charge at the ruthenium center produced after formal hydride transfer (Scheme 2, **C**) when an electron-rich NHC ligand is present. The activation of the carbonyl substrate possibly occurs via hydrogen bonding interaction between the carbonyl oxygen atom and the OH proton of the isopropanol (Scheme 2, **C**),[9a,32,33] as it would possibly facilitates the reaction by reducing the LUMO energy of the carbonyl substrate. We believe that the transfer hydrogenation of imines follows a similar mechanism.

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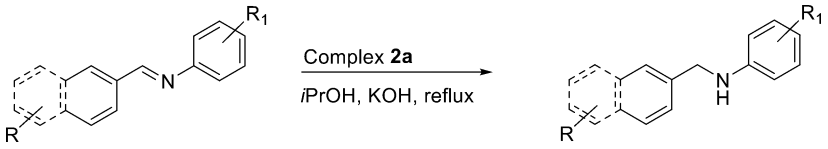
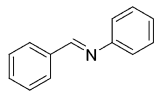
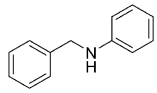
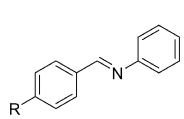
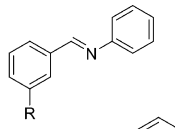
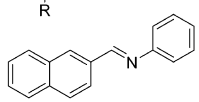
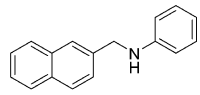
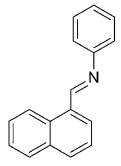
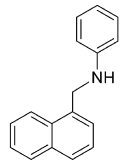
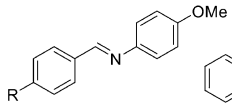
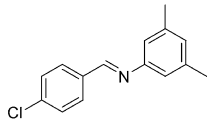
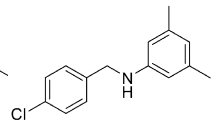
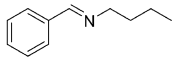
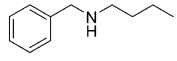
Table 6. Catalytic Transfer Hydrogenation of Various Aromatic Imines Using the Complex 2a[a]



Entry	Imine	Amine	Time (h)[b]	Yield(%)[c]
1			24	99
2	R = Cl		3	98 (95)[d]
3	Br		6	85
4	Me		20	74
5	OMe		24	90
6	R = Cl		2	99 (91)[d]
7	Br		8	98 (92)[d]
8			24 (12)	90 (79)
9			8	86
10	R = H		4	84
11	Cl		4	99 (94)[d]
12			2.5	98 (91)[d]
13			24	60

[a]General conditions: imine (0.5 mmol), complex **2a** (0.01 mmol), KOH (0.1 mmol), [i]PrOH (4 mL), reflux temperature. [b]Reaction time. [c]Determined by GC-MS using mesitylene as internal standard, average of two runs. [d]Isolated yield.

CONCLUSION

In conclusion, we have described the synthesis and characterization of air- and moisture-stable orthometalated NHC complexes **2a−c** with varying electronic properties and demonstrated that the catalytic efficiency of metal complexes can be tuned substantially by varying the stereoelectronic profile of the ancillary NHC ligands. This was exemplified by applying two different types of precatalysts featuring a planar 5-membered ruthenacycle [(*p*-cymene)(NHC)Ru^{II}(X)] (**2a−c**, containing substituted imidazolylidene NHC ligand, and **4**, containing a bulky mesoionic triazolylidene ligand) in the catalytic reduction of a library of carbonyl compounds via transfer hydrogenation strategy. *p*-OMe-substituted NHC-ligand-containing precatalyst **2c** performed significantly better than other catalysts in the reduction of ketones, whereas the precatalyst **4** was found to be superior for aldehyde reductions. In addition, precatalyst **2a** is more suited than other complexes studied here for the transfer hydrogenation of various aromatic aldimines to produce selectively the corresponding amines. We believe that this type of stereoelectronic tuning of the catalytic activity of Ru(II)−NHC catalysts would be potentially useful for the future development of efficient catalysts. Further applications of these electronically tunable Ru(II) precatalysts in other hydride transfer reactions are underway in our laboratory.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under argon atmosphere using either standard Schlenk line or Glove box techniques. Glassware was dried at 130 °C in an oven overnight before use. The solvents used for the synthesis were dried, distilled, and degassed by standard methods and stored over 4 Å molecular

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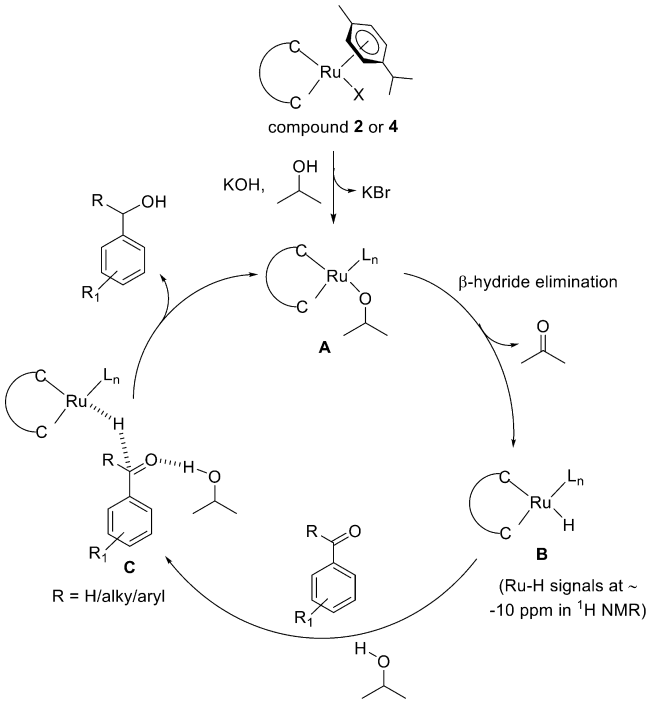
Scheme 2. Proposed Catalytic Cycle for the Transfer Hydrogenation Reaction



sieves. NMR measurements were performed on Bruker 400 and 500 MHz FT-NMR spectrometers. The chemical shifts in the ^{1}H NMR spectra were referenced to the residual proton signals of the deuterated solvents ($CDCl_3$, ^{1}H 7.26 ppm and $^{13}C\{^1H\}$ 77.16 ppm) and reported relative to tetramethylsilane. Coupling constants are expressed in Hz. ESI-MS spectra were recorded with a Micromass Q-TOF Mass spectrometer or an Agilent 6545A Q-TOF Mass spectrometer and elemental analysis were performed using PerkinElmer 24000 instrument. The starting materials $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$[34a] and imines[34b,c] were prepared according to literature procedures. 1-Phenylimidazole/4-substituted phenyl imidazoles were synthesized using modified procedure described in ref 34d. All other chemicals were purchased from commercial sources and used as received without further purification.

General Procedure for the Synthesis of Imidazolium Salts 1a−c. 1-Phenylimidazole and excess ethylbromide were taken in a 50 mL pressure tube. After adding CH_3CN, the resulting suspension was stirred at 80 °C for 12 h. After cooling to ambient temperature, the reaction mixture was dried in vacuo. The obtained residue was dissolved in DCM, and diethyl ether was added to get off-white precipitate. After decanting the solvent, the solid was dried under reduced pressure to get pure imidazolium salts **1a−c**.

Compound **1a**[35a] was synthesized using 1-phenylimidazole (1.652 g, 11.47 mmol) and ethyl bromide following the above-mentioned procedure. Yield: 2.38 g (9.405 mmol, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.88 (s, N−CH−N, 1H), 7.78−7.75 (m, 4H), 7.56−7.48 (m, 3H), 4.63 (q, $^3J_{H-H}$ = 7.4 Hz, N−CH_2CH$_3$, 2H), 1.64 (t, $^3J_{H-H}$ = 7.4 Hz, N−CH$_2$$CH_3$, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 135.8, 135.7, 134.5, 130.6, 130.3, 122.8, 121.9, 120.7, 45.8, 15.8 ppm. MS (ESI, positive ions): m/z 173.1112 (calculated for $[M - Br^-]^+$ 173.1100).

Compound **1b**[35b] was synthesized using 1-(4-trifluoromethyl)-phenylimidazole (1.00 g, 4.71 mmol) and ethyl bromide following the procedure mentioned above. Yield: 1.06 g (3.302 mmol, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.05 (s, N−CH−N, 1H), 8.14−8.10 (m, 3H), 7.88 (s, 1H), 7.76 (d, $^3J_{H-H}$ = 8.1 Hz, Ar−H, 2H), 4.57 (q, $^3J_{H-H}$ = 7.2 Hz, N−CH_2CH$_3$, 2H), 1.63 (t, $^3J_{H-H}$ = 7.3 Hz, N−CH$_2$$CH_3$, 3H) ppm. $^{13}C\{^1H\}$ (126 MHz, $CDCl_3$) δ 137.0, 136.2, 127.9 (q, J = 3.7 Hz), 123.4, 122.6, 121.1, 46.1, 15.8 ppm. MS (ESI, positive ions): m/z 241.0985 (calculated for $[M - Br^-]^+$ 241.0951).

Compound **1c** was synthesized using 1-(4-methoxy)-phenylimidazole (0.710 g, 4.08 mmol) and ethyl bromide following the procedure mentioned above. Yield: 0.921 g (3.265 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.71 (s, N−CH−N, 1H), 7.80 (s, 1H), 7.73 (s, 1H), 7.67 (d, $^3J_{H-H}$ = 8.9 Hz, Ar−H, 2H), 6.96 (d, $^3J_{H-H}$ = 8.9 Hz, Ar−H, 2H), 4.57 (q, $^3J_{H-H}$ = 7.3 Hz, N−CH_2CH$_3$, 2H), 3.78 (s, OMe, 3H), 1.60 (t, $^3J_{H-H}$ = 7.3 Hz, N−CH$_2$$CH_3$, 3H) ppm. $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$) δ 160.7, 135.2, 127.5, 123.4, 122.8, 121.1, 115.5, 55.8, 45.6, 15.8 ppm. MS (ESI, positive ions): m/z 203.1179 (calculated for $[M - Br^-]^+$ 203.1184).

Synthesis of Compound 2a. THF (15 mL) was added to a Schlenk flask containing **1a**(0.200 g, 0.79 mmol), $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$(0.242 g, 0.395 mmol), Cs_2CO_3(0.515 g, 1.58 mmol), and NaBr (0.244 g, 2.37 mmol). The resulting deep red suspension was stirred at 70 °C under argon atmosphere for 24 h. After that. the reaction mixture was cooled to room temperature and filtered through neutral alumina. The filtrate was then concentrated to 5 mL, and pentane was added to get precipitate. The precipitated solid was then dissolved in dichloromethane, filtered, and the filtrate dried under reduced pressure to get the desired product as red solid. Yield: 0.300 g (0.617 mmol, 78.1%). Crystals suitable for X-ray diffraction study were obtained by slow diffusion of hexane into a saturated solution of the compound in THF at ambient temperature. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11−8.08 (m, Ar−H, 1H), 7.36 (d, $^3J_{H-H}$ = 1.3 Hz, imidazole H5/H4, 1H), 7.06−7.05 (m, Ar−H, 1H), 7.01 (d, $^3J_{H-H}$ = 1.3 Hz, imidazole H5/H4, 1H), 6.95−6.94 (m, Ar−H, 2H), 5.57 (d, $^3J_{H-H}$ = 5.6 Hz, p-cymene−Ph, 1H), 5.54 (d, $^3J_{H-H}$ = 5.5 Hz, p-cymene−Ph, 1H), 5.40 (d, $^3J_{H-H}$ = 5.6 Hz, p-cymene−Ph, 1H), 5.31 (d, $^3J_{H-H}$ = 5.5 Hz, p-cymene−Ph, 1H), 4.65−4.41 (m, N−CH_2CH$_3$, 2H), 2.25 (sept, $^3J_{H-H}$ = 6.9 Hz, p-cymene−iPr, 1H), 2.13 (s, p-cymene−Me, 3H), 1.62 (t, $^3J_{H-H}$ = 7.3 Hz, N−CH$_2$$CH_3$, 3H), 0.91 (d, $^3J_{H-H}$ = 6.9 Hz, p-cymene−iPr, 3H), 0.76 (d, $^3J_{H-H}$ = 6.9 Hz, p-cymene−iPr, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 187.00 ($C_{carbene}$), 162.4 (C−Ru), 145.4 (C_{ar}−N), 141.9 (C_{ar}−H), 124.3 (C_{ar}−H), 122.1 (C_{ar}−H), 119.7 (C_{ar}−H/C_{im}−H), 114.5 (C_{ar}−H/C_{im}−H), 110.9 (C_{im}−H), 103.4 (C_{ar}−CH_3(cym)), 100.1 (C_{ar}−iPr(cym)), 92.4 (C_{ar}−H(cym)), 90.0 (C_{ar}−H(cym)), 87.4 (C_{ar}−H(cym)), 83.7 (C_{ar}−H(cym)), 45.6 (N-CH_2CH$_3$), 31.0 (CH-(CH$_3$)$_2$)), 23.0 (CH(CH$_3$)$_2$)), 21.7 (CH(CH$_3$)$_2$), 19.5 (CH$_3$−C_{ar}(cym), 16.7 (N-CH$_2$$CH_3$) ppm. MS (ESI, positive ions): m/z 489.0290 (calculated for $[M + H]^+$ 489.0318). Anal. Calcd (%) for **2a**: C = 51.85%, H = 5.18%, N = 5.76%. Found: C = 51.89%, H = 4.64%, N = 5.85%.

Synthesis of Compound 2b. Compound **2b** was synthesized following the procedure similar to that used for **2a** using **1b** (0.100 g, 0.312 mmol), $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$(0.096 g, 0.157 mmol), Cs_2CO_3(0.204 g, 0.625 mmol), and NaBr (0.097 g, 0.943 mmol). Yield: 0.120 g (0.217 mmol, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, Ar−H, 1H), 7.37 (d, $^3J_{H-H}$ = 1.8 Hz, imidazole H5/H4, 1H), 7.18 (d, $^3J_{H-H}$ = 8.0 Hz, Ar−H, 1H), 7.10 (d, $^3J_{H-H}$ = 8.0 Hz, Ar−H, 1H), 7.03 (d, $^3J_{H-H}$ = 1.8 Hz, imidazole H5/H4, 1H), 5.59 (m, p-cymene−Ph, 2H), 5.46 (d, $^3J_{H-H}$ = 5.9 Hz, p-cymene−Ph, 1H), 5.35 (d, $^3J_{H-H}$ = 5.8 Hz, p-cymene−Ph, 1H), 4.66−4.36 (m, N−CH_2CH$_3$, 2H), 2.22 (sept, $^3J_{H-H}$ = 6.9 Hz, p-cymene−iPr, 1H), 2.14 (s, p-cymene−Me, 3H), 1.62 (t, $^3J_{H-H}$ = 7.3 Hz, N−CH$_2$$CH_3$, 3H), 0.90 (d, $^3J_{H-H}$ = 6.9 Hz, p-cymene−iPr, 3H), 0.74 (d, $^3J_{H-H}$ = 6.9 Hz, p-cymene−iPr, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 187.98 ($C_{carbene}$), 163.4 (C−Ru), 148.2 (C_{ar}−N), 138.2−137.5 (m), 120.3, 120.0−119.7 (m), 114.8, 110.3, 104.3 (C_{ar}−CH_3(cym)), 100.8 (C_{ar}−iPr(cym)), 92.7 (C_{ar}−H(cym)), 90.3 (C_{ar}−H(cym)), 87.7 (C_{ar}−H(cym)), 84.2 (C_{ar}−H(cym)), 45.7 (N−CH_2CH$_3$), 31.1 (CH-(CH$_3$)$_2$)), 22.9 (CH(CH$_3$)$_2$), 21.7 (CH(CH$_3$)$_2$), 19.5 (CH$_3$−C_{ar}(cym), 16.6 (N−CH$_2$$CH_3$) ppm. ^{19}F NMR: (470.8 MHz, $CDCl_3$): δ −61.01 (CF_3) ppm. MS (ESI, positive ions): m/z 475.0931 (calculated for $[M - Br^-]^+$ 475.0941). Anal. Calcd (%) for **2b**: C = 47.66%, H = 4.36%, N = 5.05%. Found: C = 47.81%, H = 4.73%, N = 5.35%.

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Synthesis of Compound 2c. Compound **2c** was synthesized following the procedure similar to that used for **2a** using **1c** (0.200 g, 0.709 mmol), $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$(0.218 g, 0.354 mmol), Cs_2CO_3(0.462 g, 1.418 mmol), and NaBr (0.220 g, 2.127 mmol). Yield: 0.220 g (0.426 mmol, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, $^3J_{H-H}$ = 2.0 Hz, imidazole H4/H5, 1H), 7.29 (d, $^3J_{H-H}$ = 2.0 Hz, imidazole H5/H4, 1H), 6.99 (d, $^3J_{H-H}$ = 8.4 Hz, Ar−H, 2H), 6.47 (dd, J = 8.4 HZ, 2.0 Hz, Ar−H, 1H), 5.55 (d, $^3J_{H-H}$ = 5.7 Hz, p-cymene−Ph, 1H), 5.51 (d, $^3J_{H-H}$ = 5.5 Hz, p-cymene−Ph, 1H), 5.40 (d, $^3J_{H-H}$ = 5.7 Hz, p-cymene−Ph, 1H), 5.31 (d, $^3J_{H-H}$ = 5.5 Hz, p-cymene−Ph, 1H), 4.59−4.41 (m, N−CH_2CH$_3$, 2H), 3.85 (s, OMe, 3H), 2.26 (sept, $^3J_{H-H}$ = 6.8 Hz, p-cymene−iPr, 1H), 2.13 (s, p-cymene−Me, 3H), 1.62 (t, $^3J_{H-H}$ = 7.3 Hz, N−CH$_2$$CH_3$, 3H), 0.91 (d, $^3J_{H-H}$ = 6.8 Hz, p-cymene−iPr, 3H), 0.76 (d, $^3J_{H-H}$ = 6.8 Hz, p-cymene−iPr, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 185.41 ($C_{carbene}$), 164.2 (C−Ru), 155.6 (C_{ar}−OMe), 139.7 (C_{ar}−N), 127.6 (C_{ar}−H), 119.5, 114.3, 110.8, 106.6, 103.4 (C_{ar}−CH$_3$(cym)), 100.0 (C_{ar}−iPr(cym)), 92.3 (C_{ar}−H(cym)), 89.7 (C_{ar}−H(cym)), 87.5 (C_{ar}−H(cym)), 83.8 (C_{ar}−H(cym)), 55.4 (OCH$_3$), 45.5 (N−CH_2CH$_3$), 31.0 (CH(CH$_3$)$_2$)), 23.0 (CH(CH$_3$)$_2$), 21.7 (CH(CH$_3$)$_2$), 19.5 (CH$_3$−C_{ar}(cym), 16.7 (N−CH$_2$$CH_3$) ppm. MS (ESI, positive ions): m/z 519.0413 (calculated for $[M + H]^+$ 519.0424). Anal. Calcd (%) for **2c**·H_2O: C = 49.44%, H = 5.47%, N = 5.24%; Found: C = 49.19%, H = 4.80%, N = 5.50%.

Synthesis of Compound 4. THF (20 mL) was added to a Schlenk flask containing **3** (0.120 g, 0.326 mmol), $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$(0.100 g, 0.163 mmol), and Cs_2CO_3(0.232 g, 0.652 mmol). The resulting deep red suspension was stirred at 65 °C under argon atmosphere for 24 h. After that the reaction mixture was cooled to room temperature and was filtered through Celite. The reaction mixture was then concentrated to 5 mL, and hexane was added to precipitate the compound as yellow solid. The precipitated solid was washed with hexane and dried under reduced pressure. Yield: 0.156 g (0.261 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, $^3J_{H-H}$ = 7.3 Hz, 1H), 7.91 (d, $^3J_{H-H}$ = 6.8 Hz, 2H), 7.61 (m, 4H), 7.08 (t, $^3J_{H-H}$ = 6.8 Hz, 1H), 6.97 (t, $^3J_{H-H}$ = 7.3 Hz, 1H), 5.23 (d, $^3J_{H-H}$ = 5.4 Hz, p-cymene−Ph, 1H), 5.16 (d, $^3J_{H-H}$ = 5.4 Hz, p-cymene−Ph, 1H), 4.77 (d, $^3J_{H-H}$ = 5.4 Hz, p-cymene−Ph, 2H), 4.08 (s, 3H, N−CH$_3$), 2.31 (sep, $^3J_{H-H}$ = 6.9 Hz, p-cymene−iPr, 1H), 2.09 (s, p-cymene−Me, 3H), 0.86 (d, $^3J_{H-H}$ = 6.9 Hz, p-cymene−iPr, 3H), 0.73 (d, $^3J_{H-H}$ = 6.9 Hz, p-cymene−iPr, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 171.40 ($C_{carbene}$), 164.8 (C−Ru), 145.6, 144.6, 143.4, 130.7, 129.7, 128.8, 128.7, 127.0, 122.0, 113.8, 103.1 (C_{ar}−CH$_3$(cym)), 100.5 (C_{ar}−iPr(cym)), 89.24 (C_{ar}−H(cym)), 89.20 (C_{ar}−H(cym)), 88.3 (C_{ar}−H(cym)), 83.6 (C_{ar}−H(cym)), 37.1 (N-CH$_3$), 31.3 (CH(CH$_3$)$_2$)), 23.3 (CH(CH$_3$)$_2$), 21.3 (CH(CH$_3$)$_2$), 20.4 (CH$_3$−C_{ar}(cym) ppm. MS (ESI, positive ions): m/z 470.2096 (calculated for $[M - I]^+$ 470.1177) and m/z 598.1013 (calculated for $[M + H]^+$ 598.0300). Anal. Calcd (%) for **4**: C = 50.34%, H = 4.39%, N = 7.05%. Found: C = 49.93%, H = 3.90%, N = 6.78%.

General Procedure for the Catalytic Transfer Hydrogenation of Ketones/Aldehydes. Potassium hydroxide (0.2 mmol) and 2-propanol (5 mL) were added in a pressure tube, and the reaction mixture was heated to dissolve the potassium hydroxide fully. The mixture was then cooled to room temperature, and catalyst **2c** (0.005 mmol) followed by ketone (1 mmol) or catalyst **4** (0.002 mmol) followed by aldehyde (2 mmol) were added. The reaction mixture was then heated to reflux for the specified time. To determine the yield by GC-MS, either 1 mmol (for ketone) or 2 mmol (for aldehyde) of mesitylene was added to the reaction mixture and after the specified time, a 50 μL aliquot was taken and diluted with 1 mL of methanol for GC-MS analysis. For the isolation of the alcohols, all the volatiles were removed by rotatory evaporator after completion of the reaction. The obtained compound was then purified through silica gel column using hexane and ethyl acetate as an eluent.

General Procedure for the Catalytic Transfer Hydrogenation of Imines. To an oven-dried pressure tube with 4 Å molecular sieves, potassium hydroxide (0.1 mmol) and 2-propanol (4 mL) were added and degassed by passing argon for a few minutes. Then, to this solution was added catalyst **2a** (0.01 mmol) followed by imine (0.5 mmol). The reaction mixture was then heated to reflux for the specified time. To determine the yield by GC-MS, 0.5 mmol of mesitylene was added to the reaction mixture, and after the specified time, a 50 μL aliquot was taken and diluted with 1 mL of methanol for GC-MS analysis. For isolation, all the volatiles were removed by rotatory evaporator after completion of the reaction. The residue was then purified by silica gel flash column chromatography using ethyl acetate and hexane as eluent.

Single Crystal X-ray Crystallography. X-ray data were collected on a Bruker APEX-II or Bruker AXS Kappa APEX-II CCD diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Crystal was fixed at the tip of a glass fiber loop, and after mounting on the goniometer head, it was optically centered. The APEXII and APEXII-SAINT program were used for the data collection and unit cell determination, respectively.[36a] Processing of the raw frame data was performed using SAINT/XPREP.[36a,c] The structures were solved by SHELXT-2014/4 methods[36d] and refined against F^2 using all reflections with the SHELXL-2014/7 (WinGX) program.[36e,f] Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. The crystal data (CCDC Nos. 1856325−1856326) and refinement details are summarized in Table S1. The graphical representations were performed using the program Mercury.[36g]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b02246.

Characterization data for compounds **1**−**4** and the isolated organic compounds from catalytic run (PDF)

Accession Codes

CCDC 1856325−1856326 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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