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Dehydrogenation

Metal–Ligand Cooperation on a Diruthenium Platform: Selective Imine Formation through Acceptorless Dehydrogenative Coupling of Alcohols with Amines

Biswajit Saha, S. M. Wahidur Rahaman, Prosenjit Daw, Gargi Sengupta, and Jitendra K. Bera*[a]

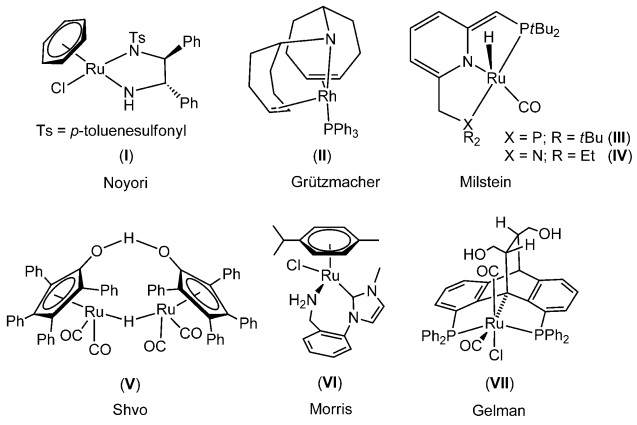
Dedicated to Dr. Ganesh Pandey on the occasion of his 60th birthday

Abstract: Metal–metal singly-bonded diruthenium complexes, bridged by naphthyridine-functionalized N-heterocyclic carbene (NHC) ligands featuring a hydroxy appendage on the naphthyridine unit, are obtained in a single-pot reaction of $[Ru_2(CH_3COO)_2(CO)_4]$ with 1-benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazolium bromide (BIN·HBr) or 1-isopropyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazolium bromide (PIN·HBr), $TlBF_4$, and substituted benzaldehyde containing an electron-withdrawing group. The modified NHC-naphthyridine-hydroxy ligand spans the diruthenium unit in which the NHC carbon and hydroxy oxygen occupy the axial sites. All the synthesized compounds catalyze acceptorless dehydrogenation of alcohols to the corresponding aldehydes in the presence of a catalytic amount of weak base 1,4-diazabicyclo[2.2.2]octane (DABCO). Further, acceptorless dehydrogenative coupling (ADHC) of the alcohol with amines affords the corresponding imine as the sole product. The substrate scope is examined with **1** (BIN, *p*-nitrobenzaldehyde). A similar complex $[Ru_2(CO)_4(CH_3COO)(3\text{-PhBIN})][Br]$, that is devoid of a hydroxy arm, is significantly less effective for the same reaction. Neutral complex **1a**, obtained by deprotonation of the hydroxy arm in **1**, is found to be active for the ADHC of alcohols and amines under base-free conditions. A combination of control experiments, deuterium labeling, kinetic Hammett studies, and DFT calculations support metal–hydroxyl/hydroxide and metal–metal cooperation for alcohol activation and dehydrogenation. The bridging acetate plays a crucial role in allowing β-hydride elimination to occur. The ligand architecture on the diruthenium core causes rapid aldehyde extrusion from the metal coordination sphere, which is responsible for exclusive imine formation.

Introduction

In metal-catalyzed reactions, the catalytic activity is mainly metal-based, whereas the ligand plays important roles in modulating electron density on the metal and controlling the steric environment around it. However, there is an emerging class of catalysts in which the ligand actively participates in bond-breaking and bond-making processes, causing a reversible structural transformation of the catalyst during substrate activation and product formation.[1] Synergistic cooperation between metal and ligand is recognized to promote superior catalytic activity both in natural and synthetic systems.[2]

The concept of metal–ligand cooperativity has been exploited to develop a new generation of bifunctional catalysts. Noyori's catalyst (Scheme 1, **I**), which utilizes metal–amine/metal–amide interconversion for the hydrogenation of carbonyl and carbonyl-type compounds, inspired much activity in this area.[3] The interplay between Lewis acidic Rh and coordinated amide nitrogen in Grützmacher's catalyst (**II**) is linked to dehydrogenative coupling of primary alcohols with water, methanol, or amine.[4] Milstein's elegant PNP–Ru (**III**) and PNN–Ru (**IV**) systems display an interesting mode of cooperation involving



Scheme 1. Metal–ligand cooperating catalysts.

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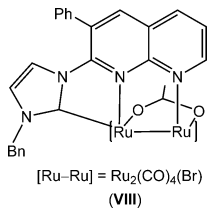
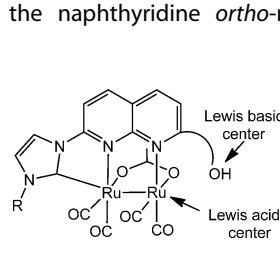
ligand aromatization/dearomatization, which is exploited for catalytic dehydrogenative synthesis of esters, acetals, imines, amines, and amides from alcohols and the reverse reactions.[5] Aliphatic PNP pincer complexes catalyze transfer hydrogenation of ketones and imines, hydrogenation of esters, and dehydrogenation of ammonia–boron adducts.[6] Shvo's catalyst (**V**) dehydrogenates secondary alcohols following a simultaneous β-elimination and proton transfer to the metal.[7] Although the original catalyst is a dinuclear complex, the active species contains a single Ru.[8] Yamaguchi and Fujita reported an Ir catalyst that contains hydroxy pyridine for acceptorless dehydrogenation of secondary alcohols.[9] Morris et al. have performed detailed mechanistic investigations of alcohol-assisted outer-sphere hydrogenation of ketones catalyzed by a Ru–NHC complex incorporating an amine appendage (**VI**).[10] Gelman introduced a dibenzobarrelene-based PC(sp^3)P pincer ligand (**VII**) that features -CH_2OH arms.[11] Intramolecular cooperation between the metal and the hydroxide functionality brings about the acceptorless dehydrogenative coupling (ADHC) of alcohols with amines.[12]

Recent activities on bifunctional catalysis have focused on the discovery of new cooperation modes and the fabrication of novel molecular platforms. Carefully designed metal–ligand cooperation has the potential to realize better performing catalysts and enable the development of new reactions. We have been exploring bimetallic reactivity with the intention of developing useful catalysts based on bimetallic systems.[13] Towards this end, naphthyridine-functionalized N-heterocyclic carbene (NHC) ligands have been incorporated on a metal–metal singly bonded [Ru^I–Ru^I] platform.[14] Site-directed anchoring of the ligand afforded a bridged complex **VIII** (Scheme 2) featuring an accessible axial site that was exploited for carbene-transfer catalysis to a variety of substrates.[14] We proposed that the introduction of a protonic arm (−XH; X = O, N) might result in cooperative action with the metal at the axial site, as illustrated in Scheme 3.

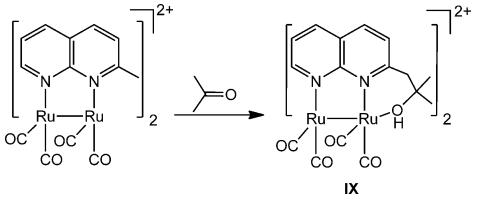


Scheme 2. Napthyridine–NHC bridged diruthenium(I) complex.

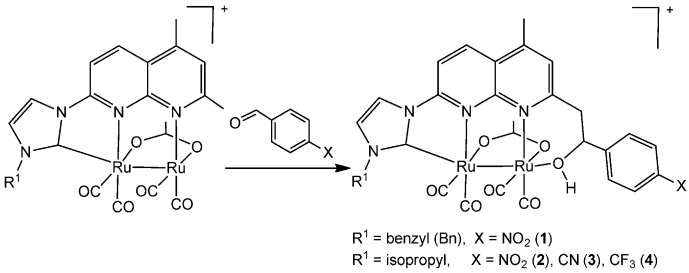
Functionalization at the *ortho*-position of the naphthyridine unit is a difficult exercise. This was, however, previously achieved through the use of an aldol-type C–C bond-formation reaction between the naphthyridine *ortho*-methyl substituent and carbonyl compounds on a $[Ru_2(CO)_4]^{2+}$ framework (Scheme 4).[15] In this work, electron-deficient aromatic benzaldehydes were found to work well with naphthyridine-NHC ligands. Four new diruthenium(I) complexes are described bearing ligands that offers a protonic arm at the site *trans* to the Ru–Ru bond (Scheme 5). These compounds activate the alcohol and catalyze ADHC of alcohols with amines for exclusive formation of the corresponding imine. The metal–ligand cooperation mechanism is also examined in this work.



Scheme 3. Proposed metal–ligand interplay at axial site of a diruthenium platform.



Scheme 4. C–C bond-forming reaction through aldol-type addition on a $[Ru_2(CO)_4]$ core.



Scheme 5. Syntheses of diruthenium–NHC complexes bearing a protonic arm at the axial site (present work).

Results and Discussion

Single-pot reaction between $[Ru_2(CO)_4(CH_3COO)_2]$, 1-benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazolium bromide (BIN·HBr) or 1-isopropyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazolium bromide (PIN·HBr), $TlBF_4$, and benzaldehydes containing an electron-withdrawing group in the *para* position, provided compounds **1**–**4**. Metal coordination of the BIN or PIN ligand is vital prior to C–C coupling. Isolation of $[Ru_2(CO)_4(CH_3COO)(3\text{-PhBIN})](Br)$ (**VIII**) confirmed the bridging disposition of the ligand on the diruthenium(I) core.[14] $TlBF_4$ removed the axial bromide, and subsequent aldol-type C–C bond formation with different aldehydes gave the desired compounds. It must be noted here that only electron-deficient benzaldehydes containing an electron-withdrawing nitro, cyanide, or trifluoromethyl group afforded coupled products; attempts to use ketones or electron-rich aldehydes failed. These results are in contrast to C–C coupled products obtained with a variety of ketones and 2-methyl-naphthyridine on the $[Ru_2(CO)_4]^{2+}$ core.[15] Natural population analysis charge (NPA) calculations on $[Ru_2(CO)_4(CH_3COO)(3\text{-PhBIN})]Br$ show that NHC-based ligands make the Ru centers sufficiently electron rich,[14] but fails to activate ketones or electron-rich aldehydes efficiently. Another plausible explanation involves the *trans* NHC unit, which

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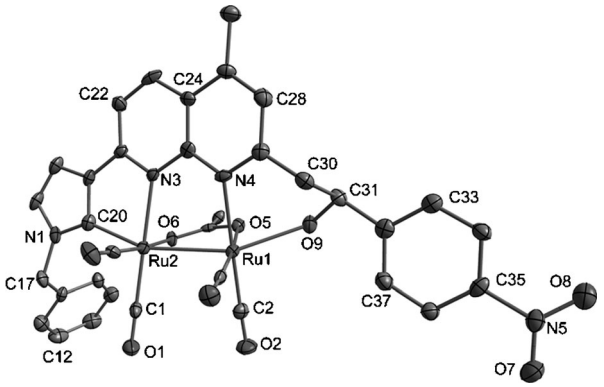

Figure 1. Molecular structure (40% probability thermal ellipsoids) of **1** with important atoms labeled. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–Ru2 2.667(1), Ru2–C20 2.061(5), Ru1–C2 1.833(6), Ru1–O5 2.134(3), Ru1–N4 2.192(4), Ru1–O9 2.338(4), Ru2–C1 1.843(5). C4-Ru1-Ru2 95.3(2), O5-Ru1-Ru2 82.9(1), N4-Ru1-Ru2 85.3(2), O9-Ru1-Ru2 152.8(1), C20-Ru2-O6 83.1(2), C20-Ru2-N3 77.3(2), C20-Ru2-Ru1 157.7(2), O6-Ru2-Ru1 84.2(9), C5-O6-Ru2 121.6(3), C31-O9-Ru1 121.8(3).

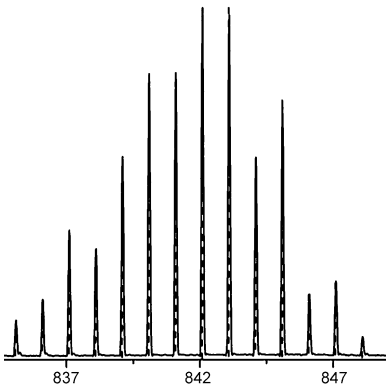

Figure 2. Simulated (dotted line) and experimental (solid line) mass distributions for $[\mathbf{1}-BF_4]^+$.

prohibits strong axial binding of the aldehyde and means that the carbonyl carbon is not electrophilic enough to be attacked by the methyl carbon.

The X-ray structure of $[Ru_2(L^1)(CO)_4(CH_3COO)][BF_4]$, in which L^1 = 2-[7-(3-benzyl-1*H*-imidazol-1-ylidene)-5-methyl-1,8-naphthyridin-2-yl]-1-(4-nitrophenyl)ethanol (**1**; Figure 1) revealed the formation of a modified naphthyridine-NHC ligand L^1 through C–C bond formation between BIN and *p*-nitrobenzaldehyde. The diruthenium unit is spanned by the ligand and is additionally bridged by an acetate unit. Two carbonyl groups are oriented *cis* to each ruthenium. The Ru–Ru distance 2.667(1) Å is similar to that previously reported for the naphthyridine-NHC bridged diruthenium complex $Ru_2(CO)_4(CH_3COO)$(3-PhBIN)Br (**VIII**; 2.691(1) Å).[14] The carbene carbon is axially coordinated and the second axial site is occupied by a weakly bound OH group, with a Ru–O distance of 2.338(4) Å. The strong *trans* effect of the carbene carbon leads to a longer Ru–O distance compared with $[Ru_2(CO)_4(L')_2][BF_4]_2$ (**IX**; L′ = 2-methyl-1-(1,8-naphthyridin-2-yl)propan-2-ol) (2.244(6) Å).[15] Similar compounds were achieved for *p*-nitrobenzaldehyde (**2**; Figure S1 in the Supporting Information), *p*-cyanobenzaldehyde (**3**; Figure S3), and *p*-trifluoromethylbenzaldehyde (**4**; Figure S5) with PIN as NHC ligand. All four compounds feature a common hydroxy arm at the axial site of the $Ru_2(CO)_4$ core.

The ^{1}H NMR spectrum of **1** reveals an interesting pattern (Figure S7). The methylene 'CH_2' protons show two apparent AB quartet signals centered at δ = 4.03 and 4.35 ppm with ^2J(H,H) values 14.4 and 14.2 Hz, respectively. The appearance of the AB pattern is due to a comparable chemical shift difference and coupling constant. The remaining ^{1}H signals are consistent with its solid-state structure. The carbene carbon is observed at δ = 173 ppm in the ^{13}C NMR spectrum, and the ESI-MS exhibits the expected signal at *m/z* 842, which is assigned for $[\mathbf{1}-BF_4]^+$ (Figure 2).

Catalysts that perform acceptorless dehydrogenation (AD) are of significant importance.[16] The process involves extraction of hydrogen from unreactive alcohol without the need for a stoichiometric amount of oxidant, thereby providing a non-polluting route to aldehydes and related products.[17] The accessible protonic arm at the axial site of the diruthenium–NHC complexes prompted us to study possible bifunctional acceptorless dehydrogenation of alcohols to aldehydes. Reaction of 1 mmol benzyl alcohol and 1 mol% catalyst **1** in toluene at reflux for 24 h in the presence of 5 mol% KOH afforded 98% conversion into benzaldehyde. More importantly, addition of 1.2 mmol benzylamine and 4 Å molecular sieves to this reaction afforded *N*-benzylidene benzylamine as a single product in high yield (>90%). First we screened a range of bases in the model reaction involving 1 mmol benzyl alcohol and 1.2 mmol benzylamine. Interestingly, conversions were very similar for a range of bases, including KOH, KO*t*Bu, NaH, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,4-diazabicyclo-[2.2.2]octane (DABCO) (Table 1). Only 5 mol% base was sufficient to afford maximum conversion with 1 mol% catalyst. Subsequent reactions were performed with DABCO as base. Molecular sieves were essential for imine formation; performing the reaction in their absence gave a mixture of products (aldehyde, amine and imine). The reaction was not efficient at room temperature and best results were obtained in toluene at reflux (110 °C). Compounds **2**–**4** were also employed for the model reaction under the optimized conditions and they afforded similar conversions (92–95%; Table 2). Remaining studies were carried out with **1** because of its easy accessibility as a pure, crystalline product.

The substrate scope was then examined under the optimized conditions (catalyst **1** (1 mol%), alcohol/amine (1:1.2 mol), DABCO (5 mol%), 4 Å molecular sieves, toluene, reflux, 24 h). Electron-rich *p*-methoxybenzyl alcohol gave excellent conversions into the corresponding imines with benzylamine (96%; Table 3, entry 1), *p*-methylbenzylamine (94%; entry 2), cyclohexylamine (94%; entry 3), and hexylamine (91%; entry 4). Substrates *p*-methylbenzyl alcohol and benzyl alcohol afforded good yields with a range of amines (92–71%; entries 6–15). Electron-deficient *p*-nitrobenzyl alcohol gave relatively lower yields compared with electron-rich alcohols (entries 16 and 17). Reaction of 2-phenylethanol with benzylamine or hexylamine provided 86 and 82% imine (entries 18 and 19). Long-chain al-

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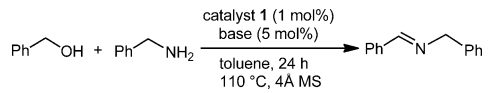
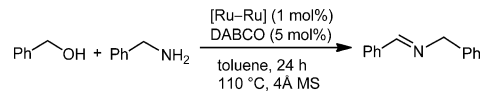
Table 1. Screening of base for imine formation catalyzed by **1**.[a]



Entry	Base	Conversion [%][b]
1	KOH	95
2	KO*t*Bu	95
3	NaH	94
4	DBU	92
5	DABCO	92

[a] Reaction conditions: benzyl alcohol (1 mmol), benzylamine (1.2 mmol), base (5 mol%), catalyst **1** (1 mol%), toluene, 4 Å molecular sieves, reflux, 24 h. [b] Conversions determined by GC analysis.

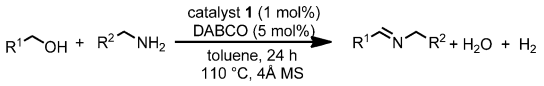
Table 2. Catalyst screening.[a]



Entry	Catalyst	Base	Conversion [%][b]
1	**1**	DABCO	92
2	**2**	DABCO	92
3	**3**	DABCO	91
4	**4**	DABCO	91
5	**1a**	DABCO	93
6	**1a**	–	66 [c]
7	**VIII**	DABCO	55
8	**IX**	DABCO	68, 86[d]

[a] Reaction conditions (unless mentioned otherwise): benzyl alcohol (1 mmol), benzylamine (1.2 mmol), DABCO (5 mol%), catalyst (1 mol%), toluene, 4 Å molecular sieves, reflux, 24 h. [b] Conversions determined by GC analysis. [c] Without any base. [d] After 48 h at 130 °C in *p*-xylene as solvent.

Table 3. Imine formation from alcohol and amine by catalyst **1**.[a]



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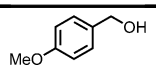
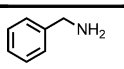
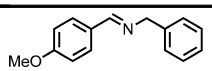
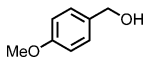
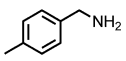
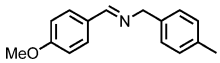
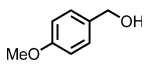
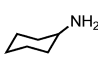
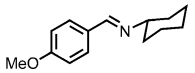
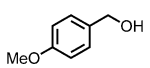
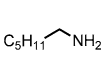
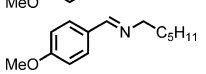
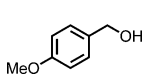
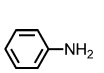
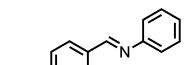
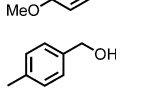
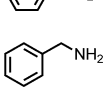
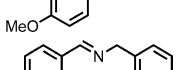
1				96
2				94
3				94
4				91
5				81
6				92

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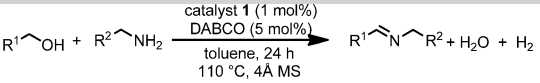
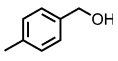
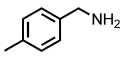
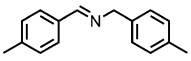
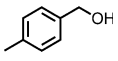
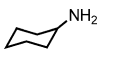
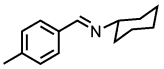
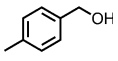
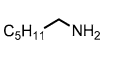
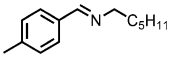
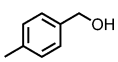
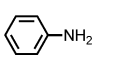
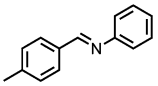
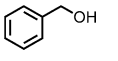
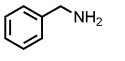
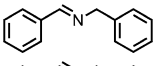
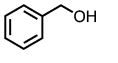
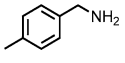
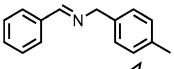


Entry	Substrate	Substrate	Product	Yield [%][b]
7				87
8				85
9				85
10				79
11				90
12				87
13				87
14				84
15				71
16				81
17				71
18				86
19				82
20				88
21				84
22				83
23				72
24				80
25				72

[a] Reaction conditions: alcohol (1 mmol), amine (1.2 mmol), DABCO (5 mol%), catalyst **1** (1 mol%), toluene, 4 Å molecular sieves, reflux, 24 h. [b] Yield determined by GC-MS analysis with nonane as internal standard.

cohols octanol and hexanol afforded lower yields than benzyl alcohol when treated with benzylamine and hexylamine (entries 20–23). With 2-ethoxyethanol, benzylamine and hexylamine provided 80 and 72% imine, respectively. Aniline converted into the corresponding imines when reacted with *p*-methoxybenzyl alcohol (81%), *p*-methylbenzyl alcohol (79%), or benzyl alcohol (71%) (entries 5, 10 and 15).

The Ru–NHC complex [$RuCl_2$(I*i*Pr)(*p*-cymene)] (I*i*Pr = 1,3-diisopropylimidazol-2-ylidene) catalyzes imine formation from alco-

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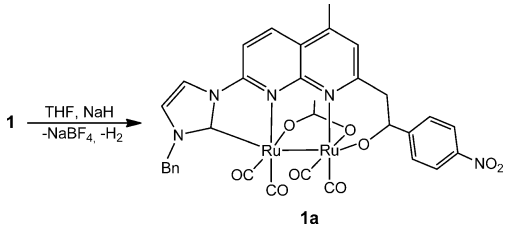
hols and amines with DABCO,[18] but gave amide in the presence of strong base KO*t*Bu (15 mol%) and additive $PCy_3{\cdot}HBF_4$ (5 mol%).[19] Bifunctional catalyst **1**, however, gave only imine, irrespective of the nature of the base. Furthermore, **1** also afforded an imine in the case of aniline, for which the Ru–NHC complex failed to give a clean product. Gelman's bifunctional catalyst (**VII**) showed catalytic activity for imine formation exploiting hydroxy/hydroxide cooperation.[12]

Diruthenium(I) catalyst $[Ru_2(CO)_4(CH_3COO)(3\text{-PhBIN})][Br]$ (**VIII**), which is devoid of a hydroxy appendage, dehydrogenated benzyl alcohol less efficiently than **1** under identical conditions (59 vs. 98%). Accordingly, lower imine conversion (55%) was observed for **VIII** than for **1** (92%) for the model reaction (Table 2, entry 7). This result implies that the hydroxy appendage promotes alcohol dehydrogenation. We further employed catalyst **IX**, which contains two naphthyridine-based ligands, but this afforded lower imine conversion (68%). The conversion improved to 86% upon prolonged heating for 48 h at elevated temperature (130 °C).

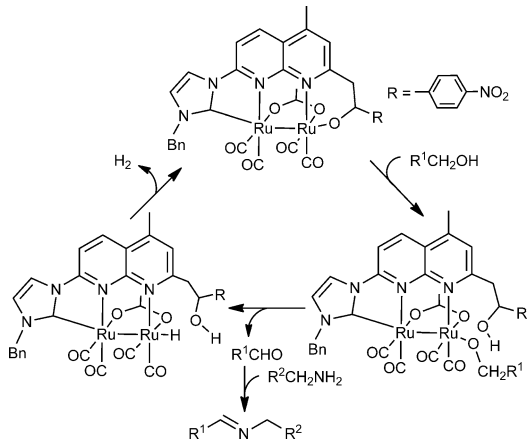
The use of base was essential for this reaction; in the absence of base, catalyst **1** gave less than 5% conversion for the reaction between benzyl alcohol and benzylamine, and unreacted alcohol and amine were recovered from the reaction mixture. Obtaining imines from alcohols and amines under base-free conditions is a challenge met by very few catalysts.[5c] A neutral complex **1a**, which exhibited high solubility in common organic solvents, was synthesized by reacting **1** with NaH in tetrahydrofuran (Scheme 6), and the ^{1}H NMR spectrum



Scheme 6. Synthesis of compound **1a**.

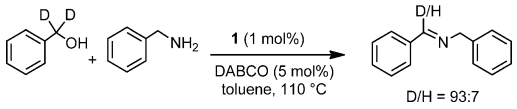
of this complex showed a downfield shift of the methylene protons by $\Delta\delta = 0.16$ and 0.28 ppm compared with **1**. The remaining proton signals in the NMR spectrum were similar to those of **1**. We could also achieve conversion of **1a** into **1** in the presence of alcohol.[20] Compound **1a** catalyzed the model ADHC reaction in the absence of any base with 55% conversion. *p*-Methoxybenzyl alcohol afforded 68 and 66% imine products with benzylamine and *p*-methylbenzylamine, respectively, under base-free conditions, and the reaction between *p*-methylbenzyl alcohol and benzylamine gave the corresponding imine in 60% conversion. Thus, the bimetallic Ru system exhibited moderate activity under acceptorless and base-free conditions for imine formation, although the yields were lower than those obtained with Milstein's PNP–Ru catalyst (**III**).[5c] The conversion improved upon the addition of base, finally matching the activity of **1**.

We propose a bifunctional mechanism to account for the conversion of alcohol into aldehyde. Because neutral **1a** exhibits substantial activity in the absence of base, it is assumed that the active catalytic species is the deprotonated form of **1**. The alcohol is activated in a bifunctional manner to form axial diruthenium-alkoxide, causing the hydroxy arm to open up (Scheme 7). Subsequent β-hydride elimination of alkoxide produces the aldehyde and the [Ru–Ru]-H intermediate. In the absence of amine, the hydride intermediate has been identified by a characteristic signal at $\delta = -7.37$ ppm in the ^{1}H NMR spectrum.[21] The active catalyst is regenerated with the liberation of hydrogen and the extruded aldehyde reacts with amine to give the imine as the final product.[22]



Scheme 7. Proposed mechanism for imine formation.

To investigate the mechanism in more detail, we carried out studies with deuterated alcohol. A model imination reaction in $[D_8]$toluene did not afford deuterated product, thus ruling out the possibility of isotope scrambling from solvent. Reaction of α,α-$[D_2]$-benzyl alcohol with benzylamine gave deuterated *N*-benzylidene benzylamine as the major product (93:7 D/H observed by GC-MS analysis; Scheme 8). The conventional metal-



Scheme 8. Imination with α,α-$[D_2]$-benzyl alcohol by catalyst **1**.

based mechanism involves a Ru^{II}-dihydride species, which undergoes reductive elimination followed by oxidative addition of alcohol to a Ru^{II}-hydride-alkoxide species (see Scheme S1).[18,23] Such a process necessarily leads to hydrogen scrambling in the product. Madsen et al. observed 42% hydrogen incorporation for the catalyst $[RuCl_2(I\textit{i}Pr)(p\text{-cymene})]$, which lacks functional attributes for metal–ligand cooperation.[18] The absence of significant isotope scrambling is indicative of a bifunctional mechanism that involves a Ru-monohydride intermediate.[24] The ^{1}H NMR spectrum reveals only one

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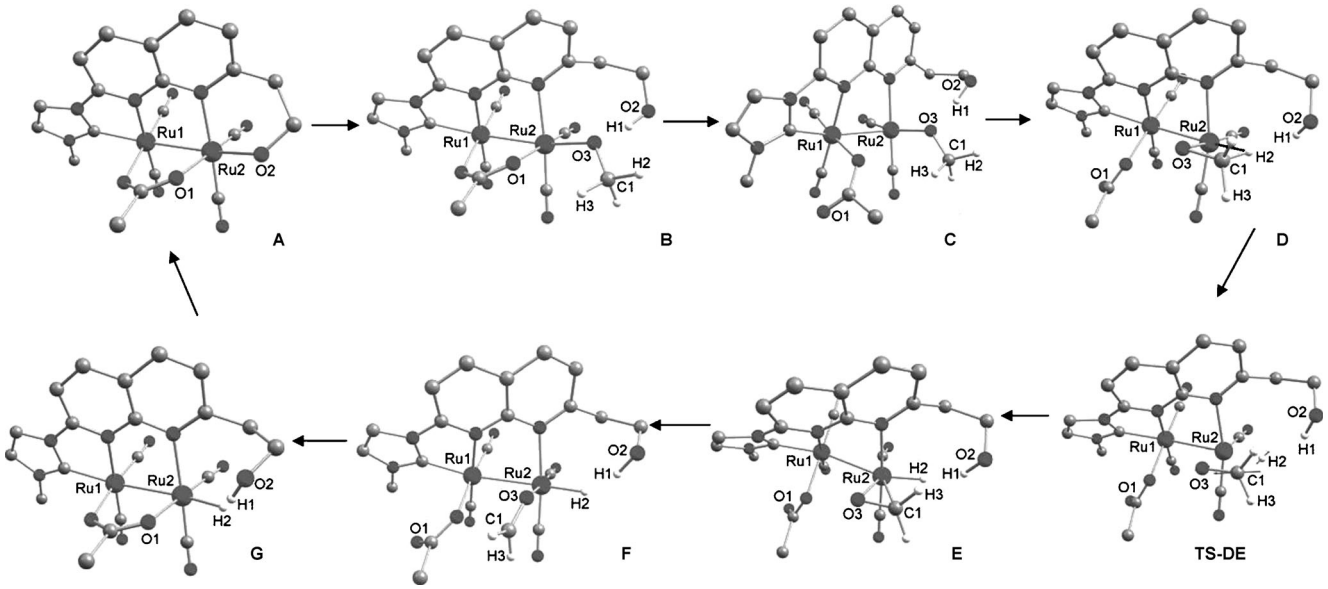
signal corresponding to the metal-hydride.[25] The dehydrogenation step involves the metal-hydride and the accessible ligand proton. The presence of the generated hydrogen gas was confirmed by GC (thermal detector) techniques.[26]

One important aspect of catalyst **1** is that it selectively affords imines without any trace of amide or other side-products. It is recognized that the ability of the metal unit to bind the intermediate product aldehyde determines the product identity.[5c,27] The amine attacks the metal-coordinated aldehyde and gives a hemiaminal that undergoes dehydration to afford an imine or, alternatively, an amide is obtained that is generated through a second dehydrogenation process.[27] The NHC-based ligand architecture on the diruthenium core ensures rapid extrusion of aldehyde from the metal coordination sphere, which, on reaction with amine, produces imine and water. A reaction of benzyl alcohol with catalyst **1** did not afford any trace of benzyl benzoate (GC-MS analysis) after 24 h, supporting the assertion that the aldehyde is rapidly extruded from the metal core.[23]

The key step in the acceptorless alcohol dehydrogenation reaction is β-hydride elimination, which requires a vacant site *cis* to the alkoxide group.[28] The bridging acetate in **1** possibly moves away from μ^2 to η^1 mode, providing a pathway for the elimination to occur. This is apparent because complex **IX**, which features hydroxy arms but does not contain acetate, gave lower yields under identical reaction conditions. The conversion improved on prolonged heating at higher temperature (Table 2, entry 8). It is assumed that one of the ligands undergoes demetallation at high temperature, paving the way for the reaction to occur.

Kinetic Hammett studies were carried out to investigate the key β-hydride elimination step. Benzyl alcohol was allowed to compete with *para*-substituted benzyl alcohols (X = OMe, Me, F, NO_2) in reaction with benzylamine (Scheme S2). The progress of the reaction was monitored by GC-MS analysis and a linear relationship was obtained for the plot of $\ln(c_0/c)$ of substituted benzyl alcohols against the same values for benzyl alcohol (Table S1), confirming first-order dependence of the reaction with respect to alcohol. The slopes of the straight lines gave relative reactivities (k_X/k_H), which were plotted against all possible σ values (σ^+, σ^-, $\sigma^\cdot$) of a particular substituent.[19a,29] A straight line was successfully generated only with σ^+ with a negative slope ($\rho = -0.703$) (Figure S9), which suggests the generation of a positive charge at the benzylic position of the alcohol, thus supporting the proposition of β-hydride elimination for the conversion of alcohol into aldehyde.

To gain further mechanistic insight on the β-hydride elimination and the role of acetate, we carried out DFT calculations at the B3LYP level of theory. A simplified system was chosen whereby the benzyl group at the imidazolyl nitrogen was replaced by a methyl group and methanol was considered as the substrate. The optimized structure of the active catalytic species (Scheme 9, **A**) showed axial coordination of the hydroxide (Ru2–O2 = 2.133 Å; ∢Ru1-Ru2-O2 = 155.4°). Methanol addition resulted in an axial [Ru–Ru]-OCH_3 species **B** (Ru2–O3 = 2.148 Å) forcing the arm to open up as the hydroxy. The bridging acetate then moved away to η^1-bound mode, paving the way for β-elimination. Because we looked for an axial hydride prior to dehydrogenation, species **C** was optimized whereby the methoxide migrated from the axial to the equatorial site (Ru2–O3 = 2.044 Å), keeping the axial site open (Ru2···H1 = 3.076 Å), and it was calculated to be marginally higher (0.82 kcal mol^{-1}) in energy than **B**. The methoxide then changes its orientation to generate an agostic complex **D** that involves C–H interaction with the metal (Ru2···H2 = 2.196 Å). Subsequent β-hydride elimination leads to an axial [Ru–Ru]-H species **E** via transition state **TS-DE**, corresponding to a free energy of activation of 16.11 kcal mol^{-1}. The **TS-DE** that connects **D** and **E** was calculated to have a single imaginary frequency of −394.21 cm^{-1}, and involved movement of one



Scheme 9. Computed reaction pathway for alcohol dehydrogenation catalyzed by **1**.

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methyl proton H2 towards Ru2 and methyl carbon C1 towards methoxide oxygen O3. The Ru–H distance in **E** was calculated to be 1.688 Å, and the Ru2–O3 (2.219 Å) and Ru2–C1 (2.248 Å) distances revealed a side-on interaction with the aldehyde. A more stable intermediate (**F**; 3.26 kcal mol^{-1}) was also computed whereby the aldehyde binds through the carbonyl oxygen (Ru2–O3 = 2.185 Å; C1–O3 = 1.159 Å). The acetate reverts to the bridging mode, expelling aldehyde from the metal coordination sphere (**G**), in a process that is energetically favorable by 8.97 kcal mol^{-1}. The active catalyst **A** is regenerated by liberation of hydrogen. Thus, catalyst **1** displays both Ru–hydroxy/hydroxide and Ru–Ru cooperation for alcohol dehydrogenation and subsequent selective imine formation.

Conclusion

Catalyst **1** exhibits both metal–metal and metal–ligand cooperation for the dehydrogenative coupling reaction between alcohols and amines. Alcohol addition at the axial site followed by β-hydride elimination produces aldehyde and hydrogen. Deuterium labeling and kinetic experiments confirm bifunctional alcohol activation and dehydrogenation in the catalytic cycle. A similar diruthenium(I)–NHC complex without the hydroxy appendage was shown to be a poor catalyst. These results underscore the metal–ligand cooperation in the activity of catalyst **1**. Furthermore, the bridging acetate on the diruthenium unit plays an important role in allowing effective β-elimination to occur. The NHC-based ligand architecture promotes aldehyde extrusion from the metal coordination sphere, and the aldehyde then reacts with amine to give the corresponding imine with the loss of a water molecule. The inability of the aldehyde to reside on the dimetal core ensures no side-products such as amides are produced. The present work demonstrates metal–hydroxy/hydroxide cooperation that is reminiscent of Gelman's system but on a [Ru^{I}–Ru^{I}] platform.[12]

Experimental Section

General Procedures

All reactions with metal complexes were carried out under an atmosphere of purified nitrogen by using standard Schlenk vessel and vacuum line techniques. Infrared spectra were recorded in the range 4000–400 cm^{-1} on a Perkin Elmer Spectrum Two with KBr pellets. ^{1}H NMR spectra were obtained on a JEOL JNM–LA 400 and 500 MHz spectrometer. ^{1}H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents. ESI-MS were recorded on a Waters Micromass Quattro Micro triple quadrupole mass spectrometer. Elemental analyses were performed on a Thermoquest EA1110 CHNS/O analyzer. GC-MS experiments were performed on an Agilent 7890A GC and 5975C MS system. The recrystallized compounds were powdered, washed several times with dry diethyl ether or hexane, and dried in vacuo for at least 48 h prior to elemental analyses. Melting points were measured in open capillaries on a JSGW melting point apparatus and are uncorrected.

Materials

Solvents were dried by conventional methods, distilled under nitrogen, and deoxygenated prior to use. $RuCl_3{\cdot}nH_2O$ (39% Ru) was purchased from Arora Matthey, India. The compounds $Ru_2(CO)_4(CH_3COO)_2$, BIN·HBr, and PIN·HBr were synthesized by following the literature procedures.[13,14,30] Benzyl alcohol-α,α-$[D]_2$ was purchased from Sigma-Aldrich and used without further purification.

Synthesis of 1: The ligand precursor BIN·HBr (69 mg, 0.17 mmol) was added to an acetonitrile solution of $Ru_2(CH_3COO)_2(CO)_4$ (75 mg, 0.17 mmol) and the mixture was stirred at 60 °C for 48 h. $TlBF_4$ (49 mg, 0.17 mmol) was then added and stirred for an additional 30 min. The resulting mixture was filtered through a small pad of Celite. The clear red solution was completely evaporated under reduced pressure. The solid mass was dissolved in 15 mL of dichloromethane. *p*-Nitrobenzaldehyde (40 mg, 0.26 mmol) was added to this solution, which was stirred at room temperature for 12 h. The solvent was evaporated to dryness, and 10 mL of hexane was added with stirring to induce precipitation. The red solid was isolated, washed with hexane, and dried in vacuo. Crystals suitable for X-ray diffraction were grown by layering petroleum ether over a concentrated dichloromethane solution of compound **1** inside an 8 mm o.d. vacuum-sealed glass tube. Yield: 126 mg (78%). M.p. > 250 °C; ^{1}H NMR (500 MHz, CD_3CN, 294 K): $\delta = 8.96$ (d, $J = 9.3$ Hz, 1H, NP), 8.49 (d, $J = 9.2$ Hz, 1H, NP), 8.11 (d, $J = 2.2$ Hz, 1H, Imdz), 8.09 (d, $J = 2.1$ Hz, 1H, Imdz), 7.64 (s, 1H, NP), 7.46–7.33 (m, 9H, 2Ph), 5.62 (s, 2H, CH_2^{benzyl}), 5.60–5.58 (m, 1H, CH^{CHOH}), 4.35 (dd, $J_1 = 14.2$ Hz, $J_2 = 2$ Hz, 1H, CH_2), 4.03 (dd, $J_1 = 14.4$ Hz, $J_2 = 2$ Hz, 1H, CH_2), 2.83 (s, 3H, CH_3^{NP}), 2.55 ppm (s, 3H, CH_3^{OAc}); ^{13}C NMR (125.8 MHz, CD_3CN, 296.2 K): $\delta = 210.2$ (*C*O), 201.8 (*C*O), 196.6 (*C*O), 191.6 (*C*O), 181.8 (OCO_{OAc}), 172.9 (NCN_{Im}), 156.9 (NCN_{NP}), 155.3 ($N_{NP}CN_{Im}$), 152.3 (CCN_{NP}), 152.3 (CCC_{NP}), 141.2 (CCC_{NP}), 140.8 (CCC_{NP}), 135.6 (CCN_{Ph}), 135.3 (CCC_{NP}), 130.5 (NCC_{Im}), 129.2 (CCC_{Ph}), 129.0 (CCC_{Ph}), 128.8 (CCC_{Ph}), 128.5 (CCC_{Ph}), 127.9 (CCC_{Ph}), 127.6 (CCC_{benzyl}), 127.3 (CCC_{benzyl}), 126.9 (CCC_{benzyl}), 126.6 (CCC_{benzyl}), 124.4 (CCC_{benzyl}), 121.4 (CCC_{benzyl}), 119.5(CCC_{NP}), 117.4 ($N_{Im}CC$), 55.6 (*C*CO), 49.6 (CCO_{OAc}), 29.8 (CH_3^{NP}), 28.1 ppm (CH_2^{NP}); IR (KBr): $\nu = 2071$ (CO), 2025 (CO), 1951 (CO), 1425 (OAc), 1060 cm^{-1} (BF_4); ESI-MS: $m/z =$ 842 corresponding to $[\mathbf{1}-BF_4]^+$; elemental analysis calcd (%) for $C_{33}H_{26}N_5O_9BF_4Ru_2$: C 42.82, H 2.83, N 7.57; found: C 42.71, H 2.72, N 7.58.

Synthesis of 1a: NaH (5 mg, 2 mmol) was added to $[Ru_2(L^1)(CO)_4(CH_3COO)][BF_4]$ (100 mg, 1 mmol) dissolved in 10 mL of THF and the mixture was stirred for 6 h at room temperature. The THF was removed and the sample evaporated to dryness, after which it was redissolved in 15 mL of dichloromethane. The resulting mixture was filtered through a small pad of Celite. The resulting filtrate was concentrated under reduced pressure and petroleum ether was added to induce precipitation. The violet-colored precipitate was washed with petroleum ether and dried under vacuum. Yield: 90 mg (90%). M.p. > 250 °C; ^{1}H NMR (500 MHz, CD_3CN, 294 K): $\delta =$ 8.96 (d, $J = 9.3$ Hz, 1H, NP), 8.49 (d, $J = 9.2$ Hz, 1H, NP), 8.11 (d, $J =$ 2.2 Hz, 1H, Im), 8.09 (d, $J = 2.1$ Hz, 1H, Im), 7.64 (s, 1H, NP), 7.46–7.33 (m, 9H, 2Ph), 5.62 (s, 2H, CH_2^{benzyl}), 5.60–5.58 (m, 1H, CH^{CHOH}), 4.49 (dd, $J_1 = 14.0$ Hz, $J_2 = 2$ Hz, 1H, CH_2), 4.1 (dd, $J_1 = 14.3$ Hz, $J_2 =$ 2 Hz, 1H, CH_2), 2.83 (s, 3H, CH_3^{NP}), 2.55 ppm (s, 3H, CH_3^{OAc}); ^{13}C NMR (125.8 MHz, CD_3CN, 296.2 K): $\delta = 210.2$ (*C*O), 201.8 (*C*O), 196.6 (*C*O), 191.6 (*C*O), 181.3 (OCO_{OAc}), 172.1 (NCN_{Im}), 156.9 (NCN_{NP}), 155.3 ($N_{NP}CN_{Im}$), 152.3 (CCN_{NP}), 152.3 (CCC_{NP}), 141.2 (CCC_{NP}), 140.8 (CCC_{NP}), 135.6 (CCN_{Ph}), 135.3 (CCC_{NP}), 130.5 (NCC_{Im}), 129.2 (CCC_{Ph}), 129.0 (CCC_{Ph}), 128.8 (CCC_{Ph}), 128.5 (CCC_{Ph}), 127.9 (CCC_{Ph}), 127.6 (CCC_{benzyl}), 127.3 (CCC_{benzyl}), 126.9 (CCC_{benzyl}), 126.6 (CCC_{benzyl}), 124.4 (CCC_{benzyl}), 121.4 (CCC_{benzyl}), 119.5 (CCC_{NP}), 117.4 ($N_{Im}CC$), 55.6 (*C*CO), 49.4 (CCO_{OAc}), 29.8 (CH_3^{NP}), 28.1 ppm (CH_2^{NP}); IR (KBr): $\nu = 2071$ (CO),

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2025 (CO), 1951 (CO), 1425 cm^{-1} (OAc); elemental analysis calcd (%) for $C_{33}H_{25}N_5O_9Ru_2$: C 47.31, H 3.01, N 8.36; found: C 47.26, H 2.98, N 8.32.

Synthesis of 2: Compound **2** was synthesized following a similar procedure employed for the synthesis of **1** by using PIN·HBr (60 mg, 0.17 mmol), $Ru_2(CO)_4(CH_3COO)_2$ (75 mg, 0.17 mmol), $TlBF_4$ (49 mg, 0.17 mmol), and *p*-nitrobenzaldehyde (40 mg, 0.26 mmol). Crystals suitable for X-ray diffraction were grown by layering hexane over a concentrated dichloromethane solution of **2** inside an 8 mm o.d. vacuum-sealed glass tube. Yield: 113 mg (74%). M.p. $>250\,^{\circ}C$; ^1H NMR (400 MHz, CD_3CN, 294 K): $\delta=8.94$ (d, $J=9.2$ Hz, 1H, NP), 8.16 (d, $J=9.2$ Hz, 1H, NP), 8.10 (d, $J=2.3$ Hz, 1H, Im), 8.0 (d, $J=8.7$ Hz, 2H, Ph), 7.90 (d, $J=8.3$ Hz, 2H, Ph), 7.79 (s, 1H, NP), 7.57 (d, $J=2.4$ Hz, 1H, Im), 5.03–5.09 (m, 1H, CH^{CHOH}), 4.35 (dd, $J_1=14.2$ Hz, $J_2=2$ Hz, 1H, CH_2), 4.01 (dd, $J_1=14.2$ Hz, $J_2=2$ Hz, 1H, CH_2), 2.82 (s, 3H, Me-NP), 2.75–2.76 (m, 1H, CH^{iPr}), 2.46 (s, 3H, CH_3^{OAc}), 1.64 (s, 3H, CH_3^{iPr}), 1.63 ppm (s, 3H, CH_3^{iPr}); ^{13}C NMR (99.5 MHz, CD_3CN, 296.2 K): $\delta=211.1$ (*C*O), 206.5 (*C*O), 202.7 (*C*O), 191.9 (*C*O), 189.4 (N*C*N_{NP}), 184.6 (N_{NP}*C*N_{Im}), 180.4 (O*C*O_{OAc}), 179.4 (N*C*N_{Im}), 162.4 (C*C*N_{NP}), 156.3 (*C*CC_{NP}), 153.2 (*C*CC_{NP}), 142.2 (*C*CC_{NP}), 141.2 (C*C*N_{Ph}), 139.1 (*C*CC_{NP}), 133.2 (N*C*C_{Im}), 129.8 (CCCPh), 127.0 (CCCPh), 125.1 (*C*CC_{Ph}), 123.0 (*C*CC_{Ph}), 121.5 (*C*CC_{Ph}), 120.4 (*C*CC_{NP}), 119.2 (N_{Im}*C*C), 54.4 (*C*CO), 49.6 (*C*CO_{OAc}), 48.9 (NC*C*^{iPr}), 29.8 (*C*H_3^{NP}), 28.1 (*C*H_2^{NP}), 23.2 (CC*C*^{iPr}), 18.5 ppm (CC*C*^{iPr}); IR (KBr): $\nu=2071$ (CO), 2025 (CO), 1951 (CO), 1426 (OAc), 1061 cm^{-1} (BF_4); ESI-MS: $m/z=792$ corresponding to $[\mathbf{2}-BF_4]^+$; elemental analysis calcd (%) for $C_{31}H_{28}N_5O_9BF_4Ru_2$: C 39.74, H 2.87, N 7.99; found: C 39.69, H 2.81, N 7.84.

Synthesis of 3: Compound **3** was synthesized following a similar procedure employed for the synthesis of **1** by using PIN·HBr (60 mg, 0.17 mmol), $Ru_2(CO)_4(CH_3COO)_2$ (75 mg, 0.17 mmol), $TlBF_4$ (49 mg, 0.17 mmol), and *p*-cyanobenzaldehyde (34 mg, 0.26 mmol). Crystals suitable for X-ray diffraction were grown by layering hexane over a concentrated dichloromethane solution of **3** inside an 8 mm o.d. vacuum-sealed glass tube. Yield: 107 mg (72%). M.p. $>250\,^{\circ}C$; ^1H NMR (400 MHz, CD_3CN, 294 K): $\delta=8.94$ (d, $J=9.1$ Hz, 1H, NP), 8.53 (d, $J=9.4$ Hz, 1H, NP), 8.20 (d, $J=2.7$ Hz, 1H, Im), 8.0 (d, $J=8.7$ Hz, 2H, Ph), 7.98 (d, $J=8.5$ Hz, 2H, Ph), 7.90 (s, 1H, NP), 7.50 (d, $J=2.4$ Hz, 1H, Im), 5.15–5.06 (m, 1H, CH^{CHOH}), 4.34 (dd, $J_1=14.1$ Hz, $J_2=2$ Hz, 1H, CH_2), 4.03 (dd, $J_1=14.2$ Hz, $J_2=2$ Hz, 1H, CH_2), 2.83 (s, 3H, Me-NP), 2.74–2.72 (m, 1H, CH^{iPr}), 2.46 (s, 3H, CH_3^{OAc}), 1.66 (s, 3H, CH_3^{iPr}), 1.61 ppm (s, 3H, CH_3^{iPr}); ^{13}C NMR (99.5 MHz, CD_3CN, 296.2 K): $\delta=210.1$ (*C*O), 206.1 (*C*O), 201.2 (*C*O), 192.0 (*C*O), 187.2 (N*C*N_{NP}), 184.1 (N_{NP}*C*N_{Im}), 179.1 (N*C*N_{Im}), 162.0 (C*C*N_{NP}), 156.7 (*C*CC_{NP}), 153.0 (*C*CC_{NP}), 142.7 (*C*CC_{NP}), 141.4 (C*C*N_{Ph}), 139.8 (*C*CC_{NP}), 133.2 (N*C*C_{Im}), 129.2 (*C*CC_{Ph}), 127.5 (*C*CC_{Ph}), 124.7 (*C*CC_{Ph}), 123.0 (*C*CC_{Ph}), 121.1 (*C*CC_{Ph}), 120.0 (*C*CC_{NP}), 119.2 (N_{Im}*C*C), 55.4 (*C*CO), 54.1 (O*C*O_{OAc}), 48.9 (*C*CO_{OAc}), 48.2 (NC*C*^{iPr}), 29.6 (*C*H_3^{NP}), 28.0 (*C*H_2^{NP}), 22.9 (CC*C*^{iPr}), 18.9 ppm (CC*C*^{iPr}); IR (KBr): $\nu=2067$ (CO), 2025 (CO), 1947 (CO), 1422 (OAc), 1060 cm^{-1} (BF_4); ESI-MS: $m/z=772$ corresponding to $[\mathbf{3}-BF_4]^+$; elemental analysis calcd (%) for $C_{30}H_{26}N_5O_7BF_4Ru_2$: C 42.02, H 3.06, N 8.17; found: C 41.99, H 3.01, N 8.09.

Synthesis of 4: Compound **4** was synthesized following a similar procedure employed for the synthesis of **1** by using PIN·HBr ligand precursor (60 mg, 0.17 mmol), $Ru_2(CO)_4(CH_3COO)_2$ (75 mg, 0.17 mmol), $TlBF_4$ (49 mg, 0.17 mmol), and *p*-trifluromethylbenzaldehyde (45 mg, 0.26 mmol). Crystals suitable for X-ray diffraction were grown by layering hexane over a concentrated dichloromethane solution of **4** inside an 8 mm o.d. vacuum-sealed glass tube. Yield: 129 mg (72%). M.p. $>250\,^{\circ}C$; ^1H NMR (400 MHz, CD_3CN, 294 K): $\delta=8.80$ (d, $J=5.5$ Hz, 1H, NP), 8.09 (d, $J=9.2$ Hz, 1H, NP), 8.08 (d, $J=2.3$ Hz, 1H, Im), 8.06 (d, $J=2.4$ Hz, 1H, Im), 7.67 (s, 1H, NP), 7.65 (d, $J=5.28$ Hz, 2H, Ph), 7.57 (d, $J=1.1$ Hz, 2H, Ph), 7.46 (d, $J=8.2$ Hz, 2H, Ph), 7.32 (d, $J=8.4$ Hz, 2H, Ph), 5.19–5.14 (m, 1H, CH^{CHOH}), 4.06 (dd, $J_1=13.9$ Hz, $J_2=4.6$ Hz, 1H, CH_2), 3.71 (dd, $J_1=14.0$ Hz, $J_2=3.2$ Hz, 1H, CH_2), 2.43 (s, 3H, Me-NP), 2.75–2.76 (m, 1H, CH^{iPr}), 1.75 (d, $J=6.6$ Hz, 3H, CH_3^{iPr}), 1.71 ppm (d, $J=6.7$ Hz, 3H, CH_3^{iPr}); ^{13}C NMR (99.5 MHz, CD_3CN, 296.2 K): $\delta=208.2$ (*C*O), 203.9 (*C*O), 202.5 (*C*O), 184.2 (*C*O), 178.3 (N*C*N_{Im}), 165.4 (N*C*N_{NP}), 163.8 (O*C*O), 156.1 (N_{NP}*C*N_{Im}), 155.2 (C*C*N_{NP}), 151.4 (*C*CC_{NP}), 145.2 (*C*CC_{NP}), 141.8 (*C*CC_{NP}), 135.7 (C*C*N_{Ph}), 129.7 (*C*CC_{NP}), 128.2 (N*C*C_{Im}), 126.4 (*C*CC_{Ph}), 125.2 (*C*CC_{Ph}), 125.2 (*C*CC_{Ph}), 125.1 (*C*CPh), 122.6 (*C*CC_{Ph}), 122.5 (*C*CC_{Ph}), 120.6 (*C*CC_{Ph}), 118.5 (*C*CC_{Ph}), 118.5 (*C*CC_{Ph}), 117.4 (*C*CC_{Ph}), 112.7 (*C*CC_{Ph}), 54.5 (F*C*C), 48.9 (NC*C*^{iPr}), 23.2 (CC*C*^{iPr}), 21.5 ppm (CC*C*^{iPr}); ^{19}F NMR (372.5 MHz, CD_3CN, 294 K): $\delta=-63.0$ ($CF_3C_6H_4COO$), -63.5 (CF_3L^4), -151.7 (BF_4); IR (KBr): $\nu=2074$ (CO), 2033 (CO), 1984 (CO), 1325 ($CF_3C_6H_4COO$), 1066 cm^{-1} (BF_4^-); ESI-MS: $m/z=945$ corresponding to $[\mathbf{4}-BF_4]^+$; elemental analysis calcd (%) for $C_{36}H_{27}N_4O_7BF_{10}Ru_2$: C 41.96, H 2.64, N 5.44; found: C 41.90, H 2.61, N 5.38.

General procedure for the catalytic reaction

Complex **1** (9.26 mg, 0.01 mmol), DABCO (5.6 mg, 0.05 mmol), alcohol (1 mmol), amine (1.2 mmol), nonane (0.2 mmol), 4 Å molecular sieves (100 mg), and toluene (3 mL) were placed in an oven-dried reaction vessel. The reaction mixture was heated at reflux at 110 °C with stirring for 24 h. It was cooled to room temperature and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (hexane/Et_2O 10:0→9:1 with 5% Et_3N) to afford the imine.

X-ray data collection and refinement

Single-crystal X-ray studies were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. All the data were collected at 100(2) K using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda_\alpha=0.71073$ Å). The frames were indexed, integrated, and scaled by using the SMART and SAINT software packages[31] and the data were corrected for absorption by using the SADABS program.[32] The structures were solved and refined with the SHELX suite of programs.[33] All hydrogen atoms were included in the final stages of the refinement and were refined with a typical riding model. Structure solution and refinement details for compounds **1**–**4** are provided in the Supporting Information. Anisotropic treatment of these three atoms resulted nonpositive definite displacement tensors and were therefore subjected to isotropic refinement. The "SQUEEZE" option in the PLATON program[34] was used to remove a disordered solvent molecule from the overall intensity data of compounds **1** and **4**. Pertinent crystallographic data for compounds **1**–**4** are summarized in Table S2 in the Supporting Information. The crystallographic figures used in this manuscript have been generated using Diamond 3.1e software.[35] CCDC-949508 (**1**), 949509 (**2**), 949510 (**3**), and 949511 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational study

Calculations were performed by using density functional theory (DFT) with Becke's three-parameter hybrid exchange functional[36] and the Lee–Yang–Parr correlation functional (B3LYP).[37] Geometry-optimized structures were characterized fully by analytical frequency calculations as minima on the potential energy surface. The

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double-ζ basis set of Hay and Wadt (LanL2DZ) with a small core (1s2s2p3s3p3d4s4p4d) effective core potential (ECP)[38] was used for Ru. The ligand atoms H, N, C, and O atoms were described by using the 6-31G(d,p) basis sets. All optimization calculations were performed with the Gaussian 09 (G09)[39] suite of programs. Atomic charges were calculated by natural population analysis (NPA) as implemented in Gaussian 03.[40] Solvent effects were accounted for by using methanol ($\varepsilon = 32.63$), taking optimized geometries from gas-phase calculations with a polarizable continuum model (PCM).[41]

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[20] *p*-Nitrobenzyl alcohol (11 mg, 0.072 mmol) and $[n\mathrm{Bu}_4\mathrm{N}]\mathrm{BF}_4$ (24 mg, 0.073 mmol) were added to a solution of **1a** (40 mg, 0.048 mmol) in toluene (3 mL) and the mixture was stirred vigorously for 6 h at room temperature. The red precipitate was isolated, washed with toluene (2×5 mL) and hexane (2×10 mL), then recrystallized and dried under vacuo to give **1**. Yield: 18 mg (40%).

[21] Benzyl alcohol (0.015 mL), DABCO (0.004 mL), catalyst **1** (14 mg) in C_6D_6 (0.6 mL) were heated at 75 °C for 4 h in a sealed NMR tube and the ^{1}H NMR spectrum was recorded.

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[25] In contrast, Madsen et al. (Ref. [19a]) reported a doublet at $\delta = -18.04$ ppm [J(H,H) = 7.1 Hz] for a Ru-dihydride intermediate.
[26] Benzyl alcohol (0.90 mL), DABCO (0.024 mL), and catalyst **1** (84 mg) in toluene (3 mL) were heated at 110 °C for 4 h in a sealed reaction vessel. The gas evolved was injected into a GC instrument and analyzed; H_2 was identified by comparison with the retention time of an authentic sample.
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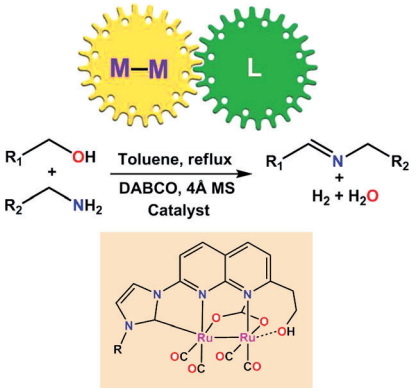
FULL PAPER

Ligand lends a hand: Metal–hydroxy/hydroxide and metal–metal cooperation is demonstrated for acceptorless dehydrogenation of alcohols to give aldehydes. The ligand architecture ensures rapid extrusion of the aldehyde from the metal core, resulting in the formation of the corresponding imine as the sole coupled product with amines (see scheme; DABCO = 1,4-diazabicyclo-[2.2.2]octane).



Dehydrogenation

*B. Saha, S. M. Wahidur Rahaman, P. Daw, G. Sengupta, J. K. Bera**

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Metal–Ligand Cooperation on a Diruthenium Platform: Selective Imine Formation through Acceptorless Dehydrogenative Coupling of Alcohols with Amines

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