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Acceptorless Dehydrogenation of Alcohols on a Diruthenium(II,II) Platform

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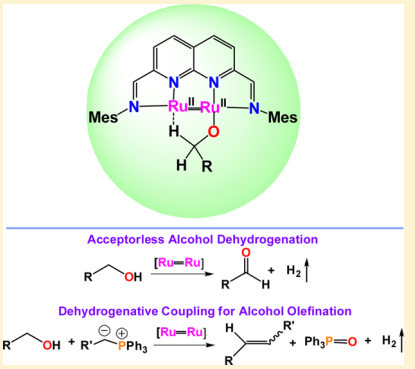
Supporting Information

ABSTRACT: The diruthenium(II,II) complex $[Ru_2(L^1)(OAc)_3]Cl$ (**1**), spanned by a naphthyridine-diimine ligand and bridged by three acetates, has been synthesized. The catalytic efficacy of complex **1** has been evaluated for the acceptorless dehydrogenation (AD) of alcohols and for the dehydrogenative coupling reactions of alcohols with Wittig reagents. The diruthenium(II,II) complex is an excellent catalyst for AD of a diverse range of alcohols, and it is shown to be particularly effective for the conversion of primary alcohols to the corresponding aldehydes without undesired side products such as esters. Triphenylphosphonium ylides in a one-pot reaction with alcohols afforded the corresponding olefins in high yields with excellent *E* selectivity. The liberated dihydrogen gas was identified and measured to be 1 equiv with respect to alcohol. Deuteration studies with $PhCD_2OH$ revealed the absence of isotope scrambling in the product, indicating the involvement of a Ru-monohydride intermediate. Kinetic studies and DFT calculations suggest a low-energy bimetallic *β*-hydride elimination pathway where rate-limiting intramolecular proton transfer from alcohol to metal-bound hydride constitutes the dehydrogenation step. The general utility of metal−metal bonded compounds for alcohol AD and subsequent coupling reactions is demonstrated here.

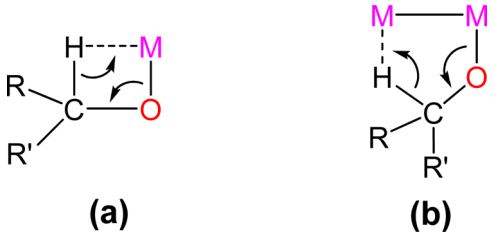


INTRODUCTION

The prospect of cooperative participation of metal ions renders the bimetallic complexes as potential catalysts for organic transformations.[1] Metal−metal bonded complexes are particularly interesting because of enforced proximity between the metals and the ability of the dimetal core to attain valence delocalization.[2] Elementary oxidative addition and reductive elimination processes are more favored on a bimetallic platform than on a single-metal entity.[3] Metal−metal singly bonded dirhodium(II,II) systems are the most prominent catalysts for a wide variety of organic reactions.[4] Although the reactions almost exclusively take place at one of the axial sites, the second metal plays a significant role. A 3c/4e bonding manifold has been proposed to explain the greater density of electronic states and consequently diverse reactivity.[5] Well-defined stoichiometric reactions of small organic and inorganic molecules across the metal−metal bonds have been widely reported.[6] Catalytic transformations on a bimetal platform utilizing equatorial sites have been relatively less explored.[7] Suitable ligands capable of holding two metals in close proximity and accommodating structural and electronic changes during the catalytic cycle are vital to exploit the benefit of bimetallic cooperativity.

Acceptorless dehydrogenation (AD) is essentially a reaction that removes one hydrogen molecule from ubiquitous yet considerably less reactive alcohols to form carbonyls—a more potent synthon. Hydrogen is liberated without the use of stoichiometric acceptor/oxidant, making AD a green and environmentally benign synthetic methodology.[8] Several catalysts based on N-heterocyclic carbene and phosphine ligands have been reported for AD reactions.[9] The use of a metal−ligand cooperation strategy in the ligand design has led to considerable improvement in the reaction conditions and selectivity.[10] However, these studies have focused primarily on a single metal center. A key step in the alcohol AD is *β*-hydride elimination of a metal−alkoxide intermediate that proceeds via a four-membered agostic species (Scheme 1a).[11] A metal−metal bond provides an interesting possibility of an alternative pathway on a bimetallic platform (Scheme 1b). To assess this proposal, we

Scheme 1. *β*-Hydride Elimination on (a) Monometallic and (b) Bimetallic Platforms



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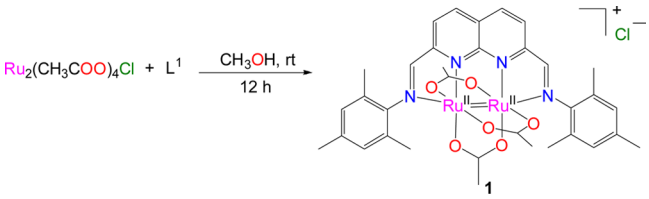
have designed a diruthenium(II,II) acetate-bridged complex incorporating a crescent-shaped naphthyridine-diimine ligand and evaluated its catalytic utility for the AD of alcohols. The catalyst is highly efficient for a range of alcohols and particularly effective for primary alcohols, affording solely the corresponding aldehydes. The AD methodology has been extended to the catalytic olefination of alcohols. Mechanistic studies and DFT calculations suggest a bimetallic pathway during the catalytic cycle.

RESULTS AND DISCUSSION

Syntheses and Structures. Synthesis of the naphthyridine-diimine ligand 2,7-bis(*N*-mesitylmethylimino)-1,8-naphthyridine (L^1) was achieved by condensation of 1,8-napthyridine-2,7-dicarbaldehyde with mesitylamine (Scheme S1 in the Supporting Information). Treatment of L^1 with $Ru_2(OAc)_4Cl$ in a 1:1 molar ratio in MeOH afforded $[Ru_2(L^1)(OAc)_3]Cl$ (**1**) as a dark green solid in 79% yield (Scheme 2). A single-electron reduction of Ru_2^{5+} to Ru_2^{4+} in methanol is consistent with the literature reports.[12]

Scheme 2. Synthesis of Complex 1



The molecular structure of **1** was confirmed by X-ray crystallography, which revealed two very similar molecules in the asymmetric unit. The salient features of only one molecule are discussed here. The diruthenium(II,II) core is spanned by the crescent-shaped L^1, and three additional acetate ligands bridge between the metal centers (Figure 1). Two imine nitrogen atoms of L^1 occupy sites trans to the Ru−Ru double bond. The

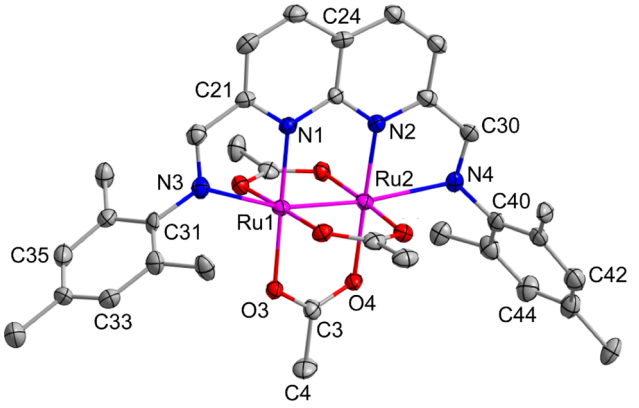


Figure 1. Molecular structure (40% probability thermal ellipsoids) of the cationic unit in **1** with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (Å) and angles (deg): Ru1−Ru2 2.2953(8), Ru2−N2 2.023(6), Ru2−O4 2.061(5), Ru2−N4 2.278(6), Ru1−N1 2.019(6), Ru1−O3 2.072(5), Ru1−N3 2.297(6); N2−Ru2−O4 179.3(2), N2−Ru2−N4 74.7(2), O4−Ru2−N4 105.0(2), N2−Ru2−Ru1 90.83(17), O4−Ru2−Ru1 89.40(14), N4−Ru2−Ru1 163.13(15), N1−Ru1−O3 178.1(2), N1−Ru1−Ru2 89.61(17), O3−Ru1−Ru2 89.00(14), N1−Ru1−N3 75.2(2), O3−Ru1−N3 106.2(2), Ru2−Ru1−N3 164.77(15).

tetradentate ligand L^1 ensures that two acetate units are disposed opposite to each other, whereas the third acetate is trans to the naphthyridine unit. The Ru1−Ru2 distance is 2.2953(8) Å and is consistent with those in similar diruthenium(II,II) complexes.[13] The imine nitrogens (axial) make longer Ru1−N3 (2.297(6) Å) and Ru2−N4 (2.278(6) Å) bond distances in comparison to naphthyridine nitrogens at the equatorial sites (Ru1−N1 = 2.019(6) Å and Ru2−N2 = 2.023(6) Å).

ESI-MS exhibits a signal at m/z 800.0799, which is assigned to $[\mathbf{1} - Cl]^+$ (Figure 2). ^{1}H NMR signals of **1** are broad and

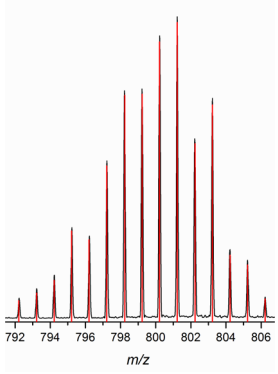


Figure 2. Simulated (red line) and experimental mass distributions (black line) for $[\mathbf{1} - Cl]^+$ at m/z 800.0799 (z = 1).

featureless because of the paramagnetic nature of the complex.[12c] The UV−vis spectrum of **1** shows intense absorption at 331 nm (ϵ = 12000 M^{-1} cm^{-1}, assigned to intraligand transitions) with the appearance of a shoulder at 425 nm possibly due to transitions from [Ru-Ru] dπ−dπ to ligand acceptor orbitals (Figure S3 in the Supporting Information). Two additional absorptions at 675 nm (ϵ = 6700 M^{-1} cm^{-1}) and at 740 nm are attributed to metal to ligand transitions. When a dichloromethane solution of **1** is excited at 331 nm, blue emissions are observed at 406 and 428 nm (Figure S4 in the Supporting Information). The cyclic voltammogram of **1** in 0.1 M TBAP/acetonitrile shows a reversible one-electron, metal-centered oxidation at 0.98 V vs Ag/AgCl (Figure S5 in the Supporting Information). The oxidation observed for **1** represents the formation of a formally mixed valence $[Ru_2]^{5+}$ species stable on the cyclic voltammetry time scale.[12a,c,14] The high potential of the metal-based oxidation indicates a greater stability of the $[Ru_2]^{4+}$ relative to that of the $[Ru_2]^{5+}$ core in the presence of L^1. Free L^1 shows a single reversible two-electron reduction at −1.29 V, which is split into two reversible one-electron reductions in **1** at −0.32 and −1.16 V, indicating significant contribution from the metal d orbitals. The effective magnetic moment of powdered **1** at 295 K is 2.81 μ_B, corresponding to two unpaired electrons per molecule and is consistent with a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ electronic configuration.[12a,14]

Catalytic Studies. A few reports of alcohol dehydrogenation reactions on a diruthenium platform using O_2 as oxidant have appeared in the literature. Naota et al. reported that the aerobic oxidation of alcohols in water could be performed efficiently in the presence of a catalytic amount of $Ru_2(\mu\text{-}OAc)_3(\mu\text{-}CO_3)$ under 1 atm of O_2.[15] The Tokii group synthesized phosphinato-bridged diruthenium complexes and tested their catalytic efficiency to oxidize cinnamyl alcohol under 1 atm of O_2.[16] The oxidation of alcohol was also achieved when iodide-bridged diruthenium complexes were employed in the presence of

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Ag_2O.[17] These studies, however, use oxidants, are limited in substrate scope, and do not reflect on the mechanistic implications. Complex **1** was tested for the acceptorless dehydrogenation (AD) of benzyl alcohol at 1 mol % catalyst loading in the presence of 10 mol % of KOH, which afforded benzaldehyde in 89% yield (Table 1). Optimization studies showed that KOH was the best choice among a variety of bases (Table S2, entry 2, in the Supporting Information). The reaction was not efficient at lower temperatures, and the best results were obtained in toluene at 70 °C. Increasing the catalyst loading or temperature did not affect the progress of the reaction.

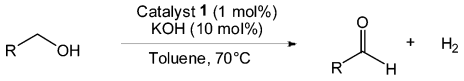
The substrate scope was then examined under the optimized conditions. Electron-rich *p*-methoxybenzyl alcohol and *p*-methylbenzyl alcohol gave excellent yields (93−98%; entries 1a,b) in comparison to benzyl alcohol (89%; Table 1, entry 1c). However, electron-withdrawing groups attached to benzyl alcohol reduced the yield of the corresponding aldehyde (61−74%; entries 1d−f). The substrate scope was then extended to polyaromatic and heterocyclic functionalized alcohols, and they showed appreciable yields (80−97%; entries 1g−k). Diols afforded corresponding lactones (86−94%, entries 1l,m) in good yields. The reaction was extended to aliphatic alcohols such as *n*-hexanol and *n*-octanol and showed moderate yields (45−65%; entries 1n,o) after extending the reaction time to 24 h. Natural products such as carveol and geraniol were also tested under AD conditions, and they gave 42−48% yields of the corresponding aldehyde (entries 1p,q). A significant amount of hydrogenated products (15−20%) were also observed, which could be accounted for on the basis of evolved hydrogen during the reaction.

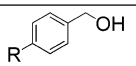
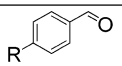
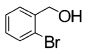
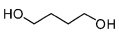
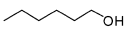
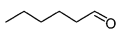
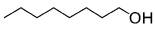
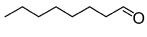
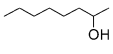
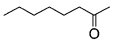
Unlike primary alcohols, secondary alcohols were poorly dehydrogenated (38−45%; Table 1, entries 1r−t) to the corresponding ketones. This is in contrast to reports where secondary alcohols were dehydrogenated easily owing to their low redox potentials.[18] Furthermore, a review of literature reports reveals that AD of primary alcohols invariably produces esters as major products by a hemiacetalyzation followed by dehydrogenation or by a Tischenko reaction.[19] No such side products were observed for the diruthenium catalyst. Catalyst **1** is clearly a superior alternative for the AD of primary alcohols.

AD of alcohol to aldehyde is accompanied by the concomitant release of one molecule of hydrogen (Scheme 3). A volumetric quantitative analysis of benzyl alcohol dehydrogenation using a gas buret revealed near-quantitative formation of hydrogen (~92% of theoretical yield; Figure S6 in the Supporting Information). The evolved hydrogen was identified by matching the retention time with an authentic sample using a thermal detector in GC. In another experiment, the AD reaction was conducted in a flask that was connected through a rubber tube to a second flask in which styrene and a catalytic amount of $RhCl(PPh_3)_3$ in benzene were placed. After the reaction was completed, ethylbenzene was produced in 76% yield in the second flask, demonstrating that the hydrogen gas generated in the AD reaction is responsible for styrene reduction (Scheme S2 and Figure S7 in the Supporting Information). This dual reaction authenticated that hydrogen is produced during the course of the reaction.[10c] When the AD reaction was done using benzyl alcohol-α,α-d_2 ($PhCD_2OH$), GC-MS analysis of the product showed a single peak at m/z 107, indicating monodeuterated ethylbenzene formed by the in situ generated HD gas (Scheme S3 and Figure S8 in the Supporting Information).

Alcohols are common starting materials for many chemical reactions, although they are largely unreactive. A convenient approach toward alcohol activation/utilization is AD to a more reactive carbonyl group.[8] Acceptorless dehydrogenative coupling

Table 1. Acceptorless Dehydrogenation of Alcohol by 1[a]



Entry	Substrate	Product	Time (h)	Yield (%)[b]
1a–1e	 R = OMe, Me, H, F, NO_2		6	98, 93, 89, 74, 71
1f			6	61
1g			6	97
1h			6	90
1i			6	94
1j			6	90
1k			6	80
1l			6	94
1m			6	86
1n			24	65
1o			24	45
1p			24	48[c]
1q			24	42[d]
1r			24	45
1s			24	40
1t			24	38

[a]Conditions: 1 mmol of alcohol, 0.01 mmol of **1**, 0.01 mol of KOH, 70 °C in toluene. [b]Yields were determined by GC using 1 mmol of dodecane as internal standard. [c]A combined 15% yield of monohydrogenated and dihydrogenated aldehydes (1:1). [d]A combined 20% yield of monohydrogenated and dihydrogenated aldehydes (1:1).

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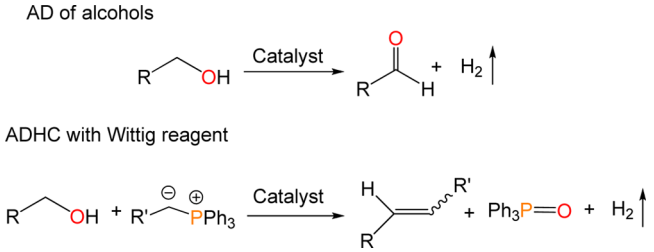
Scheme 3. Alcohol Dehydrogenation and Olefination

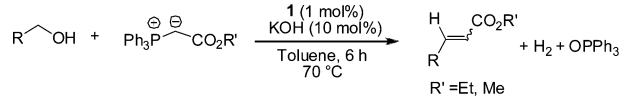


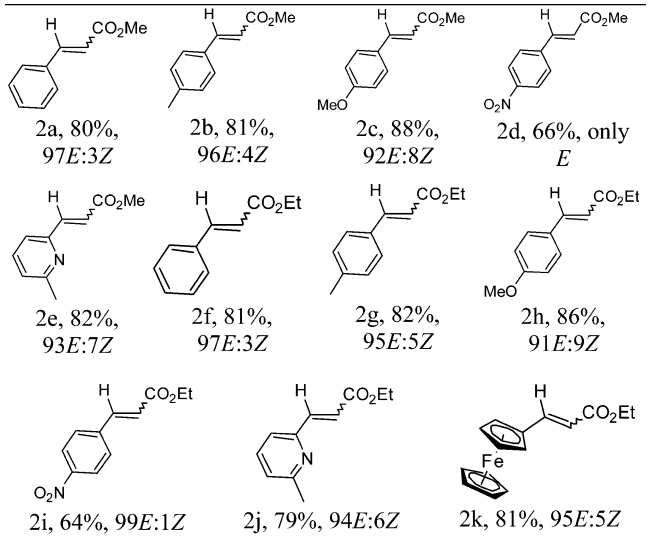
(ADHC) reactions offer environmentally benign synthetic routes for the preparation of a plethora of useful products such as esters, amides, imines, and heterocycles by the direct reaction of alcohol with an appropriate coupling reagent.[20] Direct reaction of an ylide/Wittig reagent with an alcohol to selectively form an olefin, with the liberation of hydrogen gas and avoidance of the use of oxidants, is a useful carbon−carbon bond forming reaction (Scheme 3). Alkanes were obtained as major products when iridium or ruthenium catalysts were used for similar reactions.[21] The product formation was explained on the basis of hydrogenation of generated alkenes with the concomitantly evolved hydrogen. The Milstein group has recently reported the olefination of alcohols with Wittig salt precursors using an Ru(II)-PNN pincer catalyst in an open system that allowed the escape of hydrogen for the selective synthesis of alkenes.[22] Catalyst **1** performs the same task with equal efficiency but at a significantly lower temperature.

A mixture of benzyl alcohol, 1 mol % of **1**, 10 mol % of KOH, and triphenylphosphonium methoxycarbonylmethylide (Wittig reagent, 1.5 equiv) was placed in a single vessel and heated to 70 °C in toluene for 6 h. Isolated yields were 80% (Table 2, entry 2a). NMR analysis showed predominantly (*E*)-methyl cinnamate, and only trace amounts of the *Z* isomer were present. The substrate scope of the reaction was examined. Electron-rich *p*-methoxybenzyl alcohol and *p*-methylbenzyl alcohol showed better yields (81−88%; entries 2b,c), but in the presence of an electron-withdrawing group such as *p*-nitrobenzyl alcohol, a lesser yield was obtained (66%; entry 2d). However, the selectivity of the reaction improved, yielding *E* products exclusively. The reaction was expanded to another Wittig reagent (triphenylphosphonium ethoxycarbonylmethylide), and similar trends were obtained (entries 2f−i). Heterocyclic functionalized alcohols such as 2-methyl-6-pyridinemethanol and ferrocenylmethyl alcohol were also notably tolerated under the reaction conditions (entries 2e,j,k) to provide the corresponding (*E*)-alkenes. Importantly, catalyst **1** exhibited higher *E* selectivity in comparison with other catalysts.[22]

An AD reaction with $Ru_2(OAc)_4Cl$, having an accessible axial site, yielded only 30% of benzaldehyde under identical reaction conditions. The presence of a vacant axial site does not necessarily lead to product formation. Rather, a suitably designed framework renders trans ligands labile, and consequently those equatorial sites can be accessed. We propose a mechanism that involves both metals, and the reaction proceeds on the equatorial platform (Scheme 4). Initially, the alkoxide moiety replaces the

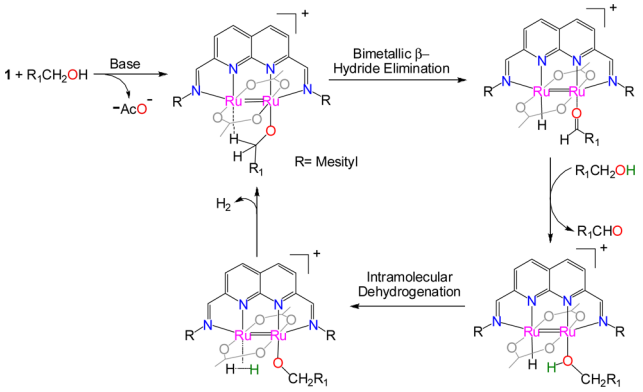
Table 2. Catalytic Olefination of Alcohols by 1 using Wittig Reagent[a]





[a]Conditions: 1 mmol of alcohol, 0.01 mmol of **1**, 0.01 mol of KOH, 1.5 mmol of Wittig reagent, 3 mL of toluene, 70 °C. All yields are reported on isolation.

Scheme 4. Proposed Mechanistic Cycle for the AD Reaction



acetate group trans to the naphthyridine. A bimetallic *β*-hydride elimination generates a Ru-hydride intermediate with the concurrent formation of aldehyde. The aldehyde is extruded, and an alcohol molecule binds to the metal. The catalytic cycle is closed via a dehydrogenation step that involves an intramolecular proton transfer from alcohol to the metal-bound hydride.

Kinetic Studies. To gain support for the proposed mechanism, kinetic studies were performed. The initial rate of reaction was monitored to determine the order with respect to catalyst **1**. Reactions were performed with varying concentrations of **1** and equimolar amounts of benzyl alcohol and dodecane (internal standard). The initial rate varied linearly with the catalyst concentration, and the reaction was found to be first order with respect to **1** (Figure 3a). Furthermore, equimolar amounts of benzyl alcohol and dodecane ($n_{alcohol} = n_{dodecane}$) were mixed with 1 mol % of catalyst **1** in 3 mL of toluene. Aliquots of 0.2 mL were taken out at regular time intervals, and the amount of unreacted alcohol was measured using GC-MS against dodecane. According to the integrated rate law for a reaction of the type A → B with the restriction [A] = 1 and [B] = 0 at $t = 0$, the ln[A] vs time plot fitted well to a first-order kinetics (Figure 3b). Both of these experiments suggest the involvement of catalyst **1** and alcohol, one molecule each, in the rate-determining

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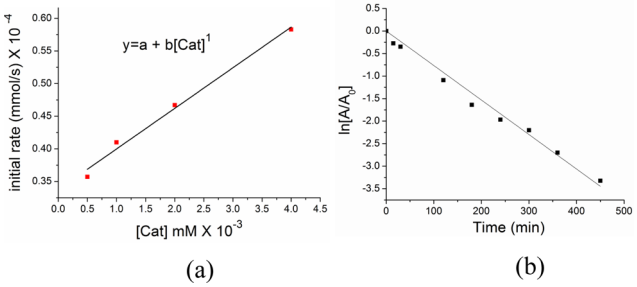

Figure 3. (a) Dependence of initial rate on **1** and (b) decay of benzyl alcohol vs time. Data are averaged over three runs.

step. As one molecule of the catalyst **1** consists of two ruthenium centers, it is reasonable to assume that the reaction takes place on the bimetallic assembly.[23] Close proximity between the metals aided by the ligand architecture allows the second metal to participate in the β-hydride elimination step.

Deuteration Studies. To garner further support in favor of the proposed mechanism, isotope scrambling studies were carried out with deuterated alcohol. A model AD reaction in toluene-d_8 did not afford deuterated product, thus ruling out the possibility of isotope scrambling from the solvent. Reaction of $PhCD_2OH$ showed deuterated benzaldehyde as the major product (92/8 D/H observed by GC-MS analysis; Figure S9 in the Supporting Information). An AD mechanism for a monometal catalyst typically involves a Ru^{II}-dihydride species generated by a sequence of elementary β-hydride elimination/reductive elimination reactions (Scheme S4 in the Supporting Information).[24] Such a process necessarily leads to hydrogen scrambling in the product. For example, for a Ru(II) catalyst bearing an N-heterocyclic carbene based ligand, 42% hydrogen incorporation was observed in deuterated imine products.[25] The absence of significant isotope scrambling for catalyst **1** strongly suggests the intermediacy of a Ru-monohydride intermediate, offering support to the proposed mechanism.[26]

Kinetic Isotope Effects. The involvement of C−H bond breaking in the rate-determining step of the catalysis is indicated by the intermolecular kinetic isotope effect (KIE).[27] A direct comparison of two reactions, (a) $PhCH_2OH$ in toluene and (b) $PhCD_2OH$ in toluene-d_8, showed k_{C-H}/k_{C-D} = 2.71 ± 0.04 (Figure 4). This proved that the C−H bond breaking is one of the slower steps of the reaction. The rate of the reaction was 4.94 ± 0.02 times slower when $PhCH_2OD$ was used as a substrate instead of $PhCH_2OH$ (Figure 4). The high k_{O-H}/k_{O-D} value suggests that hydrogen elimination during the final stage of the catalytic cycle is likely to be the rate-limiting step.

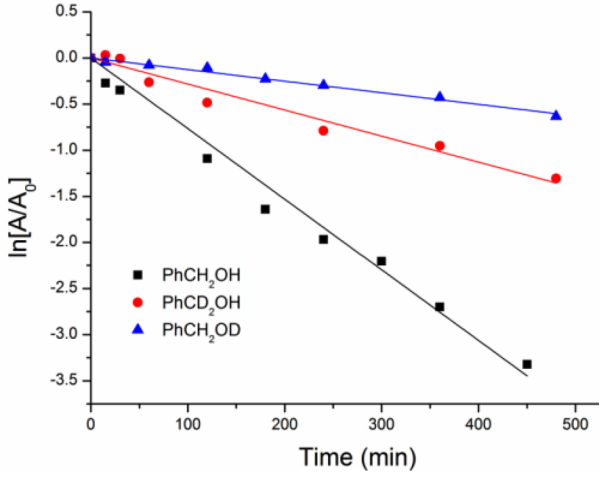

Figure 4. Reaction rates for $PhCH_2OH$, $PhCD_2OH$, and $PhCH_2OD$ vs time (min).

DFT Studies. DFT calculations at the M06 level of theory were carried out to gain insight into the reaction pathway. All DFT optimized structures of the intermediates and transition states along with the energy profile of the reaction (kcal/mol) are presented in Figures 5 and 6, respectively. A simplified system was chosen where the mesityl group was replaced by methyl and bridging acetates were replaced by formates. Methanol was considered as the substrate to reduce the computational cost. Replacement of one of the bridging formates trans to the naphthyridine by alkoxide produces intermediate **A**. The optimized structure **B** was subsequently computed where one of the H atoms of the alkoxide is engaged in an agostic interaction with the second ruthenium center.[28] The computed Ru2···H1 distance is 2.04 Å, comparable to metal−hydrogen distances in agostic complexes.[29] Subsequent β-hydride elimination leads to the metal−hydride intermediate **C**, which proceeds via the transition state **TSBC** ($\Delta G^{\ddagger}$ = 12.42 kcal/mol, Figure 6). The **TSBC** has a single imaginary frequency of 359*i* cm^{-1} and involves movement of H1 toward Ru2, resulting in a decrease in Ru2···H1 (1.67 Å) and a simultaneous increase in C1−H1 (1.75 Å). An alternate route involving a single metal center has also been considered where β-hydride elimination occurs on Ru1, affording

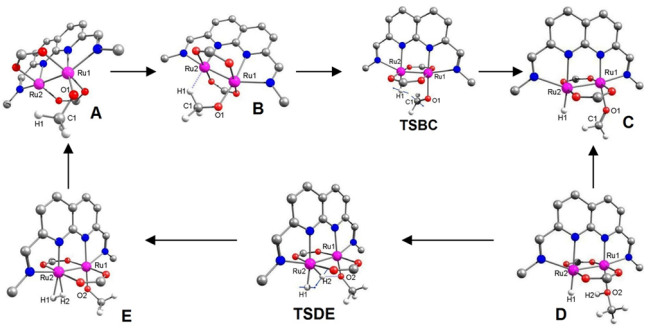

Figure 5. DFT optimized structures of all intermediates and transition states in the AD mechanism.

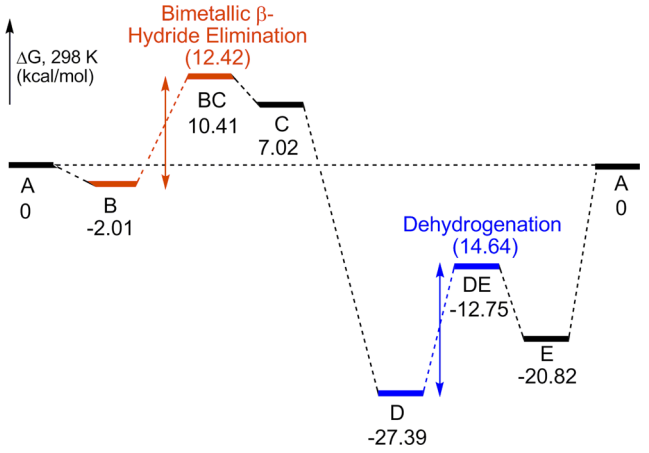

Figure 6. Computed reaction profile for AD by catalyst **1**. Energies are shown in kcal/mol relative to **A**. Values in parentheses represent activation barriers for the corresponding transition states.

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F (Figure S10 in the Supporting Information). The energy of **F** is 18.63 kcal/mol higher than that of **C**. Clearly, a bimetallic β-hydride elimination is a more energy efficient route than a pathway involving a single metal. The next step is the liberation of aldehyde from **C** followed by coordination of alcohol, a highly downhill process to form the intermediate **D**. Proton transfer from the alcohol to the metal-bound hydride gives the dihydrogen-bound species **E** via the transition state **TSDE** ($\Delta G^{\ddagger}$ = 14.64 kcal/mol, Figure 6). The endothermic nature of the dehydrogenation step was validated by DFT calculations, which revealed k_{C-H}/k_{C-D} = 2.68 and k_{O-H}/k_{O-D} = 3.73. These results are in agreement with the experimental KIE values. The final step is H_2 liberation from **E** to regenerate **A**.

CONCLUSION

A diruthenium(II,II) complex incorporating a naphthyridine−diimine ligand was synthesized. The ligand architecture offers accessible sites trans to the naphthyridine unit. The title compound is an excellent catalyst for AD of alcohols to the corresponding carbonyl compounds. This diruthenium assembly is remarkably effective for the clean conversion of primary alcohols to the corresponding aldehydes without esters as side products. A possible explanation is that the generated aldehyde is rapidly extruded from the [Ru═Ru] core and hence the hemiacetalyzation is hindered. The same catalyst was further exploited for catalytic olefination of alcohols using ylides to react with the in situ produced aldehyde. Kinetic experiments, isotope labeling studies, and DFT calculations point to a bimetallic cooperative mechanism that operates on the equatorial platform. A low-energy bimetallic β-hydride elimination makes dehydrogenation process the rate-limiting step. This study underlines the general utility of bimetallic catalysts in AD and ADHC reactions.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under a nitrogen atmosphere with the use of standard Schlenk-line techniques unless stated otherwise. Glassware was flame-dried under vacuum prior to use. ^{1}H and ^{13}C NMR spectra were obtained on JEOL JNM-LA 500 MHz and JEOL JNM-LA 400 MHz spectrometers. Chemical shift values were referenced to the residual signals of the deuterated solvents. ESI-MS were recorded on a Waters Micro mass Quattro Micro triple-quadrupole mass spectrometer. Infrared spectra were recorded on a Bruker Vertex 70 FTIR spectrophotometer in the range 400−4000 cm^{-1}. Elemental analyses were performed on a Thermoquest EA1110 CHNS/O analyzer. The crystallized compound was washed several times with dry diethyl ether, powdered, and dried under vacuum for at least 48 h prior to elemental analyses. GC-MS experiments were performed on an Agilent 7890A GC and 5975C MS system.

Cyclic voltammetric studies were performed on a BAS Epsilon electrochemical workstation in acetonitrile with 0.1 M tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. The working electrode was a BAS Pt-disk electrode, the reference electrode was Ag/AgCl, and the auxiliary electrode was a Pt wire. The ferrocene/ferrocenium couple occurs at $E_{1/2}$ = +0.51(70) V versus Ag/AgCl under the same experimental conditions. The potentials are reported in volts (V); the ΔE ($E_{p,a} - E_{p,c}$) values are in millivolts (mV) at a scan rate of 100 mV s^{-1}.

UV−visible spectra were recorded using a JASCO V-670 UV/vis absorption spectrophotometer. Emission spectra were recorded using a Fluorolog FL3-21 (Horiba Jobin Yvon) spectrofluorometer equipped with a xenon flash lamp and also using a PTI QuantaMaster Model QM-4 scanning spectrofluorometer equipped with a 75 W xenon lamp, emission and excitation monochromators, an excitation correction unit, and a PMT detector for both visible and NIR regions.

Materials. Solvents were dried by conventional methods, distilled under nitrogen, and deoxygenated prior to use. $RuCl_3 \cdot xH_2O$ (39% Ru) was purchased from Arora Matthey (India). The compounds $[Ru_2(OAc)_4Cl]$,[30] 1,8-naphthyridine-2,7-dicarboxaldehyde,[31] and $PhCH_2OD$[32] were synthesized following literature procedures.

X-ray Data Collection and Refinement. Single-crystal X-ray structural studies were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected at 100(2) K using graphite-monochromated Mo Kα radiation (λ_α = 0.71073 Å). The frames were indexed, integrated, and scaled using the SMART and SAINT software package,[33] and the data were corrected for absorption using the SADABS program.[34] The structure was solved and refined using the SHELX suite of programs. All hydrogen atoms were included in the final stages of the refinement and were refined with a typical riding model. All non-hydrogen atoms were refined with anisotropic thermal parameters. The "SQUEEZE" option in the PLATON program was used to remove a disordered solvent molecule from the overall intensity data.[35] Crystallographic data and pertinent refinement parameters for compound **1** are summarized in Table S1 in the Supporting Information. The crystallographic figures used in this paper have been generated using Diamond 3.1e software.[36] CCDC 1447839 contains 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.

Synthesis of L^1. 1,8-Naphthyridine-2,7-dicarboxaldehyde (250 mg, 1.34 mmol) was dissolved in 50 mL of methanol and placed in a 100 mL round-bottom flask equipped with a stir bar. To this suspension was introduced mesitylamine (370 mg, 2.71 mmol), and within a few minutes a yellow precipitate appeared. This mixture was stirred overnight. The yellow compound was collected by filtration and washed with methanol followed by diethyl ether: yield 470 mg (84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.56 (d, J = 8.24 Hz, 1H), 8.37 (d, J = 8.68 Hz, 1H), 6.93 (s, 2H), 2.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 158.2, 147.5, 137.6, 134.2, 129.4, 129.2, 129.1, 127.1, 120.1, 20.9, 18.4 ppm; IR (KBr) ν 2949, 2914, 2856, 1636, 1597, 1505, 1479, 1373, 1206, 864, 852, 732 cm^{-1}; ESI-MS (CH_2Cl_2) m/z 421.2453 $[M + H]^+$. Anal. Calcd for $C_{28}H_{28}N_4$: C, 79.96; H, 6.72; N, 13.33. Found: C, 79.81; H, 6.53; N, 13.18.

Synthesis of 1. $[Ru_2(OAc)_4(Cl)]$ (60 mg, 0.126 mmol) was placed in a flame-dried Schlenk flask, and 10 mL of dry methanol was added to form a brown suspension. Addition of L^1 (53 mg, 0.12 mmol) resulted in a deep green solution. The reaction mixture was stirred at room temperature for 12 h. The solution was evaporated completely under reduced pressure, and the residue obtained was redissolved in 0.5 mL of dichloromethane. Diethyl ether was added with stirring to induce precipitation. The solution was discarded by cannula filtration, and the precipitate was further washed with diethyl ether (3 × 10 mL). Finally, the precipitate was dried under vacuum to afford **1** as a green powder. Yield: 73 mg (79%). Needle-shaped green crystals suitable for X-ray diffraction were grown by layering hexane over a concentrated dichloromethane solution of **1** inside an 8 mm o.d. vacuum−sealed glass tube: IR (KBr) ν 2963, 1532, 1441, 1262, 1198, 1096, 1021, 800, 690 cm^{-1}; MS (ESI; CH_3CN) m/z 800.0799 $[M - Cl]^+$. Anal. Calcd for $C_{34}H_{37}N_4O_6Ru_2$: C, 50.93; H, 4.65; N, 6.99. Found: C, 50.79; H, 4.45; N, 6.83.

General Procedure for AD of Alcohols. A mixture of alcohol (1 mmol), **1** (0.01 mmol), potassium hydroxide (0.1 mmol), and dodecane (1 mmol) in 3 mL of toluene was placed in an oven-dried reaction vessel. The reaction mixture was heated to 70 °C with stirring for 6−24 h. The reaction mixture was cooled, diluted with EtOAc, and passed through a short column of silica for GC-MS analysis.

Volumetric Estimation of Evolved Hydrogen. Alcohol (1 mmol), **1** (0.01 mmol), and potassium hydroxide (0.1 mmol) in 3 mL of toluene was placed in an oven-dried reaction vessel, and the reaction mixture was heated to 70 °C. The headspace of the reaction vessel was connected to a gas buret. The reaction was continued until evolution of gas ceased. The experiment was repeated three times to get consistent readings, and the number of moles of hydrogen evolved was calculated by taking into account the vapor pressure of water at 293 K = 17.5424 Torr: volume of water displaced 22.6 mL, atmospheric pressure

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761.3126 Torr, R = 62.3635 L Torr K^{-1} mol^{-1}, $n(H_2) = [(P_{atm} - P_{water})V]/RT$ = 0.00092 mol, expected value 0.001 mol.

Dual Reactions Involving Hydrogenation of Styrene. The catalysis reaction using the catalyst **1** was conducted in a flask that was connected through a rubber tube to another flask in which styrene (1 mmol) and a catalytic amount of $RhCl(PPh_3)_3$ (0.05 mmol) in benzene were placed. Ethylbenzene was produced in the latter flask (76%).

Deuteration Studies with Styrene. A similar procedure was followed using $PhCD_2OH$ as substrate. GC-MS analysis of the product showed a signal for monodeuterated styrene (Scheme S3 in the Supporting Information).

General Procedure for Catalytic Olefination of Alcohols using Wittig Reagent. Alcohol (1 mmol), **1** (0.01 mmol), potassium hydroxide (0.1 mmol), and Wittig reagent (1.5 mmol) were sequentially added to 3 mL of toluene placed in an oven-dried reaction vessel. The reaction mixture was heated to 70 °C with stirring for 6 h. After the completion of the reactions, the products were purified by chromatography on a silica gel column using hexane/EtOAc (9/1 v/v) as eluent. The isolated *E* products were characterized by ^1H and ^{13}C NMR spectra.

Experimental Procedure for Kinetics Studies. A mixture of alcohol (1 mmol), **1** (0.01 mmol), potassium hydroxide (0.1 mmol), and dodecane (1 mmol) in 3 mL of toluene was placed in an oven-dried reaction vessel. The reaction mixture was heated to 70 °C. After stipulated time intervals, small aliquots (0.2 mL) were taken out from the reaction mixture, diluted with EtOAc, and passed through a short column of silica for GC-MS analysis. The experiments were repeated in triplicate with varying catalyst concentrations.

Experimental Procedure for Deuteration Studies and KIE. Deuterated alcohol (1 mmol), **1** (0.01 mmol), NaOD (0.1 mmol), and dodecane (1 mmol) in 3 mL of d_8-toluene were placed in an oven-dried reaction vessel. The reaction mixture was heated to 70 °C. After the stipulated time intervals, small aliquots of 0.2 mL were taken out and passed through silica column for GC-MS analysis.

Computational Details. Full geometry optimizations, without any symmetry constraints, were carried out using the hybrid density functional theory (DFT) method M06[37] as implemented in the program suite Gaussian 09.[38] The Stuttgart–Dresden effective core potential MWB28 and the corresponding basis set were invoked for Ru.[39] The ligand atoms H, N, C, and O were described using the 6-31+G(d,p) basis sets.[40] All structures were subjected to normal-mode vibrational analysis calculated at the same level of theory as the corresponding geometry optimization. All stationary points on the potential energy surface are either local minima with no imaginary vibrational frequency or transition states with one imaginary frequency. Solvent effects were accounted for with the SMD model.[41] Gas phase optimized structures were taken as the initial geometries for optimization in solution.[42,43] The solvation energies were calculated in toluene (ε = 2.38). The reported energies are Gibbs free energies in toluene using the M06 functional.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00085.

Experimental details and supporting figures (PDF)

Crystallographic data (CIF)

Cartesian coordinates of all computed molecules (XYZ)

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Notes

The authors declare no competing financial interest.

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