Ruthenium(II) Complex of a Tridentate Azoaromatic Pincer Ligand and its Use in Catalytic Transfer Hydrogenation of Aldehydes and Ketones with Isopropanol

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In this work, a new Ru(II) complex with the redox-active pincer 2,6-bis(phenylazo)pyridine ligand (L) is reported which acts as a metal-ligand bifunctional catalyst for transfer hydrogenation reactions. The isolated complex [(L)Ru(PMe₂Ph)₂(CH₃CN)](ClO₄)₂; [1](ClO₄)₂ is characterized by a host of spectroscopic measurements and X-ray structure determination. It is diamagnetic and single-crystal X-ray structure analysis reveals that [1]²⁺ adopts a distorted octahedral geometry where L binds Ru center in meridional fashion. The observed elongation in the coordinated azo bond length (1.29 Å) is attributed to the extensive π -back bonding, d π (Ru^{II}) \rightarrow π *(azo)L. The complex [1](ClO₄)₂ acts as an

Introduction

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Study of pincer ligands and their complexes is a continuously growing area in coordination chemistry and chemical catalysis.^[1] The natural endowment of pincers lies in the formation of thermally stable complexes that are prerequisites in homogeneous catalysis, even in harsh conditions.^[1-2] The tridentate ligands enforce meridional coordination around the transition metal center and impose structural rigidity to the metal complexes. Among these, a plethora of neutral and anionic pincers with C2v symmetry backbone, termed as palindromic pincers, have been exploited in organometallics.^[3]

In the last decade, our group has introduced a new palindromic pincer, *viz.* 2,6-bis(phenylazo)pyridine (L), which binds through a σ -bonded pyridyl N-atom and two N-atoms of two flanking π -acceptor azo (-N=N-) arms.^[4] Being a redoxactive pincer, the ligand L can store up to ($4e^- + 4H^+$) redox equivalents in the two azo components during the transformation of azo (-N=N-) to hydrazo (-NH-NH-) function without rupture of the azo bond.^[5] In its transition metal complexes, the metal to ligand back-bonding interactions further stabilizes the π^* -orbital of azo-function. As a result, it can accept the redox equivalents easily in accordance with

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efficient catalyst, which brings about catalytic transfer hydrogenation reactions of a broad array of aldehydes and ketones in isopropanol and in inert conditions. The selectivity of the catalyst for aldehyde reduction over the other reducible functional groups such as nitro, nitrile, ester etc was also investigated. Mechanistic studies, examined by suitable control reactions and isotope labelling experiments, indicate synergistic participation of both ligand and metal centres via the formation of a fleeting Ru–H intermediate and hydrogen walking to the coordinated azo function of L.

multiple potentially accessible reductive responses in the solution state. This distinctive behavior of the coordinated pincer has been utilized in synthesizing complexes that are potential storages of electrons and both electrons and protons.^[4-5] By changing the traditional idea of metal as active site and ligand as a mere spectator, many transition metal complexes of redox-active pincers make advances in several electro-catalytic transformations, small molecule activations and can mimic functions of various metalloenzymes.^[6] Using metalligand cooperative pathway or only the redox processes at ligand scaffold, transition metal complexes of L are also reported to show catalytic dehydrogenation of alcohols to aldehydes, ketones and azines based on azo-hydrazo redox couple.^[5,7] The Ni(II) and Zn(II) monoligated complexes are reported to show catalytic aerial alcohol oxidation reaction involving sole ligand participation forming mono- or bishydrazo intermediates.^[5] These catalytic processes are operative via hydrogen atom transfer (HAT) mechanism in the presence of a reducing agent. Subsequently, few Ru(II)-L complexes are also reported which efficiently furnish aldehydes/ketones by oxidizing corresponding alcohols without engaging any sacrificial reducing agent for ligand reduction and active participation of the metal center via hydride transfer and H-walking processes^[8] are proposed to be operative as evidenced from the experimental and theoretical studies.^[7b,c]

In this backdrop our present work is on the design of another mixed ligand complex, of the pincer L, [Ru-(L)(PMe₂Ph)₂(CH₃CN)](ClO₄)₂ suitable for studies for the transfer hydrogenation reactions. Among the various ways of catalytic hydrogenation of organic substrates, transfer hydrogenation is considered to be economical and safer technique, as it does not possess the threat linked with carrying molecular H_2 .^[9] Ruthenium, among other transition metals, has reportedly played a

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fundamental role in designing efficient catalysts for the reduction of aldehydes and ketones to produce alcohols.^[9a,b,d,10] The use of isopropanol as the hydrogen source is prevalent in the literature as it is both inexpensive and easy to handle.^[9a,11] We looked for a mixed ligand phosphine complex because of the previous reports on the use of metal-phosphine complexes as proficient catalysts for the anticipated catalytic reaction.^[12] Accordingly, the reference complex is designed such that it also contains a labile solvent binding for smooth substrate coordination. Our studies indicate efficient catalytic selectivity of the isolated system for transfer hydrogenation to carbonyl functions selectively over other reducible functional groups like alkene, nitro, nitrile, ester, etc. Mechanistic analysis through different control reactions, isotope labelling studies and scrutinizing the spectroscopic data suggest metal-ligand cooperativity in the catalytic cycle through hydrogen-walking pathway.

Results and Discussion

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Synthesis and Characterization

The reaction of the neutral ligand, L with equimolar quantity of RuCl₃.xH₂O in the presence of excess PMe₂Ph in refluxing ethanol afforded a brown residue, which after counter-anion exchange process (with NaClO₄) followed by recrystallization from slow evaporation of acetonitrile solution yielded [1](ClO₄)₂ as shown in Figure 1a (detailed method is given in the experimental section). The Electrospray Ionization Mass Spectrum (ESI-MS) of the dicationic complex, [1]²⁺, showed a peak at m/z 332 amu (z=2) for the [(L)Ru(PMe₂Ph)₂)]²⁺ *i.e.* [1-CH₃CN]²⁺ fragment and the simulated spectrum matches well with the isotopic distribution of the complex (Figure 1b).

Complex $[1](ClO_4)_2$ is diamagnetic (S = 0) at room temperature and displayed a resolved ¹H-NMR spectrum in CDCl₃. It exhibited thirteen aromatic proton resonances corresponding



Figure 1. (a) Synthetic scheme of complex $[1](ClO_4)_{2^{\prime}}$ (b) Segmented ESI-MS of the complex; Masses observed from the fragment $[C_{33}H_{35}N_5P_2Ru]^{2+}$ (z=2), *i.e.*, $[1-CH_3CN]^{2+}$. The simulated mass spectrum is in blue, and (c) ¹H-NMR spectrum of the complex in CDCl₃ in 500 MHz (*₁: solvent residual peak; *₂: dichloromethane) (inset: aromatic proton resonances).

to the ligand L and ten aromatic proton resonances for two PMe₂Ph groups in the range of δ =8.80–6.19 ppm (Figure 1c). The twelve methyl proton resonances of two PMe₂Ph are visible at δ =1.66 ppm and three methyl protons of the coordinated CH₃CN moiety resonates at δ =2.65 ppm. The ³¹P-NMR spectrum of the complex showed one signal for two chemically equivalent trans-PMe₂Ph ligands at δ =37.91 ppm with respect to phosphoric acid solution as standard (δ =0.00 ppm). Addition of free PMe₂Ph gives an additional peak at –44.74 ppm. (Figure S2)

Suitable crystals of [1](ClO₄)₂ for single-crystal X-ray diffraction analysis were developed by slow evaporation of its acetonitrile solution. Its molecular view is shown in Figure 2. The cationic part of the complex *i.e.* $[1]^{2+}$ adopts a distorted octahedral geometry where the tridentate ligand L binds to the Ru center in a meridional fashion using a pair of N_{azo} and a N_{pv} . The remaining three coordination sites are occupied by two trans-PMe₂Ph groups and one CH₃CN moiety trans to the pyridyl-N of L. The azo bond lengths (d_{N-N}) in the isolated complex (1.286(11) and 1.290(11) Å) are considerably longer than that of the free ligand ($d_{N-N} = 1.225(8)$ and 1.241(8) Å) which is also reflected in its IR spectrum, where the spectral transition corresponding to $\nu_{\text{N-N}}$ appears at 1428 $\text{cm}^{-1}.$ Comparing the azo stretching frequency and bond lengths of the uncoordinated ligand^[4] with that of the Ru-complex, it can be stated that a neutral azo-chromophore is present in the complex. However, the relative elongation of azo bond in the coordinated L is considered due to the metal to ligand π -back bonding^[13] [Ru(II) $d\pi \rightarrow \pi^*(azo)$] which causes lowering of the azo stretching frequency. The crystallographic details along with the selected bond parameters are collected in the supporting information (Tables S1-S2).

The redox behavior of the isolated complex $[1](ClO_4)_2$ was studied by cyclic voltammetry in acetonitrile. The cyclic voltammogram exhibits one reversible reductive response at -0.01 V, together with a quasi-reversible reduction at -0.31 V and one quasi-reversible oxidation at 1.44 V vs. Ag/AgCl (Figure S3a, Table S3). Density functional theory (DFT) studies were performed to assess the locus of plausible electron transfer. The highest occupied molecular orbital (HOMO) of the isolated complex ([1](ClO₄)₂) is localized primarily on the



Figure 2. Molecular view of $[1]^{2+}$ (hydrogen atoms, counter anions and disordered atoms are omitted for clarity).

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ruthenium center; while the lowest unoccupied orbital (LUMO) is localized on the azo moiety of coordinated L (Figure S4). Therefore, the reductive waves are ascribed to the ligand-centered reductions of the coordinated azo chromophore of pincer L; whereas the oxidative response is assigned as metal-centered *i.e.* $Ru^{II} \rightarrow Ru^{III}$. The compound shows multiple absorptions in its electronic spectrum in the range of 200–800 nm recorded in acetonitrile (Figure S3b). Time-dependent density functional theory (TD-DFT) analysis was done to assign the major spectral transitions. The spectrum displays two intense transitions at 340 and 420 nm with a broad shoulder at 532 nm and the strong absorptions are ascribed to the excitations from the metal (Ru) centered (HOMO-7) to the ligand centered (LUMO + 1) (38%) and LUMO (42%) respectively (Table S4).

Catalytic activity

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The catalytic proficiency of the Ru-complex, $[1](ClO_4)_2$, was explored in the reduction of the model substrate benzaldehyde via transfer hydrogenation. Isopropanol was used both as the source of hydrogen and solvent in the reaction medium. The initial optimization was performed by reacting 1 mmol of benzaldehyde with 2 mol% of the catalyst and 1 mol% of 'BuOK in refluxing isopropanol (Table 1). However, a trace amount of the corresponding reduced product *i.e.* benzaldehyde was observed when the reaction was carried out in the air for 6 h (Table 1, entry 1). Screening the reaction for 12 h or even increasing the catalyst-loading up to 5 mol% could not afford the desired product in a reasonable amount (Table 1, entries 2–3). On the other hand, just changing the reaction atmosphere to N₂ resulted in the isolation of 96% of benzyl alcohol (Table 1, entry 4). Decreasing the catalyst-loading gradually from 2.0 to

Table 1. Optimization by varying the reaction atmosphere, catalyst, catalyst-loading and reaction time for transfer hydrogenation of benzaldehyde $\!\!\!^{[a]}$

Entry	Catalyst	Catalyst- loading (mol%)	Atmosphere	Time (h)	lsolated Yield (%)
1	[1](CIO ₄) ₂	2	Air	6	Trace
2	[1](ClO ₄) ₂	2	Air	12	Trace
3	[1](CIO ₄) ₂	5	Air	12	12
4	[1](CIO ₄) ₂	2	N ₂	6	96
5	[(L)	2	N ₂	6	52
	Ru(CH₃CN) Cl₂]				
6	[(L) Ru(PPh₃) Cl₂]	2	N ₂	6	84
7	[1](CIO ₄) ₂	1	N ₂	6	94
8	$[1](CIO_4)_2$	0.5	N_2	6	92
9 ^b	$[1](CIO_4)_2$	2	N_2	6	20
10	[1](ClO ₄) ₂	0.5	N ₂	2	26
[a] Reaction conditions: benzaldehyde (1 mmol), ^t BuOK (1.0 mol%), isopropanol (10 mL), heated at reflux. [b] base free					

0.5 mol%, keeping other factors the same, the conversion of benzaldehyde to benzyl alcohol was achieved in reasonably good yields as mentioned (Table 1, entries 4-6). A previously reported Ru(II)-complex of L viz.[(L)Ru(CH₃CN)Cl₂]^[7b,14] was found to yield only 52% of the desired alcohol under similar reaction conditions (Table 1, entry 5). However, another Ru(II)-L monophosphine complex viz.[(L)Ru(PPh₃)Cl₂],^[7c] when screened, afforded 84% of the corresponding product (Table 1, entry 6). The enhanced catalytic activity with the increasing number of phosphine ligands indicates the effectiveness of trans-effect of phosphines. A Comparison between the three ruthenium complexes, the catalytic activity is maximum in the phosphine complex [1](ClO₄)₂. This is assumed due to higher translabilization by the two phosphine ligands.^[15] The Ru-diphosphine complex, discussed herein, *i.e.* [1](ClO₄)₂ was found preeminent and finally, the optimized condition for transfer hydrogenation was achieved where a typical catalytic reaction consists of 1 mmol of benzaldehyde to react with 0.5 mol% of catalyst [1](ClO₄)₂ (5×10⁻³ mmol) and 1.0 mol% of ^tBuOK (1× 10^{-2} mmol) in 10 mL of refluxing isopropanol under N₂ atmosphere for 6 h (Table 1, entry 8). The resultant reduced product i.e. benzyl alcohol was purified on a preparative thinlayer chromatography (TLC) plate (UV-active silica (GF-254)) by eluting with 1:5 ethyl acetate and hexane solvent mixture. The isolated yield of benzyl alcohol was 92%. These optimized conditions were then applied for the transfer hydrogenation of various aldehydes and ketones using isopropanol as the source

of hydrogen. The transfer hydrogenation of benzaldehyde produced benzyl alcohol in almost quantitative yield (Table 2, entry 3 a). Electron-withdrawing halogen (F, Cl, and Br) substituted benzaldehydes were reduced to the corresponding alcohols in 80-88% yields with the halogen atoms well tolerated (Table 2, entries 3 b-3 d). Additionally, reactions of benzaldehyde bearing electron-donating substituents such as methyl (in para position to --CHO), methoxy (in ortho, meta, and para to --CHO) groups afforded the desired products in 80-92% yields (Table 2, entries 3f-3i). The reaction was also found operational for the reduction of dialdehydes such as terphthalaldehyde and isophthalaldehyde to their corresponding diols (Table 2, entries 3j-3k). The poly-aryl aldehyde *i.e.* 1-napthylaldehyde can also be reduced smoothly to 1-naphthalenemethanol in a high isolated yield (Table 2, entry **3** I). Moreover, catalyst $[1](CIO_4)_2$ was also reactive towards the transfer hydrogenation of a heterocyclic aldehyde i.e. 2-pyridinecarboxaldehyde and 2pyridylmethanol was obtained in 70% yield (Table 2, entry 3 m). The relatively low yield of the products may be ascribed to the competitive coordination between the pyridyl and C=O moiety to the metal center.^[16]

The selectivity in hydrogenation is an important factor to get pure products. Thus intra-molecular chemoselectivity of the catalyst was examined with the transfer hydrogenation of a range of aromatic aldehydes containing other readily reducible functional groups in isopropanol. The transfer hydrogenation of α , β -unsaturated aldehyde (cinnamaldehyde) produced cinnamyl alcohol in 88% isolated yield indicating the selectivity for C=O over C=C hydrogenation (Table 2, entry **3** n). Although

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several ruthenium catalysts are known to hydrogenate nitroaryl compounds,^[9a,17] here the transformation of *p*-nitrobenzaldehyde yielded the consequent nitrobenzyl alcohol in 82% yield with exclusive retention of the nitro group (Table 2, entry 3 o). Similarly, the cyano group also remained unaffected during aldehyde to alcohol formation (Table 2, entry 3 p). In addition to these, the catalytic system also shows excellent tolerance for ester functionality and only the aldehyde group was reduced to yield the corresponding alcohol (Table 2, entry 3 g). Furthermore, absolute intermolecular chemoselectivity of catalyst [1](ClO₄)₂ towards transfer hydrogenation of aldehydes in the presence of other unsaturated organic substrates (for example nitrobenzene, benzonitrile, styrene, and phenylacetylene) was also established. In the competitive reaction comprising of an equimolar mixture of benzaldehyde and the respective cosubstrate in isopropanol, selective hydrogenation of benzaldehyde was observed without any notable conversion of the cosubstrate (Table 2ii).

To further expand the catalytic potential of $[1](CIO_4)_{2r}$ transfer hydrogenation of several ketones were carried out in isopropanol. The catalyst is found capable of converting a series of ketones (4a-4g) including one alicyclic ketone *viz.* cyclohexanone to the desired alcohols (5a-5g) in high yields, as outlined in Table 3.

To reveal the practical efficacy of this methodology, a largescale reaction was carried out where the transfer hydrogenation of 5 mmol of benzaldehyde in the presence of 0.5 mol% of catalyst $[1](ClO_4)_2$ and 1.0 mol% of ^tBuOK in refluxing isopropa-



BuoK (1.0 mol%), isopropanol (10 mL), 82 °C, 6 h, N_2 . [b] catalyst (1.0 mol%). Reported yields refer to isolated compounds.

nol under $N_{\rm 2}$ atmosphere furnished 82% isolated yield of benzyl alcohol after 10 h (Scheme 1).

Mechanistic Investigation

We have next carried out different controlled chemical reactions to gain insights into the mechanism of the possible catalytic cycle. In the catalytic transfer hydrogenation reaction, the initial step is supposedly the formation of a Ru-isopropoxide adduct in presence of a base. When the catalyst was heated with ^{*i*}PrOH and ^{*i*}BuOK in toluene a new IR stretch appeared at 744 cm⁻¹ characteristic to the Ru–O stretching.^(7c,18) As evidenced earlier,^{(7b,c]} hydride ion transfer (H⁻) is operative in the following step which involves the oxidation of isopropanol to release acetone. As shown in Figure 3, the migratory hydride ion now has two plausible acceptors; either the β -hydride transfer to the metal center generating a Ru–H intermediate which further



Scheme 1. Scalability for transfer hydrogenation of benzaldehyde in isopropanol.



Figure 3. Metal-ligand cooperativity or exclusively ligand mediated.

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Scheme 2. Transfer hydrogenation of benzophenone with isopropanol-d_ $\!\!\!\!\!\!\!_{8}$.

migrates to an azo function of the coordinated ligand *i.e.* via metal-ligand cooperativity (Pathway I), or the H^- directly migrates to the azo function *i.e.* exclusively ligand-mediated (Pathway II).

NMR spectroscopic technique was used to identify the intermediate. The Ru-catalyst was mixed with equimolar isopropanol and 0.2 equivalent ^tBuOK in THF-d⁸ solvent in an NMR tube and the solution was right away subjected to ¹H-NMR spectral analysis. The spectrum displayed a characteristic Ru-H resonance^[19,7c] at $\delta = -4.03$ ppm (Figure S30a) indicating the formation of a metal-hydride intermediate. This observation implies that the reaction proceeds through a hydride transfer to the Ru(II)-center from the coordinated alkoxide ion. A similar experiment was carried out using deuterated isopropanol *i.e.* isopropanol-d₈ (instead of isopropanol) and a broad resonance at $\delta = -1.50$ ppm characteristic^[20] Ru–D resonance was observed in the ²H-NMR spectrum of the mixture recorded in tetrahydrofuran (Figure S30b). These Ru-H or Ru-D intermediates were found to be transient and their corresponding NMR resonances were absent when checked after 30 minutes. Interestingly, the IR spectrum of the above reaction mixture containing ⁱPrOH showed two bands at 2844 and 2902 cm⁻¹ attributable to the N-H stretching frequencies^[5b,7c] (Figure S31a). This was further confirmed when the other solution having isopropanol-d₈ showed two characteristic N–D peaks^[5b,7c] at 2148 and 2246 cm⁻¹ (Figure S31b). These experimental findings substantiate the metal-ligand cooperativity in the catalytic cycle through the formation of a transitory Ru-H intermediate and subsequently a Ru-hydrazo intermediate via hydrogen-walking mechanism. The transfer hydrogenation is carried out in N₂ atmosphere and the hydrazo intermediate species is proposed to retrieve the active-catalyst form by reducing the aldehyde/ketone present. To confirm the role of isopropanol as the exclusive source of hydrogen, isotope labeling experiment for the transfer hydrogenation of benzophenone was performed (Scheme 2). The optimized condition for transfer hydrogenation, mentioned earlier, was employed where isopropanol was replaced by isopropanol-d₈. The product *i.e.* diphenylcarbinol-d₂ (5e') was characterized by its ¹H-NMR spectrum (Figure S29).

Considering the above experimental results, we propose a probable catalytic cycle (Scheme 3) for transfer hydrogenation reactions.



Scheme 3. Proposed catalytic cycle for transfer hydrogenation.

Conclusions

In this study, a Ru(II)-diphosphine complex bearing a pincer bisazo-aromatic ligand, L was isolated and characterized. Single crystal X-ray structure of the compound revealed that the tridentate ligand binds to the central Ru(II) atom in a meridional fashion and the counter cationic part of the complex adopts a distorted octahedral geometry. The Ru-complex acts as an efficient catalyst to bring about the transfer hydrogenation of a broad array of aldehydes and ketones in isopropanol in deaerated conditions. High chemoselectivity was also observed for aldehyde reduction in the presence of the other reducible functional groups, for instance, nitro, nitrile, alkene, and ester. The incorporation of phosphine entities was proven to be useful as its catalytic efficiency seemed better than the previously reported dichloro Ru(II)-L complexes. The controlled experiments including isotope-labelling studies confirm the role of isopropanol as the only source of hydrogen during transfer hydrogenation catalysis and the complex acts as a metal-ligand bifunctional catalyst where both the metal and ligand participated synergistically in the cycle.

Experimental Section

Materials

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 $RuCl_3.xH_2O, PMe_2Ph$ and tetrabutylammonium hexafluorophosphate ([Bu_4N]PF_6) were purchased from Sigma-Aldrich. Different aldehydes and ketones (including deuterated ones), used for catalysis, were purchased from either Sigma-Aldrich or Alfa Aesar. Solvents were purified and dried prior to use.

ESI-Mass spectra were recorded on a micromass Q-TOF mass spectrometer with serial no. YA 263. Room temperature magnetic moment measurement was carried out with a Gouy balance (Sherwood Scientific, Cambridge, U.K). NMR spectra were recorded using either a Bruker Avance 400 MHz or 500 MHz spectrometers using SiMe₄ as the internal standard. Infrared spectra were obtained from a Perkin-Elmer 783 spectrophotometer. A Perkin-Elmer Lambda 950 spectrophotometer was used to record UV-Vis spectra. A Perkin-Elmer 240 C elemental analyzer was used to collect micro analytical data (C, H, N). The electrochemical measurements were performed using a PC-controlled PAR model 273 A electrochemistry system. Cyclic voltammetric experiments were performed in acetonitrile solvent containing supporting electrolyte, 0.1 M [Bu₄N] PF₆ under nitrogen atmosphere and the three electrodes configuration includes Ag/AgCl as the reference electrode,Pt disk as the working electrode and Pt wire as the auxiliary electrode. $E_{1/2}$ for the ferrocenium-ferrocene couple was 0.40 V under the experimental condition.

Synthesis and Characterization Data of Complex [1](ClO₄)₂

The ligand, 2,6-bis(phenylazo)pyridine (L) was prepared following the method available in the literature where the synthetic route involves the condensation of nitrosobenzene with 2,6-diaminopyridine in 2:1 molar ratio in highly alkaline condition.^[4] 75 mg (0.26 mmol) of the ligand, L and 65 mg (0.25 mmol) of RuCl₃.xH₂O was mixed in 10 mL of ethanol and PMe₂Ph (138 mg, 1.0 mmol) was added to the solution in excess. The solution was refluxed for 2 h. The resulting reddish brown solution was then concentrated using a rotary evaporator and was added into a saturated aqueous solution (cold) of NaClO₄. The brown precipitate, thus deposited, was washed thoroughly with cold water, hexane to remove any impurity present and then dried under vacuum. The crude mass was recrystallized from slow evaporation of its acetonitrile solution at room temperature (300 K). Yield: 131 mg (58%, based on Ru). ESI-MS: m/z 332 amu for $[1-CH_3CN]^{2+}$. IR (KBr, cm⁻¹): 1428 ($v_{N=N}$). Anal. Calc. for C₃₅H₃₈Cl₂N₆O₈P₂Ru: C, 46.47; H, 4.23; N, 9.29. Found: C, 46.71; H, 4.42; N, 9.11. ¹H-NMR (500 MHz, CDCl₃): δ (ppm) 8.80 (d, J=7.5 Hz, 4H), 8.24 (d, J=8.0 Hz, 2H), 8.02 (t, J=8.0 Hz, 1H), 7.68 (t, J=8.0 Hz, 2H), 7.59 (t, J=8.0 Hz, 4H), 7.15 (t, J=7.5 Hz, 2H), 6.98 (t, J=8.0 Hz, 4H), 6.23-6.19 (m, 4H), 2.65 (s, 3H), 1.66 (s, 12H). ³¹P-NMR (162 MHz, CDCl₃): δ 37.91 ppm.

X-Ray Crystallography

Crystallographic data table for complex [1](ClO₄)₂ and selected bond parameters are provided in the Supporting Information (Tables S1-S2). Suitable crystals for X-ray diffraction analysis were developed by slow evaporation of the acetonitrile solution of the complex. Crystallographic data were collected on a Bruker SMART APEX-II diffractometer, equipped with graphite-monochromatic Mo K α radiation (λ =0.71073 Å), and was corrected for Lorentz polarization effects. Data for $[1](CIO_4)_2$: a total of 27504 reflections were collected, of which 6822 were unique ($R_{int} = 0.172$). These satisfy the $I > 2\sigma(I)$ criterion and was used in subsequent analysis. The structure was solved by employing the SHELXS-2014 program package and was refined by full-matrix least squares based on F² (SHELXL-2014).^[21] All hydrogen atoms were added at calculated positions. Crystal twining has been observed for the counter anions and phenyl ring of one of the PMe₂Ph ligand. However, we use this data as we have failed to produce better quality crystals for diffraction after repetitive attempts.

Procedure for catalytic transfer hydrogenation reaction

The transfer hydrogenation of aldehydes and ketones were carried out in isopropanol by using complex [1](ClO₄)₂ as catalyst assisted by catalytic amount of a base following a general procedure. In a schlenk tube, 1 mmol of the substrate (aldehyde/ketone), 0.005 mmol of the catalyst (4.5 mg) and 0.01 mmol of 'BuOK (1.1 mg) were mixed in 10 mL of deaerated isopropanol. The reaction mixture was stirred at 82 °C for 6 h under N₂ pressure (unless stated otherwise). After the reaction was complete, the evaporation of the solvent was done under reduced pressure followed by purification of the resultant crude product on preparative silica gel GF-254 TLC plate using 1:5 ethyl acetate: hexane solvent mixture as eluent. The reduced products were characterized by NMR spectroscopy (See Figures S7–S41).

Mechanistic analysis

In a sealed NMR tube 0.05 mmol isopropanol (3.0 mg) was mixed with 0.05 mmol of catalyst [1]²⁺ (45.0 mg) and 0.01 mmol of ¹BuOK (1.2 mg) in 0.7 ml THF-d₈. A distinct resonance of Ru–H was observed at $\delta = -4.03$ ppm (Figure S30a) in the ¹H-NMR spectrum recorded instantaneously. After 30 min, the solution was subjected to IR spectral analysis which showed two distinct peaks at 2844 and 2902 cm⁻¹ characteristic to N–H stretching for the hydrazo intermediate (Figure S31a). A similar experiment was carried out with appropriate quantity of catalyst [1]²⁺ (45.0 mg) and isopropanol-d₈ in THF. A broad signal at $\delta = -1.50$ ppm, appeared in the ²H-NMR of the reaction mixture, is characteristic to Ru–D resonance (Figure S30b) and two distinct IR bands appeared due to N–D stretching at 2148 and 2246 cm⁻¹ in its IR spectrum after stirring the reaction mixture for 30 min (Figure S31b).

Computational details

All the calculations were performed using Gaussian 09 program package.^[22] The 6-31G* (C, H, N), 6-311G* (P, Cl) and SDD (Ru) level of theory^[23] were employed for the structural optimization and vibrational analysis. Spin restricted approaches were employed for ground state singlet state. Singlet excitation energies based on the solvent-phase (acetonitrile) optimized geometry of the complexes were computed using the Time Dependent Density Functional Theory (TD-DFT) formalism^[22,24] in dichloromethane/acetonitrile solvent using Conductor-like Polarisable Continuum Model (CPCM).^[24a,25] GaussSum^[26] was used to calculate the percentage contribution of metal and ligand to the frontier orbital and the fractional contributions of various molecular orbital in the optical spectral transition.

Supporting Information

The supporting information contains spectroscopic characterizations of the Ru-complex and intermediates, voltammetric and crystallographic details of the Ru-complex, and NMR spectra of the products. Crystallographic data for complex [1](ClO₄)₂ has been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2065125. Copies of the data can be obtained free of charge on application to CCDC.

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Ruthenium(II) Complex of a Tridentate Azoaromatic Pincer Ligand and its Use in Catalytic Transfer Hydrogenation of Aldehydes and Ketones with Isopropanol