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# Effects of Ancillary Ligands on Redox and Chemical Properties of **Ruthenium Coordinated Azoaromatic Pincer**

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S Supporting Information

ABSTRACT: In this work, the effect of the electronically different ancillary ligands on the overall properties of the  $Ru^{II}L$  moiety (L = 2,6-bis(phenylazo)pyridine) in heteroleptic complexes of general formula [RuLQC1]<sup>0/+</sup> was investigated. Four different ancillary ligands (Q) with different electronic effects were used to prepare the heteroleptic compounds from the precursor complex,  $[RuL(CH_3CN)Cl_2]$  (1); Q = pcp: 2-(4-chloro-phenylazo)pyridine (strong  $\pi$ -acceptor), [2]<sup>+</sup>; bpy: 2,2'-bipyridyl (moderate  $\pi$ -acceptor), [3]<sup>+</sup>; acac<sup>-</sup>: acetylacetonate (strong  $\sigma$ -donor), 4; and DTBCat<sup>2-</sup>: 3,5-di-tert-butyl catecholate (strong  $\pi$ -donor), 5. The complexes  $[2]^+$ ,  $[3]^+$ , 4,



and 5 were fully characterized and structurally identified. The electronic structures of these complexes along with their redox partners were elucidated by using a host of physical measurements: nuclear magnetic resonance, cyclic voltammetry, electronic paramagnetic resonance, UV-vis-NIR spectroscopy, and density functional theory. The studies revealed significant effects of the coligands on azo bond lengths of the RuL moiety and their redox behavior. Aerobic alcohol oxidation reactions using these Ru complexes as catalysts were scrutinized. It was found that the catalytic efficiency is primarily controlled by the electronic effect of the coligand. Accordingly, the complex  $[2]^+$  (containing a strong  $\pi$ -acceptor coligand, pcp) brings about oxidation efficiently, producing 86% of benzaldehyde. In comparison, however, the complexes 4 and 5 (containing electron donating coligand) furnished only 15-20% of benzaldehyde under identical reaction conditions. Investigations of the reaction mechanism suggest that an unstable Ru-H species is formed, which is transformed to a Ru-hydrazo intermediate by H-walking as reported by Hall et al. (J. Am. Chem. Soc., 2015, 137, 12330). Aerial O<sub>2</sub> regenerates the catalyst via oxidation of the hydrazo intermediate.

# INTRODUCTION

Over the past two decades, transition metal complexes of the redox active ligands have drawn significant attention due to their inherent ability to acquire multiple redox states compared to coordination complexes of mere spectator ligands.<sup>1-5</sup> As a result, this class of compounds is now at the focus of several realworld applications ranging from development of efficient chemical catalysts<sup>6-9</sup> and materials<sup>10-12</sup> for next-generation digital and optical technologies. The reactivity of metal complexes bearing redox-active ligands primarily depends on the nature of metal center,  $^{13,14}$  electronic structure of the ligand backbone,<sup>15–17</sup> and secondary coordination sphere of the complex.<sup>18</sup> Strong metal-ligand  $\pi$ -interactions and redox activities of the coordinated ligands together modulate the overall electronic structures vis-á-vis chemical behaviors of such complexes.

We and others<sup>19-32</sup> have long-standing interest in the coordination chemistry of redox active azo-aromatic ligands. The neutral azo-aromatics have low lying  $\pi^*$  orbital which can strongly participate in back-bonding as well as can form metal stabilized azo-anion radical complexes. Recently, we introduced<sup>26,33</sup> a pincer azo-aromatic ligand, 2,6-bis(phenylazo)pyridine (L), which in principle can accommodate up to either four electrons or four electrons plus four protons without rupture of -N-N- bonds. We showed previously<sup>33,34</sup> that Ni(II) and Zn(II) complexes of L are capable of mimicking the enzymatic pathway for catalytic alcohol oxidation using primarily ligand-based redox couple  $(-N=N- + 2e^{-} + 2H^{+})$  $\leftrightarrow -NH-NH-$ ).

In this work, we explored the effect of ancillary ligands on the properties of RuL moiety in a hexacoordinated framework, [RuLQCl]<sup>0/+</sup> (Chart 1). Four ancillary ligands (designated as Q) of different character (strongly  $\pi$ -accepting 2-(4chlorophenylazo)pyridine (pcp), weakly  $\pi$ -accepting 2,2'bipyridine (bpy),  $\sigma$ -donating acetylacetonate (acac<sup>-</sup>), and strong  $\pi$ -donating 3,5-di-*tert*-butyl catecholate (DTBCat<sup>2-</sup>) ligands) were chosen and allowed to coordinate at the Ru center in the RuL moiety. We hypothesized that the ancillary ligands, in

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Chart 1



conjunction with completing the coordination sphere, would exert tuning effect on their overall physicochemical activities.

Accordingly, the primary aim of this paper is to follow the ancillary ligand effect on the metal ligand cooperativity between Ru(II) and the principal ligand L. Besides studying the usual metal–ligand interplay in determining the electronic structures of the heteroleptic complexes,<sup>35,36</sup> we further scrutinized the tuning effect on their chemical reactivity.<sup>37</sup> We thus set out to study aerial catalytic oxidation of benzyl alcohol using the above complexes. An interesting trend was observed: under identical reaction conditions, the compound with strongest  $\pi$ -acceptor ligand pcp produced the corresponding aldehydes in an excellent yield (>85%), whereas the compound with  $\pi$ -donor ligand, (DTBCat<sup>2–</sup>), produced the product only in 15% yield. Mechanistic studies revealed that the coordinating ligand L directly participates in the hydrogen abstraction process from alcohol using azo/hydrazo redox couple.

## RESULTS AND DISCUSSION

Synthesis and Characterization. The reaction of one equivalent ligand (L) with  $RuCl_3 \cdot xH_2O$  in refluxing ethanol resulted in a greenish brown compound. The crude mass upon recrystallization by slow evaporation of its acetonitrile solution produced a green product of composition  $Ru(L)(CH_3CN)Cl_2$ (1). Electrospray ionization mass spectrometry (ESI-MS) of the complex 1 showed an intense peak at m/z 460 amu, which corroborates with the formulation of  $(1 - (CH_3CN) + H)^+$ . The complex 1 is diamagnetic at room temperature and showed a resolved proton NMR spectrum. The aromatic proton resonances appeared in the region 8.59-7.51 ppm, and a sharp singlet at 2.70 ppm is noted due to the coordinated CH<sub>3</sub>CN moiety. The heteroleptic ruthenium complexes [Ru- $(L)(Q)Cl]^{0/+}$  (0 for anionic ligands acac<sup>-</sup> and DTBsq<sup>•-</sup>, one electron oxidized form of DTBcat<sup>2-</sup>, and + for neutral ligands pcp and bpy) were prepared as stable compounds from the

reactions between the complex 1 and the corresponding ligand (Q) (Chart 1) under refluxing conditions using either acetonitrile or methanol as solvent. Synthetic procedures along with their characterization data of the isolated compounds are collected in the Experimental Section. Micro analytical data, ESI-MS, and NMR spectral data support their formulations. The ESI-MS spectra of the complexes  $[Ru(L)(pcp)Cl]PF_{6}$  [2]PF<sub>6</sub> and [Ru(L)(bpy)Cl]PF<sub>6</sub>, [3]PF<sub>6</sub> displayed intense molecular ion peaks at m/z 641 and 580 amu, respectively (Figures S1 and S2). On the other hand, the complex [Ru(L)(acac)Cl], 4 showed an intense peaks at m/z 488 amu due to  $(4 - Cl)^+$ fragment (Figure S3) and complex [Ru(L)(DTBsq<sup>•-</sup>)Cl], 5 showed two intense peaks at m/z 644 and 424 amu due to  $(5)^+$ and  $(5 - DTBsq^{\bullet-})^+$  fragments (Figures S4a and b). All of these isolated complexes except 5 are diamagnetic. The <sup>1</sup>H NMR resonances of these compounds are overlapping, and so the unambiguous assignment of individual proton resonance was not possible. However, proton counts in the spectrum of each of the compounds corroborated well with the formulation of products (Figures S5-S7). Characteristic <sup>1</sup>H NMR signals of acetyl group in the complex 4 appeared at 2.53 and 1.26 ppm as two separate singlets for the two methyl groups, and one singlet resonance appeared at 5.08 ppm for the  $\gamma$ -C–H proton; the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of the compound 4 displayed two carbonyl carbon resonances at 190.4 and 187.2 ppm. NMR data of all compounds are included in the Experimental Section, and their spectra are submitted as Supporting Information (Figures S5-S7). Solution-state magnetic susceptibility measurement of the compound 5 by Evans method indicated that it is one electron paramagnetic<sup>38</sup> with  $\mu_{\rm eff}$  (298 K) = 1.68  $\mu_{\rm B}$ . Paramagnetic ground state of the complex 5 was further characterized by its electron paramagnetic resonance (EPR) spectrum (see below).

**Crystal Structure Analysis.** All of the molecules ( $[2]PF_6-5$ ) described herein are crystalline, and their structures were

solved by three-dimensional single crystal X-ray diffraction analyses. Suitable crystals of these complexes were developed by slow diffusion of their dichloromethane solution into hexane. Molecular views along with the atom numbering schemes are shown in Figure 1. Their ORTEP representations are presented



**Figure 1.** Molecular views of the isolated complexes:  $[2]^+$ ,  $[3]^+$ , 4, and 5. Hydrogen atoms for all the complexes and the counteranion for  $[2]^+$  and  $[3]^+$  are omitted for clarity.

in Figures S8–S11. All of them adopt distorted octahedral geometry with the N $\wedge$ N $\wedge$ N pincer ligand L coordinating meridionally in an almost planar configuration.

The ligand L is a strong  $\pi$ -acceptor, and metal to ligand  $[Ru(II)d\pi - \pi^*(azo)]$  back bonding in its complexes is a common phenomenon.<sup>24,26</sup> X-ray crystallographic analyses of the two cationic complexes  $[2]^+$  and  $[3]^+$  reveal significantly distorted octahedral geometry about the ruthenium center. The chelate bite angles are considerably smaller compared to that in ideal octahedral geometry. The average value of chelate bite angles of  $N_{azo}(L)$ -Ru- $N_{pv}(L)$  is 76.24° for complex [2]<sup>+</sup> and  $76.06^{\circ}$  for  $[3]^+$ . In the complexes  $[2]^+$  and  $[3]^+$ , the bite angles of the ancillary ligands are  $75.56^{\circ}$  and  $77.32^{\circ}$ , respectively. In complex  $[2]^+$ , the two pyridyl nitrogen atoms of the ligands L and pcp are disposed *trans* to each other. In complex  $[2]^+$ , three N-N bond lengths are 1.289(11), 1.286(10) (for ligand L), and 1.287(10) Å (for ligand pcp), while the  $d_{N-N}$  lengths of complex  $[3]^+$  are 1.299(2) and 1.293(2) Å (Table 2). The two d<sub>N-N</sub> bond lengths in the complex 4 are 1.309(3) and 1.300(2) Å. The Ru-O bond lengths in complex 4 are 2.0428(17) and 2.0821(15) Å, which are commonly observed<sup>39-43</sup> in the other Ru(II)-acac complexes. The ligand DTBCat coordinates via deprotonation and can exists in different oxidation states (catecholate, semiquinone, and quinonoid), C-O bond length of the coordinated ligand is an indicator<sup>44-48</sup> of its oxidation state. In the complex 5, the C-O bond lengths are 1.293(4) and 1.303(4) Å, which are characteristic<sup>48</sup> for the semiguinone oxidation state of the coordinated ligand. Moreover, the bond lengths of C18-C19, C19-C20, C20-C21, C21-C22, C22-C23, and C23-C18 of the phenyl ring of the DTBCat ligand are 1.410(5), 1.365(5), 1.435(5), 1.365(5), 1.439(5), and 1.439(5) Å respectively. The calculated metric oxidation state (MOS) value<sup>49</sup> is -1.141 (esd 0.0799) indicates the semiquinone state of the coordinated DTBCat ligand. Two Ru-O bond lengths in this complex are 2.078(2) Å (*trans* to  $N_{py}$  of L) and 2.023(2) Å (*trans* to Cl atom), respectively. The  $d_{N-N}$  of coordinated L are 1.299(4) and 1.300(4) Å, respectively. The dianionic DTBCat<sup>2–</sup> ligand was anticipated to have strongest electron donor ability via  $\sigma$ - and  $\pi$ -donation, but its one electron oxidized semiguinone

# Table 1. Crystallographic Details of the Complexes [2]PF<sub>6</sub>, [3]PF<sub>6</sub>, 4, and 5

compound	[2]PF <sub>6</sub>	[3]PF <sub>6</sub>	4	5
CCDC no.	1846398	1846399	1846400	1846401
empirical formula	C <sub>28</sub> H <sub>21</sub> Cl <sub>2</sub> F <sub>6</sub> N <sub>8</sub> PRu	C27H21ClF6N7PRu	$C_{22}H_{20}ClN_5O_2Ru$	C31H33ClN5O2Ru
formula weight	786.47	725.00	522.95	644.14
crystal system	monoclinic	triclinic	monoclinic	triclinic
space group	P21/c	Pī	P21/c	PĪ
a (Å)	8.1668(14)	8.1792(5)	13.2910(18)	8.7710(11)
b (Å)	29.650(5)	11.6400(7)	9.8527(13)	9.9940(13)
c (Å)	12.725(2)	15.7389(10)	16.737(2)	17.362(2)
α	90	87.749(2)	90	83.592(4)
β	95.997(5)	79.667(1)	93.249(3)	80.279(3)
γ	90	71.001(2)	90	82.210(4)
Ζ	4	2	4	2
$V(Å^3)$	3064.4(9)	1393.54(15)	2188.2(5)	1480.1(3)
$D_{\rm cal}~({\rm g/cm^3})$	1.705	1.728	1.587	1.445
$\mu \ (\mathrm{mm}^{-1})$	0.810	0.789	0.868	0.656
<i>T</i> (K)	293	293	293	293
heta range (deg)	1.4-27.3	1.9-32.4	1.5-27.5	1.2-27.5
GOF	1.04	1.18	0.80	0.84
no. of reflections collected	42 137	22 350	23 416	19 992
no. of unique reflections	6945	8443	4976	6512
final <i>R</i> indices $((I > 2\sigma(I))$	0.0901	0.0296	0.0251	0.0396
$R_1$ , $wR_2$	0.2330	0.0816	0.0853	0.1075

#### Table 2. Selected Bond Distances of the Complexes [2]PF<sub>6</sub>, [3]PF<sub>6</sub>, 4, and 5

	$\pi$ -accepting ligands			$\sigma/\pi$ -donating ligands				
	[RuL(pcp)Cl]F	PF <sub>6</sub> ; [ <b>2</b> ]PF <sub>6</sub>	[RuL(bpy)Cl]PF <sub>6</sub> ; [3]PF <sub>6</sub>		[RuL(acac)Cl]; 4		[RuL(DTBsq <sup>•-</sup> )Cl]; 5	
bond parameters	expt	calc	expt	calc	expt	calc	expt	calc
			effects on 2,6-bis(ph	enylazopyridine	e) ligand (L)			
Ru-N1	2.044(7)	2.140	2.0204(15)	2.117	2.0440(19)	2.091	2.087(3)	2.097
Ru–N3	1.904(6)	1.945	1.9075(15)	1.934	1.8853(18)	1.898	1.894(3)	1.902
Ru-N5	2.089(6)	2.112	2.1038(15)	2.120	2.0852(17)	2.091	2.067(3)	2.097
N1-N2	1.289(11)	1.283	1.299(2)	1.289	1.309(3)	1.296	1.299(4)	1.296
N4-N5	1.286(10)	1.288	1.293(2)	1.287	1.300(2)	1.296	1.300(4)	1.296
Ru-Cl1	2.367(3)	2.399	2.3653(7)	2.399	2.3583(7)	2.393	2.3489(10)	2.385
	effects on ancillary coligands (Q)							
Ru–N6	2.079(8)	2.068	2.1087(15)	2.146				
Ru–N7			2.0476(16)	2.103				
Ru–N8	2.015(6)	2.115						
N7-N8	1.287(10)	1.282						
Ru–O1					2.0428(17)	2.081	2.023(2)	2.123
Ru–O2					2.0821(15)	2.120	2.078(2)	2.061
O1-C18					1.278(3)	1.283	1.293(4)	1.300
O2-C20					1.267(3)	1.272		
C18-C19					1.389(3)	1.399		
C19-C20				2.146	1.394(3)	1.410		
O2-C23				2.103			1.303(4)	1.304
C18-C23				2.117			1.439(5)	1.450

state (DTBsq<sup>•-</sup>) essentially acts as comparatively weak  $\pi$ -donating ligand.

Being a redox-active ligand, L can adopt multiple oxidation states upon coordination to the metal center. Such complexes exhibit ligand-based redox processes which were influenced by the metal-to-ligand  $\pi$ -back-donations. Presence of the ancillary ligands of different nature influence the back-donation and *vis-á-vis* the redox properties of both metal and ligand (see later). Crystallographic details and selected bond lengths of the complexes [2]<sup>+</sup>, [3]<sup>+</sup>, 4, and 5 are collected in Tables 1 and 2.

**Cyclic Voltammetry and EPR Spectroscopy.** Cyclic voltammograms of the isolated complexes  $[2]^+$  and  $[3]^+$  were investigated in acetonitrile, whereas those of 4 and 5 were studied in dichloromethane solvent containing 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. In all cases, platinum was used as the working electrode and Ag/AgCl as reference electrode.  $E_{1/2}$  of the ferrocene/ferrocinium couple appeared at 0.4 V under the experimental conditions. Their cyclic and differential pulse voltammograms are displayed in Figure 2, and the results are summarized in Table 3. All of these complexes showed multiple single electron redox processes in the potential window of  $\pm 2.5$  V.

Coordination of more than one redox active ligand to metal center is reflected in the cyclic voltammograms of the complexes  $[2]^+$  and  $[3]^+$ . Each of these complexes exhibits 5 single electron transfer waves: for  $[2]^+$ , 5 redox waves appeared at 1.70, 0.08, -0.42, -0.81, and -1.35 V, while those for complex  $[3]^+$  appeared at 1.43, -0.18, -0.70, -1.44, and -1.69 V. In the case of complex  $[2]^+$ , the wave that appeared at 0.08 V is reductive, as evidenced by exhaustive electrolysis at -0.25 V. Electrochemically generated one electron reduced complex 2 showed a rhombic EPR spectrum (Figure 3(a) and Table 4) at  $g_{av} = 1.974$  ( $g_1 = 2.003$ ,  $g_2 = 1.974$ ,  $g_3 = 1.945$ ) with notable g anisotropy, 50,51  $\Delta g = 0.058$ , indicating a ligand-based EPR spectrum. A similar situation is also observed in the case of coulometrically generated complex 3 (Figure 3(c) and Table 4).



**Figure 2.** Cyclic (black) and differential pulse (red) voltammograms of the complexes  $[2]^+$ –5.

In this case, the signal appeared at  $g_{av} = 1.967$  ( $g_1 = 2.015$ ,  $g_2 = 1.957$ ,  $g_3 = 1.929$ ) with  $\Delta g = 0.084$ . Similarities in the EPR spectrum indicate that the locus of reduction is same in both the cases. This is further supported by DFT and spectro-electro-chemical studies (see below). The 2e<sup>-</sup> reduced complex [2]<sup>-</sup> is

 Table 3. Cyclic Voltammetry Data<sup>a</sup>

complex	reduction $E_{1/2}^{b}$ V ( $\Delta E_{p}$ , mV)	$egin{array}{l} { m oxidation} \ E_{1/2} \ { m V} \ (\Delta E_{ m p}, \ { m mV}) \end{array}$
[ <b>2</b> ]PF <sub>6</sub>	0.08 (70), -0.42(78), -0.81(69), -1.35 (73)	1.70 (126)
[3]PF <sub>6</sub>	$-0.18 (86), -0.70 (116), -1.44 (63), -1.69 (143)^{c}$	$1.43 (172)^c$
4	-0.49 (130)	1.16 (132)
5	-0.13 (64), -0.50 (64), -0.87 (86)	0.73(67), 1.78 (158)

"Conditions: cyclic voltammetry was performed in acetonitrile solution; for complexes [2]PF<sub>6</sub> and [3]PF<sub>6</sub> and in dichloromethane solution; for complexes 4 and 5. Supporting electrolyte [Bu<sub>4</sub>N]ClO<sub>4</sub>, working electrode: Platinum, reference electrode: Ag/AgCl, scan rate: 50 mV/s.  ${}^{b}E_{1/2}$ = ( $E_{pa} + E_{pc}$ )/2, where  $E_{pa}$  and  $E_{pc}$  are anodic and cathodic peak potentials respectively,  $\Delta E_{p}$ = ( $E_{pa} - E_{pc}$ ) (in mV). <sup>c</sup>Quasireversible.

also EPR active and showed a broad ligand-based spectrum with  $g_{av} = 1.973$  ( $g_1 = 2.009$ ,  $g_2 = 1.972$ ,  $g_3 = 1.938$ ) (Figure 3(b) and Table 4). Interestingly, the similar complex [3]<sup>-</sup> is EPR inactive. Here, we anticipate that in the complex [2]<sup>+</sup>, the second reduction occurs at the ancillary ligand (pcp), resulting in an S = 1 ground state. However, our repeated attempts to identify the "spin forbidden" signal<sup>11,12</sup> (from S = 1 ground state of the complex [2]<sup>-</sup>) were unsuccessful. The second reduction in the complex [3]<sup>+</sup>, on the other hand, occurs at the same ligand L, generating a spin coupled system, 52-54 [3]<sup>-</sup>. Our attempts to study the EPR spectra of further reduced species of the complexs [2]<sup>+</sup> and [3]<sup>+</sup> were unsuccessful due to their hyper reactivity.

The complex 4 exhibits a cathodic response at -0.49 V and an anodic response at 1.16 V. To ascertain the locus of reduction, we performed exhaustive electrolysis at -0.6 V of the complex 4. The reduced complex [4]<sup>-</sup> exhibits an EPR spectrum at  $g_{ay} = 1.970$  ( $g_1 = 2.023$ ,  $g_2 = 1.916$ ) with significant g anisotropic<sup>35,56</sup>

#### Table 4. EPR Data Table<sup>a</sup>

complex	2	[2]-	3	<sup>b</sup> [4] <sup>-</sup>	<sup>c</sup> 5	<sup>b</sup> [5] <sup>2-</sup>
$g_1$	2.003	2.009	2.015	2.023	2.002	
$g_2$	1.974	1.972	1.957	1.916	1.987	
$g_3$	1.945	1.938	1.929		1.973	
$\langle g \rangle^d$	1.974	1.973	1.967	1.969 <sup>e</sup>	1.987	1.992 <sup>g</sup>
$\Delta g^{f}$	0.058	0.071	0.085	0.107	0.029	

<sup>*a*</sup>Unless noted otherwise, EPR data were obtained for CH<sub>3</sub>CN-toluene glass (containing [Bu<sub>4</sub>N]ClO<sub>4</sub> as supporting electrolyte), measurements at 77 K. <sup>*b*</sup>EPR data were obtained for CH<sub>2</sub>Cl<sub>2</sub>, measurements at 77 K (containing [Bu<sub>4</sub>N]ClO<sub>4</sub> as supporting electrolyte). <sup>*c*</sup>EPR data were obtained for CH<sub>2</sub>Cl<sub>2</sub>, measurements at 77 K. <sup>*d*</sup>Unless noted otherwise,  $\langle g \rangle = [1/3(g_1^2 + g_2^2 + g_3^2)]^{1/2}$ . <sup>*c*</sup> $\langle g \rangle = [1/2(g_1^2 + g_2^2)]^{1/2}$ . <sup>*f*</sup> $\Delta g = g_1 - g_3$ . <sup>*g*</sup>No *g* anisotropy observed.

value,  $\Delta g = 0.11$  (Figure 3(d) and Table 4). Such a high value of  $\Delta g$  is an indication of high metal-azoaromatic L interactions. The magnitude of  $\Delta g$  among the series of the complexes  $[\mathbf{2}]^+$  $[3]^+$ , and 4 are as follows: complex 4 ( $\Delta g = 0.11$ ) > complex  $[3]^+$  $(\Delta g = 0.084)$  > complex  $[2]^+(\Delta g = 0.058)$ . In complex 4,  $Ru(d\pi)$ - $L_{azo}(p\pi)$  back-donation is maximum, and the effect is reflected on the reduction potential of the coordinated ligand L  $(E_{1/2}^{red} = 0.49 \text{ V})$  as discussed above. An opposite effect was observed in the cases of complex  $[2]^+$  and  $[3]^+$ . The ligands pcp and bpy are both  $\pi$ -acceptors, and so the extent of  $\pi$ -backdonation to coordinated L in the two complexes are lower. In all these three complexes, the first reduction occurs at the coordinated L, which varies systematically as follows: 0.08 V  $([2]^+) < -0.18 \text{ V} ([3]^+) < -0.49 \text{ V} (4)$ . While making this comparison of redox potential, we must note here that the overall charges of all complexes, discussed herein, are not identical. The compound 4 is a molecular compound, while the other two ( $[2]^+$  and  $[3]^+$ ) are monocationic. However, they are all ruthenium(II) complexes, which are isostructural and



**Figure 3.** EPR spectra of the electrogenerated species (a) 2, (b)  $[2]^-$ , and (c) 3 at 77 K in acetonitrile-toluene glass; (d)  $[4]^-$  and (f)  $[5]^{2-}$  in dichloromethane at 77 K; and isolated complex (e) 5 at 77 K in dichloromethane.

isoelectronic compounds, and hence, the comparison appears reasonable.<sup>57</sup> The reduction potential of the complex containing an ancillary ligand with maximum  $\pi$ -acceptor ability occurs at lower potential which monotonically shifted cathodic with increasing donor ability of ancillary ligand.

An opposite trend, however, was observed in the oxidation potential of the above four complexes. In all of these complexes, oxidation is primarily metal centered ( $Ru^{II}/Ru^{III}$ ), which is supported by DFT calculations (see Supporting Information, Theoretical Calculations), and the trend is as anticipated: 1.69 V ( $[2]^+$ ) > 1.42 V ( $[3]^+$ ) > 1.16 V (4). Thus, both L and the ancillary ligand pcp being strong  $\pi$ -acceptor ligand in the complex [2]<sup>+</sup>, the Ru–L delocalization is least; the main ligand L is most redox noninnocent, and the metal is most electron deficient among the series of the complexes [2]<sup>+</sup>, [3]<sup>+</sup>, and 4.

Electrochemical behavior of the complex 5 is somewhat different than that of the previously described complexes viz.,  $[2]^+$ ,  $[3]^+$ , and 4. It is isolated as a stable free radical complex, [RuL(DTBsq<sup>•-</sup>)Cl], which is paramagnetic and displayed a typical rhombic EPR spectrum (Figure 3(e) and Table 4) for a Ru(II) coordinated semiquinone radical<sup>58</sup> with  $g_{av} = 1.987$  ( $g_1 =$ 2.002,  $g_2 = 1.987$ ,  $g_3 = 1.973$ ) and with  $\Delta g = 0.029$ . It exhibits three reductive waves at -0.13, -0.50, and -0.87 V and two oxidative waves appeared at 0.73 and 1.78 V. Exhaustive electrolysis at -0.35 V leads to a diamagnetic compound  $[5]^$ due to the reduction of DTBsq<sup>•–</sup> ligand. This corroborates well by Density Functional Theory (DFT) calculations (see below). The two electron reduced complex ( $[5]^{2-}$ ) is EPR active and showed a typical azo-anion ligand-based single line EPR spectrum<sup>26</sup> at g = 1.992, indicating the reduction of coordinated azo-aromatic L (see Figure 3(f) and Table 4). The one electron oxidized complex  $[5]^+$  is EPR inactive, and DFT calculations suggest that the first oxidation occurs at DTBsq<sup>•-</sup> ligand.

**Density Functional Theory (DFT) Studies.** To have an insight into the electronic description of the isolated complexes, we performed full geometry optimization using DFT at the B3LYP level.<sup>59–62</sup> The ground state of the complexes  $[2]^+$ ,  $[3]^+$ , and 4 are diamagnetic (S = 0), as evidenced by the room temperature magnetic moment, and thus, optimizations were performed for the singlet state only. The computed bond distances were collected in Table 2 and are found to be in good agreement with those obtained in the X-ray crystallographic analysis.

DFT calculations for these ruthenium complexes, considering multiple valence states were performed to discount their alternative electronic structures. Owing to the presence of two redox active ligands, the electronic structure landscapes for these complexes are rather more complex. In the cases of complexes  $[2]^+$  and  $[3]^+$ , the diamagnetism of the isolated systems is, in principle, consistent with a range of formulations: (i)  $[Ru^{II}(L) (Q)Cl]^+$  (Q = pcp or bpy), (ii)  $[Ru^{III}(L^{\bullet-})(Q)Cl]^+$ , and (iii)  $[Ru^{III}(L)(Q^{\bullet-})Cl]^+$ . DFT analyses indicate that the  $[Ru^{II}(L)-$ (Q)Cl<sup>+</sup> electronic description is preferential over its other two spin-coupled redox congeners. The optimized structures of both the complexes are also in good agreement with the electronic configuration. To have an insight into the center of first reduction, we scrutinized the LUMO of the optimized structures. In both the complexes, the LUMO was primarily localized on the ligand L (complex  $[2]^+$  (77%) and complex  $[3]^+$ (80%)). This further supports the experimentally observed ligand-based EPR spectra of the coulometrically generated one electron reduced complexes, 2 and 3. Additionally, these redox partners were also optimized where major spin population was

observed on the L backbone (see Figures 4a,b). Notably, electrogenerated complex  $[2]^-$  is also EPR active, which is in



Figure 4. Spin density plots of (a) 2, (b) 3, (c) [4]<sup>-</sup>, and (d) 5.

agreement with the most stable electronic configuration of  $[\tilde{R}u^{II}(L^{\bullet-})(pcp^{\bullet-})Cl]^{-}$  (S = 1) state<sup>26</sup> (see Supporting Information, Theoretical Calculations). Thus, the second electron transfer occurred at coordinated pcp ligand, generating an S = 1 state which is well-justified<sup>26</sup> by the orthogonal arrangement of two ligands. On the other hand, electrogenerated complex [3]<sup>-</sup> is EPR inactive. The DFT analysis indicates a spin pairing situation over the coordinated L. It is well-documented that the bpy is a poorer<sup>12,63</sup> acceptor than pcp, and thus, the second reduction occurred on coordinated ligand L<sup>•–</sup> rather than bpy, resulting in the formation of a spin-coupled S = 0 state.<sup>64</sup> On the other hand, the highest occupied molecular orbital (HOMO) of the isolated complexes  $[2]^+$  and  $[3]^+$  are primarily localized on the metal center. Thus, the oxidative waves of complexes  $[2]^+$  and  $[3]^+$  are assigned to Ru(II)/ Ru(III) redox couple. The presence of two strong electron withdrawing ligands (L and pcp) in  $[2]^+$  imparts electron deficiency on the central ruthenium center. As a result, the oxidative redox couple in  $[2]^+$  appears at a high redox potential, 1.70 V. The corresponding couple for  $[3]^+$  appears at a lower potential of 1.43 V. Complex 4 is diamagnetic and is consistent with the two electronic structure descriptions: (i) [Ru<sup>II</sup>(L)-(acac)Cl] and (ii)  $[Ru^{III}(L^{\bullet-})(acac)Cl\bar{]}.$  DFT calculations indicate that [Ru<sup>II</sup>(L)(acac)Cl] is energetically favored over its spin-coupled redox congener. The HOMO of the optimized structure is located on the metal center while LUMO is predominated by L contribution. Thus, the oxidation is associated with the  $Ru^{II} \rightarrow Ru^{III}$ , while the reduction occurs at the azo-aromatic L. This is in line with the EPR spectral feature of the electrogenerated complex  $[4]^-$ . Examination of the spin density plot of the complex  $[\hat{4}]^-$  also shows 84% spin is localized on the L backbone (Figure 4c).

On the contrary to above, complex **5** is an example of stable uncoupled radical<sup>65</sup> with  $S = {}^{1}/{}_{2}$ . This feature of the complex is consistent with the following two formulations: (i) [Ru<sup>II</sup>(L)-(DTBsq<sup>•-</sup>)Cl] and (ii) [Ru<sup>II</sup>(L<sup>•-</sup>)(DTBq)Cl] (DTBq = one electron oxidation state of DTBsq<sup>•-</sup>). DFT calculations favor the former description over the latter, which is also in line<sup>56</sup> with the structural parameters and the characteristic room temperature EPR spectrum of Ru–semiquinone radical systems. The spin density plot of the complex **5** is also an indicative of semiquinone radical state and is shown in Figure 4d. To



**Figure 5.** UV-vis-NIR spectra of the complexes: in acetonitrile, (a)  $[2]^n$  (n = +1, 0, -1) and (b)  $[3]^n$  (n = +1, 0, -1); in dichloromethane, (c) 4 and (d)  $[5]^n$  (n = +1, 0, -1, -2).

ascertain the locus of first oxidation/reduction, we examined the SOMO and LUMO of the complex **5**. Both the orbitals are predominantly localized on the semiquinone ligand, and thus, it is inferred that the first oxidation and reduction both occur at the semiquinone ligand. Notably, the single electron reduced state was also computed, and the  $[Ru^{II}(L)(DTBCat)Cl]^-$  is found to be energetically favorable over  $[Ru^{II}(L^{\bullet-})(DTBsq^{\bullet-})Cl]^-$  electronic description. The second electron reduction univocally occurs at the L and is consistent with the observed single line EPR spectrum. DFT calculations for one electron oxidized complex  $[\mathbf{5}]^+$  are consistent with  $[Ru^{II}L(DTBq)Cl]^+$  formulation.

**Electronic Spectra.** UV-vis-NIR spectra of the compounds  $[2]^+$  and  $[3]^+$  were recorded in acetonitrile, while those of compounds 4 and 5 were recorded in dichloromethane solvent. These data are summarized in Table S1, and their spectra are depicted in Figure 5. All of the compounds show multiple absorptions in the range of 200-800 nm. Time-dependent density functional theory (TDDFT) analyses were done to assign the major spectral transitions.

Beginning with  $[2]^n$  (n = 1, 0, -1), the isolated complex  $([2]^+)$  exhibits an absorption at 560 nm, which is ascribed as a metal-to-ligand charge transfer (MLCT) transition. Upon reduction, a broad transition appears at 1860 nm in 2, which is associated with ligand-to-ligand charge transfer (LLCT) transition from partially reduced ligand L to pcp. The doubly

reduced complex ([2]<sup>-</sup>) displays a transition at 565 nm, which is ascribed as  $d\pi(Ru) \rightarrow \pi^*(L/pcp)$  transition.

The complex  $[3]^+$ , on the other hand, shows an broad transition at 395 nm. TDDFT analysis indicate that the absorption is associated with the excitation from orbitals primarily localized on the phenyl ring of the L to the azobackbone. Upon reduction, the complex 3 shows a broad weak absorption at a NIR region (~2000 nm), attributed to a  $L(\pi) \rightarrow L(\pi^*)$  transition, and MLCT transition appears at 500 nm. Upon subsequent reduction to  $[3]^-$ , the  $L(\pi) \rightarrow L(\pi^*)$  band diminishes, and the MLCT transition is red-shifted to 530 nm.

The isolated neutral complex 4 displays a strong LLCT  $[acac(\pi) \rightarrow L(\pi^*)]$  transition at 430 nm and a relatively broad MLCT  $[Ru(d\pi) \rightarrow L(\pi^*)]$  transition at 628 nm. The 1e<sup>-</sup> reduced species  $[4]^-$  is hyper reactive for recording its absorption spectrum.

Complex **5** contains a semiquinone radical along with a  $\pi$ -acceptor L. It exhibits a LLCT transition<sup>58</sup> ( $\pi$ (DTBsq<sup>•-</sup>)  $\rightarrow \pi^*$ (L)) at 635 nm. Upon reduction of the semiquinone ligand, two broad transitions appeared at 660 and 1100 nm, which are attributed as MLCT [Ru( $d\pi$ )  $\rightarrow$  L( $\pi^*$ )] and DTBCat  $\rightarrow$  L charge transfer, respectively. Upon two electron reduction, the electrogenerated complex [S]<sup>2-</sup> showed two characteristic transitions at 640 and 1115 nm due to LMCT [ $\pi$ (cat/L)  $\rightarrow$  Ru( $d\pi$ )] and MLCT [Ru( $d\pi$ )  $\rightarrow$  L( $\pi^*$ )] transitions,

respectively. On the other hand, the one electron oxidized complex  $[5]^+$  exhibits a  $L(\pi) \rightarrow L(\pi^*)$  transition at 430 nm.

**Chemical Catalysis.** To understand the chemical tuning of RuL moiety by different ancillary ligands, we explored a comparative study on aerobic alcohol oxidation reactions<sup>66–68</sup> by using of four heterolaptic complexes *viz.* [2]PF<sub>6</sub>, [3]PF<sub>6</sub>, 4, and 5 as catalysts. We hypothesized that increasing the  $\pi$ -acceptor ability of the ancillary ligand would increase the electrophilic character of RuL moiety and thus promote enhancement of substrate activation for catalytic alcohol oxidation reaction.

In literature, (re)development of homogeneous catalyst is commonly made either by changing the metal ion or by introducing large modification on the primary ligand framework. However, the effect of using different ancillary ligands in tuning catalytic activity has been addressed only in recent years.<sup>37</sup> Moreover, we wish to note here that precedents for homogeneous Ru catalyzed aerobic alcohol oxidation reactions are only few<sup>69–77</sup> and mostly substrate specific.

In our study, we chose benzyl alcohol as a model substrate, and the catalytic reactions using the four aforementioned catalysts were performed under identical conditions. In a typical experiment, a mixture of 1 mmol of benzyl alcohol, 2 mol % (0.02 mmol) of catalyst, 4 mol % (0.04 mmol) of <sup>1</sup>BuOK, and 10 mL of toluene was heated at 343 K for 6 h under positive pressure of oxygen. The corresponding benzaldehyde was purified by preparative thin layer chromatographic technique using 1:10 dichloromethane and hexane mixture as eluent. The isolated yields from each of the above reactions are collected in Table 5.

 Table 5. Effect of Ancillary Coligand on the Catalytic

 Dehydrogenation of Alcohols



The yields of the above reactions follow the following order:  $[2]^+ \gg [3]^+ \gg 4$  and 5. Subsequently, the scope of catalytic activities of the most efficient catalyst in the series  $([2]PF_6)$  was further evaluated by using a variety of primary and secondary alcohols, including aromatic, polyaromatic, and cyclic aliphatic alcohols. A series of halogenated benzyl alcohols (Table 6, entries b-d) afforded the respective aldehydes in high yields (>70%). This was also found to be equally effective even for alcohols for strong electron withdrawing CF<sub>3</sub> and NO<sub>2</sub> substituents (Table 6, entries f and g). All of the above experiments were performed using an identical protocol as noted above, and the yields of the products are collected in Table 6. Optimization table of catalyst loading, nature of bases, solvent, and temperature are given in Tables S2 and S3. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectral data of the isolated oxidized products (aldehydes/ketones) noted in Table 6 are submitted in the Supporting Information (Figures S12–S30).

Table 6. [2] PF<sub>6</sub> Catalyzed Aerobic Oxidation of Alcohols into Ketones/Aldehydes<sup>a</sup>



<sup>*a*</sup>Reaction conditions: complex [2]PF<sub>6</sub> = 0.02 mmol, substrate = 1 mmol, <sup>*t*</sup>BuOK = 0.04 mmol, 10 mL of dry toluene (solvent). Reactions were studied under positive  $O_2$  pressure for 6 h at 343 K. Detailed reaction procedure is collected in the Experimental Section. All the yields mentioned herein are isolated yields.

Mechanistic Studies. To have an insight into the mechanism of the catalytic activity of the complexes, we performed a series of experiments including radical clock reaction, isotope labeling experiments. DFT analyses were also used to discount alternate pathways. Following the literature reports  $^{78-80}$  on similar catalytic reactions, we propose that the catalytic cycle begins with the substitution of Ru–Cl by alkoxide ion (in alkaline condition), to generate a hexacoordinated Rualkoxide complex. The formation of metal alkoxide bond was monitored<sup>81</sup> by IR spectroscopic analysis. An equimolar mixture of the complex  $[2]PF_6$  and <sup>t</sup>BuOK was heated to 343 K in toluene. The initial brown color of the solution became violet in 1 h. A Ru–O stretching frequency at 755 cm<sup>-1</sup> was observed indicated the formation of the Ru-alkoxide intermediate (Figures S31 and S32). Its ESI-MS spectrum also signifies the formulation, an intense molecular ion peak at m/z 679 amu appeared due to formation of the base adduct of  $[2]^+$ , i.e.  $[RuL(pcp)(^{t}BuO)]^{+}$  (Figure S33). In the subsequent step, we analyzed the most crucial step of migration of  $\beta$ -H of coordinated alkoxide. We considered two possibilities: (i) hydrogen atom transfer and (ii) hydride ion transfer. Here, strategically, we examined oxidation of radical clock substrates<sup>8</sup> viz. cyclopropanemethanol and cyclopropyl phenylmethanol. The reactions yielded cyclopropanecarboxaldehyde and cyclopropyl phenylketone, respectively, as exclusive products (Figures S29 and S34). Absence of any ring opening product





implies that hydride transfer pathway is operative<sup>69</sup> for the above oxidation reaction. Notably, after the  $\beta$ -H elimination, the C–H departing from the alkoxide is optimally lined up with the empty orbital on the ruthenium center and subsequently generated Ru–H intermediate. This was further supported by the fact that the radical scavenger like (2,2,6,6-tetramethylpiperidin-1-yl)-oxyl (TEMPO) did not affect the yield of isolated product.

Next, we attempted to trap the metal hydride intermediate using NMR spectroscopy which, however, failed possibly due to its transient existence (see below). To understand the reaction steps we then plan to follow a stoichiometric reaction between equimolar amount of catalyst  $[2]PF_6$  and benzyl alcohol in an anaerobic condition (in the presence of 2 equiv. <sup>t</sup>BuOK). The reaction mixture after 3 h was subjected to IR spectral analysis. Interestingly, the IR spectrum showed two characteristic N-H vibrations modes at 2924 and 2853 cm<sup>-1</sup> (Figure S35). To have a closer view, we then performed an identical reaction using d<sup>12</sup> cyclohexanol as a substrate. Notably, in the later experiment, the two N—D modes were shifted to 2203 and 2105  $cm^{-1}$  (Figure \$36). From the above isotope labeling experiments, we propose that the catalytic reaction involves<sup>33</sup> the formation of mono hydrazo intermediate. Here again, we considered the two plausible acceptors for migratory hydride ion: (i) the  $\beta$ -hydride transfer to the metal center generating a transient Ru-H intermediate which follows another migration from Ru-H to an azo function of coordinated L (pathway I) and (ii) direct H<sup>-</sup> migration to the azo function (pathway II), as shown in Scheme 1.

To discard one of the above two pathways, we considered DFT calculated energetics for this step. It was observed that the migration of hydride ion from ruthenium alkoxide intermediate (I) to ruthenium (II) center necessitates an activation energy of 26.5 kcal/mol and it goes through transition state TS1 (Figure 6). The other possibility of direct H-migration to the azo function is found to be comparatively more energetic (28.9 kcal/mol via TS1'). Thus, pathway I is energetically preferred one. We must admit here that the difference of activation energy between the two above possibilities is too low (2.4 kcal/mol) to identify the pathway conclusively.

Similar metal–ligand cooperativity for H<sup>-</sup> migration was previously reported<sup>83,84</sup> separately by Grützmacher and Hall group in a Ru–diimine complex. This process was termed as "hydrogen walking" from Ru–H to a redox acceptor function.



**Figure 6.** Energy profile diagrams of the two pathways mentioned here (I and II).

The azo functional group of coordinated L in the catalyst [2]PF<sub>6</sub> has low lying  $\pi^*$  orbitals with acceptor ability superior to that of an imine function. Thus, it is most likely that similar consecutive hydrogen migration occurs in our system. DFT analysis indicates that in the walking process, hydrogen migration from Ru–H to adjacent azo-nitrogen occurs over a free energy barrier of 18.5 kcal/mol via transition state **TS2** (Figure S37). Further electronic analysis also shows that the hydrogen becomes protonic in **TS2** as confirmed by its NBO charge of 0.31. In either way, the reaction leads to the formation of intermediate **V** (from **III** or **II**'), where the N–H bond was formed. Computed Gibbs free energy diagram of the proposed catalytic cycle is shown in Figure S41. The optimized structures of all intermediates and transition states involved are shown in Figures S38–S40.

Finally, catalyst regeneration in the cycle occurs by aerobic oxidation<sup>33</sup> of hydrazo intermediate with the formation of  $H_2O_2$ . Formation of  $H_2O_2$  in the catalytic reaction was identified chemically<sup>85–87</sup> (for details, see the Experimental Section and Figure S41). Considering the above findings, we propose that the following catalytic cycle (Scheme 2) is operative for alcohol dehydrogenation reaction.

**Effect of Ancillary Ligands on the Reaction Coordinates.** In the above catalytic cycle, the abstraction of hydride from alcohol by the catalyst is thus found to be the ratedetermining step. From our foregoing discussion, it is evident Scheme 2. Proposed Mechanism for the Alcohol Oxidation Reaction with Catalyst  $[2]PF_6$ 



that rate of hydride abstraction from coordinated alkoxide is directly related to the degree of electrophilicity of the Ru(II) center in the catalyst. Herein, we considered the Ru–L moiety which actually participated in the chemical catalysis by abstraction of hydride ion from the coordinated alkoxide. All of the isolated complexes are isostructural and most importantly the central ruthenium ion is in +2 oxidation state, whereas the azo-aromatic L retains its neutral oxidation state (+0). Although the complexes [2]<sup>+</sup> and [3]<sup>+</sup> are cationic, whereas complex 4 and 5 are neutral in nature and might influence the overall electrophilicity of the ruthenium center, a comparison between a catalyst bearing a neutral coligand vs anionic coligand is worth noting, which might be helpful in design and selection of coordinated ligand for an alcohol oxidation catalyst. To have a better understanding of the ligand effect on the reaction, we also compared the energetics of H<sup>-</sup> migration to ruthenium for complex [2]PF<sub>6</sub> (containing strong  $\pi$ -accepting ligand pcp) with that of the complex 4 (containing strong  $\sigma$ -donating ligand acac<sup>-</sup>). As shown in Figure 7, the energy barrier for the hydride ion migration to Ru from the attached alkoxide in the complex [2]PF<sub>6</sub> is computed to be 6 kcal/mol lower compared to complex 4 (TS1 vs TS1<sub>acac</sub>). Therefore, coligand pcp can significantly boost the formation of Ru–H intermediate by stabilizing the associated transition state TS1.

## CONCLUSION

Herein, we described an investigation on isostructural ruthenium complexes where the ancillary ligands do exert significant electronic effects on the redox noninnocence of Ru<sup>II</sup> coordinated bis-azoaromatic ligand moiety. The effect of electron-withdrawing and -donating ability of four different ancillary ligands systematically tune the overall electronic and redox properties of the isolated complexes. Our results on catalytic oxidation of alcohols demonstrate that the properties of coordinated L, engineered for a chemical reaction, can be substantially tuned by the incorporation of suitable ancillary ligand(s). Thus, the ligand pcp with strongest acceptor ability induced maximum electron deficiency in the complex,  $[2]PF_6$  by effectively engaging itself in the  $\pi$ -system of the principal L. There was a parallel effect on its redox behavior, accordingly, in CV, the cathodic reductive and anodic oxidative waves of the compound appeared at lowest and highest potentials, respectively. Completely opposite effects were observed in the case of strongly donating  $\pi$ -donor ligand, [DTBCat]<sup>2-</sup>, and the complex 5 displayed most poor catalytic activity in the series. The results described herein represent a less-explored area in the participation of redox active ligands in chemical catalysis, which appears to have a huge scope<sup>6,88</sup> in bioinspired catalytic reactions.

# EXPERIMENTAL SECTION

**Materials.** The metal precursor RuCl<sub>3</sub> was purchased from Arora Matthey Limited. All alcohols were purchased from Sigma-Aldrich. Other chemical and solvents were of reagent grade and used as received.



**Figure** 7. Gibbs free energy diagram of formation of Ru–H intermediate for the complexes [2]PF<sub>6</sub> and 4.

For spectrochemical studies, high-performance liquid chromatography (HPLC)-grade solvents were used. Tetrabutylammonium perchlorate was prepared and recrystallized as reported earlier.<sup>89</sup> Caution! Perchlorates have to be handled with care and appropriate safety precautions.

Physical Measurements. A PerkinElmer Lambda 950 spectrophotometer was used to record UV-vis spectra. Infrared spectra were obtained using a PerkinElmer 783 spectrophotometer. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance 300, 400, or 500 MHz spectrometer, and SiMe4 was used as the internal standard. A PerkinElmer 240C elemental analyzer was used to collect microanalytical data (C, H, N). ESI mass spectra were recorded on a micromass Q-TOF mass spectrometer (serial no. YA 263). All electrochemical measurements were performed using a PC-controlled PAR model 273A electrochemistry system. Cyclic voltammetric experiments were performed under the nitrogen atmosphere using an Ag/AgCl reference electrode with a Pt disk working electrode and a Pt wire auxiliary electrode either in dichloromethane or in acetonitrile solution containing supporting electrolyte, 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>. A Pt wire gauge working electrode was used for exhaustive electrolyses.  $E_{1/2}$  for the ferrocenium-ferrocene couple under our experimental conditions was 0.40 V. X-band EPR spectra were recorded with a JEOL JES-FA200 spectrometer.

**Synthesis.** The ligand 2,6-bis(phenylazo)pyridine was prepared<sup>26</sup> according to a procedure reported in the literature.

**Preparation of Complexes.** [*Ru*(*L*)(*CH*<sub>3</sub>*CN*)*CI*<sub>2</sub>]; **1**. In a roundbottom flask equipped with a condenser, a mixture of 165 mg of L (0.57 mmol) and 150 mg RuCI<sub>3</sub>·xH<sub>2</sub>O (150 mg,0.57 mmol) in 20 mL of ethanol was refluxed for 3 h. During this time, the color of the solution slowly changed from red to green. The resulting green solution was then evaporated to dryness, and the excess ligand was washed with hexane. The green product was then extracted with acetonitrile. Yield: 213 mg (75%). ESI-MS: *m*/*z* 459.8470 (1 – (CH<sub>3</sub>CN) + H)<sup>+</sup>. IR (KBr, cm<sup>-1</sup>): 1448 cm<sup>-1</sup> ( $\nu$ (N==N)). Anal. Calcd for C<sub>19</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>6</sub>Ru: C, 45.61; H, 3.22; N, 16.80. Found: C, 45.78; H, 3.34; N, 16.71. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 8.59 (d, *J* = 8 Hz, 2H), 8.30 (d, *J* = 8 Hz, 4H), 8.08 (t, *J* = 8 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 2H<sub>2</sub>), 7.52 (t, *J* = 8 Hz, 4H), 2.70 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): 168.7(2C), 154.8(1C), 133.2(2C), 129.9 (2C), 129.2 (4C), 124.8 (4C), 120.9 (2C), 117.1 (1C), 4.8 (1C).

All the complexes reported below were prepared from the precursor complex [RuLCl<sub>2</sub>(CH<sub>3</sub>CN)], **1**.

 $[Ru(L)(pcp)Cl]PF_6$ ; [2](PF\_6). The precursor complex 1 (100 mg, 0.20 mmol) and pcp, 2-(4-chlorophenylazo)pyridine (50 mg, 0.23 mmol) were mixed in 20 mL acetonitrile and refluxed for 3 h. The resulting solution was concentrated to 5 mL followed by saturated aqueous solution of NH<sub>4</sub>PF<sub>6</sub> was added. The mixture was left in a refrigerator for 1 h; the resulting precipitate was filtered and washed thoroughly with chilled water to remove excess NH<sub>4</sub>PF<sub>6</sub> and dried in vacuum. The product was purified on a preparative silica gel TLC plate using acetonitrile-dichloromethane (1:10) as eluent. A brown band at the middle part of TLC plate was collected. The compound, thus obtained, was recrystallized by slow diffusion of its dichloromethane solution into hexane. Its yield and characterization data are as follows. Yield: 113 mg (72%). ESI-MS: m/z 640.8040 ([2]PF<sub>6</sub> – PF<sub>6</sub>)<sup>+</sup>. IR (KBr, cm<sup>-1</sup>): 1456  $cm^{-1}(\nu(N=N) \text{ of } L)$ , 1406  $cm^{-1}(\nu(N=N) \text{ of pcp})$ . Anal. Calcd for C<sub>28</sub>H<sub>21</sub>Cl<sub>2</sub>F<sub>6</sub>N<sub>8</sub>PRu: C, 42.76; H, 2.69; N,14.25. Found: C, 42.88; H, 2.64; N, 14.13. <sup>1</sup>H NMR(500 MHz, CD<sub>3</sub>CN): 9.87 (d, J = 5 Hz, 1H), 8.91 (d, J = 8 Hz, 2H), 8.79 (d, J = 8 Hz, 1H), 8.54 (t, J = 8 Hz, 1H), 8.20 (t, J = 8 Hz, 1H), 7.66 (t, J = 8 Hz, 1H), 7.61 (t, J = 7 Hz, 1H), 7.54 (t, J)= 7 Hz, 2H), 7.28(t, J = 8 Hz, 3H), 7.22 (t, J = 7 Hz, 2H), 7.11 (d, J = 8 Hz, 4H), 6.38 (d, J = 7 Hz, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR(125 MHz, CD<sub>3</sub>CN): 165.0 (2C), 153.2 (1C), 151.7 (1C), 142.1 (1C), 139.1 (2C), 135.1 (2C), 130.8 (2C), 130.7 (4C), 130.3 (1C), 130.0 (2C), 127.8 (2C), 125.5 (1C), 125.1 (1C), 124.4 (4C), 123.9 (1C), 122.2 (1C).

[*Ru*(*L*)(*bpy*)*Cl*]*PF*<sub>6</sub>; [*3*]*PF*<sub>6</sub>. This was prepared similarly to [*Ru*(*L*)-(pcp)*Cl*]*PF*<sub>6</sub> using appropriate quantity of bpy in place of pcp. Its yield and characterization data are as follows. Yield: 119 mg (82%). ESI-MS: m/z 579.8936 ([3]PF<sub>6</sub> – PF<sub>6</sub>)<sup>+</sup>. IR (KBr, cm<sup>-1</sup>): 1450 cm<sup>-1</sup> ( $\nu$ (N=N)). Anal. Calcd for C<sub>27</sub>H<sub>21</sub>ClF<sub>6</sub>N<sub>7</sub>PRu: C, 44.73; H, 2.92; N,13.52. Found: C, 44.84; H, 2.72; N, 13.33. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):

10.11 (d, J = 5 Hz, 1H), 9.01 (d, J = 8 Hz, 2H), 8.55 (t, J = 8 Hz, 1H), 8.46 (d, J = 8 Hz, 1H), 8.36 (t, J = 8 Hz, 1H), 8.20 (d, J = 8 Hz, 1H), 8.06 (t, J = 7 Hz, 1H), 7.85 (t, J = 7 Hz, 1H), 7.47–7.44 (m, 2H), 7.25–7.20 (m, 8H), 7.11 (t, J = 7 Hz, 1H), 6.70 (d, J = 6 Hz, 1H);  $^{13}C{^{1}H}$ NMR(125 MHz, CD<sub>3</sub>CN): 167.6 (2C), 157.2 (1C), 155.0 (1C), 154.2 (1C), 153.5 (1C), 152.9 (1C), 140.6 (1C), 140.2 (1C), 137.3 (2C), 133.8 (2C), 130.3 (4C), 129.3 (1C), 128.4 (1C), 125.2 (2C), 125.0 (2C), 124.1 (4C).

[Ru(L)(acac)Cl]; 4. The precursor complex 1 (100 mg, 0.20 mmol) and acetylacetone (20 mg, 0.20 mmol) were taken in 20 mL methanol; 2 drops NEt<sub>3</sub> were added into it, and the mixture was heated to reflux for 3 h. Then, the mixture was cooled at room temperature, and the product was purified on a preparative silica gel TLC plate using dichloromethane as eluent. A green band at the upper part of TLC plate was collected. The compound, thus obtained, was recrystallized by slow diffusion of its dichloromethane solution into hexane. Its yield and characterization data are as follows. Yield: 70 mg (67%). ESI-MS: m/z488.3649 (4 - Cl)<sup>+</sup>. IR (KBr, cm<sup>-1</sup>): 1427 cm<sup>-1</sup> ( $\nu$ (N=N)). Anal. Calcd for C22H20ClN5O2Ru: C, 50.53; H, 3.85; N,13.39. Found: C, 50.82; H, 3.98; N, 13.30.<sup>1</sup>H NMR(500 MHz, CDCl<sub>3</sub>): 8.55 (d, J = 8 Hz, 2H), 8.45 (d, J = 8 Hz, 4H), 8.08 (t, J = 8 Hz, 1H), 7.58 (t, J = 7 Hz, 2H), 7.45 (t, J = 8 Hz, 4H), 5.08 (s, 1H), 2.53 (s, 3H), 1.26 (s, 3H);  ${}^{13}C{}^{1}H{}$ NMR(125 MHz, CDCl<sub>3</sub>): 190.4 (1C), 187.2 (1C), 169.3 (2C), 154.0 (1C), 131.8 (2C), 130.8 (2C), 129.3 (4C), 124.8 (4C), 120.2 (2C), 99.8 (1C), 28.8 (1C), 26.0 (1C).

[*Ru*(*L*)(*DTBsq*<sup>•-</sup>)*Cl*]; **5**. This was prepared similarly to [Ru(L)(acac)-Cl] using an appropriate quantity of H<sub>2</sub>DTBcat in place of Hacac. Its yield and characterization data are as follows. Yield: 93 mg (72%). ESI-MS: 643.9383 (**5**)<sup>+</sup>, 423.8699 (**5** – DTBsq<sup>•-</sup>)<sup>+</sup>. IR (KBr, cm<sup>-1</sup>): 1436 cm<sup>-1</sup> ( $\nu$ (N=N)). Anal. Calcd for C<sub>31</sub>H<sub>33</sub>ClN<sub>5</sub>O<sub>2</sub>Ru: C, 57.80; H, 5.16; N,10.87. Found: C, 57.45; H, 5.32; N, 11.05. This compound is paramagnetic in nature,  $\mu_{eff}$  = 1.68  $\mu_{B}$  (calculated by Evans method),  $g_{av}$ = 1.987.

General Procedure for Catalysis Using Catalyst [2]PF<sub>6</sub>. The catalytic reactions were performed following a general procedure. In a round-bottom flask, a mixture of 1 mmol of substrate in 10 mL of dry toluene solvent, 0.02 mmol of catalyst (15.7 mg), and 0.04 mmol of K<sup>t</sup>BuO (4.5 mg) was heated at 343 K at a positive pressure of oxygen with continuous stirring for 6 h. The crude product, thus obtained, was purified on preparative silica gel GF-254 TLC plate using hexane as eluent.

**Isotope Labeling Experiments.** In an argon atmosphere Schlenk tube, 0.1 mmol of the complex [2]PF<sub>6</sub> (79 mg) was mixed with the equimolar quantity of d<sup>12</sup>-cyclohexanol (22 mg) and 0.2 mmol of K<sup>t</sup>BuO (22 mg) in dry and deoxygenated toluene solvent. The solution was stirred at 343 K for 3 h. The resulting light green colored solution was then evaporated under vacuum. The IR spectrum of the resultant compound showed characteristic stretching due to N–D bonds. IR (KBr disk, cm<sup>-1</sup>):  $\nu$ (N=N): 1446 cm<sup>-1</sup>, 1435 cm<sup>-1</sup>,  $\nu$ (N–N): 1178 cm<sup>-1</sup>,  $\nu$ (N–D): 2203 cm<sup>-1</sup>, 2105 cm<sup>-1</sup>.

A similar experiments performed with benzyl alcohol showed following characteristic bands. IR (KBr disk, cm<sup>-1</sup>):  $\nu$ (N=N): 1452 cm<sup>-1</sup>,1420 cm<sup>-1</sup>,  $\nu$ (N-N): 1195 cm<sup>-1</sup>,  $\nu$ (N-H): 2924 cm<sup>-1</sup>, 2853 cm<sup>-1</sup>.

Detection of Hydrogen Peroxide During the Catalytic Reactions.  $H_2O_{22}$ , produced in the catalytic reaction, was detected spectro-photometrically by following the gradual development of the characteristic band for  $I_3^-$  ( $\lambda_{max}$  (observed) = 360 nm) upon reaction with I<sup>-</sup>. In a round-bottom flask containing 1 mmol of benzyl alcohol in 10 mL of dry toluene was mixed with 0.02 mmol of catalyst and 0.04 mmol of 'BuOK, and the mixture was heated at 343 K for 3 h with continuous stirring. To the reaction mixture an equal volume of water was added subsequently and extracted with dichloromethane to remove the leftover reactants and products from the reaction mixture. The separated aqueous layer was then acidified with  $H_2SO_4$  to pH 2 to stop further oxidation. Then, 1 mL of a 10% KI solution and three drops of a 3% of ammonium molybdate solution were added. Hydrogen peroxide oxidizes I<sup>-</sup> to I<sub>22</sub> which reacts with excess I<sup>-</sup> to form I<sub>3</sub><sup>-</sup> according to the following chemical reactions: (i)  $H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_{22}$  (ii)

 $I_2(aq) + I^- \rightarrow I_3^-$ . Increasing acid concentration increases the reaction rate. Oxidation reaction is catalyzed by ammonium molybdate solution.

Computational Details. All calculations were performed using Gaussian 09<sup>90</sup> suite of programs. B3LYP/6-31+G(d)<sup>91</sup> (C, H, N, O, Cl), LANL2DZ (Ru)<sup>92</sup> level of theory were employed for all structural optimization and vibrational analysis. The broken-symmetry approach<sup>93–97</sup> was employed to establish the singlet state S = 0 of the compound(s). The calculations of the ground singlet states were performed using either spin-restricted or spin-unrestricted approaches (in G09W, combined with GUESS = MIX). Mulliken spin densities were used for analysis of the spin populations on ligand and metal centers.<sup>98</sup> Singlet excitation energies based on the solvent-phase (CH<sub>3</sub>CN/dichloromethane) optimized geometry of the complexes were computed using the TDDFT formalism  $^{99-101}$  in acetonitrile/ dichloromethane using the conductor-like polarizable continuum model (CPCM).<sup>102-105</sup> GaussSum<sup>106</sup> was used to calculate the percentage contribution of ligand and metal to the frontier orbital and the fractional contributions of various molecular orbitals in the optical spectral transition. Stationary points were characterized by the absence of any imaginary frequency. All the transition states were identified by a unique imaginary frequency that connects corresponding reactant and product. Intrinsic reaction coordinate (IRC) calculations were carried out for further confirmation of the transition state. For a better estimation of the electronic energy, single point calculations over the B3LYP/6-31+G(d)(C, H, N, O, Cl), LANL2DZ (Ru) optimized geometry were done by using  $M06^{107}/6-31++G(d,p)$  (C, H, N, O, Cl), LANL2TZ(f) (Ru)<sup>108</sup> method. Solvent effects were incorporated using an implicit PCM solvation model (SMD)<sup>109</sup> for toluene. All the reported energies given are in SMD/M06/6-31++G(d,p) (C, H, N, O, Cl), LANL2TZ(f) (Ru) // B3LYP/6-31+G(d)(C, H, N, O, Cl), LANL2DZ (Ru) level of theory.

**X-ray Crystallography.** Crystallographic data for compounds [2]PF<sub>6</sub>, [3]PF<sub>6</sub>, 4, and 5 are collected in Table 1. Suitable crystals for X-ray diffraction were obtained by slow diffusion of dichloromethane solution into hexane for rest compounds. All data were collected on a Bruker SMART APEX-II diffractometer, equipped with graphitemonochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å), and were corrected for Lorentz polarization effects.

[2]PF<sub>6</sub>: a total of 42137 reflections were collected, of which 6945 were unique ( $R_{int} = 0.194$ ), satisfying the  $I > 2\sigma(I)$  criterion, and were used in subsequent analysis. [3]PF<sub>6</sub>: a total of 22 350 reflections were collected, of which 8443 were unique ( $R_{int} = 0.020$ ), satisfying the  $I > 2\sigma(I)$  criterion, and were used in subsequent analysis. 4: a total of 23 416 reflections were collected, of which 4976 were unique ( $R_{int} = 0.032$ ), satisfying the  $I > 2\sigma(I)$  criterion and were used in subsequent analysis. 5: a total of 19 992 reflections were collected, of which 6512 were unique ( $R_{int} = 0.043$ ), satisfying the  $I > 2\sigma(I)$  criterion and were used in subsequent analysis.

The structures were solved by employing the SHELXS-97 program package<sup>110</sup> and were refined by full-matrix least-squares based on  $F^2$ (SHELXL-97).<sup>111</sup> All hydrogen atoms were added in calculated positions.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b01558.

Supporting tables and figures for experimental and computational data (PDF)

#### **Accession Codes**

CCDC 1846398–1846401 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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