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# Contrasting Reactivity of 2-Mesityl-1,8-Naphthyridine (Mes-NP) with Singly-Bonded [Rh<sup>II</sup>–Rh<sup>II</sup>] and [Ru<sup>I</sup>–Ru<sup>I</sup>] Compounds

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Reaction of *cis*-[Rh<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>(CH<sub>3</sub>CN)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> with two equivalents of 2-mesityl-1,8-naphthyridine (Mes-NP) affords *trans*-[Rh<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>(Mes-NP)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (1). X-ray structure reveals weak Rh–C(ipso) interaction, and a short Rh–Rh distance. The same ligand, in contrast, oxidatively cleaves the Ru–Ru bond in *cis*-[Ru<sub>2</sub>(CO)<sub>4</sub>(CH<sub>3</sub>CN)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> and results in *trans*-[Ru(Mes-NP)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (2). Both compounds adopt *trans* geometry to relieve the steric strain. Compound **2** exhibits moderate activity for the alcohol oxidation and aldehyde olefination reactions.

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# Introduction

The 1,8-naphthyridine (NP) ligand and its derivatives, has been demonstrated to be an excellent in the formation of a variety of dimetal systems; from non-bonded dicopper(II) to quadruply bonded dimolybdenum(II) compounds.<sup>[1]</sup> The flexibility and adaptability are the key attributes of NP ligands which make them suitable for use in bimetallic catalysis.<sup>[2–4]</sup> We explored NP-R (2-(2-R)-1,8-naphthyridine) ligands in our pursuit of dimetallic chemistry.<sup>[5–7]</sup> Covalent attachment of a donor group, for example, the thiazolyl at 2-position of the NP (tz-NP), provides a tridentate ligand that bridges the dimetal unit and simultaneously binds one axial site, as illustrated in Fig. 1a. By varying the donor appendages, we have examined the effects of axial ligands on metal-metal distances,<sup>[8]</sup> and investigated the role of axial donors in ligand isomerization processes.<sup>[9,10]</sup> Introduction of an aryl group at the axial site of the RuI-RuI single bond resulted in the cyclometalated complex via C–H bond activation (Fig. 1b).<sup>[11]</sup> A bulky *t*-butyl group, however, led to the oxidative cleavage of the Ru-Ru single bond.<sup>[12]</sup> To gain further insight on the ligand-assisted metal-metal bond scission, we sought to introduce mesityl group at sites trans to the metal-metal single bond. Accordingly, the synthesis of



Fig. 1. Dimetal unit bridged by tz-NP (1a) and C-H bond cleavage by dimetal unit (1b).

2-mesityl-1,8-naphthyridine (Mes-NP) is described (Fig. 2), and its subsequent reaction with  $[Rh^{II}-Rh^{II}]$  and  $[Ru^{I}-Ru^{I}]$  compounds have been studied. The present work reveals that the dirhodium(II) platform remains intact, whereas the Mes-NP causes the oxidative cleavage of the  $Ru^{I}-Ru^{I}$  single bond, affording a new  $Ru^{II}$  compound, the catalytic potential of which has been evaluated.

### **Results and Discussion**

Reaction of *cis*-[Rh<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>(CH<sub>3</sub>CN)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> with two equivalents of Mes-NP afforded *trans*-[Rh<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>(Mes-NP)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (1) in high yield. The <sup>1</sup>H NMR spectrum of complex 1 displays six resonances in the aromatic region, corresponding to five aromatic protons from the NP unit and one set of aromatic protons corresponding to the mesityl group, indicating the equivalence of two Mes-NP ligands on the NMR time scale. All methyl protons appear in the region  $\delta$  1.72–2.00 ppm. The *trans* geometry of compound 1 was confirmed by X-ray crystallography. The molecular structure of 1, depicted in Fig. 3, consists of two bidentate bridging Mes-NP ligands and two acetate groups. Only half of the molecule is observed in the asymmetric unit related to the other half by a centre of inversion located at the centre of the Rh–Rh vector. The Mes-NP ligands are arranged in a head-to-tail (HT) fashion placing mesityl



Fig. 2. Mes-NP ligand used in this work.



**Fig. 3.** *ORTEP* diagram (40% probability thermal ellipsoid) of the cationic unit *trans*-[Rh<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>(Mes-NP)<sub>2</sub>] in compound **1** with key atoms labeled. Hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and angles [°]: Rh(1)–Rh(1') 2.3866(5), Rh(1)–N(1) 2.001(3), Rh(1)–O(2) 2.016(2), Rh(1)–Mesityl (centroid) 3.410, N(1)–C(15) 1.361(4), N(1)–C(18) 1.334(4), C(1)–C(2) 1.496(5), O(2)–C(1) 1.276(4), C(18)–C(19) 1.491(5). Rh(1)–N(1)–C(15) 123.9(2), Rh(1)–N(1)–C(18) 115.6(2), N(2)–C(15)–N(1) 116.4(3), N(1)–C(18)–C(19) 113.6(3), C(17)–C(18)–C(19) 125.2(3), O(2)–Rh(1)–N(1) 88.31(10), N(1)–Rh1–Mesityl (centroid) 78.94. Rh(1')–Rh(1)–Mesityl (centroid) 167.85, Rh(1)–N(1)–C(15)–N(2) 4.8(4), Rh(1)–N(1)–C(18)–C(19) 6.9(3), Rh(1)–O(2)–C(1)–O(1) 1.7(3), Rh(1)–O(2)–C(1)–C(2) 179.1(3). Symmetry code 1/2 - x, 3/2 - y, 2 - z.



 $[Rh-Rh] = [Rh_2(CH_3COO)_3]$ 

Fig. 4. Agostic interaction of the *ortho*-hydrogen of the phenyl appendage with the [Rh–Rh] core.

groups at the axial sites.  $Rh_2(CH_3COO)_2$  complexes are in general *cis*, whereas compound **1** possesses a rare *trans* geometry which we attribute to the steric crowding of the mesityl groups.

We demonstrated earlier that the *ortho*-hydrogen of the phenyl appendage interacts with the [Rh–Rh] unit in an agostic fashion as shown in Fig. 4.<sup>[11]</sup> Such possibility does not exist in compound **1**. Analysis of the bond parameters reveals interaction of the *ipso*-carbon with the metal (Rh(1)–C(19); 2.833(3) Å). The C(2) rim carbons make longer distances with Rh (Rh(1)–C(20) 3.308(3); and Rh(1)–C(26) 3.332(3) Å). Marina and co-workers have described the axial interaction of a variety of aromatic  $\pi$ -donors to the dirhodium core.<sup>[13–15]</sup> It is shown that the metal interacts with the 'rim' carbons and 'hub' carbons, however, predominant metal- $\pi$  interactions were not observed. With regards to the disposition of the mesityl groups (see Fig. 3), the Rh–X separation of 3.410 Å and the Rh'–Rh–X angle 167.85°, where X is defined as the centroid of the mesityl group, is indicative of weak Rh- $\pi$  interaction. The Rh–Rh distance (2.387(1) Å) is the shortest<sup>[16]</sup> amongst similar paddle-wheel Rh<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub> complexes listed in Table 1.<sup>[17–30]</sup> It is

our assertion that weak axial interactions lead to shorter metalmetal distance in compound 1.<sup>[8,9]</sup>

The reaction of cis-[Ru<sub>2</sub>(CO)<sub>4</sub>(CH<sub>3</sub>CN)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> with Mes-NP in the presence of  $[n-Bu_4N][BF_4]$  at room temperature afforded trans-[Ru(Mes-NP)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (2) in high yield. The four carbonyls do not allow cis to trans isomerization, and as a result the Ru-Ru bond is cleaved. We offer a tentative mechanism which involves the homolytic cleavage of the Ru-Ru bond, followed by metal oxidation at the expense of the acetonitrile solvent, resulting in compound 2. Addition of [n-Bu<sub>4</sub>N][BF<sub>4</sub>] afforded cleaner and better yield which is required for the charge balance. A similar mechanism was proposed for the oxidative scission of the Ru-Ru bond, assisted by the *t*-butyl appendage on the NP unit.<sup>[12]</sup> The X-ray structure of 2 reveals that two Mes-NP ligands occupy four equatorial sites in trans fashion, while the axial sites are engaged by two acetonitrile molecules (Fig. 5). Only half of the molecule is observed in the asymmetric unit and is related to the other half by a centre of inversion at the metal centre. Interestingly, the Ru–N axial distances (2.018(3) Å) are marginally shorter than the Ru–N equatorial distances (2.100(3), 2.086(3) Å).

The *trans* orientation of the ligands in compound **2** deserves comment. The 2,2'-bipyridine analogue  $[Ru(bpy)_2(CH_3CN)_2]^{2+}$  is *cis*, although the *trans* isomer has also been characterized structurally, obtained from the *cis* isomer upon prolonged heating under reflux condition.<sup>[31–35]</sup> The *trans* geometry of **2** is again attributed to the steric constraints exerted by the Mes-NP ligands.

We have reported two cases in which Ru–Ru single bond is oxidatively cleaved. The *t*-butyl group at 2-position of NP causes homolytic cleavage of the metal-metal bond resulting in a Ru(II) complex. The anti- $[NC(Me)C(Me)N]^{2-}$  is identified as the product resulting from the two-electron reductive coupling of two acetonitrile molecules. Incorporation of

No.	Compound	$d_{ m Rh-Rh}$ [Å]	Ref.
1	cis-[Rh <sub>2</sub> (µ-O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> (py) <sub>6</sub> ](CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	2.653(1)	17, 18
2	$cis$ -[Rh <sub>2</sub> ( $\mu$ -O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> (bpy) <sub>2</sub> I <sub>2</sub> ]	2.5903(3)	19
3	$cis$ -[Rh <sub>2</sub> ( $\mu$ -O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> ( $\eta^2$ -ampy) <sub>2</sub> (py) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub> ]	2.587(1)	20
4	<i>cis</i> -[Rh <sub>2</sub> (µ-O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> (bpy) <sub>2</sub> Cl <sub>2</sub> ]3H <sub>2</sub> O	2.574(1)	21-25
5	cis-[Rh <sub>2</sub> (µ-O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> (phen) <sub>2</sub> (Me-Im) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	2.565(1)	26
6	cis-[Rh <sub>2</sub> (µ-O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> (phen) <sub>2</sub> (py) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> CO	2.559(1)	27-29
7	$cis$ -[Rh <sub>2</sub> ( $\mu$ -O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> ( $\eta^{3}$ -pynp) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub> C <sub>7</sub> H <sub>8</sub>	2.407(2)	16, 30
8	trans-[Rh <sub>2</sub> (µ-O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> (Mes-NP) <sub>2</sub> (BF <sub>4</sub> ) <sub>2</sub> ]CH <sub>2</sub> Cl <sub>2</sub>	2.387(1)	This work

 Table 1. Rh–Rh bond distances in selected dirhodium(II) complexes

 Bpy (2,2'-bipyridine), phen (1,10-phenanthroline), py (pyridine), ampy (2-amino pyridine); pynp (2-(2-pyridyl)-1,8-naphthyridine)



**Fig. 5.** *ORTEP* diagram (40% probability thermal ellipsoid) of the cationic unit *trans*-[Ru(CH<sub>3</sub>CN)<sub>2</sub>(Mes-NP)<sub>2</sub>] in compound **2** with key atoms labeled. Hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and angles [°]: Ru(1)–N(1) 2.100(3), Ru(1)–N(2) 2.086(3), Ru(1)–N(3) 2.018(3), N(1)–C(15) 1.362(4), N(1)–C(11) 1.322(5). Ru(1)–N(1)–C(15) 93.8(2), Ru(1)–N(1)–C(11) 148.7(3), N(1)–Ru(1)–N(2) 63.58(12), N(1)–Ru(1)–N(1') 180.0(3), N(1)–Ru(1)–N(3) 89.25(12), N(1)–C(15)–N(2) 108.3(3). Ru(1)–N(1)–C(15)–N(2) 2.4(3), Ru(1)–N(2)–C(18)–C(19) 7.3(7), N(3)–Ru(1)–N(2)–C(18) 88.3(5). Symmetry code 1/2 - x, 1/2 - y, -z.

naphthyridine-functionalized *N*-heterocyclic carbene is also shown to oxidatively cleave the Ru–Ru bond in  $[Ru_2(CO)_4 (CH_3CN)_6(OTf)_2]$ .<sup>[58]</sup>

## Catalysis

Metal catalyzed oxidation of alcohol to their corresponding aldehyde has remained a topic of considerable interest.<sup>[36–38]</sup> Ruthenium(II) compounds, in conjunction with a variety of oxidants, such as iodosobenzene, methylmorpholine *N*-oxide, 2,2,6,6-tetramethylpiperidin *N*-oxyl (TEMPO), bromate, hypochlorite, peroxides, are widely used as the oxidation catalysts.<sup>[39–47]</sup> We have evaluated the catalytic efficacy of compound **2** for alcohol to aldehyde oxidation and aldehyde olefination reactions, and the results are presented in Tables 2 and 3. Treatment of benzylalcohol (1 mmol), TEMPO (2 mmol) and catalyst 2 (0.01 mmol) provided benzaldehyde in 78% yield at 80°C after 6 h (Table 2, entry 1). The reaction does not proceed, as indicated by the non-consumption of alcohol, in absence of either the catalyst **2** or TEMPO.<sup>[58]</sup> Use of catalytic amount of TEMPO (0.1 equiv.) under an oxygen atmosphere did not afford the aldehyde in any significant quantity. 4-nitrobenzylalcohol (entry 2) afforded the highest yield (84%), and the conversion was lowest for 4-methoxybenzylalcohol (72%) among the alcohols studied (Table 2). It is apparent that alcohols containing electron rich phenyl groups resulted in reduced yields.

The C=C double bond formation is an important synthetic transformation as olefins find vast utility, especially in the areas of natural product and polymer synthesis.<sup>[48]</sup> Transition-metal catalyzed olefination of aldehydes with diazoacetate in the presence of triarylphosphine has emerged as an efficient method for the construction of C=C double bonds.<sup>[49–58]</sup> Ruthenium and rhodium complexes are well known carbene-transfer catalysts from commercially available ethyl diazoacetate (EDA). Reaction of benzaldehyde (1 mmol), triphenylphosphine (Ph<sub>3</sub>P,

1.2 mmol), EDA (1.5 mmol) and catalytic amount of 2 (0.01 mmol) gave ethyl cinnamate in 68% conversion after 6 h (Table 3, entry 3). Ethyl maleate and fumarate were also observed in the GC-MS spectra as side products resulting from dimerization of the carbene with a combined yield of less than 10%. Ph<sub>3</sub>P is found to be essential in this reaction, as no olefin formed in its absence. No aldehyde was observed in the absence of catalyst 2 as revealed in the GC-MS. In absence of catalyst 2, azine is found as the only product. The presence of an electronwithdrawing nitro group on the aromatic ring provided quantitative conversion after 1 h (entry 1), with excellent E/Zselectivity of 99/1. The 4-cyanobenzaldehyde afforded 82% yield after 6 h at 80°C with moderate E/Z selectivity of 82/18 (entry 2). The electron rich aldehydes such as 4-bromo-, 4methyl- and 4-methoxy-benzaldehydes showed poor reactivity and selectivity (entries 4-6).

Compound 2 catalyzes the formation of ylide  $Ph_3P=$ CHCOOEt via carbene transfer to triphenyl phosphine. Subsequent reaction of the phosphorane,  $Ph_3P=$ CHCOOEt, with an aldehyde affords the new olefin. Wittig-type reactions between phospho ylides and aldehydes are known to afford olefins with high *trans* to *cis* ratios.<sup>[51–55]</sup> The selectivity reported here are in close agreement with the reported works.

Prompted by the success of the catalyst **2** for the oxidation of alcohols oxidation and the olefination of aldehydes, we attempted the one-pot synthesis of  $\alpha$ , $\beta$ -unsaturated esters from

Table 2. Oxidation of alcohols catalyzed by 2<sup>A</sup>



<sup>&</sup>lt;sup>A</sup>Catalyst **2** (9 mg, 0.01 mmol) was dissolved in 1 mL dichloroethane and 3 mL toluene was added to it. Then alcohol (1 mmol) and TEMPO (292 mg, 2 mmol) were added. The reaction mixture was heated to 80°C for 6 h.

alcohols (Scheme 1). In a typical reaction, an alcohol (1 mmol), TEMPO (2 mmol) and catalyst **2** (0.02 mmol) were reacted in a dichloroethane/toluene mixture at 80°C. After 6 h, the reaction mixture was cooled to room temperature and  $Ph_3P$  added to the reaction mixture. A diluted EDA solution was then added dropwise and the reaction mixture heated to 80°C for additional 6 h under a nitrogen atmosphere. The maximum overall olefin conversion of 35% was achieved for 4-nitrobenzylalcohol, while a poor yield of less than 10% was estimated for electron rich 4-methoxybenzylalcohol. The overall yields for other alcohols were mixed. The addition of fresh catalyst after the first step (i.e., oxidation) improved the yields only marginally (less than 5%).

## Summary and Conclusion

Reaction of *cis*-[Rh<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>(CH<sub>3</sub>CN)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> with two equivalents of Mes-NP affords *trans*-[Rh<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>(Mes-NP)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (1) which exhibits short Rh–Rh distance. The same ligand, in contrast, causes the oxidative scission of the Ru–Ru bond resulting in *trans*-[Ru(Mes-NP)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (2). The unusual *trans* geometry of both complexes is attributed to the steric constraint exerted by the mesityl group attached to the naphthyridine ring. Compound 2 exhibits moderate catalytic activity for the oxidation of alcohols and the olefination of aldehydes.

## **Experimental Section**

# General Procedures

All reactions with metal complexes were carried out under an atmosphere of purified nitrogen using standard Schlenk-vessel and vacuum line techniques. Infrared spectra were recorded in the range 4000–400 cm<sup>-1</sup> on a Vertex 70 Bruker spectrophotometer as KBr pellets. <sup>1</sup>H NMR spectra were obtained on a JEOL JNM-LA 500 MHz spectrometer. <sup>1</sup>H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents. Elemental analyses were performed on a Thermoquest EA1110 CHNS/O analyzer. GC–MS experiment was performed on an Agilent 7890A GC and 5975C MS system. The recrystallized compounds were powdered, washed several times with dry diethyl ether or hexane and dried in vacuum for at least 48 h before elemental analyses were conducted.

#### Materials

Solvents were dried by conventional methods, distilled over nitrogen, and deoxygenated before use. Cis-[Rh<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub> (CH<sub>3</sub>CN)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> was synthesized by literature procedure.<sup>[59]</sup> The compound cis-[Ru<sub>2</sub>(CO)<sub>4</sub>(CH<sub>3</sub>CN)<sub>6</sub>][BF<sub>4</sub>]<sub>2</sub> was synthesized by following a procedure similar to the synthesis of cis-[Ru<sub>2</sub>(CO)<sub>4</sub>(CH<sub>3</sub>CN)<sub>6</sub>][PF<sub>6</sub>]<sub>2</sub>.<sup>[60]</sup>

# Synthesis of trans- $[Rh_2(CH_3COO)_2(Mes-NP)_2](BF_4)_2$ (1)

The Mes-NP ligand (27 mg, 0.1 mmol) was added to a dichloromethane solution of *cis*-[Rh<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>(CH<sub>3</sub>CN)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub>



Scheme 1. The one-pot synthesis of  $\alpha$ ,  $\beta$ -unsaturated esters from alcohols.



<sup>A</sup>3 mL toluene solution of EDA (1.5 mmol, 0.14 mL) was added drop-wise to the mixture of triphenylphosphine (1.2 mmol, 314 mg), aldehyde (1 mmol) and catalyst **2** (9 mg, 0.01 mmol) in toluene and dichloromethane mixture over a period of 30 min under nitrogen atmosphere. Then the solution was heated for 6 h (1 h for entry 1) at 80°C.

	$1 \cdot CH_2Cl_2$	$2 \cdot CH_2Cl_2$
Empirical formula	$C_{39}H_{40}B_2Cl_2F_8N_4O_4Rh_2$	C <sub>39</sub> H <sub>40</sub> B <sub>2</sub> Cl <sub>2</sub> F <sub>8</sub> N <sub>6</sub> Ru
Formula weight	1079.09	938.36
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
a [Å]	14.2399(12)	19.642(6)
b [Å]	20.8555(17)	13.499(4)
<i>c</i> [Å]	15.4788(13)	15.647(5)
α [°]	90.00	90.00
β[°]	111.4540(10)	92.344(6)
γ [°]	90.00	90.00
$V[Å^3]$	4278.4(6)	4145(2)
Z	4	4
$\rho_{\rm calcd}  [\rm g  cm^{-3}]$	1.675	1.504
$\mu [\mathrm{mm}^{-1}]$	0.976	0.580
F(000)	2160	1904
Reflections		
Collected	13883	18169
Independent	5235	5137
Observed $[I > 2\sigma(I)]$	4100	3488
No. of variables	280	268
Goodness of fit	1.078	1.048
R <sub>int</sub>	0.0379	0.0633
Final <i>R</i> indices $[I > 2\sigma(I)]^{A}$	$R_1 = 0.0414$	$R_1 = 0.0558$
	$wR_2 = 0.0952$	$wR_2 = 0.0938$
R indices (all data) <sup>A</sup>	$R_1 = 0.0584$	$R_1 = 0.1263$
	$wR_2 = 0.1120$	$wR_2 = 0.1521$

#### Table 4. Crystallographic data and pertinent refinement parameters for compounds 1 and 2

 ${}^{A}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}| \text{ with } F_{o}^{2} > 2\sigma(F_{o}^{2}). wR_{2} = [\Sigma w(|F_{o}^{2}| - |F_{c}^{2}|)^{2} / \Sigma |F_{o}^{2}|^{2}]^{1/2}.$ 

(40 mg, 0.05 mmol) and the solution was stirred for 8 h at room temperature. The red solution was concentrated under reduced pressure and hexane was added to induce precipitation. Red precipitate was washed with hexane and dried under vacuum. 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 (44 mg, 82%).  $\delta_{\rm H}$  (500 MHz, CDCl<sub>3</sub>, 294 K) 9.71 (d, *J* 5.5 Hz, 1H, NP), 9.26 (d, *J* 5.2 Hz, 1H, NP), 8.56 (d, *J* 8.55 Hz, 1H, NP), 7.96 (q, *J* 3.05 Hz, 1H, NP), 7.67 (d, *J* 8.25 Hz, 1H, NP), 7.35 (s, 2H, Mesityl), 2.00 (s, 3H, Methyl<sub>mesityl</sub>), 1.96 (s, 6H, Methyl<sub>mesityl</sub>), 1.72 (s, 3H, Methyl<sub>acetate</sub>).  $\nu$ (KBr)/cm<sup>-1</sup> (BF<sub>4</sub>) 1055;  $\nu$ (KBr)/cm<sup>-1</sup> (OAc) 1432. Anal. Calcd for C<sub>38</sub>H<sub>38</sub>N<sub>4</sub>O<sub>4</sub>B<sub>2</sub>F<sub>8</sub>Rh<sub>2</sub>: C 45.91, H 3.85, N 5.64. Found: C 45.86, H 3.78, N 5.57%.

# Synthesis of $[Ru(Mes-NP)_2(CH_3CN)_2](BF_4)_2$ (2)

The Mes-NP (27 mg, 0.1 mmol) and  $[n-Bu_4N][BF_4]$  (16 mg, 0.05 mmol) were added to a dichloromethane solution of *cis*-[Ru<sub>2</sub>(CO)<sub>4</sub>(CH<sub>3</sub>CN)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> (40 mg, 0.05 mmol) and the solution was stirred for 24 h at room temperature. The red solution was concentrated under reduced pressure and hexane was added to induce precipitation. The red precipitate was washed with hexane and dried under vacuum. Crystals suitable for X-ray diffraction were grown by layering hexane over a concentrated dichloromethane solution of **2** inside an 8 mm o.d. vacuum-sealed glass tube (37 mg, 80%).  $\delta_{\rm H}$  (500 MHz, CD<sub>3</sub>CN, 294 K) 9.45 (d, *J* 9.5 Hz, 1H, NP), 8.50 (d, *J* 4.25 Hz, 1H, NP), 8.47 (d, *J* 5.2 Hz, 1H, NP), 7.68 (q, *J* 3.2 Hz, 1H, NP), 7.14 (s, 2H, Mesityl), 2.49 (s, 3H, Methyl<sub>mesityl</sub>), 2.33 (s, 6H, Methyl).  $v({\rm KBr}/{\rm cm^{-1}}$  (BF<sub>4</sub><sup>-</sup>) 1055. Anal. Calcd for C<sub>38</sub>H<sub>38</sub>N<sub>6</sub>B<sub>2</sub>F<sub>8</sub>Ru: C 53.48, H 4.49, N 9.85. Found: C 53.42, H 4.41, N 9.79%.

# X-Ray Data Collection and Refinement

Single-crystal X-ray studies were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. All data were collected at 100(2) K using graphite monochromated  $Mo_{K\alpha}$  radiation ( $\lambda \alpha 0.71073$  Å). The frames were indexed, integrated, and scaled using the SMART and SAINT software packages,<sup>[61]</sup> and the data were corrected for absorption using the SADABS programs.<sup>[62]</sup> Structures were solved and refined with the SHELX suite of programs<sup>[63]</sup> as implemented in *X-Seed*.<sup>[64]</sup> The figures were drawn using ORTEP.<sup>[65]</sup> All the hydrogen atoms were included at geometrically calculated positions in the final stages of the refinement and were refined according to the 'riding model'. All non-hydrogen atoms were refined with anisotropic thermal parameters unless mentioned otherwise. Pertinent crystallographic data for compounds 1 and 2 are summarized in Table 4. CCDC 810328(1) and 810329(2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

# **Accessory Publication**

The accessory publication contains mechanism of alcohol oxidation to aldehyde, general procedures for the catalysis reactions and relevant metrical parameters for compounds 1 and 2.

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