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Hydrogenation and hydrogenolysis of furfural and furfuryl alcohol catalyzed by ruthenium(II) bis(diimine) complexes

Anitha S. Gowda, Sean Parkin and Folami T. Ladipo*

The catalytic activity of ruthenium(II) bis(diimine) complexes *cis*-[Ru(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](Z)$_2$ (1, Z = CF_3SO_3; 2, Z = (3,5-$(CF_3)_2C_6H_3)_4$B, i.e. BArF) and *cis*-[Ru(4,4′-Cl_2bpy)$_2$(OH_2)$_2$](Z)$_2$ (3, Z = CF_3SO_3; 4, Z = BArF) for the hydrogenation and/or the hydrogenolysis of furfural (FFR) and furfuryl alcohol (FFA) was investigated. The molecular structures of *cis*-[Ru(4,4′-Cl_2bpy)$_2$(CH_3CN)$_2$](CF_3SO_3)$_2$ (3′) and dimeric *cis*-[(Ru(4,4′-Cl_2bpy)$_2$Cl)$_2$](BArF)$_2$ (5) were characterized by X-ray crystallography. The structures are consistent with the anticipated reduction in steric hindrance about the ruthenium centers in comparison with corresponding complexes containing 6,6′-Cl_2bpy ligands. While compounds 1–4 are all active and highly selective catalysts for the hydrogenation of FFR to FFA under modest reaction conditions, 3 and 4 showed decreased activity. This is best explained in terms of reduced Lewis acidity of the Ru^{2+} centers and reduced steric hindrance about the metal centers of catalysts 3 and 4. *cis*-[Ru(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](BArF)$_2$ (2) also displayed high catalytic efficiency for the hydrogenation of FFA to tetrahydrofurfuryl alcohol. Presumably, this is because coordination of C=C bonds of FFA to the ruthenium center is poorly inhibited by non-coordinating BArF counterions. Interestingly, *cis*-[Ru(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](CF_3SO_3)$_2$ (1) showed some catalytic activity in ethanol for the hydrogenolysis of FFA to 2-methylfuran, albeit with fairly modest selectivity. Nonetheless, these results indicate that ruthenium(II) bis(diimine) complexes need to be further explored as catalysts for the hydrogenolysis of C-O bonds of FFR, FFA, and related compounds. Copyright © 2012 John Wiley & Sons, Ltd.

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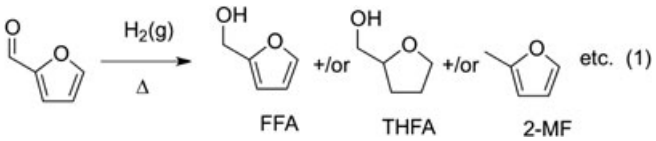
Keywords: catalytic hydrogenation; carbon–oxygen bond hydrogenolysis; ruthenium bis(diimine) complexes; furfuryl alcohol; tetrahydrofurfuryl alcohol

Introduction

Continuing depletion of nonrenewable fossil resources has spurred intense demand for a shift of feedstock for energy and chemical production towards renewable biomass resources.[1–5] However, since biomass-derived raw materials usually have a high oxygen content, efficient technologies are needed for selectively tailoring their oxygen content and functionality so that carbohydrate biomass, the world's most abundant renewable carbon resource, may be effectively utilized. In this context, furan derivatives, such as furfural (FFR) and 5-hydroxymethylfurfural are highly attractive as renewable chemical platforms for the production of fuels and chemical intermediates.[1,5,6] FFR, produced by acidic degradation of hemicellulose,[7] is a versatile industrial chemical[6] and its catalytic hydrogenation/hydrogenolysis is often used to produce furfuryl alcohol (FFA),[8,9] tetrahydrofurfuryl alcohol (THFA),[10] and 2-methylfuran, (2-MF)[8,9,11] all of which are important intermediates in the chemical industry.[8,11,12] Only a few catalysts have been reported to be selective for hydrogenation of FFR to FFA[9,13] or for hydrogenolysis of FFR or FFA to 2-MF.[12,14,15] Depending on the catalyst used, vapor phase hydrogenation of FFR yields not only the desired products but also a variety of by-products, including furan, tetrahydrofuran, and even ring-opening products, such as pentanols and pentanediols (equation (1)):[16]



While copper chromite catalysts are most often employed in industry,[1,6] disposal of deactivated copper chromite catalysts in landfill sites is restricted by new environmental regulations because of the high toxicity of Cr. Hence there is strong incentive for the development of new Cr-free catalysts that exhibit high selectivity for FFA and 2-MF formation. While carbon-supported copper (Cu/C)[9,17] and ruthenium (Ru/C)[18] catalysts, and amorphous alloy catalysts, such as Ni–Cu or Fe–Cu alloy catalysts,[19,20] have been developed as possible replacements for Cu–Cr catalysts, most are unsuitable for industrial application owing to severe deactivation phenomena.[16,19–21] Moreover, given the heterogeneous nature of the catalysts, the potential for achieving improvements in selectivity for the desired products by concentrating on the composition of catalysts and the operating conditions for FFR hydrogenation appears somewhat limited. In addition, experimental data on the reaction pathway(s) of vapor phase hydrogenation of FFR are scarce. Thus there is a current need for the development of soluble catalysts for FFR hydrogenation or hydrogenolysis in order to gain a better understanding of the reaction mechanism(s) and the origin of by-products, as well as to ultimately obtain catalysts that display high activity and product selectivity. In this context, homogeneous ruthenium-based catalysts, such as ruthenium–carbene

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complexes[22,23] and $RuCl_2(PPh_3)_3$,[24] have recently been reported to be active for FFR hydrogenation.

The potential of *cis*-[Ru(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](CF_3SO_3)$_2$ (**1**)[25] as a promising catalyst for the hydrogenation of carbonyl compounds and alkenes has previously been recognized.[2,26,27] Based on isotopic labeling studies with D_2O, which showed deuterium incorporation into both H_2 gas and the product alcohols, Lau and Cheng[25,28] proposed a hydrogenation mechanism wherein a metal hydride species *cis*-[Ru(6,6′-Cl_2bpy)$_2$H(Z)]$^{+/0}$ (**II**, Z = H_2O, substrate, solvent, $CF_3SO_3^-$) is generated via heterolytic activation of H_2 by a transiently formed dihydrogen complex *cis*-[Ru(6,6′-Cl_2bpy)$_2$(η^2-H_2)Z]$^{2+/+}$ (**I**). The hydride transfer step was postulated to occur via coordination of the carbonyl or alkene substrate *cis* to a hydride ligand followed by insertion into a Ru-H bond; product release then occurs through protonation of the resulting Ru-O or Ru-C bond. However, an alternative hydrogenation pathway involving direct transfer of a hydride ligand from the ruthenium center to a protonated substrate without binding of the substrate to ruthenium is also possible, as has been observed in the reaction between the related complex [Ru(bpy)(terpy)H]$^+$ (terpy = terpyridine) and CO_2.[29,30] Although there is currently no direct experimental evidence for either species **I** or **II**, the proposed mechanism seems feasible, particularly since alternatives that involve oxidative addition of H_2 to give a Ru^{4+} species appear more unlikely.

In this study, we have explored the potential of ruthenium(II) bis(diimine) complexes, including some which can potentially generate more electron-rich ruthenium hydride species than obtained from **1**, as catalysts for the hydrogenation and/or hydrogenolysis of FFR and FFA. We have also examined the effect of the nature of the counterion on reactivity of the complexes. Specifically, we compared the effect of weakly coordinating [B(3,5-$(CF_3)_2C_6H_3)_4$]$^-$ (BArF) anion versus $CF_3SO_3^-$ anion. It is now well recognized that the rate or even probability of a reaction at a cationic metal center may be attenuated by coordination of counterion.[31] Herein we demonstrate that ruthenium(II) bis(diimine) complexes are effective homogeneous catalysts for the chemoselective hydrogenation of FFR and FFA to furfuryl alcohol and THFA, respectively. In addition, we show that the complexes display good promise as catalysts for the hydrogenolysis of FFR and FFA to 2-MF.

Results and Discussion

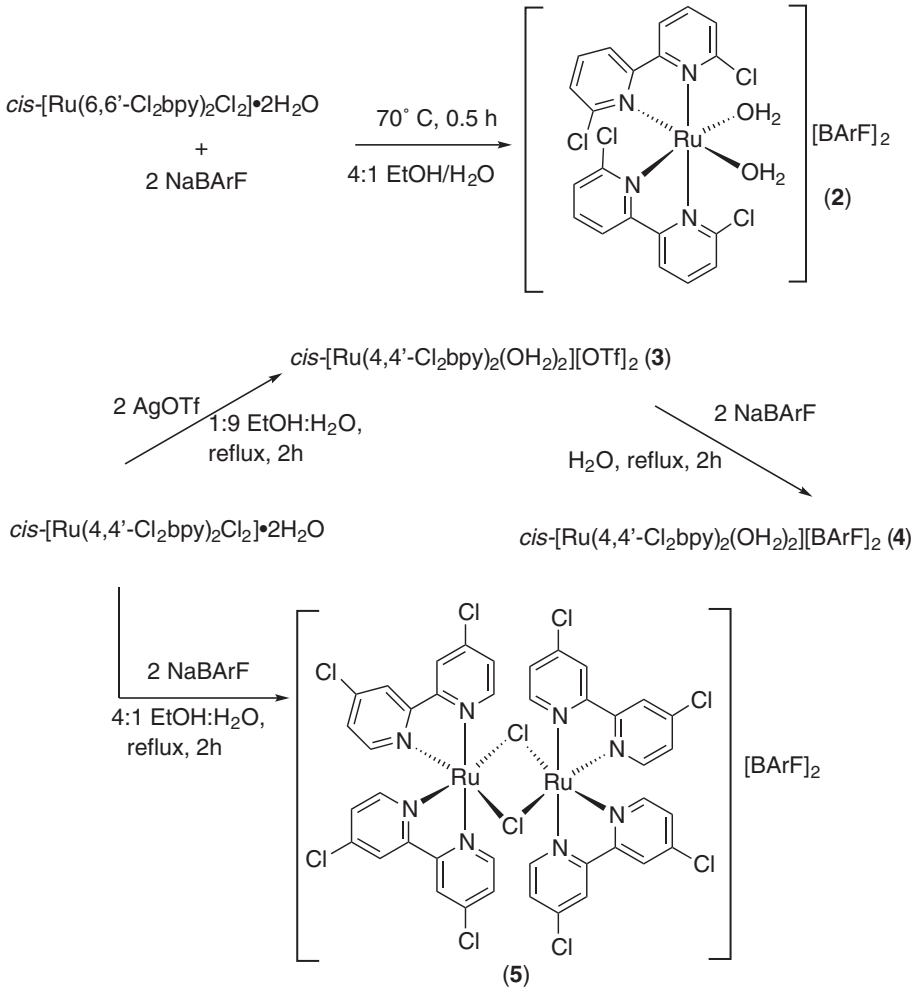
Synthesis and Characterization of Ruthenium(II) Bis(diimine) Complexes

Ruthenium(II) bis(diimine) complexes *cis*-[Ru(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](BArF)$_2$ (2, BArF = (**3**,5-$(CF_3)_2C_6H_3)_4$B) and *cis*-[Ru(4,4′-Cl_2bpy)$_2$(OH_2)$_2$](CF_3SO_3)$_2$ (**3**) were prepared in excellent yield via modification of the method reported by Che and Leung for the preparation of *cis*-[Ru(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](CF_3SO_3)$_2$ (**1**),[32] by metathesis of the corresponding ruthenium dichloride with two equivalents of NaBArF[33,34] or Ag(CF_3SO_3) in ethanol/water, respectively (Scheme 1). In contrast, similar reaction between *cis*-[Ru(4,4′-Cl_2bpy)$_2$$Cl_2$].2$H_2O$[35] and NaBArF (2 equiv.) in 4:1 ethanol–water at reflux for 2 h produced a red solution which after work-up furnished dimeric *cis*-[(Ru(4,4′-Cl_2bpy)$_2$Cl)$_2$](BArF)$_2$ (**5**, Scheme 1; similar preparation of the related compound *cis*-[Ru(Cl_2bpy)$_2$$Cl]_2$($PF_6$)$_2$ has previously been reported).[36] Apparently, dimerization is more facile for the initially formed *cis*-[Ru(4,4′-Cl_2bpy)$_2$Cl(Z)]$^+$ species than for *cis*-[Ru(6,6′-Cl_2bpy)$_2$Cl(Z)]$^+$ species (Z = H_2O, EtOH). This is presumably due to reduced steric bulk of 4,4′-Cl_2bpy compared with 6,6′-Cl_2bpy since the more electron-donating 4,4′-Cl_2bpy ligand should generate a less electrophilic ruthenium center than 6,6′-Cl_2bpy ligand.[37] Thus *cis*-[Ru(4,4′-Cl_2bpy)$_2$(OH_2)$_2$](BArF)$_2$ (**4**) was instead obtained in 81% yield via metathetical reaction of **3** with NaBArF in water at reflux for 2 h (Scheme 1). Compounds **1–5** dissolve well in polar organic solvents, such as ethanol, DMSO, acetonitrile (MeCN), sulfolane, and *N*-methylpyrrolidone (NMP). However, **2**, **4** and **5** were only sparingly soluble in $CHCl_3$ and insoluble in water, while **3** was insoluble in $CHCl_3$ but partially soluble in water.

The formulation and structure of compounds **2–4** were established by microanalysis and solution (^{1}H, ^{13}C, and ^{19}F) NMR data. Since the compounds readily exchanged their H_2O ligands in acetonitrile-d_3, NMR data were recorded for the resultant *bis* (acetonitrile) complexes (after letting the solutions sit for 1–4 h). Both the ^{1}H and ^{13}C NMR data for each compound displayed sharp resonances that are consistent with the expected C_2 symmetry. For example, the ^{1}H NMR spectrum of each compound displayed six aromatic resonances, which integrate as two protons each, for the disubstituted 2,2′-bipyridine ligands (analogous to data previously reported for *cis*-[Ru(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](CF_3SO_3)$_2$ (**1**)).[28,32] Consistent with weak or non-coordination of the counterions, **3** and **4** each displayed a single ^{19}F NMR signal at d-78.0 ($CF_3SO_3^-$)[38] and −62.0 ($BArF^-$)[39] ppm, respectively. As shown in Fig. 1, X-ray analysis of single crystals of *cis*-[Ru(4,4′-Cl_2bpy)$_2$(CH_3CN)$_2$](CF_3SO_3)$_2$ (**3′**) confirmed the structure assigned by spectroscopy; the compound adopts a distorted octahedral structure with the two bidentate 4,4′-dichloro-2,2′-bipyridine ligands coordinated *cis* at the ruthenium center. The distortion from idealized octahedral geometry arises from the acute bite angle of the bipyridine ligands [e.g. N(1)-Ru-N(2) = ~79°]. All of the Ru-N bond distances are within the expected range and comparable to those (2.04–2.07 Å) observed for related complexes *cis*-[Ru(bpy)$_2$(CH_3CN)$_2$](ClO_4)$_2$[40] and *cis*-[Ru(6,6′-Cl_2bpy)$_2$(κ^2-acac)$_2$](ClO_4).[41] Crystallographic data and selected metrical parameters for compounds **3′** and *cis*-[(Ru(4,4′-Cl_2bpy)$_2$$Cl)_2$](BArF)$_2$ (**5**) are given in Tables 1 and 2, respectively. The structure of **5** was unequivocally established by X-ray crystallography (Fig. 2) and its ^{1}H NMR data in $CDCl_3$ (which displayed six equally intense aromatic resonances for the 4,4′-Cl_2bpy ligands, consistent with D_2 symmetry) showed that the solid-state structure of **5** is maintained in $CDCl_3$ solution (see supporting information). As shown in Fig. 2, a distorted octahedral environment exists about each Ru^{2+} center in **5**, owing to the acute bite angles resulting from the 4,4′-Cl_2bpy ligands [e.g. N(1)-Ru-N(2) = ~79°] and the bridging chlorides [Cl(1)-Ru-Cl(2) = ~84°]. All of the Ru-N and Ru-Cl bond distances (2.02–2.07 Å and ~2.43 Å, respectively) are within the expected ranges and comparable to those observed for the related complex [Ru(phen)(CO)Cl_2]$_2$.[42]

Hydrogenation/Hydrogenolysis Activity Studies

As shown in Table 3 (entries 1–6), compounds **1–4** are all active catalysts for the hydrogenation of FFR in ethanol, exhibiting essentially 100% conversion of FFR and near-complete selectivity for FFA formation at modest temperatures. *cis*-[Ru(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](CF_3SO_3)$_2$ (**1**) displayed better selectivity than *cis*-[Ru(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](BArF)$_2$ (**2**) for C=O bond (versus C=C bond) hydrogenation. For example, whereas the hydrogenation of FFR in the presence of 1 mol% of catalyst **1** proceeded at 100°C/51 atm H_2 pressure for 2 h to furnish FFA in near-quantitative yield (Table 3, entry 1), FFR hydrogenation proceeded in the presence of catalyst **2** (0.40 mol%) at lower temperature and pressure (85°C/10.2 atm H_2)



Scheme 1. Synthesis of ruthenium(II) bis(diimine) complexes **1–5**

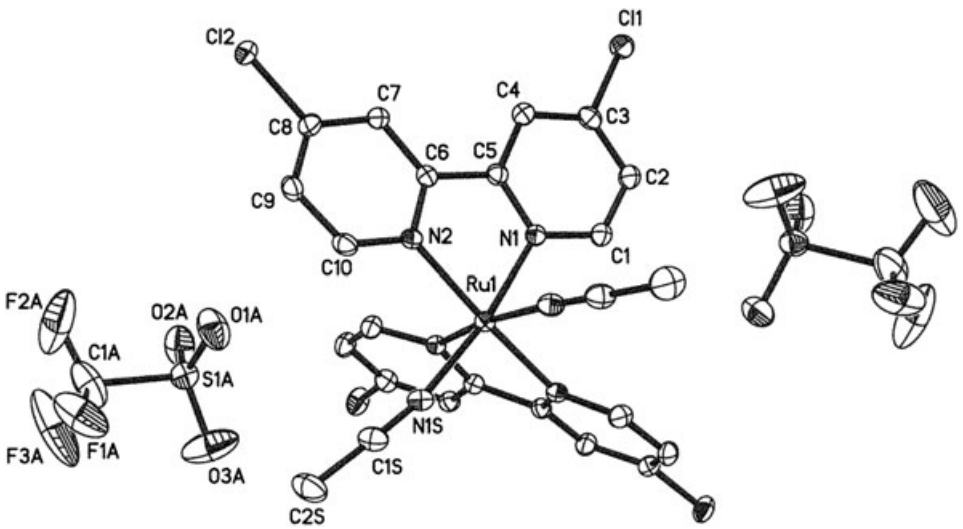


Figure 1. Molecular structure of **3′**

to give 93% yield of FFA and 7% yield of THFA; Table 3, entry 3). The yield of THFA increased when the reaction was conducted under similar conditions for a longer duration (cf. entry 3 vs. 4 in Table 3), suggesting that THFA formation is preceded by FFA formation (i.e. C=O bond hydrogenation is more facile than C=C bond hydrogenation under the reaction conditions). Consistent

Table 1. Crystallographic and refinement data for **3′** and **5**

Compound	**3′**	**5**
Empirical formula	$C_{26}H_{18}Cl_4F_6N_6O_6RuS_2$	$C_{107}H_{51}B_2Cl_{19}F_{48}N_8Ru_2$
Formula weight	931.45	3257.87
Crystal system	Monoclinic	Triclinic
Space group	C 2/c	P −1
a (Å)	18.9102(1)	13.5881(2)
b (Å)	10.8163(1)	17.1304(3)
c (Å)	18.8782(2)	27.0993(5)
a (deg.)	90	82.9755(8)
b (deg.)	118.5306(4)	89.5023(7)
g (deg.)	90	88.0876(7)
Volume ($Å^3$)	3392.41(5)	6256.99(18)
Z	4	2
D_c (Mg m^{-3})	1.824	1.729
m (mm^{-1})	0.984	0.769
F (000)	1 848	3 204
Crystal size (mm)	0.20 × 0.20 × 0.20	0.18 × 0.12 × 0.06
Reflections collected	47 530	131 393
Unique reflections	3 899	22 032
GOF on F^2	1.192	1.047
R indices [$I > 2s(I)$] R1, wR2	0.0460, 0.1173	0.0632, 0.1558
R indices (all data) R1, wR2	0.0524, 0.1235	0.1179, 0.1823
CCDC no.	828086	828087

Table 2. Selected bond lengths (Å) and angles (°) for **3′** and **5**

3′		**5**	
Ru(1)-N(1S)	2.035(3)	Ru(1)-N(3)	2.035(5)
Ru(1)-N(1)	2.054(2)	Ru(1)-N(2)	2.042(5)
Ru(1)-N(2)	2.067(2)	Ru(1)-N(4)	2.043(4)
N(1S)-Ru(1)-N(1)	171.68(9)	Ru(1)-N(1)	2.052(5)
N(1S)-Ru(1)-N(2)	92.83(10)	Ru(1)-Cl(1)	2.4325(15)
N(1)-Ru(1)-N(2)	78.91(9)	Ru(1)-Cl(2)	2.4384(15)
N(1S)#1-Ru(1)-N(1S)	94.55(14)	Ru(2)-N(6)	2.023(5)
N(1S)-Ru(1)-N(1)#1	87.18(10)	Ru(2)-N(7)	2.030(5)
N(1)#1-Ru(1)-N(1)	92.27(13)	Ru(2)-N(5)	2.040(5)
N(1S)#1-Ru(1)-N(2)	94.80(10)	Ru(2)-N(8)	2.050(5)
N(1)#1-Ru(1)-N(2)	93.25(9)	Ru(2)-Cl(1)	2.4297(15)
N(2)-Ru(1)-N(2)#1	168.76(14)	Ru(2)-Cl(2)	2.4377(15)
N(1S)#1-Ru(1)-N(1)#1	171.67(9)	N(3)-Ru(1)-N(2)	100.65(19)
N(1S)#1-Ru(1)-N(1)	87.18(10)	N(3)-Ru(1)-N(4)	79.31(18)
N(1S)#1-Ru(1)-N(2)#1	92.82(10)	N(2)-Ru(1)-N(4)	93.28(18)
N(1S)-Ru(1)-N(2)#1	94.80(10)	N(3)-Ru(1)-N(1)	97.80(18)
N(1)#1-Ru(1)-N(2)#1	78.91(9)	N(2)-Ru(1)-N(1)	79.58(18)
N(1)-Ru(1)-N(2)#1	93.25(9)	N(4)-Ru(1)-N(1)	171.74(19)
N(2)-Ru(1)-N(2)#1	168.76(14)	N(3)-Ru(1)-Cl(1)	171.01(14)
		Cl(1)-Ru(1)-Cl(2)	84.26(5)
		Cl(1)-Ru(2)-Cl(2)	84.33(5)
		Ru(2)-Cl(1)-Ru(1)	95.81(5)
		Ru(2)-Cl(2)-Ru(1)	95.45(5)
		N(7)-Ru(2)-N(5)	95.12(18)
		N(6)-Ru(2)-N(8)	96.37(19)
		N(7)-Ru(2)-N(8)	79.49(19)
		N(5)-Ru(2)-N(8)	172.69(19)

with this suggestion, the hydrogenation of FFA in the presence of 0.40 mol% of catalyst **2** at 130°C in ethanol for 4 h gave THFA in quantitative yield (Table 3, entry 7). The propensity displayed by **2** for hydrogenation of the C=C bonds of FFA is likely due to the non-coordinating nature of the BArF counterion.[34] As discussed before, one of the proposed pathways for carbonyl or alkene hydrogenation by catalyst **1** involves substrate coordination *cis* to a hydride ligand followed by insertion into a Ru-H bond. Evidently, coordination of a furan ring C=C bond to the electrophilic Ru^{2+} center of a metal hydride species generated from catalyst **2** is competitive with coordination of H_2O and/or EtOH. We presume that **1** did not similarly catalyze the hydrogenation of FFA to give THFA (*cf.* Table 3, entry 7 vs. 9) because coordination of triflate prevails against coordination of a furan ring C=C bond.

Even though *cis*-[Ru(4,4′-Cl_2bpy)$_2$(OH_2)$_2$](CF_3SO_3)$_2$ (**3**) and *cis*-[Ru(4,4′-Cl_2bpy)$_2$(OH_2)$_2$](BArF)$_2$ (**4**) both catalyzed FFR hydrogenation to produce FFA in near-quantitative yield for 100% FFR conversion, each catalyst is significantly less active than the corresponding 6,6′-Cl_2bpy-based derivative **1** and **2**, respectively (cf. Table 3, entries 1 and 3 vs. entries 5 and 6). Moreover, unlike **2**, which catalyzed FFA hydrogenation to produce THFA in near-quantitative yield (Table 3, entry 7), no reaction was observed when FFA was heated in the 130–150° C range in the presence of H_2 (51 atm) and 1 mol% of catalyst **4** for up to 23 h. The decreased activity of catalysts **3** and **4** most probably derives from a combination of reduced Lewis-acidic character of the Ru^{2+} centers and reduced steric hindrance about the metal centers.

First, ligation of Ru^{2+} by more electron-donating 4,4′-$Cl_2$by ligands would likely lower the equilibrium concentration of the dihydrogen complexes *cis*-[Ru(4,4′-Cl_2bpy)$_2$(η^2-H_2)Z]$^{2+/+}$ (Z = H_2O, substrate, solvent, or $CF_3SO_3^-$) generated from **3** and **4**, and would undoubtedly increase the pK_a values (i.e. decrease acidity) of the dihydrogen complexes.[43] Second, triflate would almost certainly compete more effectively with the C=O group of FFR for coordination to Ru^{2+} in the metal hydride species *cis*-[Ru(4,4′-Cl_2bpy)$_2$H(Z)]$^{+/0}$ (Z = H_2O, substrate, solvent, $CF_3SO_3^-$) than in *cis*-[Ru(6,6′-Cl_2bpy)$_2$H(Z)]$^{+/0}$ (**II**) since 4,4′-Cl_2bpy is sterically less demanding than 6,6′-Cl_2bpy; such behavior could possibly decrease the catalytic activity of **3** relative to **1**. Third, given the non-coordinating nature of BArF counterion, dimerization of *cis*-[Ru(4,4′-Cl_2bpy)$_2$H(Z)]$^{+/0}$ species (Z = H_2O, substrate, solvent) generated from *cis*-[Ru(4,4′-Cl_2bpy)$_2$(OH_2)$_2$](BArF)$_2$ (**4**) would likely be more facile than dimerization of *cis*-[Ru(6,6′-Cl_2bpy)$_2$H(Z)]$^{+/0}$ species generated from *cis*-[Ru(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](BArF)$_2$ (**2**). Consistent with this suggestion, we noted earlier that *cis*-[Ru(4,4′-Cl_2bpy)$_2$Cl(Z)]$^+$ species (Z = H_2O, EtOH) readily dimerized to furnish *cis*-[(Ru(4,4′-Cl_2bpy)$_2$Cl)$_2$](BArF)$_2$ (**5**) while *cis*-[Ru(6,6′-Cl_2bpy)$_2$Cl(Z)]$^+$ species reacted further with NaBArF in ethanol/water to give **2** (see above).

Dimerization of ruthenium hydride species would effectively reduce the concentration of active catalyst in solution, which would account for decrease activity of **4** relative to **2**. Also, more facile dimerization of the ruthenium hydride species generated from **4** (versus **2**) would account for why **4** did not catalyze the hydrogenation of FFA to THFA when **2** did. Presumably, dimerization of the *cis*-[Ru(4,4′-Cl_2bpy)$_2$H(Z)]$^+$ species prevails against coordination of FFR ring C=C bond under our reaction conditions.

Given that hydrogenolysis of FFR (a trace of 2-MF) was observed in the reaction of FFR with H_2 (51 atm) catalyzed by *cis*-[Ru(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](CF_3SO_3)$_2$ (**1**) at 100°C, we have briefly investigated the hydrogenolysis of FFR (and FFA) in the 125–130°C range in ethanol (the decomposition temperature for *cis*-[Ru(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](CF_3SO_3)$_2$ (**1**) has been reported to be 135° C),[44] as well as

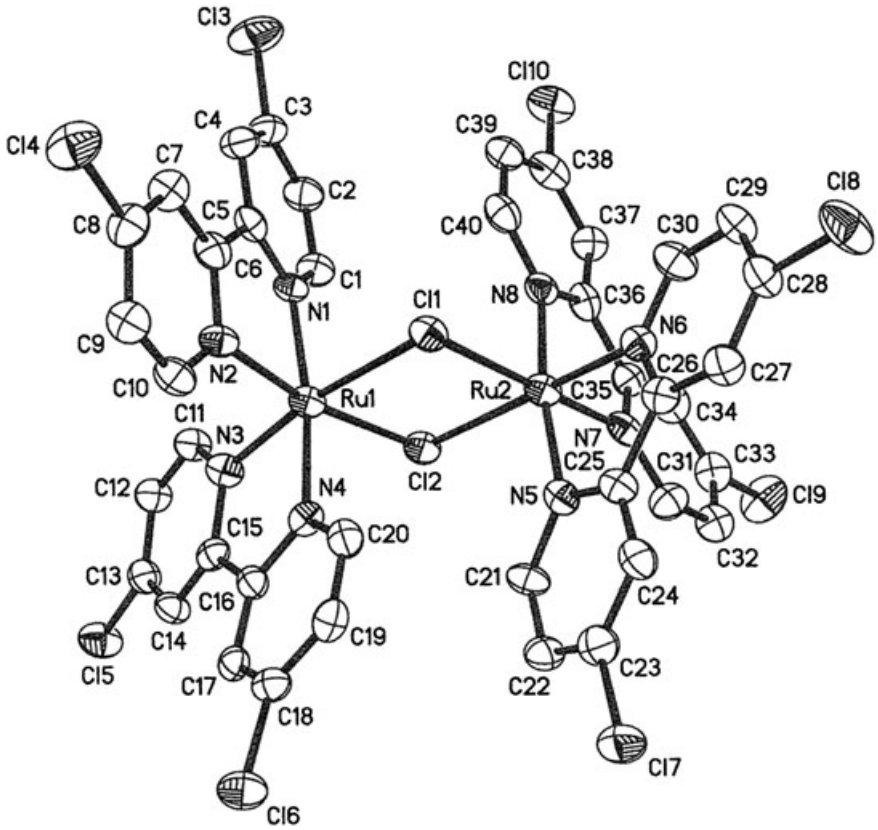


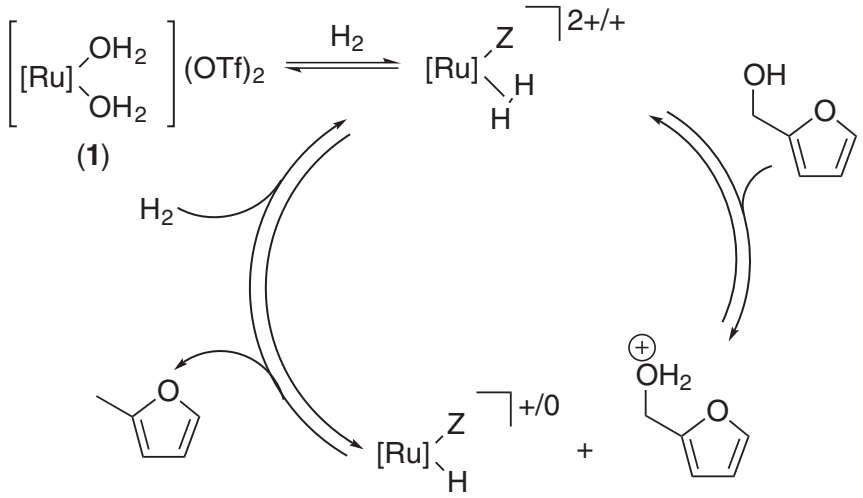
Figure 2. Molecular structure of **5**

Table 3. Ru(II) bis(diimine) catalyzed hydrogenation/hydrogenolysis of FFR and FFA

Entry	Cat.	Substrate	Solvent[f]	*T* (°C)	*t* (h)	Conv. (%)[g,h]	Selectivity (%)[g,i]		
							FFA	THFA	2-MF
1[a]	**1**[c]	FFR	EtOH	100	2	99	>99	—	Trace
2[a]	**1**[d]	FFR	EtOH	100	4	100	96	—	Trace
3[b]	**2**[e]	FFR	EtOH	85	2	100	93	7	
4[b]	**2**[e]	FFR	EtOH	90	9	100	74	26	
5[a]	**3**[c]	FFR	EtOH	110	18	100	98	<1	
6[a]	**4**	FFR	EtOH	125	23	100	99	<1	
7[a]	**2**[e]	FFA	EtOH	130	4	100	—	>99	
8[a]	**1**[c]	FFR	EtOH	130	4	100	17	Trace	20
9[a]	**1**[c]	FFA	EtOH	130	4	90	—	5	25
10[a]	**1**[c]	FFR	NMP	130	4	98	99		
11[a]	**1**[c]	FFR	Sulfolane	125	6	100	100		

[a]H_2 pressure = 51 atm.
[b]H_2 pressure = 10.2 atm.
[c]1.0 mol% catalyst.
[d]0.28 mol% catalyst.
[e]0.40 mol% catalyst.
[f]10 ml solvent.
[g]Average of ≥3 experiments.
[h]Determined by GC analysis using *n*-octane as internal standard.
[i]Product selectivity = (mol product formed/mol substrate consumed) × 100.

in solvents that would preclude formation of acetal and/or ether by-product(s). Reaction of FFR with H_2 (51 atm) in the presence of 1 mol% of **1** at 130°C in ethanol for 4 h proceeded to 100% FFR conversion and furnished a mixture of products (Table 3, entry 8), including FFA (17% yield), 2-MF (20% yield), and 2-(diethoxymethyl) furan (furfural diethyl acetal, 14% yield). (Typically, four to five



Scheme 2. A plausible mechanism for FFA hydrogenolysis

additional products are also formed. While the products have not yet been fully identified, they appear to derive from reactions between ethanol and substrate followed by different extents of furan ring hydrogenation and or hydrogenolysis. Similar results were obtained using isopropyl alcohol as solvent.) Analogous reaction of FFA with H_2 in ethanol catalyzed by 1 mol% of **1** also produced a mixture of products (Table 3, entry 9), which included 2-MF and THFA in 25% and 5% yield, respectively. Initial attempts to improve the efficiency of FFR hydrogenolysis by using catalyst **1** in the 125–130°C range in polar organic solvents, such as NMP or sulfolane (thus precluding formation of acetal and ether by-products) led to exclusive production of FFA (Table 3, entries 10 and 11).

A plausible mechanism for catalytic formation of 2-MF via FFR hydrogenolysis, which involves protonation of FFA followed by hydride attack on the electrophilic carbon of protonated FFA, is depicted in Scheme 2. A similar acid-assisted nucleophilic substitution (S_N2) mechanism has been proposed to explain Pd-catalyzed hydrogenolysis of benzyl alcohol in acidic medium.[45] In connection with the hydrogenolysis of FFA (and FFR) occurring in ethanol but not in NMP or sulfolane, we note that a transiently formed dihydrogen species *cis*-[Ru(6,6′-Cl_2bpy)$_2$(η^2-H_2)Z]$^{2+/+}$ (**I**) is the only acid present under our reaction conditions; hence the rate (hence efficacy) of FFA hydrogenolysis is probably slowed by the rather low concentration of acid. Furthermore, while protonated FFA and protonated ethanol possess similar acid strengths ($pK_a \cong -2$), protonated NMP is a significantly weaker acid ($pK_a \cong -0.5$).[46] Thus the concentration of protonated FFA would be negligible in NMP solution due to the solvent leveling effect, causing the hydrogenolysis reaction to be much less effective.

Conclusions

Ruthenium(II) bis(diimine) complexes *cis*-[Ru(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](Z)$_2$ (**1**, Z = CF_3SO_3; **2**, Z = BArF) and *cis*-[Ru(4,4′-Cl_2bpy)$_2$(OH_2)$_2$](Z)$_2$ (**3**, Z = CF_3SO_3; **4**, Z = BArF) are all active and highly selective catalysts for the hydrogenation of FFR to FFA under modest reaction conditions. Due to a combination of reduced Lewis acidity of the Ru^{2+} centers and reduced steric hindrance about the metal centers, catalysts **3** and **4** (containing 4,4′-Cl_2bpy ligands) are less active than 6,6′-Cl_2bpy-containing catalysts **1** and **2**, respectively. *cis*-[Ru(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](BArF)$_2$ (**2**) is also an efficient catalyst for the hydrogenation of FFA to THFA. Presumably, this is because coordination of C=C bonds of FFA to the ruthenium center is not inhibited by non-coordinating BArF counterions. Our initial studies demonstrate that *cis*-[Ru(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](CF_3SO_3)$_2$ (**1**) is an active catalyst in ethanol for the hydrogenolysis of FFA to 2-MF, albeit the selectivity is poor. However, given the low concentration of acid under the reaction conditions and acid-catalyzed side reactions involving ethanol, we are currently investigating the effects of added acid and polar aprotic solvent media on the reaction. In contrast to **1**, *cis*-[Ru(4,4′-Cl_2bpy)$_2$(OH_2)$_2$](CF_3SO_3)$_2$ (**3**) did not catalyze hydrogenolysis of FFA (or FFR) in ethanol under similar conditions. Since the reduced steric hindrance about the electrophilic Ru^{2+} center of **3** likely increases the propensity for dimerization of generated metal hydride species (thereby removing active catalyst from solution), we are currently exploring approaches to stabilizing complexes of type **3** (and the resultant hydrides) to dimerization.

Experimental

Materials and Instruments

All experiments were performed under dry nitrogen atmosphere using standard Schlenk techniques (unless stated otherwise). All solvents were dried and distilled by standard methods[47] prior to use and stored in a glovebox over 4A molecular sieves that had been dried in a vacuum oven at 150°C for at least 48 h. Unless otherwise stated, all reagents were purchased from Sigma-Aldrich Chemical Co. and used as received. FFR and FFA were distilled under vacuum prior to use. $RuCl_3.3H_2O$ was purchased from Pressure Chemical Co. and hydrogen gas (99.9% purity) was purchased from Scott-Gross Co. The compounds NaBArF,[33,34] *cis*-[Ru(6,6′-Cl_2bpy)$_2$$Cl_2$].2$H_2O$,[32] *cis*-[Ru(4,4′-$Cl_2$bpy)$_2$$Cl_2$].2$H_2O$,[35] and *cis*-[Ru(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](CF_3SO_3)$_2$ (**1**)[32] were prepared by the literature methods (or modification thereof).

^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on a Varian VXR-400 spectrometer at room temperature unless otherwise stated. All chemical shifts are reported in units of δ (downfield from tetramethylsilane) and ^{1}H and ^{13}C chemical shifts were referenced to residual solvent peaks. ^{19}F NMR chemical shifts were referenced to $CFCl_3$ internal standard and ^{31}P NMR chemical shifts were referenced to 85% H_3PO_4 internal standard. Analyses by gas chromatography (GC) were performed on a Shimadzu GC-17A instrument with flame ionization detection (FID), a 60 m $\times$ 0.32 mm (0.25 mm film thickness) Agilent JW Scientific DB-5 GC column, and helium as carrier gas. An injection temperature of 140°C was employed, which was found to be sufficiently low to avoid the occurrence of secondary reactions in the injection port. GC-MS analyses were performed on an Agilent Technologies 6890/5973N inert gas GC/mass selective detection system at an ionizing potential of 70 eV. Elemental analysis for C, H, and N was performed by Robertson Microlit Laboratories (Ledgewood, NJ, USA).

Synthesis of *cis*-[Ru(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](BArF)$_2$ (**2**, BArF = (3,5-(CF_3)$_2$$C_6H_3$)$_4$B)

A mixture of *cis*-[Ru(6,6′-Cl_2bpy)$_2$$Cl_2$].2$H_2O$ (0.100 g, 0.152 mmol) and NaBArF (0.267 g, 0.304 mmol) in 4:1 ethanol–water (40 ml) was heated at 70°C for 0.5 h. The resulting red solution was then cooled to ambient temperature and the solvent was removed under vacuum. The red residue was washed three times with an excess of water (~ 20 ml) and then dried under vacuum to give a dark-red sticky powder. Yield = 0.34 g, 97%. ^{1}H NMR (CD_3CN, recorded after letting the solution sit for 1 h; see Discussion section): δ 8.38 (dd, 2 H, ^{3}J = 8.0 Hz, ^{4}J = 1.2 Hz, 6,6′-Cl_2bpy), 8.32 (dd, 2 H, ^{3}J = 8.0 Hz, ^{4}J = 1.2 Hz, 6,6′-Cl_2bpy), 8.16 (t, 2 H, ^{3}J = 8.0 Hz, 6,6′-Cl_2bpy), 8.08 (t, 2 H, ^{3}J = 8.0 Hz, 6,6′-Cl_2bpy), 7.79 (dd 2 H, ^{3}J = 8.0 Hz, ^{4}J = 1.2 Hz, 6,6′-Cl_2bpy), 7.64–7.72 (m, 24 H, BArF), 7.58 (dd, 2 H, ^{3}J = 8.0 Hz, ^{4}J = 1.2 Hz, 6,6′-Cl_2bpy). ^{13}C NMR (CD_3CN): δ 162.7 (q, $^{1}J_{BC}$ = 50 Hz, C_{ipso}, BArF), 161.1, 160.3, 160.1, 159.8, 141.9, 141.8, 135.7 (C_o, BArF), 129.9 (m, C_m, BArF), 129.0, 128.6, 125.5 (q, $^{1}J_{CF}$ = 272 Hz, CF_3), 124.3, 123.9, 118.8 (C_p, BArF). A sample of **2** isolated as **2**.2H_2O was characterized by microanalysis. Anal. Calcd for $C_{84}H_{44}B_2Cl_4F_{48}N_4O_4Ru$: C, 42.94; H, 1.89; N, 2.38. Found: C, 42.51; H, 1.56; N, 2.53.

Synthesis of *cis*-[Ru(4,4′-Cl_2bpy)$_2$(OH_2)$_2$](CF_3SO_3)$_2$ (**3**)

A mixture of *cis*-[Ru(4,4′-Cl_2bpy)$_2$$Cl_2$].2$H_2O$ (0.480 g, 0.729 mmol) and Ag[CF_3SO_3] (0.412 g, 1.603 mmol) in 1:9 ethanol–water (80 ml) was heated at reflux for 2 h. The resulting red solution was cooled to ambient temperature and then filtered to remove AgCl. The filtrate was concentrated to dryness under reduced pressure and the red residue was dried under vacuum for 12 h. Yield = 0.64 g, 99%. ^{1}H NMR (CD_3CN, recorded after letting the solution sit for 4 h; see Discussion section): δ 9.18 (d, 2 H, ^{3}J = 6.4 Hz, 4,4′-Cl_2bpy), 8.61 (d, 2 H, ^{4}J = 2.0 Hz, 4,4′-Cl_2bpy), 8.48 (d, 2 H, ^{4}J = 2.0 Hz, 4,4′-Cl_2bpy), 7.93 (dd, 2 H, ^{3}J = 6.4 Hz, ^{4}J = 2.0 Hz, 4,4′-Cl_2bpy), 7.57 (d, 2 H, ^{3}J = 6.4 Hz, 4,4′-Cl_2bpy), 7.36 (dd, 2 H, ^{3}J = 6.4 Hz, ^{4}J = 2.0 Hz, 4,4′-Cl_2bpy). ^{13}C NMR (CD_3CN): d 159.3, 158.5, 155.4, 154.5, 147.5, 147.0, 129.2, 128.2, 126.1, 125.7. ^{19}F NMR (CD_3CN): d −78.0 ($CF_3SO_3^-$). Anal. Calcd for (**3**.2H_2O) $C_{22}H_{20}Cl_4F_6N_4O_{10}RuS_2$: C, 28.68; H, 2.19; N, 6.08. Found: C, 29.06; H, 1.80; N, 6.27.

Single crystals of *cis*-[Ru(4,4′-Cl_2bpy)$_2$(CH_3CN)$_2$](CF_3SO_3)$_2$ (**3′**) suitable for X-ray diffraction study were obtained via slow recrystallization of **3** from acetonitrile and diethyl ether at ambient temperature.

Synthesis of *cis*-[Ru(4,4′-Cl_2bpy)$_2$(OH_2)$_2$](BArF)$_2$ (**4**, BArF = (3,5-(CF_3)$_2$$C_6H_3$)$_4$B)

A mixture of *cis*-[Ru(4,4′-Cl_2bpy)$_2$(OH_2)$_2$](CF_3SO_3)$_2$ (3, 0.100 g, 0.113 mmol) and NaBArF (0.202 g, 0.228 mmol) in water (50 ml) was heated at reflux for 2 h. The reaction mixture was cooled to room temperature and then filtered. The dark-red precipitate was washed three times with water (3 $\times$ 20 ml). The product was then dried under vacuum overnight. Yield = 0.210 g, 81%. ^{1}H NMR (CD_3CN, recorded after letting the solution sit for 1 h; see Discussion section): δ 9.16 (d, 2H, ^{3}J = 6.4 Hz, 4,4′-Cl_2bpy), 8.60 (d, 2 H, ^{4}J = 2.0 Hz, 4,4′-Cl_2bpy), 8.47 (d, 2 H, ^{4}J = 2.4 Hz, 4,4′-Cl_2bpy), 7.91 (dd, 2 H, ^{3}J = 6.0 Hz, ^{4}J = 2.0 Hz, 4,4′-Cl_2bpy), 7.70 (m, 16 H, BArF) 7.66 (m, 8 H, BArF), 7.56 (d, 2 H, ^{3}J = 6.8 Hz, 4,4′-Cl_2bpy), 7.34 (dd, 2 H, ^{3}J = 6.0 Hz, ^{4}J = 2.4 Hz, 4,4′-Cl_2bpy). ^{13}C NMR (CD_3CN): δ 162.7 (q, $^{1}J_{BC}$ = 50 Hz, C_{ipso}, BArF), 159.3, 158.6, 155.4, 154.5, 147.6, 147.1, 135.7 (C_o, BArF), 129.9 (m, C_m, BArF), 129.1, 128.2, 126.1, 125.7, 125.5 (q, $^{1}J_{CF}$ = 272 Hz, CF_3), 118.8 (C_p, BArF). ^{19}F NMR (CD_3CN): d −62.0 (BArF). Anal. Calcd. for (**4**.2H_2O) $C_{84}H_{44}B_2Cl_4F_{48}N_4O_4Ru$: C, 42.94; H, 1.89; N, 2.38. Found: C, 42.33; H, 1.97; N, 2.27.

Typical Procedure for Hydrogenation/Hydrogenolysis Activity Tests

Hydrogenation/hydrogenolysis activity tests were performed in a 125 ml stainless steel Parr reactor. In a typical reaction, solvent (10 ml), *n*-octane (20 μl, internal standard), substrate (1.21 mmol), catalyst (1 mol%), and a stirrer bar were charged into the reactor. After sealing the reactor, the air content was purged by flushing thrice with 51 atm hydrogen. The reactor was pressurized with hydrogen, immersed in a preheated silicone oil bath, and magnetically stirred (reaction conditions are described for each result and the stirring rate was ~450 rpm). The pressure inside the chamber was maintained at the specified pressure throughout the course of the reaction. After the appropriate reaction time, the reactor was cooled to room temperature, vented, and the products were analyzed quantitatively by GC-FID (and further identified by comparison of GC-MS data with corresponding data for authentic samples).

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