Inorganic Chemistry Cite This: Inorg. Chem. XXXX, XXX, XXX-XXX

Reduction of Dinitrogen to Ammonia and Hydrazine on Low-Valent **Ruthenium Complexes**

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S Supporting Information

ABSTRACT: The ruthenium(0) dinitrogen complexes [Ru- $(N_2)(PP_3^R)$] $[PP_3^R = P(CH_2CH_2PR_2)_3; R = Pr \text{ or } Cy] \text{ react}$ with triflic acid and other strong acids to afford mixtures of ammonia and hydrazine. In this reaction, Ru(0) is oxidized to Ru(II), and depending on the solvent, Ru(II) benzene or triflate complexes are isolated and characterized from the reactions with triflic acid as the final metal-containing products from the reaction. The Ru(II) products are isolated and reduced back to Ru(0) dinitrogen complexes providing a cycle for the reduction of coordinated dinitrogen.

$N_2H_5^+ + NH_4^+$ TfOH / C₆H₆ (OTf)₃ PR₂ Ru(0) base + reductant $R = {}^{i}Pr$, cyclohexyl Ru(II) + N₂

INTRODUCTION

There have been advances in the conversion of dinitrogen to ammonia or hydrazine in homogeneous solutions containing complexes of vanadium,¹ molybdenum,² chromium,³ iron,⁴⁻ and cobalt.⁸ Only recently has the chemical transformation of dinitrogen to ammonia been reported for complexes of ruthenium and osmium.⁵

While ruthenium is not found in biological systems, it is a component of the catalyst in some industrial processes for ammonia production such as the Kellogg Brown & Root Advanced Ammonia Process-Plus (KAAP-plus).¹⁰ Advances have also been reported in heterogeneous nitrogen fixation¹¹ as well as in nitrogen reduction by electrochemical means,¹² all utilizing ruthenium as the key reactive metal.

In an important set of experiments, Peters et al.⁹ have demonstrated that the Ru(0) and Os(0) complex $[M(SiP_3) N_2$]⁻ [where M = Ru or Os; SiP₃ = (Si(o-P(i Pr)₂)C₆H₄)₃] can reduce coordinated N₂ and the system also behaves catalytically to produce ammonia in the presence of acid and $Cp_{2}^{*}Co$ as a reducing agent.

In this paper, we report the chemistry of N_2 bound to Ru(0)complexes containing the bulky tetraphosphine ligands [Ru- $(N_2)(PP_3^R)$ { $PP_3^R = P(CH_2CH_2PR_2)_3$ [$R = {}^{i}Pr(1)$, Cy (2), or Ph (3)]} and demonstrate that the isopropyl- and cyclohexylsubstituted complexes produce ammonia and hydrazine upon treatment with triflic acid, TfOH (Scheme 1), in single-batch experiments.

Many of the metal complexes of the PP₃ ligands are known to act as catalysts in a range of different organic transformations.¹³ The PP₃ ligands constrain the geometry of octahedral complexes

Scheme 1. $Ru(PP_3)(N_2)$ Complexes Produce Hydrazine and Ammonia upon Treatment with TfOH



such that the remaining non-PP3 donor atoms must occupy adjacent sites in the coordination sphere.¹⁴ Our interest lies in the ruthenium PP₃ complexes containing dinitrogen as a ligand; little has been reported about the reactivity of the dinitrogen ligand itself.¹

For Ru(0) phosphines containing a N_2 ligand, there are often multiple possible competing reaction pathways (such as relatively facile substitution of N₂, reactions at the metal center, and reaction of the coordinated N_2). The rationale for testing PP₃-type ligands with bulky substituents on the terminal phosphorus donors was that this type of ligand partially encapsulates the metal and provides steric protection to shut down or slow down alternate reaction pathways at the metal center and to direct reaction to the coordinated dinitrogen.

We recently reported an investigation of the reaction of iron(0) dinitrogen complexes containing bidentate phosphine ligands, $[Fe(N_2)(PP)_2][PP = 1,2$ -bis(diethylphosphino)ethane

Received: October 10, 2018

(depe) or 1,2-bis(dimethylphosphino)ethane (dmpe)], with acid. In this study, we observed primarily protonation at the metal center to afford metal hydride complexes instead of reaction at the coordinated dinitrogen ligand.¹⁸ Treatment of $[Fe(N_2)(dmpe)_2]$ with trimethylsilyl triflate (TMSOTf), however, did result in reaction at dinitrogen to give NH4⁺ on subsequent treatment with acid.¹⁸ Tyler et al. have reported reaction of a related system, $[Fe(N_2)(DMeOPrPE)_2]$ {DMeOPrPE = 1,2-bis[di(methoxypropyl)phosphino]ethane}, with acids such as triflic acid (TfOH), HBF₄, and HCl to give ammonium in yields of $\leq 17\%$ with respect to Fe.^{5,7} More recently, Ashley has reported that treatment of $[Fe(N_2) (dmpe)_2$ with TfOH affords hydrazine in yields of $\leq 9.1\%$ while a similar treatment of $[Fe(N_2)(depe)_2]$ afforded $\leq 24\%$ hydrazine and ≤10.5% ammonia. Interestingly, treatment of the dinitrogen-bridged complex $[Fe(dmpe)_2]_2(\mu-N_2)$ with TfOH afforded only low yields of hydrazine and ammonia.¹⁹

 $Ru(N_2)(PP_3^{Ph})$ 3 was synthesized by treatment of the dichloro complex $[RuCl_2(PP_3^{Ph})]$ with KC₈ in toluene under an atmosphere of nitrogen (Scheme 2).





The ruthenium(0) dinitrogen complex containing the isopropyl-substituted PP₃ ligand $[Ru(N_2)(PP_3^{'pr})]$ 1 and the ¹⁵N₂-labeled analogue 1-¹⁵N₂ were synthesized from the chloro

complex [RuCl(PP₃^{'Pr})]⁺Cl⁻ as previously reported.¹⁵

 $Ru(N_2)(PP_3^{Cy})$ **2** was synthesized by reduction of the chloro complex $[RuCl(PP_3^{Cy})]^+X^-$ (X = Cl or BPh₄) with KC₈ by a modification of the previously reported method.¹⁷ $[RuH_2(PP_3^{Cy})]$ **4** was always formed as a minor byproduct in the reaction, an authentic sample of the dihydrido complex **4** synthesized independently, and the complex fully characterized (see the Supporting Information).

■ REACTION OF [RU(N₂)(PP₃^{'PR})] 1 WITH TFOH

Treatment of $[Ru(N_2)(PP_3^{Pr})]$ 1 with triflic acid in pentane immediately precipitates an oily maroon-brown solid that on dissolution in dimethyl sulfoxide- d_6 (DMSO- d_6) shows the distinctive three-line multiplet at 7.0 ppm in the ¹H nuclear magnetic resonance (NMR) spectrum characteristic of NH₄⁺. Routine quantification of NH₄⁺ by ¹H NMR spectroscopy was carried out using 1,4-dioxane and/or 1,3,5-trimethoxybenzene as the internal standard. NH₄⁺ was also quantified by ¹⁴N{¹H} NMR spectroscopy using tetramethylammonium iodide as an internal standard.

While NH_3 is relatively easily detected as NH_4^+ by NMR spectroscopy, the case for hydrazine is not so straightforward. Chemical exchange with H_2O and residual TfOH as well as quadrupolar broadening means that the ¹H NMR signal for $N_2H_5^+$ is typically broadened and usually overlaps with the signal for residual H_2O and TfOH. ¹⁴N NMR spectroscopy is also not useful for analyzing hydrazine because ¹⁴N is a quadrupolar nucleus and, in the absence of high symmetry around the ¹⁴N nucleus, quadrupolar relaxation makes the ¹⁴N resonance too

broad to be conveniently quantified. Tyler and Ashley have used colorimetric methods to quantify $N_2H_5^{+,7,20}$ while Mock has used a fitting program to quantify $N_2H_5^{+}$ by ¹H NMR.³

Our method of choice for quantification of both NH₃ and N₂H₄ is gas chromatography—mass spectrometry (GC–MS). NH₃ can be detected directly by GC–MS, and N₂H₄ was analyzed after derivatization with acetone to form acetone azine $[Me_2C=N-N=CMe_2, 2-(1-methylethylidene)$ hydrazone 2-propanone].²¹ Table 1 summarizes the reaction of different

Table 1. Yields of Ammonia and Hydrazine from Reactions of $[Ru(N_2)(PP_3R)]$ with Acids

	compound	acid		$^{\%}_{\mathrm{NH_4}^{+a}}$	$N_2H_5^{+a}$	$% N_2 converted^b$
1	1	TfOH	с	3	18	20
2	1	TfOH	d	2	18	19
3	2	TfOH	С	4	5	7
4	2	TfOH	d	<1	2	2
5	1	TfOH	с, е	7	17	21
6	1	LutHOTf	f	0	0	0
7	1	HCl	g	0	0	0
8	1	HBF_4	h	<1	0	<1
9	1	CF ₃ COOH	i	<1	0	<1
10	1	$H(OEt_2)_2^+$	С	2	0	1
11	1	$H(OEt_2)_2^+$	d	5	3	6
12	3	TfOH	i	0	0	0

^aYield in moles of NH_4^+ or $N_2H_5^+$ per mole of metal complex as quantified by GC. ^bPercentage of complexed dinitrogen from the starting material that ends up as NH_4^+ or $N_2H_5^+$ (calculated as half % yield $NH_4^+ + \%$ yield of $N_2H_5^+$). ^cPentane solvent. ^dBenzene solvent. ^eWith 6 equiv of Cp*₂Co. ^fTHF solvent. ^gPentane or benzene with ether. ^hPentane with ether. ⁱPentane or benzene solvent.

Ru(0) PP₃ complexes containing bound N₂ with a range of acids. In the reaction of complex 1 with TfOH in pentane, NH₃ was formed in approximately 3% yield and N₂H₄ was formed in approximately 18% yield (entry 1, Table 1).

The combined yields of NH_3 and N_2H_4 are best expressed as "% N_2 converted", which reveals the percentage of complexed dinitrogen from the starting material that is converted to reduced products.¹⁹ We note that this measure of % N_2 converted does not take into account the electrons required to fuel the production of NH_3 and N_2H_4 products.

In batch reactions (with no added reducing agents), all of the required electrons must derive from the low-oxidation state metals in the starting materials. In the reaction of complex 1 with TfOH in pentane as the solvent, the $\% N_2$ converted was 20%.

Treatment of the ¹⁵N-labeled analogue $[Ru(^{15}N_2)(PP_3^{i}Pr)]$ 1-¹⁵N₂ with triflic acid in pentane afforded ¹⁵N-labeled ammonium as observed in the ¹H NMR spectrum as a doublet with a ¹J_{NH} of 72 Hz at 7.04 ppm. Signals for ammonium and hydrazinium at δ 358.8 and -328.7, respectively, are observed in the ¹⁵N{¹H} NMR spectrum.

The reaction of $[Ru(N_2)(PP_3^{i}Pr)]$ 1 with TfOH in benzene as the solvent afforded hydrazine (as $N_2H_5^+$) as the major nitrogencontaining product (approximately 18% yield) with only a minor amount of ammonia (approximately 2%) (entry 2, Table 1) and thus a % N_2 converted of 19% similar to that for the reaction in pentane.

At the end of the reaction, the main Ru-containing product was the η^6 -benzene complex $[Ru^{II}(\eta^6$ -benzene)(κ^3 - PP₃ⁱPrH)]³⁺(OTf⁻)₃ 5. An X-ray crystal structure of complex 5 (Figure 1) was obtained from crystals grown from a solution of



Figure 1. ORTEP plot of $[Ru(\eta^6-benzene)(\kappa^3-PP_3^{ipr}H)]^{3+}$ **5** (50% ellipsoid probability; three triflate counterions, dichloromethane solvate, and hydrogen atoms excluded for the sake of clarity). Selected bond lengths (angstroms) and angles (degrees): Ru–P3, 2.374(2); Ru–P1, 2.3019(19); Ru–P2, 2.3771(19); Ru–C, 2.282(6)–2.303(6); C–C, (benzene) 1.366(10)–1.411(10); P3–Ru–P2, 97.29(7); P1–Ru–P3, 82.02(8); P1–Ru–P2, 81.31(6).

dichloromethane layered with diethyl ether. There are no known X-ray crystal structures for Ru arene complexes containing three additional phosphorus ligands; however, there are structures of Ru benzene complexes containing two phosphorus ligands²² or two phosphorus ligands with an additional ligand such as hydride,²³ methyl,²⁴ chloride,²⁵ acetonitrile,²⁶ or substituted ethylene²⁷ that are available for comparison.

The Ru–P bond lengths in complex **5** range from 2.3020 to 2.3772 Å, which are within the range of the corresponding bond lengths in $[\text{Ru}(\eta^6\text{-benzene})(\text{P}_2)\text{X}]$ complexes (2.176-2.402 Å). The Ru–C bond lengths for complex **5** range from 2.282 to 2.303 Å, which are also within the range of those of the analogous bonds in $[\text{Ru}(\eta^6\text{-benzene})(\text{P}_2)\text{X}]$ complexes (2.201-2.353 Å).

■ REACTION OF [RU(N₂)(PP₃^{CY})] 2 WITH TFOH

The reaction of $[Ru(N_2)(PP_3^{Cy})]$ **2** with TfOH in pentane afforded small amounts of NH_4^+ (~4%) and $N_2H_5^+$ (~5%) (entry 3, Table 1), and the total % N_2 converted was approximately 7%. Only trace amounts of NH_4^+ (<1%) and $N_2H_5^+$ (2%) were obtained when the reaction was carried out in benzene (entry 4, Table 1). The yields of NH_3 and N_2H_4 were consistently lower for $[Ru(N_2)(PP_3^{Cy})]$ **2** than those for the analogous complex containing isopropyl substituents {[Ru-($N_2)(PP_3^{'Pr})$] **1**}, highlighting the fact that even a small change in the ligand structure does have a significant impact on the course of the reaction.

Unlike the reaction in benzene, in the reaction of $[Ru(N_2)-(PP_3^{Cy})]$ **2** with TfOH in pentane, which is a noncoordinating solvent, two Ru-containing products are observed at the end of the reaction. One product is the Ru(II) triflate complex $[Ru(OTf)(PP_3^{Cy})]^+$ **6** whose structure was determined by X-ray crystallographic analysis (Figure 2).

The geometry about the Ru center is a distorted square pyramid with the central phosphorus (P4), two terminal phosphines (P1 and P3), and the triflate ligand as the square base of the pyramid with the remaining terminal phosphine (P2) at the apex of the pyramid. The Ru–O bond length of 2.2572 Å is within the range reported for similar Ru triflate complexes $(2.231-2.411 \text{ Å})^{.28}$ The ${}^{31}P{}^{1}H{}$ NMR spectrum of triflate complex 6 displays a quartet at 144.5 ppm for the central phosphorus atom and a broad resonance at 64.5 ppm for the three terminal phosphorus atoms. Only one signal at -77.8 ppm



Figure 2. ORTEP plot of $[Ru(OTf)(PP_3^{Cy})]^+$ 6 (50% ellipsoid probability; triflate counterion, and hydrogen atoms excluded for the sake of clarity). Selected bond lengths (angstroms) and angles (degrees): Ru-P1, 2.3867(5); Ru-P2, 2.2749(5); Ru-P3, 2.4127(5); Ru-P4, 2.2271(5); Ru-O1a, 2.2572(14); P1-Ru-P3, 153.925(18); P2-Ru-P1, 96.524(18); P2-Ru-P3, 103.466(18); P4-Ru-P1, 82.939(18); P4-Ru-P2, 83.839(18); P4-Ru-P3, 82.748(19); P4-Ru-O1a, 173.24(4); O1a-Ru-P1, 99.87(4); O1a-Ru-P2, 101.85(4); O1a-Ru-P3, 92.31(4).

in the 19 F NMR spectrum was observed for the triflate anions even at a low temperature (193 K), indicating rapid exchange between the coordinated and uncoordinated triflate anions in solution.

While we have not been able to isolate and fully characterize the second product, it is probably a Ru(II) triflate complex containing a κ^3 -coordinated PP₃ ligand with a protonated pendant phosphine with two coordinated triflate anions, [Ru(OTf)₂(κ^3 -PP₃^{Cy}H)]⁺(OTf⁻) 7. The ³¹P NMR shifts at δ 109.5, 78.0, and 28.5 are consistent with this formulation, and the single ¹⁹F NMR signal at δ –76.8 for the triflates indicates rapid anion exchange.

In the reaction of $[Ru(N_2)(PP_3^{Cy})]$ **2** with benzene as the solvent, two Ru-containing products were formed at the end of the reaction: the triflate complex **6** and the benzene complex $[Ru(\eta^6\text{-benzene})(\kappa^3\text{-}PP_3^{Cy}H)]^{3+}$ **8** that is an analogue of complex **5**.



Crystals of 8 were formed preferentially from a solution of the mixture in dichloromethane and diethyl ether, and the complex was characterized by X-ray crystallography (see the Supporting Information).

The isolation of Ru(II) complexes **5–8** at the end of reaction sequence is important because these complexes all indicate that the oxidation of the Ru(0) starting materials to Ru(II) products provides the electrons necessary to fuel the reduction of the coordinated N_2 to $N_2H_5^+$ and NH_4^+ in batch reactions with no added reductants.

When any one of the Ru(II) complexes (5, 6, or 7) is treated with excess KC_8 or with $Cp*_2Co$ (i.e., strong reductants) under N_2 , each gives the respective starting Ru(0) dinitrogen complex 1 or 2. While the reduction is not quantitative, this reaction does open up the possibility that a catalytic cycle could be devised in which Ru(0) is oxidized to Ru(II) that could then be cycled back to Ru(0) with an appropriate reductant to re-bind more N_2 (Scheme 3).

Scheme 3. Reaction Cycle for Reduction of Coordinated $\rm N_2$ to Ammonia and Hydrazine



When the reaction of $[Ru(N_2)(PP_3^{i_Pr})]$ 1 with TfOH in pentane was repeated with an added 6 equiv of decamethylcobaltocene (Cp*₂Co) as a potential external electron source, we observed no significant increases in the yields of ammonia or hydrazine (entry 5, Table 1). Cp*₂Co is not an effective external source of electrons for this reaction at least under the reaction conditions we have explored so far, and this probably reflects the fact that Cp*₂Co reacts rapidly with the strong acid in the reaction mixture.

REACTION OF [RU(N₂)(PP₃^{'PR})] WITH OTHER ACIDS/ELECTROPHILES

The dinitrogen complex $[Ru(N_2)(PP_3^{'Pr})]$ **1** has been previously reported to react preferentially at the metal center to form the Ru(II) hydrido dinitrogen complex $[RuH(N_2)(PP_3^{'Pr})]^+BF_4^- 9$ upon protonation with mild acids such as 2,6-lutidinium tetrafluoroborate.¹⁵ We repeated this protonation reaction with lutidinium triflate (LutHOTf) in THF, and no NH₄⁺ or N₂H₅⁺ was formed (entry 6, Table 1). Similarly when complex 9 was treated with triflic acid, neither NH₄⁺ nor N₂H₅⁺ was formed, so complex 9 is not itself a species on the reaction path from metal-bound N₂ to N₂H₅⁺ or NH₄⁺.

So while we know that $[Ru(N_2)(PP_3^{'Pr})]$ 1 reacts with weaker acids to protonate on the metal, it is apparent that stronger acids, such as triflic acid, react preferentially at the coordinated N₂ leading eventually to N₂ reduction products (Scheme 4). There are multiple sites, probably competing, for reaction of the Ru(0) dinitrogen complexes with H⁺.

Treatment of $[Ru(N_2)(PP_3^{'Pr})]$ **1** with HCl in either pentane or benzene produced neither NH₄⁺ nor N₂H₅⁺ (entry 7, Table 1). Only trace amounts of NH₄⁺ (<1%) were formed upon treatment of **1** with acids such as HBF₄ and trifluoroacetic acid,

Scheme 4. Competing Reaction Pathways for the Reaction of $[Ru(N_2)(PP_3^{'Pr})]$ 1 with Acids



although no $N_2H_5^+$ was detected in any case (entries 8 and 9, Table 1).

Significant amounts of NH₄⁺ and N₂H₅⁺ were detected only when TfOH was used as the proton source. The protonation reaction with oxonium acid $[H(OEt_2)_2][B(C_6F_5)_4]$ in pentane or benzene afforded NH₄⁺ in approximately 2 and 5% yields, respectively (entries 10 and 11, respectively, Table 1). Interestingly, no N₂H₅⁺ was detected in the reaction with pentane as the solvent, while N₂H₅⁺ was formed in a low yield in the reaction with benzene as the solvent.

Treatment of $[Ru(N_2)(PP_3^{Ph})]$ 3 with TfOH did not produce $N_2H_5^+$ or NH_4^+ under the reaction conditions (entry 12, Table 1).

There is a slow but complete conversion of $[Ru(N_2)(PP_3^{'Pr})]$

1 to the dihydrido complex²⁹ $[RuH_2(PP_3^{i_{Pr}})]$ 10 under an atmosphere of hydrogen gas over several days with no formation of either NH₄⁺ or N₂H₅⁺. Hydrogen gas alone is not able to produce ammonia or hydrazine by the reduction of coordinated dinitrogen in these systems. The slow formation of 10 from 1 is not surprising because the loss of N₂ from 1 generates an electron-deficient $[Ru^0(PP_3^{i_{Pr}})]$ species and oxidative addition of H₂ gives rise to 10.

SUMMARY AND CONCLUSIONS

In this work, we have synthesized a series of $[\text{Ru}(N_2)(\text{PP}_3^R)]$ complexes $[\text{PP}_3^R = \text{P}(\text{CH}_2\text{CH}_2\text{PR}_2)_3$; $R = {}^{i}\text{Pr}$, Cy, or Ph] and treatment of the isopropyl- and cyclohexyl-substituted complexes with acid afforded hydrazine and/or ammonia in yields of ≤ 18 and $\leq 5\%$, respectively, with the highest nitrogen conversion from $[\text{Ru}(N_2)(\text{PP}_3^{\ ipr})]$.

As a high-level generalization, the $P_4Ru(0)$ core can both bind and activate dinitrogen, and in the presence of a strong acid such as TfOH, Ru(0) is a sufficiently strong reducing agent to reduce the coordinated dinitrogen.

In this system, because we observe hydrazine and ammonia as the reduction products, it appears that the reaction involves a stepwise metal-mediated reduction of a coordinated N_2 probably through a diazene, to hydrazine and eventually ammonia. It is also clear that in batch reactions of this type, the reaction is limited by the availability of electrons and the observed distribution of the hydrazine and ammonia products probably reflects the progress of the reduction as the supply of electrons is exhausted.

While we examined a range of different acids, triflic acid provided the highest conversion of coordinated N_2 to reduced products, Weaker acids afforded no (or negligible amounts of) hydrazine or ammonia, and a stronger acid is probably required to protonate a weakly activated coordinated dinitrogen and trigger electron transfer from the metal to nitrogen.

It is well-known that $Ru(0)-N_2$ complexes can be protonated at the metal center to give $[H-Ru(II)-N_2]^+$ complexes particularly with weaker acids. We isolated $[H-Ru(II)-N_2]^+$ complexes and demonstrated that they did not produce NH_4^+ or $N_2H_5^+$ when treated with strong acids, so while $[H-Ru(II)-N_2]^+$ complexes may be formed by the reaction of $Ru(0)-N_2$ complexes with acids, these compounds are not on the pathway for reduction of coordinated N_2 to NH_4^+ and $N_2H_5^+$.

The reduction of dinitrogen coordinated to Ru(0) is fueled by oxidation of Ru(0) to Ru(II), and in this work, Ru(II)complexes with coordinated solvent (benzene) and Ru(II) triflate complexes were isolated and characterized as the final Ru-containing products.

The fact that we have identified stable Ru(II) complexes as products is important because we have demonstrated that these complexes can be treated with an appropriate reductant under N_2 to re-form the starting Ru(0) dinitrogen complexes. This reaction sequence does open up the possibility that a catalytic system could be devised in which Ru(0) is oxidized to Ru(II)that could then be recycled with an appropriate reductant back to Ru(0) to re-bind more N_2 .

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b02850.

Detailed experimental procedures for the synthesis of all new compounds; experimental procedures for the reaction of metal complexes with acids; quantification of hydrazine and ammonia by GC–MS; crystallographic data for $[\text{RuH}_2(\text{PP}_3^{\text{Cy}})]$ **4**, $[\text{Ru}(\eta^6\text{-benzene})(\kappa^3\text{-}\text{PP}_3^{\text{i}}\text{PrH})]^{3+}(\text{OTf}^-)_3$ **5**, $[\text{Ru}(\text{OTf})(\text{PP}_3\text{Cy})]^+(\text{OTf}^-)$ **6**, and $[\text{Ru}(\eta^6\text{-benzene})(\kappa^3\text{-PP}_3\text{CyH})]^{3+}(\text{OTf}^-)_3$ **8** (PDF)

Accession Codes

CCDC 1570095–1570098 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, or 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.

ACKNOWLEDGMENTS

The authors gratefully acknowledge UNSW for funding. The authors also thank Dr. Martin Bucknall (Bioanalytical Mass Spectrometry Facility, Mark Wainwright Analytical Centre, University of New South Wales) and Dr. Samantha Furfari (School of Chemistry, University of New South Wales) for their assistance with GC–MS analysis. The authors also thank Mr. Thomas O. Peters for assistance with the synthesis of compound **4**.

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