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Article

# Synthesis of Ruthenium Carbonyl Complexes with Phosphine or Substituted Cp Ligands, and Their Activity in the Catalytic Deoxygenation of 1,2-Propanediol

**Prasenjit Ghosh,**[†,∥] **Paul J. Fagan,**[§] **William J. Marshall,**[§] **Elisabeth Hauptman,**[§,⊥] **and R. Morris Bullock***[,†,‡]

[†]*Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973-5000,* [‡]*Chemical and Materials Sciences Division, Pacific Northwest National Laboratory, P.O. Box 999, K2-57, Richland, Washington 99352, and* [§]*Central Research and Development, E. I. DuPont de Nemours & Co. Inc., Experimental Station, Wilmington, Delaware 19880.* [∥] *Current address: Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India.* [⊥]*Current address: Firmenich, Inc., P.O. Box 5880, Princeton, New Jersey 08543*

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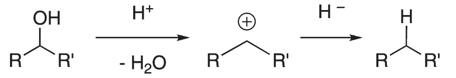
A ruthenium hydride with a bulky tetra-substituted Cp ligand, $(Cp^{iPr_4})Ru(CO)_2H$ ($Cp^{iPr_4} = C_5(i\text{-}C_3H_7)_4H$) was prepared from the reaction of $Ru_3(CO)_{12}$ with 1,2,3,4-tetraisopropylcyclopentadiene. The molecular structure of $(Cp^{iPr_4})Ru(CO)_2H$ was determined by X-ray crystallography. The ruthenium hydride complex $(C_5Bz_5)Ru(CO)_2H$ ($Bz = CH_2Ph$) was similarly prepared. The Ru−Ru bonded dimer, $[(1,2,3\text{-trimethylindenyl})Ru(CO)_2]_2$, was produced from the reaction of 1,2,3-trimethylindene with $Ru_3(CO)_{12}$, and protonation of this dimer with HOTf gives $\{[(1,2,3\text{-trimethylindenyl})Ru(CO)_2]_2(\mu\text{-H})\}^+OTf^-$. A series of ruthenium hydride complexes $CpRu(CO)(L)H$ [$L = P(OPh)_3$, $PCy_3$, $PMe_3$, $P(p\text{-}C_6H_4F)_3$] were prepared by reaction of $Cp(CO)_2RuH$ with added L. Protonation of $(Cp^{iPr_4})Ru(CO)_2H$, $Cp^*Ru(CO)_2H$, or $CpRu(CO)[P(OPh)_3]H$ by HOTf at −80 °C led to equilibria with the cationic dihydrogen complexes, but $H_2$ was released at higher temperatures. Protonation of $CpRu[P(OPh)_3]_2H$ with HOTf gave an observable dihydrogen complex, $\{CpRu[P(OPh)_3]_2(\eta^2\text{-}H_2)\}^+OTf^-$ that was converted at −20 °C to the dihydride complex $\{CpRu[P(OPh)_3]_2(H)_2\}^+OTf^-$. These Ru complexes serve as catalyst precursors for the catalytic deoxygenation of 1,2-propanediol to give *n*-propanol. The catalytic reactions were carried out in sulfolane solvent with added HOTf under $H_2$ (750 psi) at 110 °C.

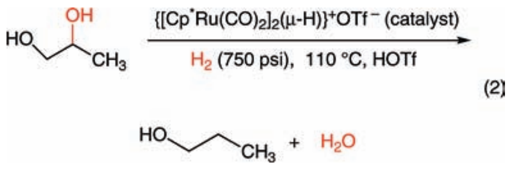
## Introduction

Catalytic reactions that convert biomass to useful chemicals or fuels are needed to effectively and efficiently use abundant, renewable resources.[1] Selective functionalization of C−H bonds is needed to convert hydrocarbons like methane to functionalized organic compounds.[2] In contrast, the conversion of carbohydrates to higher-value chemicals usually requires the *removal* of functionality, since sugars typically are "overfunctionalized,"[3] with an OH group on nearly every carbon atom. As shown in eq 1, one approach to deoxygenation is protonation, loss of water, and hydride transfer, thereby converting an OH to H. Making such a reaction catalytic requires metal complexes that can deliver protons and hydrides, and a metal species that can heterolytically cleave $H_2$ to regenerate the catalyst. As a model for the deoxygenation of polyols and more complex carbohydrates, we have studied the catalytic deoxygenation of diols. The ruthenium complex $\{[Cp^*Ru(CO)_2]_2(\mu\text{-H})\}^+OTf^-$ ($Cp^* = \eta^5\text{-}C_5Me_5$; $OTf = OSO_2CF_3$) catalyzes the selective deoxygenation of 1,2-propanediol to *n*-propanol (eq 2) in sulfolane solvent at 110 °C under $H_2$ with added HOTf.[4,5] A key step in the conversion of the hydride-bridged bimetallic catalyst precursor to the reactive mononuclear ruthenium dihydrogen complex is the reaction with $H_2$, as shown in Scheme 1. Under the reaction



(1)

R, R' = $CH_3$, $CH_2OH$, $(CHOH)_nCH_2OH$, . . .



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*To whom correspondence should be addressed. E-mail: morris.bullock@pnl.gov.

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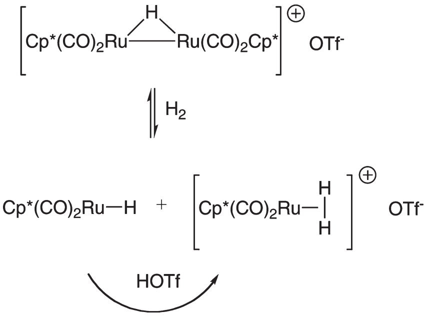
**Scheme 1**



conditions, protonation of the neutral ruthenium hydride produces the cationic dihydrogen complex[6] such that the overall reaction converts *both* of the Ru fragments to the highly acidic dihydrogen complex $[Cp^*Ru(CO)_2(\eta^2\text{-}H_2)]^+OTf^-$.

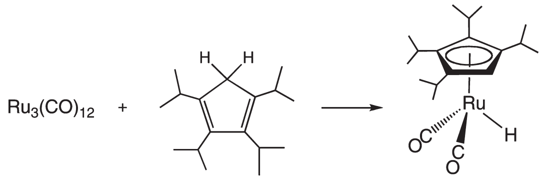
Our studies[4,5] focused on the $Cp^*Ru(CO)_2$ system, and we have expanded the scope to examine ligands with a wider range of steric and electronic properties. Since our studies had shown that the bimetallic catalyst precursor $\{[Cp^*Ru\text{-}(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$ had to be converted to mononuclear Ru complexes during the reaction, we thought that Ru complexes with bulky ligands might be more likely to exist as mononuclear species in the catalyst resting state, and hence might exhibit improved reactivity. Mononuclear complexes such as $[cis\text{-}Ru(6,6'\text{-}Cl_2\text{-}2,2'\text{-}bipy)_2\text{-}(OH_2)_2]^{+2}$ have been shown to catalyze the deoxygenation of diols; alcohols were formed in most cases but in some cases further hydrogenation to alkanes was observed.[7]

Our studies[4,5] showed that $\{[Cp^*Ru(CO)_2]_2(\mu\text{-}H)\}^+$ can be deprotonated by water to give $[Cp^*Ru(CO)(\mu\text{-}CO)]_2$, which is catalytically inactive. Since water is produced in the deoxygenation reaction, deprotonation of $\{[Cp^*Ru\text{-}(CO)_2]_2(\mu\text{-}H)\}^+$ is a pathway for catalyst deactivation, though carrying out the reactions with added HOTf helps to diminish this pathway. Complexes with stronger donor ligands should be less acidic, so that deprotonation of their hydrides should be less favorable. Angelici and co-workers reported extensive studies of the enthalpies of protonation of a series of metal complexes by HOTf.[8] Calorimetric studies on protonation of Ru−Ru bonded dimers showed that $[Cp^*Ru(CO)(\mu\text{-}CO)]_2$ is more basic than $[CpRu(CO)_2]_2$.[9] In this work we have prepared complexes containing tetra- and penta-substituted Cp ligands ($Cp^{iPr_4}$ and $C_5Bz_5$) that are more sterically demanding than Cp*. We compare these to the catalytic activity obtained with $Tp^*Ru(CO)_2H$ (Tp* = hydridotris(3,5-dimethylpyrazolyl). In addition, we synthesized CpRu(CO)(L)H (L = phosphine or phosphite) Ru complexes that have a higher electron density at the metal compared to $CpRu(CO)_2H$. This electronic property should decrease the acidity of the dihydrogen complex, as well as that of the bridging hydride complexes that are analogues of $\{[Cp^*Ru(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$. We report here the synthesis and characterization of several new Ru hydride and Ru−Ru dimer complexes, studies of their protonation, and an evaluation of their activity in the catalytic deoxygenation of 1,2-propanediol.

## Results and Discussion

**Synthesis and Characterization of ($Cp^{iPr_4}$)Ru(CO)$_2$H.** While unsubstituted $\eta^5\text{-}C_5H_5$ (Cp) ligands and pentamethyl substituted $\eta^5\text{-}C_5Me_5$ (Cp*) ligands are familiar in organometallic chemistry and homogeneous catalysis, numerous substituted Cp ligands have also been prepared,[10] including some that have very bulky substituents.[11] We synthesized ($Cp^{tBu_2}$)Ru(CO)$_2$H, but it was obtained as an impure oil, so we sought a derivative that would be available in pure form, preferably as a solid. Sitzmann reported the synthesis of 1,2,3,4-tetraisopropylcyclopentadiene ($C_5(i\text{-}C_3H_7)_4H_2$, abbreviated as $HCp^{iPr_4}$) and some Fe and Mo complexes with the $Cp^{iPr_4}$ ligand.[12] Hanusa and co-workers synthesized a series of stable calcium complexes with $Cp^{iPr_4}$ ligands.[13,14]

$CpRu(CO)_2H$ can be prepared by the reaction of $Ru_3(CO)_{12}$ with cyclopentadiene in refluxing heptane.[15] Using similar conditions, we found that the ruthenium hydride ($Cp^{iPr_4}$)Ru(CO)$_2$H can be synthesized by reacting $HCp^{iPr_4}$ with $Ru_3(CO)_{12}$ in refluxing heptane, leading to the isolation of ($Cp^{iPr_4}$)Ru(CO)$_2$H in 45% yield as a yellow solid (eq 3). The IR bands for the CO ligands appear at at slightly higher energy in ($Cp^{iPr_4}$)Ru(CO)$_2$H (2015, 1956 cm$^{-1}$, hexane solution) compared to those of $Cp^*Ru(CO)_2H$ (2013, 1955 cm$^{-1}$, hexane solution), indicating that the $Cp^{iPr_4}$ ligand is very slightly less electron-donating than Cp*. For comparison, the $\nu$(CO) bands of $CpRu(CO)_2H$ in heptane appear at substantially higher energy, 2033 and 1973 cm$^{-1}$, as expected in view of the unsubstituted Cp being a poorer electron donor than the alkyl-substituted Cp ligands. Similar results were reported for tungsten methyl complexes, in which the energy of the CO bands of ($Cp^{iPr_4}$)W-(CO)$_3$CH$_3$ (2010.1, 1919.2 cm$^{-1}$, pentane solution) appear at slightly higher energy than those of ($C_5Et_5$)-W-(CO)$_3$CH$_3$ (2008.3, 1917.3 cm$^{-1}$, pentane solution).[16] IR band positions of CO ligands of ($C_5Me_5$)Mn(CO)$_3$ versus



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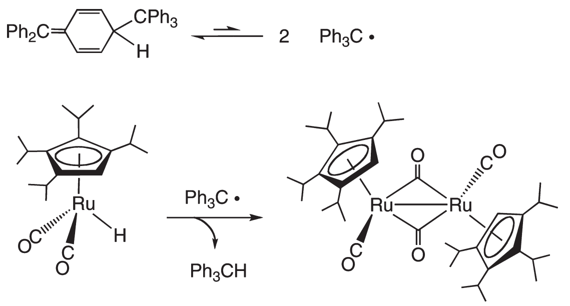
**Scheme 2**



$(C_5Et_5)Mn(CO)_3$ in heptane differ by no more than 2 $cm^{-1}$.[17] These comparisons suggest that for complexes with Cp ligands substituted with saturated alkyl groups, the electron density on the metal is influenced more by the *number* of alkyl groups than by their *identity* (Me vs Et vs $^{i}Pr$).

The ruthenium hydride $(Cp^{iPr_4})Ru(CO)_2H$ is readily converted to the Ru−Ru bonded dimer, $[(Cp^{iPr_4})Ru(CO)(\mu\text{-}CO)]_2$, through reaction with Gomberg's dimer,[18] which exists in equilibrium with trityl radical, $Ph_3C\bullet$ (Scheme 2). Following hydrogen atom transfer from ruthenium to carbon,[19] the metal-centered radicals dimerize, producing $[(Cp^{iPr_4})Ru(CO)(\mu\text{-}CO)]_2$.

**Molecular Structure of $(Cp^{iPr_4})Ru(CO)_2H$.** The molecular structure of the $(Cp^{iPr_4})Ru(CO)_2H$ complex has been determined by X-ray diffraction (Figure 1). Crystallographic data is given in Table 1. The hydride ligand was located and refined. The Ru−H distance found in the X-ray structure was 1.531(37) Å, though this may not be accurate since distances determined by X-ray can be as much as 0.2−0.3 Å shorter than the distances determined more accurately by neutron diffraction.[20,21] For comparison, the Ru−H distance found by neutron diffraction of $CpRu(PMe_3)_2H$ is 1.630(4) Å.[21]

The overall structure is similar to $(C_5Me_4Et)Ru(CO)_2Br$[22] and the cationic complex $[Cp^*Ru(CO)_2(OH_2)]^+OTf^-$.[23] Very small differences were found in the Ru−C distances in $CpRu(CO)_2Br$ compared to $(C_5Me_4Et)Ru(CO)_2Br$[22] despite the steric and electronic differences in Cp versus $C_5Me_4Et$. The $(CH_3)_2C$ plane of the *i*-Pr groups of $(Cp^{iPr_4})Ru(CO)_2H$ are roughly perpendicular to the substituted Cp ring, as found in $(Cp^{iPr_4})_2Ca$[13] and $(Cp^{iPr_4})W(CO)_3CH_3$.[16]

**Synthesis of $(C_5Bz_5)Ru(CO)_2H$.** The ruthenium hydride complex $(C_5Bz_5)Ru(CO)_2H$ (Bz = $CH_2Ph$) was synthesized from the reaction of $C_5Bz_5H$ with $Ru_3(CO)_{12}$, analogous to the method shown in eq 3. The reaction was very slow, requiring about 10 days in refluxing heptane, and $(C_5Bz_5)Ru(CO)_2H$ was isolated in 24% yield. The IR bands for the CO ligands appeared at 2020 and 1963 $cm^{-1}$, placing them roughly at the midpoint between the energies found for $CpRu(CO)_2H$ and $Cp^*Ru(CO)_2H$, indicating that the five benzyl groups on the substituted Cp ligand donate significantly less electron density to the metal compared to the five $CH_3$ groups in the Cp* ligands. This conclusion is in agreement with

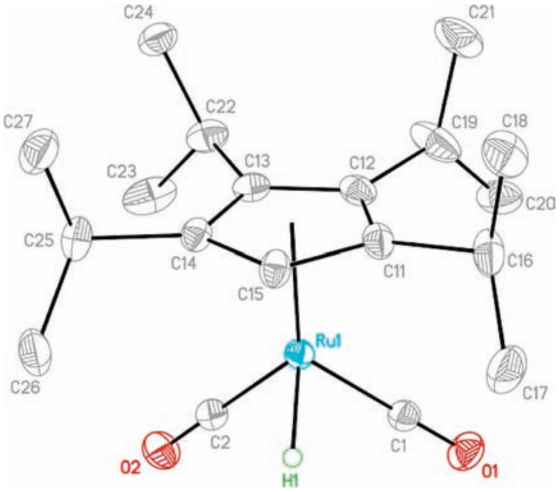


**Figure 1.** Molecular structure of $(Cp^{iPr_4})Ru(CO)_2H$ (30% probability ellipsoids). Hydrogen atoms are omitted except for the hydride ligand. Selected bond lengths (Å): Ru(1)−C(1) 1.865(2); Ru(1)−C(2) 1.872(2); Ru(1)−C(11) 2.252(2); Ru(1)−C(12) 2.288(2); Ru(1)−C(13) 2.291(2); Ru(1)−C(14) 2.263(2); Ru(1)−C(15) 2.244(2). Selected bond angles (deg): Ru(1)−C(1)−O(1) 179.4(2); Ru(1)−C(2)−O(2) 178.3(2); C(1)−Ru-C(2) 90.71(10). Disordered positions for one of the isopropyl groups are not shown.

**Table 1.** Crystal Data Collection and Refinement Parameters for $(Cp^{iPr_4})Ru(CO)_2H$

| | |
|---|---|
| empirical formula | $C_{19}H_{30}O_2Ru$ |
| FW | 391.50 |
| cryst. color, form | colorless, parallelepiped |
| cryst system | monoclinic |
| space group | *C*2/*c* |
| *a* (Å) | 20.8773(12) |
| *b* (Å) | 16.1646(9) |
| *c* (Å) | 14.3727(9) |
| α (deg) | 90. |
| *β* (deg) | 127.498(1) |
| *γ* (deg) | 90 |
| *V* ($Å^3$) | 3848.2(4) |
| *Z* | 8 |
| density ($g/cm^3$) | 1.351 |
| abs. *μ* ($mm^{-1}$) | 0.820 |
| *F*(000) | 1632 |
| cryst size (mm) | 0.46 × 0.32 × 0.32 |
| temp (°C) | −100 |
| scan mode | Ω |
| detector | Bruker-CCD |
| $\theta_{max}$ (deg) | 28.30 |
| no. obsrvd. refs | 11704 |
| no. uniq. refs | 4416 |
| $R_{merge}$ | 0.0361 |
| no. params | 228 |
| GoF[b] | 1.06 |
| R indices [$I > 2\sigma(I)$] | wR2 = 0.078, R1 = 0.032 |
| R indices (all data)[a] | wR2 = 0.082, R1 = 0.038 |
| Max min diff peak, hole ($e/Å^3$) | 0.60, −0.76 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$. [b] $GoF = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}$.

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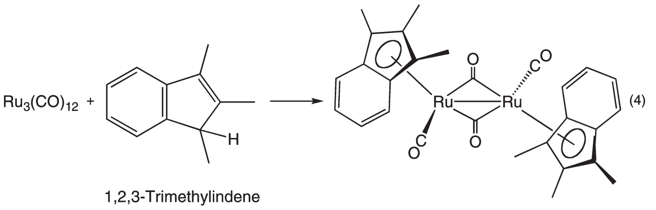
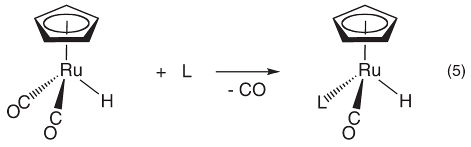
the energies of IR bands reported by Rausch and co-workers[24] for ($\eta^4$-$C_5Bz_5H$)Fe$(CO)_3$ versus ($\eta^4$-$C_5H_6$)Fe$(CO)_3$. In contrast, Martins and co-workers synthesized ($C_5Bz_5$)Mo$(CO)_3$H and found that its CO bands were at lower energy than those for Cp*Mo$(CO)_3$H.[25] Molybdenum complexes with $C_5Bz_5$ ligands have been used in the catalytic epoxidation of olefins[26] and in the catalytic ionic hydrogenation of ketones.[27] Astruc and co-workers reported electrochemical data for iron compounds which showed that $C_5Bz_5$ was not as electron-donating as Cp*.[28]

**Synthesis of [(1,2,3-Trimethylindenyl)Ru(CO)($\mu$-CO)]$_2$.** Metal complexes with indenyl ligands can show significantly different reactivity compared to Cp ligands. For example, catalysis of tail-to-tail dimerization of methyl acrylate was substantially faster with a Rh catalyst with a trimethylindenyl ligand compared to an analogous catalyst with a Cp* ligand.[29] While the divergent reactivity of Cp/Cp* versus indenyl ligands is often attributed to the much higher propensity for ring-slippage reactions of indenyl ligands,[30] it is not clear that ring-slippage is involved in the catalysis of this Rh reaction, so the different steric and electronic properties of indenyl versus Cp ligands can affect catalysis in multiple ways. Repeated attempts to prepare (1,2,3-trimethylindenyl)Ru$(CO)_2$H were made (analogous to eq 3) by refluxing 1,2,3-trimethylindene with $Ru_3(CO)_{12}$ in heptane, but this route was not successful. Methyl *iso*-butyl ketone was chosen as an alternative solvent based on a report indicating higher yields of [($\eta^5$-indenyl)Ru(CO)($\mu$-CO)]$_2$ being obtained in that solvent compared to heptane.[31] When 1,2,3-trimethylindene was refluxed with $Ru_3(CO)_{12}$ in methyl *iso*-butyl ketone for 4 h, the ruthenium dimer [(1,2,3-trimethylindenyl)Ru(CO)($\mu$-CO)]$_2$ was produced (eq 4). It was purified and isolated as an analytically pure yellow solid in 42% yield. The IR bands of [(1,2,3-trimethylindenyl)Ru(CO)($\mu$-CO)]$_2$ in $CH_2Cl_2$ appear at 1941 (terminal CO) and 1771 cm$^{-1}$ (bridging CO), which are significantly higher energies than those found in the same solvent for [Cp*Ru(CO)($\mu$-CO)]$_2$ (1925, 1744 cm$^{-1}$). A study of the electronic spectra and photoelectron spectroscopy of a series of rhodium complexes showed that the order of electron donating ability is 1,2,3-trimethylindenyl>indenyl>Cp.[32] The ruthenium dimer [(1,2,3-trimethylindenyl)Ru(CO)($\mu$-CO)]$_2$ was protonated by HOTf in dichloromethane to give the bridging hydride complex {[(1,2,3-trimethylindenyl)Ru$(CO)_2$]$_2$($\mu$-H)}$^+$ OTf$^-$.



**Synthesis of CpRu(CO)(L)H.** A series of ruthenium hydride complexes CpRu(CO)(L)H [L = P$(OPh)_3$, $PCy_3$, $PMe_3$, P($p$-$C_6H_4F$)$_3$] were prepared to examine the effect of differing amounts of electron density at the metal. These complexes were prepared by displacement of one CO ligand of CpRu$(CO)_2$H[15] by addition of a phosphine or phosphite ligand (eq 5). The hydrides CpRu(CO)($PMe_3$)H and CpRu(CO)($PCy_3$)H were previously prepared by Chinn and Heinekey.[33] Similar procedures were employed for the synthesis of the new complexes CpRu(CO)[P$(OPh)_3$]H and CpRu(CO)[P($p$-$C_6H_4F$)$_3$]H. All of these hydride complexes exhibit characteristic hydride resonances in the $^1$H NMR spectrum, with coupling to the phosphine or phosphite ligand. For example, CpRu(CO)[P$(OPh)_3$]H exhibits a doublet at $\delta$ −11.34 (d, $^2J_{HP}$ = 35 Hz). In the (proton coupled) $^{13}$C NMR spectrum, the resonance for the CO of CpRu(CO)-[P$(OPh)_3$]H appeared at $\delta$ 204.1 as a doublet of doublets, exhibiting coupling to both the hydride ($^2J_{CH}$ = 8 Hz) and the phosphite ($J_{CP}$=26 Hz). The bis-phosphite hydride CpRu[P$(OPh)_3$]$_2$H was prepared by reacting 2 equiv of P$(OPh)_3$ with CpRu$(CO)_2$H. It was isolated as yellow crystals after purification by chromatography and recrystallization.



L = P$(OPh)_3$, $PCy_3$, $PMe_3$, P($p$-$C_6H_4F$)$_3$

Cp*Ru(CO)($PMe_3$)H was prepared by reaction of $PMe_3$ with Cp*Ru$(CO)_2$H at room temperature. This hydride can be purified by sublimation to give a yellow solid.

**Protonation of Ruthenium Hydrides to Give Dihydrogen Complexes.** Cationic dihydrogen complexes are often prepared by protonation of neutral metal hydrides.[6,33,34] Heinekey and co-workers carried out detailed studies of the protonation of a series of ruthenium complexes with a phosphine ligand, CpRu(CO)($PR_3$)H, as well as diphosphine complexes [CpRu(diphosphine)H], and found that they are protonated at low temperature by $HBF_4 \cdot OEt_2$ to generate dihydrogen complexes. Intramolecular isomerization at higher temperatures occurs to produce dihydrides that are in equilibrium with the dihydrogen complexes.

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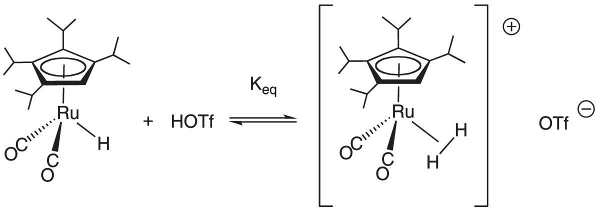
Addition of HOTf to $(Cp^{iPr_4})Ru(CO)_2H$, $Cp^*Ru(CO)_2H$, or $CpRu(CO)[P(OPh)_3]H$ at −80 °C leads to mixtures of the neutral hydride and cationic dihydrogen complexes being observed at −80 °C by $^1H$ NMR (eq 6). For example, protonation of $(Cp^{iPr_4})Ru(CO)_2H$ with HOTf in $CD_2Cl_2$ leads to a broad ($\omega_{1/2} \approx 69$ Hz) new resonance at $\delta$ −5.85 assigned to the $H_2$ resonance of $\{(Cp^{iPr_4})Ru(CO)_2(\eta^2\text{-}H_2)\}^+OTf^-$, which is very similar to the $H_2$ resonance at $\delta$ −5.69 reported for $\{Cp^*Ru(CO)_2(\eta^2\text{-}H_2)\}^+$.[6] The new dihydrogen complex was formed in 65% yield, with the remaining 35% being the neutral hydride, which displays a sharp resonance at $\delta$ −11.02. In addition, resonances for HOTf were observed, and integration of these resonances leads to the determination of $K_{eq}$ values as shown in Table 2. The HOTf appears as two separate resonances. In these NMR spectra at −80 °C, the proton resonance for $(HOTf)_n$ appears around $\delta$ 12 and that for $([Ru(\eta^2\text{-}H_2)]^+\ TfO^-\cdots\underline{H}\text{-}OTf)$ is around $\delta$ 17. We previously found[35] that the chemical shift of HOTf in $CD_2Cl_2$ is dependent on concentration, moving progressively more downfield with increasing concentration because of hydrogen bonding of the HOTf to itself. Hydrogen bonding of HOTf to an $OTf^-$ counterion leads to $TfO^-\cdots H\text{-}OTf$ which exhibits a resonance around $\delta$ 17.[35]



(6)

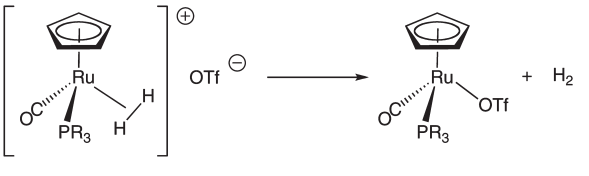
$$K_{eq} = \frac{[Ru(H_2)^+OTf^-]}{[Ru\text{-}H]\ [HOTf]}$$

When the solution from protonation of $(Cp^{iPr_4})Ru(CO)_2H$ by HOTf was warmed to −60 °C the C$\underline{H}$ of the $Cp^{iPr_4}$ ligand resonances of both the dihydrogen and hydride broadened, as did the RuH resonance of $(Cp^{iPr_4})Ru(CO)_2H$, suggesting proton transfer exchange between the neutral hydride and the cationic dihydrogen complex. Further warming to −40 °C led to coalescence of the two C$\underline{H}$ resonances, and the resonances for both the $[Ru(\eta^2\text{-}H_2)]^+$ and RuH broadened. A sharp resonance at $\delta$ 4.57 was observed for $H_2$ gas, and a new C$\underline{H}$ of a $Cp^{iPr_4}$ ligand resonance observed at $\delta$ 5.06 is assigned to $(Cp^{iPr_4})Ru(CO)_2OTf$ resulting from loss of $H_2$ and coordination of the trifluoromethanesulfonate (triflate) anion. Higher temperatures led to the disappearance of resonances because of the dihydrogen complex and the neutral hydride, together with increased intensity of resonances of the products, $H_2$ and $(Cp^{iPr_4})Ru(CO)_2OTf$. Similar results were obtained from protonation of $Cp^*Ru(CO)_2H$ and $CpRu(CO)[P(OPh)_3]H$ with HOTf at −80 °C, with a broad resonance being produced in both cases for the dihydrogen ligand at low temperature and subsequent release of $H_2$ gas at higher temperatures and concomitant formation of a ruthenium triflate complex.

**Table 2.** Equilibrium Constants for the Protonation of Ruthenium Hydride Complexes at −80 °C

| metal hydride | $K_{eq}$ ($M^{-1}$) |
|---|---|
| $(Cp^{iPr_4})Ru(CO)_2H$ | $5 \times 10^1$ |
| $Cp^*Ru(CO)_2H$ | $2 \times 10^2$ |
| $CpRu(CO)[P(OPh)_3]H$ | $4 \times 10^2$ |
| $CpRu(CO)[P(p\text{-}C_6H_4F)_3]H$ | $> 10^4$ |

While the actual equilibrium constants measured in these experiments will be subject to uncertainties owing to the nature of HOTf at low temperatures in this solvent, the trends observed in relative $K_{eq}$ values are as expected in view of the corresponding electron density at the metal. The equilibria we measured upon partial protonation of $(Cp^{iPr_4})Ru(CO)_2H$, $Cp^*Ru(CO)_2H$, and $CpRu(CO)[P(OPh)_3]H$ by 1.2 equiv. of HOTf contrasts with the complete protonation of $Cp^*Ru(CO)_2H$ by 1.2 equiv. of $HBF_4\cdot OEt_2$ found by Heinekey and co-workers. While HOTf is a stronger acid than $HOEt_2^+$, the effective acidity of HOTf at low temperature in $CD_2Cl_2$ may be influenced by the aggregation of HOTf through its hydrogen bonding to itself and to the triflate anion. The slightly larger $K_{eq}$ found for protonation of $Cp^*Ru(CO)_2H$ compared to $(Cp^{iPr_4})Ru(CO)_2H$ is in agreement with the conclusion based on IR bands for the CO ligands that Cp* is a slightly better electron donor than $Cp^{iPr_4}$. Protonation of the phosphine complex $CpRu(CO)[P(p\text{-}C_6H_4F)_3]H$ was complete with 1.2 equiv of HOTf, so the $K_{eq}$ in Table 2 is a lower limit. The resultant dihydrogen complex, $\{CpRu(CO)[P(p\text{-}C_6H_4F)_3](\eta^2\text{-}H_2)\}^+OTf^-$ was stable at −20 °C, but began to decompose upon warming to 0 °C. This reactivity is similar to that observed by Heinekey and co-workers in dihydrogen complexes prepared by protonation of complexes of formula $CpRu(CO)(L)H$ (L = $PCy_3$, $PPh_3$, $PMe_3$, etc.).[33] Heinekey's complexes were prepared by protonation of the ruthenium hydrides with $HBF_4\cdot OEt_2$, leading to dihydrogen complexes $[CpRu(CO)(PR)_3(\eta^2\text{-}H_2)]^+BF_4^-$, with $BF_4^-$ counterions. The decomposition products they observed were bimetallic complexes with bridging hydride ligands, $\{[CpRu(CO)L]_2(\mu\text{-}H)\}^+BF_4^-$. In contrast, our studies using HOTf as the acid led to decomposition to ruthenium complexes with triflate ligands (eq 7), which is understood on the basis of the higher coordinating ability of $OTf^-$ compared to $BF_4^-$.



(7)

Protonation of the bis-phosphite complex, $CpRu[P(OPh)_3]_2H$, with HOTf at −80 °C led to the dihydrogen complex $\{CpRu[P(OPh)_3]_2(\eta^2\text{-}H_2)\}^+OTf^-$, which exhibits a broad ($\omega_{1/2} \approx 151$ Hz) singlet at $\delta$ −8.67 in the $^1H$ NMR spectrum. This dihydrogen complex is more stable than the others studied here, but after the solution is warmed to −20 °C, the dihydrogen ligand oxidatively

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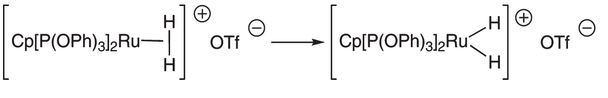
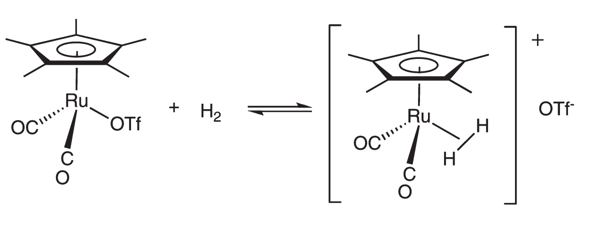
[35] Bullock, R. M.; Song, J.-S.; Szalda, D. J. *Organometallics* **1996**, *15*, 2504–2516.

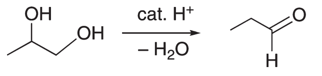
adds to the metal to produce a dihydride complex, $\{CpRu[P(OPh)_3]_2(H)_2\}^+OTf^-$ (eq 8). The higher stability of the dihydride complex in this case, compared to the dihydrogen complexes discussed above, is likely due to the higher electron density on the metal due to the two phosphite ligands, which stabilizes the dihydride compared to the dihydrogen form. Closely related conversions of dihydrogen complexes to dihydrides were studied in detail by Chinn and Heinekey for a series of $[CpRu(diphosphine)(\eta^2\text{-}H_2)]^+$ complexes.[33] The dihydride resonance of $\{CpRu[P(OPh)_3]_2(H)_2\}^+$ appears as a triplet ($^2J_{PH}$ = 19 Hz) at $\delta$ −7.68. A $^{31}P$ NMR spectrum of the dihydride displays a triplet ($^2J_{PH}$ = 19 Hz) at $\delta$ 141.2. Release of $H_2$ from $\{CpRu[P(OPh)_3]_2(\eta^2\text{-}H_2)\}^+OTf^-$ was not detected, unlike other systems in which decomposition of the dihydrogen complex to the triflate derivative took place with the evolution of hydrogen.


(8)

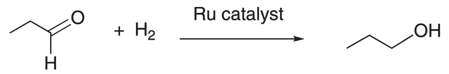
**Catalytic Deoxygenation of 1,2-Propanediol with Ru Catalysts.** The ruthenium complexes described above were used as catalyst precursors for the deoxygenation of 1,2-propanediol (cf. eq 2). These experiments were carried out using a 1.0 M solution of 1,2-propanediol in sulfolane solvent at 110 °C under $H_2$ (750 psi pressure before heating). In most cases the catalyst precursor was loaded as a mononuclear metal hydride (10 mM), along with 65 mM HOTf. For $\{[CpRu(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$ and $\{[(1,2,3\text{-trimethylindenyl})Ru(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$, in which the catalyst precursor was a bimetallic bridging hydride, the initial concentration of the bimetallic catalyst precursor was 5 mM, and the reactions were carried out with 60 mM HOTf added, providing equivalent concentrations of total Ru (10 mM) for both mononuclear and dinuclear ruthenium catalyst precursors (1 mol % Ru). These are the same conditions employed in our studies of $\{[Cp^*Ru(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$,[4,5] permitting a direct comparison of this new series of catalytsts with the $\{[Cp^*Ru(CO)_2]_2(\mu\text{-}H)\}^+$ system studied in detail earlier. We showed that essentially identical catalytic rates were obtained from $Cp^*Ru(CO)_2OTf$ or from $\{[Cp^*Ru(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$, which suggests that under the reaction conditions, $[Cp^*Ru(CO)_2(\eta^2\text{-}H_2)]^+OTf^-$ forms in the reaction of $Cp^*Ru(CO)_2OTf$ with $H_2$ (eq 9), or from $\{[Cp^*Ru(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$ as outlined in Scheme 1.


(9)

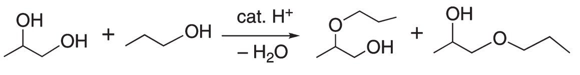
Acid-catalyzed dehydration of 1,2-propanediol generates propionaldehyde (eq 10), which was observed under the reaction conditions. In most of the catalytic experiments the maximum concentration of propionaldehyde observed was less than 100 mM. For example, in the reaction using $Cp^*Ru(CO)(PMe_3)H$ as the catalyst precursor, 53 mM of propionaldehyde was detected at *t* = 7 h, and its concentration decreased at later reaction times. In a few cases, a higher build-up of propionaldehyde was detected. The reaction catalyzed by $\{[(1,2,3\text{-trimethylindenyl})Ru(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$ led to 295 mM propionaldehyde at *t* = 2 h, and 300 mM of propionaldehyde was detected at *t* = 2 h for the reaction catalyzed by $CpRu(CO)(PMe_3)H$.


(10)

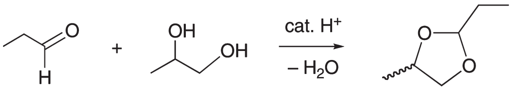
Hydrogenation of the C=O bond of propionaldehyde to give *n*-propanol (eq 11) is proposed to occur through an ionic hydrogenation mechanism involving proton transfer to the aldehyde from the cationic dihydrogen complex of Ru, followed by hydride transfer from the neutral ruthenium hydride to the protonated aldehyde. Ionic hydrogenations of ketones[36] have been studied in detail for molybdenum and tungsten catalysts.[37]


(11)

A small amount of condensation of *n*-propanol was observed, giving di-*n*-propyl ether; the highest amount of this condensation product was 44 mM observed at *t* = 72 h for the reaction catalyzed by $\{[CpRu(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$. Another ether product observed in larger amounts was propylene glycol propyl ether (two isomers as shown in eq 12), which forms through acid-catalyzed cross-condensation of *n*-propanol with the starting material, 1,2-propanediol. In the catalytic reactions reported here, 80−190 mM of propylene glycol propyl ether was typically detected.


(12)

In addition to these deoxygenation/hydrogenation products, two isomers of the acetal, *cis*/*trans*-2-ethyl-4-methyl-1,3-dioxolane (eq 13) were formed; the maximum concentration observed was 153 mM at *t* = 2 h in the reaction catalyzed by $CpRu(CO)(PCy_3)H$. This substituted dioxolane forms


(13)

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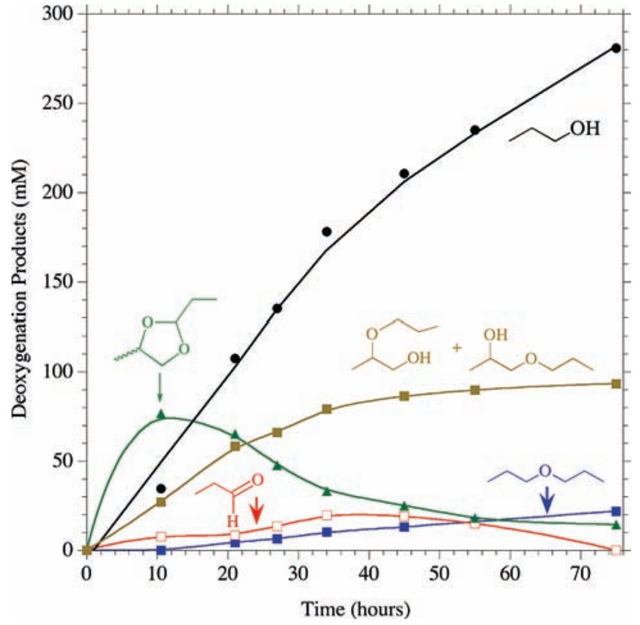


**Figure 2.** Time-dependence of intermediates and products formed from the deoxygenation of 1,2-propanediol (1.0 M) catalyzed by Tp*Ru-$(CO)_2H$ (10 mM) and HOTf (65 mM) in sulfolane at 110 °C under 750 psi $H_2$.

through acid-catalyzed condensation of 1,2-propanediol with propionaldehyde. We previously identified this acetal in our studies using $\{[Cp^*Ru(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$[4,5] and showed that it is readily converted to products under the reaction conditions.

Along with studies of Ru complexes containing Cp and Cp* ligands, we also studied catalysis by Ru complexes with a Tp* ligand (Tp* = hydridotris(3,5-dimethylpyrazolyl). The time-dependence of the intermediates and products from deoxygenation of 1,2-propanediol catalyzed by Tp*$Ru(CO)_2H$ is shown in Figure 2. In this example, the acetal, 2-ethyl-4-methyl-1,3-dioxolane builds up to 77 mM at 10 h, and its concentration decreases at later reaction times. The maximum concentration of propionaldehyde observed in this reaction is 20 mM (at $t$ = 34 h).

Figures 3 and 4 show the total deoxgenation products, defined as [Deoxygenation Products] = [*n*-propanol] + 2 [di-*n*-propyl ether] + [propylene glycol propyl ether]. Each equivalent of di-*n*-propyl ether produced represents two deoxygenation equivalents, since production of 1 equiv of di-*n*-propyl ether requires 2 equiv of *n*-propanol. All of the catalytic reactions shown in Figures 3 and 4 were carried out under the same experimental conditions for comparison of relative activity. Under these conditions, not all of the 1,2-propanediol is consumed. In our earlier studies using $\{[Cp^*Ru(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$,[4,5] we carried out a study of the catalytic rate as a function of acid concentration, and showed that higher rates and conversions are observed using higher concentrations of HOTf. For the reaction catalyzed by $CpRu(CO)[P(p\text{-}C_6H_4F)_3]H$, 0.15 M 1,2-propanediol remained at $t$ = 53 h. In contrast, deoxygenation catalyzed by $Cp^*Ru(CO)(PMe_3)H$, a catalyst of lower activity, had 0.32 M 1,2-propanediol remaining after 68 h. Concentrations of the organic intermediates and products were determined by gas chromatography using an internal standard for integration. All of the catalysts reported in Figures 3 and 4 showed 78−100% mass balance throughout the reaction. The deoxygenation reaction catalyzed by $\{[(1,2,3\text{-trimethylindenyl})Ru(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$ gave poor performance and resulted in only 60% mass balance. Tables of concentrations of the products from each of these reactions are provided in the Supporting Information, Tables S1−S12.

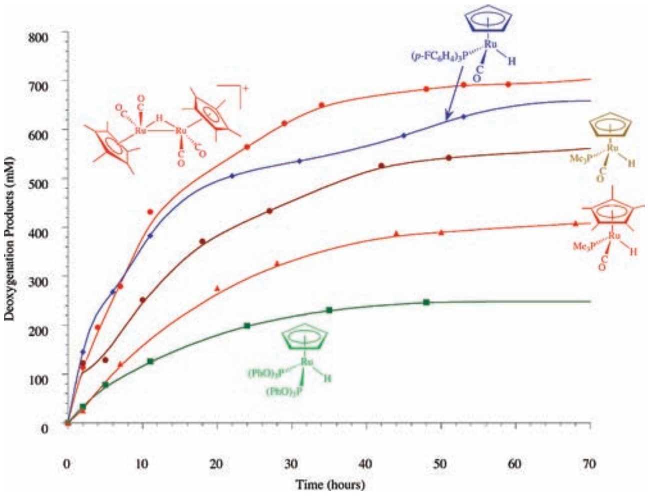


**Figure 3.** Catalytic deoxygenation of 1,2-propanediol (1.0 M) in sulfolane at 110 °C under 750 psi $H_2$. Mononuclear metal hydride catalyst precursors used at initial concentrations of 10 mM RuH and 65 mM HOTf. $\{[Cp^*Ru(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$ was used at 5 mM and 60 mM HOTf.

Excellent regioselectivity is found for the deoxygenation, as there is a high preference for dehydration of the secondary OH rather than the primary OH of the diol. An upper limit of 0.5% yield is estimated for isopropyl alcohol. We cannot completely exclude the possibility that a small amount of isopropyl alcohol could be formed in the reaction, since it would be more reactive under the reaction conditions than *n*-propanol. Further evidence against the formation of significant amounts of isopropyl alcohol having been formed is that no di(isopropyl) ether or mixed ether (*n*-propyl isopropyl ether) was detected.

Among the three complexes with one phosphine ligand, similar activity profiles were observed for $CpRu(CO)[P(p\text{-}C_6H_4F)_3]H$, $CpRu(CO)(PCy_3)H$, and $CpRu(CO)(PMe_3)H$. Figure 3 shows the time dependence for reaction catalyzed by $CpRu(CO)[P(p\text{-}C_6H_4F)_3]H$ and $CpRu(CO)(PMe_3)H$, and a plot showing all of these complexes, including $CpRu(CO)(PCy_3)H$ and $CpRu(CO)[P(OPh)_3]H$, is shown in the Supporting Information, Figure S1. Each of these three phosphine-substituted complexes produced a higher conversion to total deoxygenation products compared to the dicarbonyl catalyst $\{[CpRu(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$, which gave 0.45 M after 72 h. For example, the yield of deoxygenation products at $t$ = 72 h was 0.60 M for $CpRu(CO)[P(p\text{-}C_6H_4F)_3]H$. None of these gave as high of conversion to deoxygenation products as $\{[Cp^*Ru(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$, which produced 0.68 M of deoxygenation products after 78 h. The electronic effects alone do not explain all the trends in reactivity found, however, as the activity decreased on going from the dicarbonyl catalyst $\{[CpRu(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$ to the more electron rich

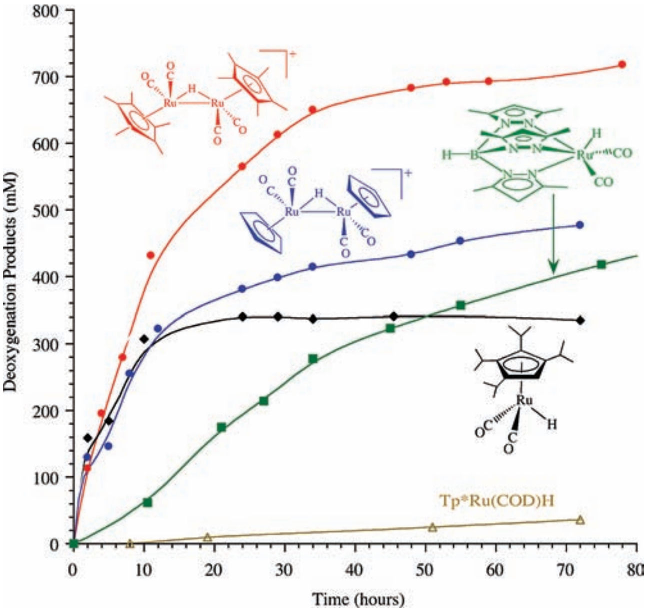


**Figure 4.** Catalytic deoxygenation of 1,2-propanediol (1.0 M) in sulfolane at 110 °C under 750 psi $H_2$. Mononuclear metal hydride catalyst precursors used at initial concentrations of 10 mM RuH and 65 mM HOTf. $\{[Cp^*Ru(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$ and $\{[CpRu(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$ were used at 5 mM and 60 mM HOTf.

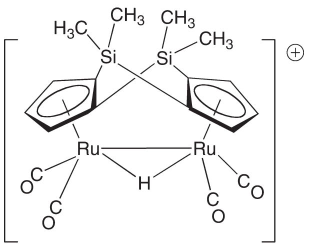
monophosphite complex $CpRu(CO)[P(OPh)_3]H$ to the even more electron rich diphosphite complex $CpRu[P(OPh)_3]_2H$.

The productivity of $Cp^*Ru(CO)(PMe_3)H$ (0.41 M deoxygenation products after 68 h) was inferior to that of $CpRu(CO)(PMe_3)H$ (0.54 M deoxygenation products after 51 h), providing further evidence that too much electron density on the metal (higher for Cp* than for Cp) is not conducive to higher catalytic activity. Higher electron density at the metal compared to $\{[CpRu(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$ can increase performance, as both $\{[Cp^*Ru(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$ and $CpRu(CO)(PMe_3)H$ provided better catalysis than $\{[CpRu(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$. But $Cp^*Ru(CO)(PMe_3)H$, in which the electron density was increased by changing to a Cp* system *and* having a strongly electron-donating phosphine, apparently has too much electron density since the performance of $Cp^*Ru(CO)(PMe_3)H$ was poorer than that of either $CpRu(CO)(PMe_3)H$ or $\{[CpRu(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$.

The two complexes with bulky substituted ligands, $(Cp^{iPr_4})Ru(CO)_2H$ and $(C_5Bz_5)Ru(CO)_2H$, gave a lower number of turnovers than either the Cp* system $[Cp^*Ru(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$ or the Cp system $\{[CpRu(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$. After 50 h, 0.38 M of deoxygenation products were produced by $(C_5Bz_5)Ru(CO)_2H$, and 0.30 M deoxygenation products were produced by $\{[(1,2,3\text{-trimethylindenyl})Ru(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$ after 74 h. Plots of the time-dependence of these and other catalysts are shown in the Supporting Information, Figure S2.

Tp*Ru(COD)H showed a much inferior performance (Figure 4) compared to $Tp^*Ru(CO)_2H$, underscoring the preference for strongly bound ligands over the weakly bound COD ligand. Presumably the weakly bound COD ligand dissociated from the catalyst during the reaction, leading to decomposition.

The dinuclear complex $\{[(C_5H_3)_2(SiMe_2)_2]Ru_2(CO)_4(\mu\text{-}H)\}^+BF_4^-$, in which the two Cp ligands are joined by two $SiMe_2$ bridges, has been synthesized and studied in detail by Angelici and co-workers.[38] This complex exhibits



essentially no catalytic activity for deoxygenation of 1,2-propanediol, producing less than 2% *n*-propanol after 71 h (not shown in Figure 4). The two $SiMe_2$ groups linking the substituted Cp ligands may prevent this complex from readily forming a mononuclear catalyst. Thus, the low activity observed suggests that successful catalysis in this system requires access to a mononuclear metal species, as concluded from our earlier mechanistic studies with the Cp* system.[4,5]

Thus, the observed order of decreasing activity for total amount of deoxygenation product in this series of $Ru(CO)_2$ complexes is $\{[Cp^*Ru(CO)_2]_2(\mu\text{-}H)\}^+OTf^- >$ $\{[CpRu(CO)_2]_2(\mu\text{-}H)\}^+OTf^- > Tp^*Ru(CO)_2H >$ $(C_5Bz_5)Ru(CO)_2H$ > $(Cp^{iPr_4})Ru(CO)_2H$ > $\{[(1,2,3\text{-trimethylindenyl})Ru(CO)_2]_2(\mu\text{-}H)\}$ > Tp*Ru(COD)H > $\{[(C_5H_3)_2(SiMe_2)_2]Ru_2(CO)_4(\mu\text{-}H)\}BF_4$.

**Fe, Os, and Re Complexes as Catalysts for the Deoxygenation of 1,2-Propanediol.** Our studies have concentrated on the use of Ru catalysts, but a few experiments were carried out to assess the activity using other metals. No more than 12 turnovers were observed under any conditions using $[Cp^*Fe(CO)_2]_2$ at 750 psi hydrogen pressure at temperatures up to 150 °C. Moving to the third row of the periodic table, a few experiments were conducted using $Cp^*Os(CO)_2H$. Up to 30 turnovers were observed with $Cp^*Os(CO)_2H$ at 750 psi $H_2$ pressure at 100°C (at 52 h), so catalysis with Os can be obtained, though it is slower than Ru and was not pursued in detail. Heinekey and co-workers found that Cp*Re(CO)(NO)H can be protonated to give a dihydrogen complex and the corresponding dihydride, which decompose at higher temperatures to generate the bridging hydride bimetallic complex $\{[Cp^*Re(CO)\text{-}(NO)]_2(\mu\text{-}H)\}^+$.[6] The similarity of this reactivity to that observed for $Cp^*Ru(CO)_2H$ led us to consider whether the Re complexes might have catalytic activity. Cp*Re-(CO)(NO)H (10 mM) + 55 mM HOTf at 750 psi $H_2$ (1.0 M diol) for 98 h at 110 °C gave a maximum of 22 turnovers of the catalyst, again less reactive than the Ru catalysts.

## Conclusions

Ruthenium hydride complexes with highly substituted Cp ligands were prepared, including $(Cp^{iPr_4})Ru(CO)_2H$ and

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$(C_5Bz_5)Ru(CO)_2H$. Cationic dihydrogen complexes were observed by NMR at low temperatures from protonation of $(Cp^{iPr_4})Ru(CO)_2H$, $Cp^*Ru(CO)_2H$, or $CpRu(CO)[P(OPh)_3]H$ by HOTf. At higher temperatures the $H_2$ ligand is lost, generating ruthenium triflate complexes. These new Ru complexes were used as catalyst precursors in the presence of added HOTf for the catalytic deoxygenation of 1,2-propanediol to give *n*-propanol. Increasing the electron density at the metal can improve performance of the catalyst, as shown by the higher conversion to products obtained with $CpRu(CO)(PMe_3)H$, $CpRu(CO)(PCy_3)H$, or $CpRu(CO)[P(p\text{-}C_6H_4F)_3]H$, compared to $\{[CpRu(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$. Similarly, changing from Cp to Cp* improves performance, as $\{[Cp^*Ru(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$ provides better results than $\{[CpRu(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$. Too much electron density at the metal (and perhaps increased steric interference), however, results in a poorer performance since $Cp^*Ru(CO)(PMe_3)H$ gives worse results than those obtained from either $\{[CpRu(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$ or $CpRu(CO)(PMe_3)H$. Similarly, the bis-phosphite complex $CpRu[P(OPh)_3]_2H$ does not give high conversions as a catalyst precursor, suggesting that the lower acidity of the corresponding dihydrogen or dihydride complex, or increased steric demands of the ligands, is deleterious to catalytic activity.

## Experimental Section

All manipulations were carried out under an atmosphere of argon using Schlenk or vacuum-line techniques, or in a Vacuum Atmospheres drybox. Quantitative analysis of the intermediates and products was carried out by gas chromatography, using an internal standard for integration, following protocols previously described in detail.[4,5] Preparations of $HCp^{iPr_4}$,[13] $HC_5Bz_5$,[28] 1,2,3-trimethylindene,[39] $Tp^*Ru(COD)H$,[40] $Tp^*Ru(CO)_2H$,[40] $Cp^*Ru(CO)_2H$,[41] and $\{[CpRu(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$[9] were carried out according to the literature procedures. $CpRu(CO)(PCy_3)H$ was prepared by a minor modification of the route described by Heinekey.[33] The head-to-tail dimer of trityl radical (Gomberg's dimer,[18] 1-diphenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene; see Scheme 2) was prepared by reaction of $Ph_3CBr$ with Cu, as described for a substituted derivative.[19]

**Synthesis of $(Cp^{iPr_4})Ru(CO)_2H$.** A solution of $HCp^{iPr_4}$ (0.300 g, 1.28 mmol) and $Ru_3(CO)_{12}$ (0.273 g, 0.427 mmol) in heptane (25 mL) was refluxed for 9 h, and the extent of the reaction was monitored by IR spectroscopy. The dark brown reaction mixture was filtered, and the filtrate was evaporated to give an oil, which was dissolved in pentane and filtered though silica gel to obtain a clear yellow solution. The solvent was evaporated to give obtain a yellow oil, which was cooled at −40 °C to give $(Cp^{iPr_4})Ru(CO)_2H$ as a yellow solid (0.226 g, 45%). $^1H$ NMR $(C_6D_6)$: $\delta$ 4.80 (s, 1H, $\underline{H}C_5^{iPr_4}$), 2.57 (sept, $^3J_{HH} = 7$ Hz, 2H, $C\underline{H}Me_2$); 2.49 (sept, $^3J_{HH} = 7$ Hz, 2H, $C\underline{H}Me_2$); 1.24 (d, $^3J_{HH} = 7$ Hz, 6H, $CH\underline{Me}_2$); 1.18 (d, $^3J_{HH} = 7$ Hz, 6H, $CH\underline{Me}_2$); 1.11 (d, $^3J_{HH} = 7$ Hz, 6H, $CH\underline{Me}_2$); 0.94 (d, $^3J_{HH} = 7$ Hz, 6H, $CH\underline{Me}_2$); −10.3 (s, 1H, Ru-$\underline{H}$). $^{13}C$ NMR $(C_6D_6)$: $\delta$ 203.6 (d, $^2J_{CH} = 9$ Hz, CO); 113.7 (s, Cp-ring-$\underline{C}$-$Pr^i$); 112.4 (s, Cp-ring-$\underline{C}$-$Pr^i$); 75.9 (dt, $^1J_{CH} = 171$ Hz, $^2J_{CH} = 5$ Hz, Cp-ring-$\underline{C}H$); 26.7 (q, $^1J_{CH} = 127$ Hz, $CH\underline{Me}_2$); 26.2 (q, $^1J_{CH} = 126$ Hz, $CH\underline{Me}_2$); 25.7 (d, $^1J_{CH} = 133$ Hz, $\underline{C}HMe_2$); 25.5 (q, $^1J_{CH} = 126$ Hz, $CH\underline{Me}_2$); 25.4 (d, $^1J_{CH} = 127$ Hz, $\underline{C}HMe_2$); 25.2 (q, $^1J_{CH} = 126$ Hz, $CH\underline{Me}_2$). IR (hexane) $\nu$(CO): 2015 (s) $cm^{-1}$, 1956 (s) $cm^{-1}$. Anal. Calcd for $C_{19}H_{30}O_2Ru$: C 58.27%; H 7.72%. Found: C 58.45%; H 7.67%.

**Synthesis of $[(Cp^{iPr_4})Ru(CO)(\mu\text{-}CO)]_2$.** A solution of $(Cp^{iPr_4})$-$Ru(CO)_2H$ (0.100 g, 0.255 mmol) and Gomberg's dimer (0.062 g, 0.128 mmol) were stirred in hexane (15 mL) at room temperature in the dark for 1 day, giving a yellow precipitate. The reaction mixture was concentrated to 10 mL for further precipitation, and the precipitate was isolated by filtration to give $[(Cp^{iPr_4})Ru(CO)(\mu\text{-}CO)]_2$ as a yellow solid (0.052 g, 52%). $^1H$ NMR $(C_6D_6)$: $\delta$ 4.51 (s, 1H, $\underline{H}C_5^{iPr_4}$), 3.07 (sept, $^3J_{HH} = 7$ Hz, 2H, $C\underline{H}Me_2$); 2.87 (sept, $^3J_{HH} = 7$ Hz, 2H, $C\underline{H}Me_2$); 1.58 (d, $^3J_{HH}=7$ Hz, 6H, $CH\underline{Me}_2$); 1.27 (d, $^3J_{HH} = 7$ Hz, 6H, $CH\underline{Me}_2$); 1.23 (d, $^3J_{HH} = 7$ Hz, 6H, $CH\underline{Me}_2$); 1.06 (d, $^3J_{HH} = 7$ Hz, 6H, $CH\underline{Me}_2$). $^{13}C$ NMR $(C_6D_6)$: $\delta$ 229 (br, CO); 118.0 (s, Cp-ring-$\underline{C}$-$Pr^i$); 111.1 (s, Cp-ring-$\underline{C}$-$Pr^i$); 82.4 (dt, $^1J_{CH} = 171$ Hz, $^2J_{CH} = 4$ Hz, Cp-ring-$\underline{C}H$); 26.8 (d, $^1J_{CH} = 126$ Hz, $\underline{C}HMe_2$); 26.3 (q, $^1J_{CH} = 126$ Hz, $CH\underline{Me}_2$); 25.3· (d, $^1J_{CH} = 131$ Hz, $\underline{C}HMe_2$); 24.7 (q, $^1J_{CH}=126$ Hz, $CH\underline{Me}_2$); 24.5 (q, $^1J_{CH} = 126$ Hz, $CH\underline{Me}_2$); 22.7 (q, $^1J_{CH} = 126$ Hz, $CH\underline{Me}_2$). IR $(C_6D_6)$ $\nu$(CO): 1936 (s) $cm^{-1}$, 1761 (s) $cm^{-1}$. IR (toluene) $\nu$(CO): 1938 (s) $cm^{-1}$, 1762 (s) $cm^{-1}$. IR (hexane) $\nu$(CO): 1943 (s) $cm^{-1}$, 1768 (s) $cm^{-1}$. Anal. Calcd for $C_{38}H_{58}O_4Ru_2$: C 58.42%; H 7.48%. Found: C 58.17%; H 7.79%.

**Protonation of $(Cp^{iPr_4})Ru(CO)_2H$ by HOTf at Low Temperatures.** HOTf (4.0 $\mu$L, 0.045 mmol) was added to $(Cp^{iPr_4})Ru(CO)_2H$ (0.015 g, 0.038 mmol) in $CD_2Cl_2$ (0.69 mL) at −80 °C in an NMR tube, and the reaction was monitored by $^1H$ NMR spectroscopy. At −80 °C, the dihydrogen complex $\{(Cp^{iPr_4})Ru(CO)_2(\eta^2\text{-}H_2)\}^+OTf^-$ (65%) was found to be in equilibrium with $(Cp^{iPr_4})Ru(CO)_2H$ (35%) and with the unreacted HOTf $[TfO^- \cdots H\text{-}OTf$ and $(HOTf)_n]$. The equilibrium constant ($K_{eq}$) for the reaction was found to be 51 $M^{-1}$ at −80 °C. There was only a small change in the observed equilibrium constant on warming to −60 °C as the $K_{eq}$ value only changed to 61 $M^{-1}$. Upon further elevating the temperature, broadening of $\{(Cp^{iPr_4})Ru\text{-}(CO)_2(\eta^2\text{-}H_2)\}^+OTf^-$ and $(Cp^{iPr_4})Ru(CO)_2H$ resonances were observed, suggesting the occurrence of proton transfer exchange between these complexes. Coalescence of the $\underline{H}C_5^{iPr_4}$ resonances was observed at −40 °C, and decomposition to $(Cp^{iPr_4})Ru(CO)_2OTf$ ($\underline{H}C_5^{iPr_4}$ resonance at $\delta$ 5.08), accompanied by the formation of $\underline{H}_2$ ($\delta$ 4.60), was observed upon warming to 27 °C. $\{(Cp^{iPr_4})Ru(CO)_2(\eta^2\text{-}H_2)\}^+OTf^-$: $^1H$ NMR $(CD_2Cl_2)$ −80 °C: $\delta$ 5.48 (s, 1H, $\underline{H}C_5^{iPr_4}$), 2.3−3.0 ($C\underline{H}Me_2$ not resolved); 0.8−1.5 ($CH\underline{Me}_2$ not resolved); −5.85 (s broad $w_{1/2} = 69$ Hz, 2H, Ru-($\eta^2$-$\underline{H}_2$)).

**Synthesis of $(C_5Bz_5)Ru(CO)_2H$.** A solution of $HC_5Bz_5$ (0.500 g, 0.969 mmol) and $Ru_3(CO)_{12}$ (0.207 g, 0.324 mmol) in heptane (25 mL) was refluxed for 10 days, and the extent of the reaction was monitored by IR spectroscopy. The brownish-yellow reaction mixture was filtered through alumina inside a drybox, and the solvent was evaporated to give a dark brown oil. The oil was dissolved in pentane (5 mL), and cooled to−30 °C. A brown oily solid precipitated. The supernatant pentane extract was decanted, and the solvent was evaporated to obtain $(C_5Bz_5)Ru(CO)_2H$ as an oily yellow solid (0.154 g, 24%). $^1H$ NMR $(C_6D_6)$: $\delta$ 7.02−6.87 (m, 25H, $C_6\underline{H}_5$), 3.61 (s, 10H, $C\underline{H}_2C_6H_5$), −9.92 (s, 1H, Ru-$\underline{H}$). IR (hexane) $\nu$(CO): 2020 (s) $cm^{-1}$, 1963 (s) $cm^{-1}$.

**Synthesis of $CpRu(CO)[P(OPh)_3]H$.** A solution of freshly cracked cyclopentadiene (9.00 mL, 109 mmol) and $Ru_3(CO)_{12}$ (0.900 g, 1.41 mmol) was refluxed in heptane (70 mL) for 4.5 h.[15] The color of the solution changed from dark orange to lemon yellow. An aliquot taken for IR spectroscopy showed predominant formation of $CpRu(CO)_2H$ (2033 and 1973 $cm^{-1}$) along with the minor amounts of $[CpRu(CO)_2]_2$ (1944 and 1793 $cm^{-1}$) and $(\eta^4\text{-}C_5H_6)Ru(CO)_3$ (2064, 1998, and 1987 $cm^{-1}$).[15] The reaction mixture was cooled to −78 °C, and a solution of

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$P(OPh)_3$ (0.510 g, 1.65 mmol) in heptane (25 mL) was added to it over 30 min. The reaction mixture was stirred overnight at −78 °C. The solvent was evaporated to obtain a yellow oil, which was chromatographed inside a drybox over silica gel and eluted with 5% $Et_2O$: 95% hexane. The first yellow band was collected, and the solvent was removed to obtain a yellow oil. The yellow oil was washed with hexane (5 mL), and $CpRu(CO)[P(OPh)_3]H$ precipitated out as a a light yellow solid (0.087 g). The supernatant hexane solution was decanted and again left at −30 °C for further crystallization (0.135 g of microcrystals were obtained). The overall yield was 27% (0.222 g, 0.439 mmol) with respect to $P(OPh)_3$. $^1H$ NMR ($C_6D_6$): $\delta$ 7.30 (d, $^3J_{HH}=8$ Hz, 6H, $-OC_6\underline{H}_5$ ortho H's); 7.03 (virtual triplet, $^3J_{HH}=8$ Hz, 6H, $-OC_6\underline{H}_5$ meta H's); 6.86 (t, $^3J_{HH}=8$ Hz, 3H, $-OC_6\underline{H}_5$ para H's); 4.43 (d, $^3J_{HP}=1$ Hz, 5H, $C_5\underline{H}_5$); −11.34 (d, $^2J_{HP}=35$ Hz, 1H, Ru-$\underline{H}$). $^{13}C$ NMR ($C_6D_6$): $\delta$ 204.1 (dd, $^2J_{CH}=8$ Hz, $^2J_{CP}=26$ Hz, $\underline{C}O$); 152.7 (d, $^2J_{CP}=6$ Hz, $\underline{C}$-1(ipso) of Ph); 129.8 (dd, $^1J_{CH}=161$ Hz, $^2J_{CH}=8$ Hz, *m*-$\underline{C}$ of Ph); 124.9 (dt, $^1J_{CH}=163$ Hz, $^2J_{CH}=8$ Hz, *p*-$\underline{C}$ of Ph); 122.6 (dd, $^1J_{CH}=163$ Hz, $^3J_{CP}=5$ Hz, *o*-$\underline{C}$ of Ph); 83.7 (dd, $^1J_{CH}=177$ Hz, $^2J_{CP}=2$ Hz, $\underline{C}p$). $^{31}P$ NMR ($C_6D_6$): $\delta$ 160.9 (d, $^2J_{PH}=35$ Hz). IR (hexane) $\nu$(CO): 1967 (br) cm$^{-1}$. Anal. Calcd for $C_{24}H_{21}O_4P_1Ru_1$: C 57.02%; H 4.19%. Found: C 57.65%; H 4.40%.

**Protonation of $CpRu(CO)[P(OPh)_3]H$ by HOTf at Low Temperature.** HOTf (4.0 $\mu$L, 0.045 mmol) was added to $CpRu(CO)[P(OPh)_3]H$ (0.020 g, 0.039 mmol) was reacted with at −80 °C in an NMR tube in $CD_2Cl_2$ (0.68 mL). Partial protonation of $CpRu(CO)[P(OPh)_3]H$ was observed at low temperatures. The dihydrogen complex $\{CpRu(CO)[P(OPh)_3](\eta^2\text{-}H_2)\}^+OTf^-$ (86%) was found to be in equilibrium with $CpRu(CO)[P(OPh)_3]H$ (12%), and with the unreacted HOTf. A decomposition product, presumably $CpRu(CO)[P(OPh)_3]OTf$, constituted the remaining about 2% of the reaction mixture. The equilibrium constant ($K_{eq}$) for the reaction was measured to be 348 M$^{-1}$ at this temperature. At −60 °C the $K_{eq}$ value decreased to 157 M$^{-1}$. Upon further elevating the temperature, broadening of the resonances of $\{CpRu(CO)[P(OPh)_3](\eta^2\text{-}H_2)\}^+OTf^-$ and $CpRu(CO)[P(OPh)_3]H$ were observed, suggesting a rapid exchange between these complexes. Coalescence of the Cp resonances was observed at −20 °C. Complete decomposition, presumably to $CpRu(CO)[P(OPh)_3]OTf$ (Cp resonance at $\delta$ 4.65) was observed upon warming to 27 °C, accompanied by the formation of $H_2$ ($\delta$ 4.60). Characterization of $\{CpRu(CO)[P(OPh)_3](\eta^2\text{-}H_2)\}^+OTf^-$: $^1H$ NMR ($CD_2Cl_2$) −60 °C: $\delta$ 7.49 (virtual triplet, $^3J_{HH}=8$ Hz, 6H, $-OC_6\underline{H}_5$ meta H's); 7.35 (t, $^3J_{HH}=7$ Hz, 3H, $-OC_6\underline{H}_5$ para H's); 7.29 (d, $^3J_{HH}=8$ Hz, 6H, $-OC_6\underline{H}_5$ ortho H's); 5.02 (s, 5H, $C_5\underline{H}_5$); −7.52 (s broad $w_{1/2}=52$ Hz, 2H, Ru-($\eta^2$-$\underline{H}_2$)). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) −60 °C: $\delta$ 143.4.

**Synthesis of $CpRu[P(OPh)_3]_2H$.** A mixture of freshly cracked cyclopentadiene (5.00 mL, 60.6 mmol) and $Ru_3(CO)_{12}$ (0.450 g, 0.704 mmol) was refluxed in heptane (35 mL) for 3 h. The color of the solution changed from dark orange to lemon yellow. The reaction mixture was cooled to room temperature and a solution of $P(OPh)_3$ (1.309 g, 4.22 mmol) in hexane (25 mL) was added. The reaction mixture was stirred at room temperature for 1 day. The solvent was evaporated to obtain a yellow oil which was chromatographed over silica gel inside a drybox, and eluted with 5% $Et_2O$: 95% hexane. The first yellow band was collected in two fractions (100 mL each). $CpRu[P(OPh)_3]_2H$ crystallized out as light yellow microcrystals from the second fraction (0.458 g, 28%). Another crop of $CpRu[P(OPh)_3]_2H$ could be obtained from the first fraction (0.370 g, 11%) but it was contanimated with triphenylphosphite (50:50 mixture by $^1H$ NMR). $^1H$ NMR ($C_6D_6$): $\delta$ 7.36 (d, $^3J_{HH}=8$ Hz, 12H, $-OC_6\underline{H}_5$ ortho H's); 7.04 (virtual triplet, $^3J_{HH}=8$ Hz, 12H, $-OC_6\underline{H}_5$ meta H's); 6.87 (t, $^3J_{HH}=8$ Hz, 3H, $-OC_6\underline{H}_5$ para H's); 4.27 (s, 5H, $C_5\underline{H}_5$); −12.06 (t, $^2J_{HP}=36$ Hz, 1H, Ru-$\underline{H}$). $^{13}C$ NMR ($C_6D_6$): $\delta$ 153.2 (t, $^2J_{CP}=3$ Hz, $\underline{C}$-1(ipso) of Ph); 129.5 (dd, $^1J_{CH}=160$ Hz, $^2J_{CH}=9$ Hz, *m*-$\underline{C}$ of Ph); 124.0 (td, $^1J_{CH}=162$ Hz, $^2J_{CH}=8$ Hz, *p*-$\underline{C}$ of Ph); 122.4 (d, $^1J_{CH}=160$ Hz, *o*-$\underline{C}$ of Ph); 81.9 (d, $^1J_{CH}=177$ Hz, $\underline{C}p$). $^{31}P$ NMR ($C_6D_6$): $\delta$ 155.7 (d, $^2J_{PH}=36$ Hz). Anal. Calcd for $C_{41}H_{36}O_6P_2Ru_1$: C 62.51%; H 4.61%. Found: C 62.70%; H 4.83%.

**Protonation of $CpRu[P(OPh)_3]_2H$ by HOTf at Low Temperature.** HOTf (3.0 $\mu$L, 0.034 mmol) was added to $CpRu[P(OPh)_3]_2H$ (0.025 g, 0.032 mmol) at −80 °C in an NMR tube in $CD_2Cl_2$ (0.66 mL). Complete protonation produced the dihydrogen complex $\{CpRu[P(OPh)_3]_2(\eta^2\text{-}H_2)\}^+OTf^-$ (81%) as a major component along with the dihydride complex $\{CpRu[P(OPh)_3]_2(H)_2\}^+OTf^-$ (19%). Unlike in other systems where the dihydrogen complex would start decomposing on warming above about −40 °C, this dihydrogen complex $\{CpRu[P(OPh)_3]_2(\eta^2\text{-}H_2)\}^+OTf^-$ cleanly converted to the dihydride complex $\{CpRu[P(OPh)_3]_2(H)_2\}OTf$ upon reaching 27 °C. At −20 °C, about 50% conversion of the dihydrogen complex to the dihydride complex was observed. No formation of $H_2$ was observed. Characterization of $\{CpRu[P(OPh)_3]_2(\eta^2\text{-}H_2)\}^+OTf^-$: $^1H$ NMR ($CD_2Cl_2$) −80 °C: $\delta$ 7.40 (virtual triplet, $^3J_{HH}=7$ Hz, 12H, $-OC_6\underline{H}_5$ meta H's); 7.28 (t, $^3J_{HH}=7$ Hz, 6H, $-OC_6\underline{H}_5$ para H's); 7.11 (d, $^3J_{HH}=7$ Hz, 12H, $-OC_6\underline{H}_5$ ortho H's); 4.49 (s, 5H, $C_5\underline{H}_5$); −8.67 (s, broad, $w_{1/2}=151$ Hz, 2H, Ru-($\eta^2$-$\underline{H}_2$)). $^{31}P$ NMR ($CD_2Cl_2$) −80 °C: $\delta$ 145.5 (s).

Characterization of $\{CpRu[P(OPh)_3]_2(H)_2\}^+OTf^-$: $^1H$ NMR ($CD_2Cl_2$): $\delta$ 7.46 (virtual triplet, $^3J_{HH}=8$ Hz, 12H, $-OC_6\underline{H}_5$ meta H's); 7.36 (t, $^3J_{HH}=7$ Hz, 6H, $-OC_6\underline{H}_5$ para H's); 7.07 (d, $^3J_{HH}=8$ Hz, 12H, $-OC_6\underline{H}_5$ ortho H's); 4.73 (s, 5H, $C_5\underline{H}_5$); −7.68 (t, $^2J_{HP}=19$ Hz, 2H, Ru-$\underline{H}$). $^{13}C$ NMR ($CD_2Cl_2$): $\delta$ 151.0 (t, $^2J_{CP}=4$ Hz, $\underline{C}$-1(ipso) of Ph); 131.1 (dd, $^1J_{CH}=163$ Hz, $^2J_{CH}=9$ Hz, *m*-$\underline{C}$ of Ph); 127.0 (dt, $^1J_{CH}=163$ Hz, $^2J_{CH}=8$ Hz, *p*-$\underline{C}$ of Ph); 121.8 (dt, $^1J_{CH}=164$ Hz, $^3J_{CP}=2$ Hz, *o*-$\underline{C}$ of Ph); 88.8 (d, $^1J_{CH}=184$ Hz, $\underline{C}p$). $^{31}P$ NMR ($CD_2Cl_2$): $\delta$ 141.2 (t, $^2J_{PH}=19$ Hz).

**Synthesis of $CpRu(CO)[P(p\text{-}C_6H_4F)_3]H$.** A solution of freshly cracked cyclopentadiene (5.00 mL, 60.6 mmol) and $Ru_3(CO)_{12}$ (0.450 g, 0.704 mmol) was refluxed in heptane (50 mL) for 4 h,[15] and the color of the solution changed from dark orange to lemon yellow. The reaction mixture was then cooled to room temperature followed by the addition of a solution of $P(p\text{-}C_6H_4F)_3$ (0.467 g, 1.48 mmol) in heptane (30 mL). The mixture was stirred overnight at room temperature. The solvent was then removed under vacuum to obtain a orangish-yellow oil, which was chromatographed over silica gel inside the drybox and eluted with 5% $Et_2O$: 95% hexane. The first yellow band was collected and the solvent was evaporated to obtain a yellow oil. The yellow oil was washed with hexane (ca. 3 mL), leading to the separation of $CpRu(CO)[P(p\text{-}C_6H_4F)_3]H$ as a light yellow microcrystalline solid (0.070 g). The supernatant hexane solution was cooled again to −30 °C for further crystallization (0.270 g of microcrystals). Total yield was 45% (0.34 g, 0.665 mmol) based on $P(p\text{-}C_6H_4F)_3$. $^1H$ NMR ($C_6D_6$): $\delta$ 7.34 (multiplet, 6H, $C_6\underline{H}_4$ ortho H's); 6.69 (virtual triplet, $^3J_{HH}=8$ Hz, 6H, $C_6\underline{H}_4$ meta H's); 4.68 (s, 5H, $C_5\underline{H}_5$); −11.17 (d, $^2J_{HP}=33$ Hz, 1H, Ru-$\underline{H}$). $^{13}C$ NMR ($C_6D_6$): $\delta$ 206.2 (dd, $^2J_{CH}=9$ Hz, $^2J_{CP}=18$ Hz, $\underline{C}O$); 163.9 (dd, $^1J_{CF}=251$ Hz, $^4J_{CP}=2$ Hz, *p*-$\underline{C}$ of $C_6H_4F$); 135.5 (ddm, $^1J_{CH}=158$ Hz, $^2J_{CP}=22$ Hz, $^3J_{CF}=8$ Hz, *o*-$\underline{C}$ of $C_6H_4F$); 134.9 (dd, $^1J_{CP}=49$ Hz, $^4J_{FC}=3$ Hz, $\underline{C}$-1(ipso) of $C_6H_4F$); 115.3 (ddd, $^1J_{CH}=165$ Hz $^2J_{CF}=32$ Hz, $^3J_{CP}=11$ Hz, *m*-$\underline{C}$ of $C_6H_4F$); 83.7 (dm, $^1J_{CP}=176$ Hz, $^2J_{CP}=1$ Hz, $\underline{C}p$). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 66.5 (s). $^{19}F\{^1H\}$ NMR ($C_6D_6$): $\delta$ −110.8 (d, $^5J_{PF}=2$ Hz). IR (hexane) $\nu$(CO): 1940 (br) cm$^{-1}$.

**Protonation of $CpRu(CO)[P(p\text{-}C_6H_4F)_3]H$ with HOTf at Low Temperatures.** HOTf (4.0 $\mu$L, 0.045 mmol) was added to $CpRu(CO)[P(p\text{-}C_6H_4F)_3]H$ (0.020 g, 0.039 mmol) at −80 °C in an NMR tube in $CD_2Cl_2$ (0.61 mL), giving complete protonation to yield the dihydrogen complex $\{CpRu(CO)[P(p\text{-}C_6H_4F)_3](\eta^2\text{-}H_2)\}^+OTf^-$. This dihydrogen complex was stable until about 0 °C. At higher temperatures, the triflate derivate (Cp resonance at $\delta$ 5.04) was observed, accompanied by the formation of $H_2$ ($\delta$ 4.60).

Characterization of $\{CpRu(CO)[P(p\text{-}C_6H_4F)_3](\eta^2\text{-}H_2)\}^+OTf^-$: $^1H$ NMR ($CD_2Cl_2$) −60 °C: δ 7.31−7.21 (m, 12H, $[P(p\text{-}C_6H_4F)_3]$); 5.44 (s, 5H, $C_5\underline{H}_5$); −7.01 (s, broad, $w_{1/2}$ = 66 Hz, 2H, Ru-($\eta^2$-$\underline{H}_2$)). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) −60 °C: δ 44.6.

**Synthesis of [(1,2,3-Trimethylindenyl)Ru(CO)(*μ*-CO)]$_2$.** A solution of 1,2,3-trimethylindene (0.300 g, 1.90 mmol) and $Ru_3(CO)_{12}$ (0.405 g, 0.633 mmol) in methyl *iso*-butyl ketone (50 mL) was refluxed for 4 h during which time the formation of a dark brown precipitate was observed. The reaction mixture was concentrated to 10 mL. The precipitate was isolated by filtration, washed with hexane, and dried under vacuum to obtain [(1,2,3-trimethylindenyl)Ru(CO)($\mu$-CO)]$_2$ as a brown solid (0.253 g, 42%). Further purification of the dimer can be obtained by Soxhlet extraction using toluene to obtain [(1,2,3-trimethylindenyl)Ru(CO)($\mu$-CO)]$_2$ as a yellow solid. $^1H$ NMR ($CD_2Cl_2$): δ 7.18 (m, 2H, $C_6\underline{H}_4$-ring); 6.99 (m, 2H, $C_6\underline{H}_4$-ring); 2.09 (s, 3H, $\underline{Me}$ $C_5$-ring); 2.05 (s, 6H, two $\underline{Me}$ groups of $C_5$-ring). $^1H$ NMR ($C_6D_6$): δ 7.06 (m, 2H, $C_6\underline{H}_4$-ring); 6.83 (m, 2H, $C_6\underline{H}_4$-ring); 1.85 (s, 3H, $\underline{Me}$ $C_5$-ring); 1.82 (s, 6H, two $\underline{Me}$ groups of $C_5$-ring). $^{13}C$ NMR ($CD_2Cl_2$): δ 126.0 (dd, $^1J_{CH}$ = 162 Hz, $^2J_{CH}$ = 7 Hz, 2C, $\underline{C}_6H_4$-ring); 119.0 (dd, $^1J_{CH}$ = 167 Hz, $^2J_{CH}$ = 6 Hz, 2C, $\underline{C}_6$-ring); 109.1 (s, 1C, $\underline{C}_5$-ring); 108.5 (s, 2C, $\underline{C}_5$-ring); 95.8 (s, 2C, $\underline{C}_5$-ring); 10.2 (q, $^1J_{CH}$ = 128 Hz, 2C, Me groups of $C_5$-ring); 9.3 (q, $^1J_{CH}$ = 128 Hz, 1C, $\underline{Me}$ $C_5$-ring). IR ($CH_2Cl_2$) ν(CO): 1941 and 1771 cm$^{-1}$. Anal. Calcd for $C_{28}H_{26}O_4Ru_2$: C 53.48%; H 4.17%. Found: C 53.71%; H 4.39%.

**Protonation of [(1,2,3-Trimethylindenyl)Ru(CO)(*μ*-CO)]$_2$ with HOTf.** HOTf (2 μL; 0.02 mmol) was added to [(1,2,3-trimethylindenyl)Ru(CO)($\mu$-CO)]$_2$ (0.01 g, 0.02 mmol) in $CD_2Cl_2$ at room temperature to give the bimetallic bridging hydride complex $\{[(1,2,3\text{-trimethylindenyl})Ru(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$. $^1H$ NMR ($CD_2Cl_2$): δ 7.46 (m, 4H, $C_6\underline{H}_4$-ring); 7.41 (m, 4H, $C_6\underline{H}_4$-ring); 2.38 (s, 12H, two $\underline{Me}$ groups of $C_5$-ring); 2.26 (s, 6H, $\underline{Me}$ $C_5$-ring); −17.5 (s, 1H, $\mu$-$\underline{H}$). IR ($CD_2Cl_2$) ν(CO): 2103 (w), 2080 (w), 2049 (w), 2030 (s) and 1995 (s) cm$^{-1}$.

**Synthesis of Cp*Ru(CO)(PMe$_3$)H.** This complex was previously prepared by reaction of Cp*Ru(CO)(PMe$_3$)Cl with NaBH$_4$,[42] and also by a photochemical reaction between [Cp*Ru(CO)($\mu$-CO)]$_2$ and PMe$_3$.[43] We report here a new route that provides Cp*Ru(CO)(PMe$_3$)H through displacement of a CO ligand by PMe$_3$. PMe$_3$ (0.250 g, 3.28 mmol) was added to a solution of Cp*Ru(CO)$_2$H (0.500 g, 1.70 mmol) in hexane (30 mL), and the reaction mixture was stirred at room temperature for 90 min. The solvent was evaporated to obtain an orange solid. The orange solid was sublimed (60 °C, 30 mTorr) to give Cp*Ru(CO)(PMe$_3$)H as a yellow solid (0.412 g, 71%). $^1H$ NMR ($CD_2Cl_2$): 1.97 (d, $^4J_{HP}$ = 2 Hz, 15H, $C_5\underline{Me}_5$); 1.37 (d, $^2J_{HP}$ = 9 Hz, 9H, $P\underline{Me}_3$); −12.38 (d, $^2J_{HP}$ = 39 Hz, 1H, Ru-$\underline{H}$). $^{13}C$ NMR ($CD_2Cl_2$): δ 204.1 (dd, $^2J_{CH}$ = 9 Hz, $^2J_{CP}$ = 17 Hz, $\underline{C}O$); 95.8 (d, $^2J_{CP}$ = 2 Hz, $\underline{C}_5Me_5$); 22.7 (dq, $^1J_{CH}$ = 128 Hz, $^1J_{CP}$ = 31 Hz, $P\underline{Me}_3$); 11.8 (q, $^1J_{CH}$=127 Hz, $C_5\underline{Me}_5$). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): δ 9.9 (s, $\underline{P}Me_3$). IR (hexane) ν(CO): 1924 (br) cm$^{-1}$.

**Catalytic Deoxygenation Experiments.** This is a representative example of the procedure used for the catalytic reactions, following procedures very similar to those developed earlier for reactions catalyzed by $\{[Cp^*Ru(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$.[5] CpRu(CO)[P($p$-$C_6H_4F$)$_3$]H (0.128 g, 0.250 mmol) was added to 25 mL of 1.0 M solution of 1,2-propanediol (containing 0.1 M toluene as an internal standard) in sulfolane in a 300 mL Parr (Model 4561) minireactor. HOTf (122 μL, 1.37 mmol) was added slowly dropwise to the reaction mixture. The autoclave was then sealed tightly inside the glovebox, taken out and was pressurized with $H_2$ gas to 750 psi. The system was then heated to 110° C. The reaction was monitored by removing samples at various time intervals and subjecting them to GC analysis. After 94 h, 0.03 M (3%) of the 1,2-propanediol remained, and the concentrations and yields of hydrogenated products were *n*-propanol (0.46 M, 46%), di-*n*-propyl ether (0.053 M, 5%), and propylene glycol propyl ether (0.06 M, 6%). The total yield of deoxygenation products from this experiment indicated 62 catalyst turnovers (62% yield).

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**Supporting Information Available:** Plots of time-dependence of intermediates and products from all catalysts (Figures S1 and S2); Tables of product distributions for each catalyst (Tables S1−S12); cif file from X-ray crystal structure of $(Cp^{iPr_4})Ru(CO)_2H$. This material is available free of charge via the Internet at http://pubs.acs.org.

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