Coupling H$_2$ to Electron Transfer with a 17-Electron Heterobimetallic Hydride: A "Redox Switch" Model for the H$_2$-Activating Center of Hydrogenase

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Abstract: A meta-stable heterobimetallic mixed-valence ion, [Fe(II),Ru(III)], is formed by the one-electron oxidation of Cp*(dppf)RuH {**1**, dppf = 1,1′-bis(diphenylphosphino)ferrocene, Cp* = pentamethylcyclopentadienide}. A remarkable stability toward one-electron oxidation is revealed by the cyclic voltammetry of **1** which contains two reversible oxidations at +0.073 and +0.541 V and a quasireversible oxidation at +0.975 V (vs NHE) assigned to Ru(III/II), Ru(IV/III), and Fe(III/II), respectively. The isolable Ru(III) metal hydride, [Cp*(dppf)RuH]PF$_6$ (**1**$^+$), is characterized by a NIR absorption at 912 nm (ϵ = 486 M^{-1} cm^{-1}) assigned to an intervalence transfer band and a series of atom transfer reactions yielding the even electron derivatives [Cp*(dppf)RuXH]PF$_6$ (X = H, Cl, Br, I). A crystallographically determined Fe–Ru distance of 4.383(1) Å in **1** is consonant with the classification of **1**$^+$ as a weakly coupled, Type II mixed-valence ion (H_{ab} = 627 cm^{-1}, α^2 = 3.3 × 10^{-3}). This is the first reported example of a mixed-valence bimetallic complex containing the widely used dppf ligand. The ability of **1** to serve as a heterobimetallic catalyst for the reduction of methyl viologen with H$_2$ makes it a unique functional model of [NiFe] hydrogenase enzymes.

Introduction

The capacity of hydrogenase enzymes to couple H$_2$ with electron transfer pathways that reduce one-electron acceptors, such as cytochrome c_3 or methyl viologen (MV^{2+}), poses a considerable challenge to the development of functional hydrogenase models (eq 1).[1] In general, reductions in which H$_2$ is used solely as a source of electrons are not well studied beyond the early work of Halpern and his co-workers.[2] A credible hydrogenase reactivity model not only must use H$_2$ to perform one-electron reductions but must do so with high thermodynamic efficiency. For instance, in the hydrogenase of *D. gigas* an Fe$_4$S$_4$ cluster proximal to the putative H$_2$-activating site, the Ni center, is reduced at a midpoint redox potential of −445 mV (vs NHE),[3] only 35 mV positive of the thermodynamic reduction potential of H$_2$ at pH = 8.

$$H_2 \xrightarrow{H_2ase} 2e^- + 2H^+ \qquad (1)$$

A further challenge to understanding and modeling the activation of H$_2$ by [NiFe]H$_2$ase is raised by recent structural studies which show that the nickel resides in a heterobimetallic site linked to a second metal, believed to be iron, by cysteinate bridges.[4] Speculation that interaction of these two metals is involved in the activation of H$_2$ has prompted our interest in the study of a heterobimetallic complex, Cp*(dppf)RuH (**1**, dppf = 1,1′-bis(diphenylphosphino)ferrocene, Cp* = pentamethylcyclopentadienide, Figure 1), to examine the influence of a proximal Fe(II) on the Cp*L$_2$RuH catalyzed reduction of NAD model compounds by H$_2$.[5] In this paper we report the preparation of the Ru(II) hydride, **1**, its ability to catalyze the one-electron reduction of MV^{2+} with H$_2$ (TMP = tetramethylpiperidine, eq 2), and the isolation and characterization of its 17-electron Ru(III) counterpart, **1**$^+$, as a delocalized mixed-valence metal hydride.[6]

$$H_2 + 2MV^{2+} + 2TMP \xrightarrow[\text{acetone}]{\mathbf{1}\,(0.1\%)} 2MV^+ + 2HTMP^+ \qquad (2)$$
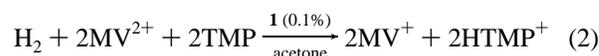
Experimental Section

General Procedures. All manipulations were performed under an atmosphere of nitrogen (high purity, 99.995%) or argon prepurified by passage through BASF-BTS catalyst and molecular sieves (3Å-Linde). Gasses were measured using a mercury manometer against atmospheric pressure so an "atmosphere of gas" indicates about 735 Torr. Prepurified hydrogen (99.995%) was passed through a column containing a BASF-BTS catalyst and molecular sieves (3Å-Linde). Degassed solutions were prepared by freezing in liquid nitrogen, evacuating, and thawing three times. NMR tube reactions were performed in resealable 5-mm NMR tubes (Brunfeldt Glass).

Benzene, hexane, THF, and pentane were distilled under nitrogen or vacuum from sodium or potassium benzophenone. Methylene chloride and acetonitrile were distilled from P$_4$O$_{10}$. Methanol was distilled under nitrogen from freshly activated magnesium turnings. Acetone was dried and vacuum transferred from MgSO$_4$. THF-d_8 was stored over sodium benzophenone ketyl under vacuum in a flask with a Teflon valve and transferred at reduced pressure to reaction samples.

Cp*(PPh$_3$)$_2$RuCl,[8] Cp(dppf)RuH,[9] Cp*(Ph$_2$PMe)$_2$RuH,[10] [MV][I]$_2$,[11] and [Fc]PF$_6$[12] were prepared as described in the literature. The hexafluorophosphate salts were generated by metathesis with NH$_4$PF$_6$. TMP was purchased from Aldrich and distilled from P$_4$O$_{10}$. Cobaltocene was purchased from Strem Chemicals Inc., Bu$_3$SnH from Aldrich, and ruthenium trichloride hydrate from Colonial Metals, Inc.

Analyses. Elemental analyses were performed by Midwest Microlabs, Indianapolis, IN. Crystallographic data was collected at Crysta-

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(4) The distance from Ni to the second metal (X) is 2.7 Å in the *D. gigas* [NiFe] hydrogenase: Volbeda, A.; Charon, M.-H.; Piras, C.; Hatchikian, E. C.; Frey, M.; Fontecilla-Camps, J. C. *Nature* **1995**, *373*, 580–87.

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(7) Li, Z. W.; Yeh, A.; Taube, H. *Inorg. Chem.* **1994**, *33*, 2874–81.

a.

b.

c.

d.
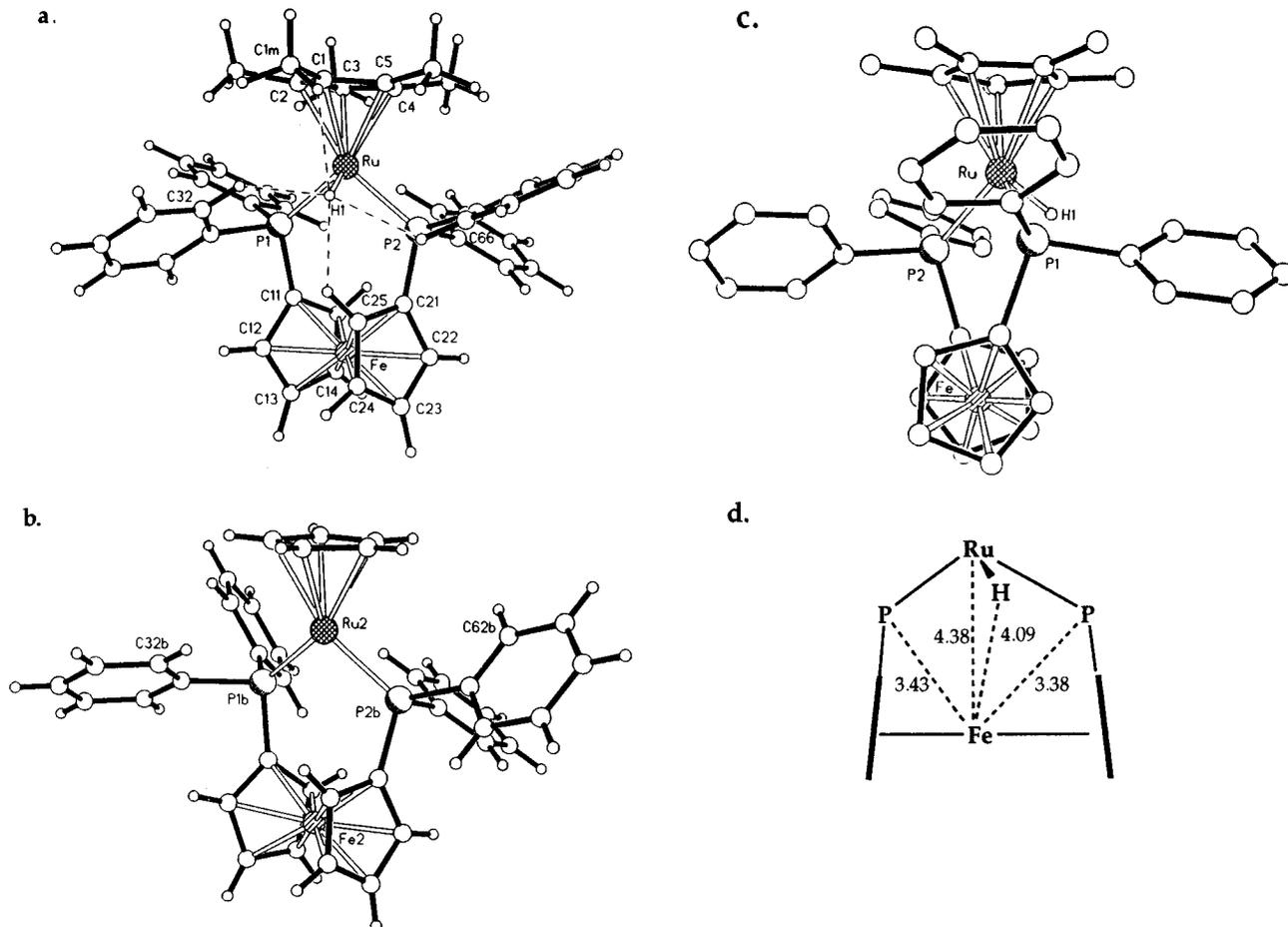
Figure 1. (a) Perspective drawing of the solid-state structure of Cp*(dppf)RuH, **1**. For clarity, Ru, Fe, and P atoms are represented by large cross-hatched, striped, and shaded spheres, respectively; carbon and hydrogen atoms are represented by medium-sized and small open spheres. (b) Perspective drawing of the solid-state structure of Cp(dppf)RuH, **2**, viewed, labeled, and represented as in part a (the hydride was not crystallographically located).[9] (c) Perspective drawing of **1** showing staggered conformation of the ferrocene group in the dppf ligand. For clarity all hydrogen atoms except the hydride ligand have been omitted. (d) Schematic of the Fe−P₂−RuH core of **1**.

lytics Co., Lincoln, NE. IR spectra were recorded on an Analect RFX-65 FT-IR spectrometer using a CaF₂ cell for liquid samples. NMR spectra were recorded on GE Omega 300 and 500 (^{13}C, ^{1}H, and ^{31}P) spectrometers. Solvent adsorptions were used as internal standards {δ ^{1}H: THF-d_7, δ = 3.58, 1.73; CHD₂CN, δ = 1.93; C₆D₅H, δ = 7.15; CDHCl₂, δ = 5.32 ppm}. A 3% aqueous H₃PO₄ solution was used as an external standard for ^{31}P spectra. Near-IR and UV−vis measurements were made on a Cary 14 UV−vis apparatus with an Olis upgrade for NIR measurements.

Cyclic voltammograms were obtained on a Cypress Systems Potentiostat Model CYSY-1R equipped with a Model CS-1090 computer-controlled electroanalytical system. A glassy carbon or 0.15 mm diameter platinum wire electrode was used as the working electrode, a silver wire as the reference electrode, and a platinum wire as the counter electrode. All solutions were prepared and measurements were performed in a drybox under a nitrogen atmosphere. Samples were prepared in THF with the concentration of electrolyte, [Bu₄N][PF₆], at 0.1 M and that of the analyte and reference, [Cp₂Co][PF₆], at 0.4 mM.

Cp*(dppf)RuH, 1. Method 1. A benzene solution (25 mL) containing [Cp*RuCl₂]$_n$ (247 mg, 0.81 mmol), dppf (520 mg, 0.95

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mmol), and zinc (455 mg, 7.0 mmol) was stirred for 48 h under nitrogen. A methanolic solution (15 mL) containing Na (130 mg, 5.6 mmol) was added via cannula and heated at reflux for 4 h. The solvent was removed at reduced pressure and the residue was extracted with benzene. The benzene was removed at reduced pressure and the resulting residue washed with methanol and dried in vacuo yielding 553 mg of an orange powder (87% yield).

Method 2. A benzene solution (30 mL) of Cp*Ru(PPh₃)₂Cl (500 mg, 0.63 mmol) and dppf (378 mg, 0.68 mmol) was heated at reflux under nitrogen for 10 h. A dark yellow solid formed and when cooled was filtered, washed with benzene twice, and dried in vacuo. A methanolic solution containing Na (120 mg, 5.2 mmol) was added via cannula to a suspension of the collected solid, Cp*Ru(dppf)Cl, in methanol and heated at reflux for 48 h. Allowing the suspension to cool resulted in the precipitation of a yellow solid which was filtered under nitrogen, washed three times with methanol, and dried in vacuo yielding 385 mg of an orange powder (78% yield). A crystalline solid suitable for X-ray analysis was obtained by layering methanol on a saturated benzene solution in a tube sealed with a Teflon valve. ^{1}H NMR (C₆D₆) δ −12.31 (t, J = 35.8 Hz, 1H), 1.40 (s, 15 H), 3.70 (s, 2 H), 3.82 (s, 2 H), 4.09 (s, 2 H), 4.65 (s, 2 H), 7.19 (m, Ph), 8.03 (br s, Ph), 8.19 (br s, Ph). ^{31}P NMR (C₆D₆) δ 64.8 (s). IR (THF) $\nu_{Ru−H}$ = 1946 cm^{-1} (br, w). Anal. Calcd for (C₄₄H₄₄P₂RuFe): C, 66.7; H, 5.6. Found: C, 66.3; H, 5.5.

This hydride is not soluble in acetonitrile or methanol but is soluble in THF, benzene, methylene chloride, and acetone. Dissolution of **1** in chloroform or dichloroethane results in the formation of Cp*(dppf)-RuCl within an hour. In methylene chloride **1** is stable for days at ambient temperature but slowly decomposes at 80 °C. A low-temperature NMR study showed no broadening of the cyclopentadienyl

protons of the ferrocene ligand at −80 °C. The staggered conformation of the dppf ligand present in the solid state must, therefore, undergo a rapid "ring flip".

[Cp*(dppf)Ru(H)]PF$_6$, [1]PF$_6$. To a THF (20 mL) solution of **1** (256 mg, 0.32 mmol) was added [Fc]PF$_6$ (100 mg, 0.30 mmol) at −78 °C under nitrogen. The solution was stirred for 4 h in which time it became a dark maroon color. Cold pentane was added via cannula causing the precipitation of the product which was filtered, washed three times with cold pentane, and dried in vacuo yielding 278 mg (98% yield) of a light maroon solid. The broadened peaks of the ^{1}H NMR of the solid in CD$_2$Cl$_2$ was consistent with a paramagnetic product. No hydride resonance or ^{31}P signal was observed. Allowing the NMR tube to sit for several hours resulted in a lighter colored solution and very faint ^{31}P signals at 44 and 38 ppm. After 12 h, NMR indicated the formation of [Cp*(dppf)Ru(H)$_2$]$^+$ and [Cp*(dppf)Ru-(THF)]$^+$.

[Cp*(dppf)Ru(H)(Cl)]PF$_6$. To a 25-mL flask containing [**1**]PF$_6$ (27 mg, 30 μmol) was added carbon tetrachloride (1.5 mL) and THF (4 mL). After an hour of stirring the solvent was removed at reduced pressure and the residue dried for 2 h under vacuum. ^{1}H NMR (CD$_2$-Cl$_2$) δ −7.45 (t, J = 32 Hz, 1H), 1.22 (s, 15H), 4.15 (s, 2H), 4.18 (s, 2H), 4.39 (s, 2H), 4.97 (s, 2H), 7.40−7.75 (m, 20H). {^{1}H}^{31}P NMR (CD$_2$Cl$_2$) δ 38.3. Anal. Calcd for C$_{44}$H$_{44}$ClF$_6$FeP$_3$Ru: C, 54.3; H, 4.5. Found: C, 54.1; H, 4.7.

[Cp*(dppf)Ru(H)(Br)]PF$_6$. To a foil-wrapped resealable NMR tube was added [**1**]PF$_6$ (8 mg, 9 μmol), BrMn(CO)$_5$ (6 mg, 22 μmol), and THF. The dark gold solution was analyzed by ^{31}P NMR indicating the formation of one major product at δ 37.6 ppm which was assumed to be the correct product from the similarity in chemical shift to the chloride and iodide derivatives. ^{1}H NMR (CD$_3$CN) δ −7.50 (t, J = 32 Hz, 1H), 1.40 (t, J = 1.5 Hz, 15H), 4.18 (s, 2H), 4.24 (s, 2H), 4.43 (s, 2H), 5.09 (s, 2H), 7.46 (m, 20H). {^{1}H}^{31}P NMR (CD$_3$CN) δ 37.6.

[Cp*(dppf)Ru(H)(I)]PF$_6$. To a THF solution (2 mL) containing [**1**]PF$_6$ (28 mg, 3 μmol) was added an iodine/THF (0.1 M) solution (0.5 mL) with stirring for 75 min. A dark red solid was isolated by precipitation with hexanes. Recrystallization from MeOH/benzene afforded crystals. ^{1}H NMR (CD$_3$CN) δ −7.50 (t, J = 32 Hz, 1H), 1.40 (t, J = 1.5 Hz, 15H), 4.18 (s, 2H), 4.24 (s, 2H), 4.43 (s, 2H), 5.09 (s, 2H), 7.46 (m, 20H). {^{1}H}^{31}P NMR (CD$_3$CN) δ 37.6. Anal. Calcd for C$_{44}$H$_{44}$F$_6$FeIP$_3$Ru: C, 49.6; H. 4.2. Found: C, 50.0; H, 4.4.

[Cp*(dppf)Ru(H)$_2$]PF$_6$. To a solution (0.5 mL) containing [**1**]PF$_6$ (9 mg, 9 μmol) in THF-d_8 was added Bu$_3$SnH (18 mg, 62 μmol). After 30 min ^{1}H and ^{31}P NMR spectra indicated the formation of [Cp*(dppf)-RuH$_2$]PF$_6$. ^{1}H NMR (THF) δ −7.76 (t, J = 25.7 Hz, 1H), 1.26 (s, 15H), 4.21 (s, 4H), 4.22 (s, 4H), 7.4 (m), 7.62 (br s), and 7.92 (m). {^{1}H}^{31}P NMR (THF) δ 59.2. Anal. Calcd for C$_{44}$H$_{45}$F$_6$FeP$_3$Ru: C, 56.2; H, 4.8. Found: C, 55.9; H, 4.9.

Disproportionation of [1]PF$_6$ in Solution. Into a flask with a Teflon valve and a quartz cuvette fused to a side-arm was placed 12 mg of [**1**]PF$_6$ (13 μmol), and 4 mL of THF was placed in the sidearm. To begin the reaction the flask was tilted upright allowing the THF to run into the bulb. The reaction was followed by the decreasing absorbance at 912 nm for 570 min at 23 °C. Extrapolation based on the rate of disproportionation yielded an extinction coefficient of 468. Analysis of a plot of the reciprocal of [**1**$^+$] vs time yielded a second-order rate constant of 3.5 × 10^{-2} M^{-1} s^{-1}.

A retardation in the decomposition rate of [**1**-H]PF$_6$ was measured by following a reaction prepared in the same manner as above, but with 44 mg of **1** (0.056 mmol) added prior to the addition of THF. After 10 h 50% of [**1**]PF$_6$ remained.

Reduction with H$_2$ Catalyzed by 1. **1** (6.2 mg, 0.01 mmol) and [Cp$_2$Fe][PF$_6$] (337 mg, 1.0 mmol) were placed in a flask with a Teflon valve and acetone (10 mL) was added by vacuum transfer. TMP (200.0 μL, 1.2 mmol) was added by syringe under a flow of argon, and the solution was degassed and then placed under an atmosphere of H$_2$. Progress of the reaction was followed by the dissolution of the insoluble [Cp$_2$Fe]PF$_6$. After 2 h the solution was concentrated to a residue and extracted with hexanes (3 × 10 mL). Following the removal of the hexanes 176 mg of ferrocene (94% yield) was obtained.

In the same fashion, **1** (3 μmol), [MV][PF$_6$]$_2$ (45.0 mg, 0.10 mmol), and TMP (50 μL, 0.30 mmol) were combined and placed under H$_2$

Table 1. Crystallographic Data for Cp*(dppf)RuH (**2**-H)^a

C$_{44}$H$_{44}$P$_2$RuFe   791.71 amu
$P2_1/n$ {an alternate setting of $P2_1/c-C_{2h}^5$ (No. 14)}
density = 1.557 g cm^{-3}
monoclinic (T = 20 °C)
V = 3616(1) Å^3
Z = 4
a = 12.913(2) Å
b = 15.041(3) Å
c = 18.831(4) Å
α = 90.0
β = 98.62(2)°
γ = 90.00°
R(unweighted) = 0.019
(8305 independent absorption corrected
    reflections having 2θ < 55°) GOF = 1.02

^{a} The complete data set is available from the Crystalytics Co., Lincoln, NE.

with acetone (10 mL) as the solvent. After 5 h at 23 °C the initially light yellow solution became very dark blue.

Crystallographic Study of 1. At 20 ± 1 °C, single crystals of **1** are monoclinic, space group $P2_1/n$ [an alternate setting of $P2_1/c-C^5_{2h}$ (No. 14)] with a = 12.913(2) Å, b = 15.041(3) Å, c = 18.831(4) Å, β = 98.62(2)°, V = 3616(1) Å^3, and Z = 4 {d_{calcd} = 1.557 g cm^{-3}; $μ_a$(Mo Kα) = 1.32 mm^{-1}}. A total of 8305 independent absorption corrected reflections having 2θ(Mo Kα) < 55.0° (the equivalent of 1.0 limiting Cu Kα spheres) were collected on a computer-controlled Nicolet autodiffractometer using full (0.90° wide) ω scans and graphite-monochromated Mo Kα radiation. The computer programs and procedures used for data collection, data reduction, structure solution, and refinement of **1** have been reported elsewhere;[13] a summary of the crystallographic data for the present study is given in Table 1.

The structure was solved using "heavy atom" techniques with the Siemens SHELXTL-PC software package as modified at Crystalytics Company. The resulting structural parameters have been refined to convergence {R_1(unweighted, based on F) = 0.036 for 5419 independent absorption-corrected reflections having 2θ(Mo Kα) < 55.0° and $I > 3σ(I)$} using counter-weighted full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms.

The hydride hydrogen atom (H$_1$) was located from a difference Fourier map and refined as an independent isotropic atom. The five methyl groups (C$_{1m}$, C$_{2m}$, C$_{3m}$, C$_{4m}$, C$_{5m}$ and their hydrogens) were refined as rigid rotors with sp^3-hybridized geometry and a C−H bond length of 0.96 Å. The initial orientation of each methyl group was determined from difference Fourier positions for the hydrogen atoms. The final orientation of each methyl group was determined by three rotational parameters. The refined positions for the rigid rotor methyl groups gave C−C−H angles which ranged from 102° to 114°. The remaining hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp^2 hybridization of the carbon atoms and a C−H bond length of 0.96 Å) "riding" on their respective carbon atoms. The isotropic thermal parameter for H$_1$ refined to a final value of 3(1) Å^2. The isotropic thermal parameter of each remaining hydrogen atom was fixed at 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which it is covalently bonded.

Results and Discussion

Synthesis and Characterization of Cp*(dppf)RuH, 1. Established procedures, with minor adaptation, work well for the synthesis of **1**. Its chloride counterpart, Cp*(dppf)RuCl, is prepared in good yield by either the Bruce or Suzuki methods.[14] In the former dppf displaces triphenylphosphine from Cp*(Ph$_3$P)$_2$-RuCl and in the latter dppf reacts with a Ru(III) polymer, [Cp*RuCl$_2$]$_n$, in the presence of zinc. Treatment of Cp*(dppf)-RuCl with NaOMe yields the hydride, **1**, as an orange powder,

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insoluble in methanol or acetonitrile, but readily dissolved in THF, benzene, and acetone. Reaction with chlorinated solvents such as chloroform or dichloroethane limits their usage, but methylene chloride solutions are stable for a couple of days at ambient temperature.

X-ray analysis of a crystal of **1** revealed the molecular structure of the heterobimetallic hydride, Cp*(dppf)RuH, as shown in Figure 1 with a Ru−H bond length of 1.43(4) Å. Both d^6 metals in **1** are pseudooctahedral 18-electron centers with nine of their twelve formal coordination sites occupied by three substituted cyclopentadienyl rings.[15] The steric properties of the chelating dppf ligand[16] require a nearly linear C_{1g}−Ru⋯Fe[17] arrangement with the ferrocenyl group situated opposite the C_5Me_5 bound to ruthenium ($\angle C_{1g}$−Ru⋯Fe = 175.6°). Thus the hydride ligand, both phosphorus atoms, and the four phenyl rings of the dppf ligand occupy positions in a band perpendicular to this nearly linear C_{1g}−Ru⋯Fe grouping and between the Ru-bonded cyclopentadienyl ligand and the ferrocenyl group.[18]

The Cp rings in the dppf ligand of **1** are within 3° of perfectly staggered (Figure 1c). For instance, the dihedral angle defined by P_1−C_{11}−C_{21}−P_2 is 38.3°. In solution rapid flipping between pseudoenvelope conformations renders these phosphorus atoms symmetry equivalent, even at −80 °C. The dimensions of the heterobimetallic core, of interest in the redox properties of **1**, are defined by the nonbonded distances of ∼3.40 Å between the iron and the two phosphorus atoms, 4.38 Å between the iron and ruthenium atoms, and 4.09 Å between the iron and the metal hydride ligand (Figure 1d). Along with a P−Ru−P angle of 98° the coordination of dppf to Ru(II) in **1** is as expected for an 18-electron complex. It is interesting to note, however, that the structure of [(dppf)Pd(PPh₃)][BF₄]₂, with a dative interaction between the iron of dppf and Pd(II), has been reported by Sato.[20] The Fe−Pd distance of 2.88 Å and a P−Pd−P angle of 156° in this complex demonstrates that the geometry of the heterobimetallic core of **1** is surprisingly flexible.

The structure of **1** (Figure 1a) may be compared with that of four related Ru(II) hydrides of the CpL₂RuH family {L₂ = (PMe₃)₂,[21a] (PPh₃)₂,[21b] dppp,[21c] and dppf[9]}, but none of these contain the pentamethylcyclopentadienide ligand. In a careful analysis of the structures of this class of metal hydrides Lemke and Bremmer compare several structural features of the "three-legged piano stool" geometry.[21a] First, the 98° P_1−Ru−P_2 angle

in **1** (Table 2) is similar to that in the other Ru(II) hydrides (96−101°). Likewise, **1** is typical of this group in the angles at which the metal hydride bond intersects the P_1−Ru−P_2 plane and the H_1−Ru−C_{g1} plane intersects the P_1−Ru−P_2 plane: 76.9° vs 73.6−85.4° and 89.6° vs 87.4−88.8°, respectively.[22] The angle of intersection of the P_1−Ru−P_2 plane with the plane defined by the cyclopentadienyl carbons is a bit higher in **1** (73.5°) than in the C_5H_5 derivatives (65.6−68.9°) which may reflect the influence of the methyl groups of Cp*. For instance, the same angle in [Cp*(PPh₃)₂RhH]PF₆ is increased to 79.2°.[23]

The steric crowding imposed in a half-sandwich derivative of C_5Me_5 is nicely demonstrated by comparison of **1** with Cp-(dppf)RuH, **2** (Figure 1b).[24] The metric parameters of their Ru coordination spheres and heterobimetallic cores, Fe−P_2−RuH, are essentially identical (Figure 1d).[25] The only striking structural difference between **1** and **2** is that two of the four dppf phenyl rings have rotated about their P−C bonds to adopt orientations more nearly parallel to the C_5Me_5 plane. Replacing the hydrogens of a cyclopentadienyl ligand with methyls dramatically increases its "cone angle".[26] This added "radial bulk" allows the C_5Me_5 to act as a van der Waals "cap" for the ruthenium octahedron which prevents the ortho hydrogens on the phenyl rings from approaching this portion of the coordination sphere. As a result the orientation of the phenyl rings for the dppf ligands is more restricted in **1** than in **2**. In essence, the substitution of methyl groups for hydrogen on the Ru-bonded cyclopentadienyl ring of **2** has compressed the phenyl groups of dppf and introduced a preferred orientation in which the phenyl rings are "flattened", i.e., perpendicular to the Ru−C_{1g} vector. One of these phenyl rings is adjacent to the hydride ligand and produces a smaller hydrophobic pocket for this ligand in **1** than **2**.[29] As discussed below, we attribute the unusual stability of the Ru(III) derivative of **1**, at least in part, to this

(15) Each of the five-membered rings for these cyclopentadienyl ligands are coplanar to within 0.006 Å. The least-squares mean planes for the two cyclopentadienyls of the dppf ligand are within 7.2° of being parallel to each other with the Fe(II) atom between them, 1.64 Å from each mean plane. Phosphorus atoms P_1 and P_2 are displaced by 0.04 and 0.09 Å from these mean planes toward the Fe atom. The Ru(II) atom is 1.91 Å from the C_5 ring of the C_5Me_5 ligand and the five methyl carbons are displaced by 0.17−0.25 Å on the opposite side.

(16) Gan, K.-S.; Hor, T. S. A. In *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, 1995; pp 3−104.

(17) The symbols C_{1g}, C_{2g}, and C_{3g} are used to represent the centers-of-gravity for the five-membered rings of the Cp* and each of the two cyclopentadienyl rings of the dppf ligand, respectively.

(18) The average[19] Ru−C, Ru−P, and Fe−C bond lengths are 2.263(4, 18, 30, 5), 2.265(1, 6, 6, 2), and 2.045(4, 16, 27, 10) Å. The P_1−Ru−P_2, H_1−Ru−C_{1g},[17] and C_{2g}−Fe−C_{3g}[17] angles are 97.9(1)°, 121.0°, and 176.0°. The average P−Ru−H_1 and P−Ru−C_{1g} angles are 82(2, 1, 1, 2)° and (−, 3, 3, 2)°. The average P−C aryl dicyclopentadienyl and phenyl C−C bond lengths are 1.848(4, 9, 23, 6), 1.427(6, 10, 27, 10) and 1.387(7, 7, 21, 24) Å. The average ring C−C and ring-to-methyl C−C bond lengths for the Cp* ligand are 1.427(6, 8, 16, 5) and 1.503(6, 3, 7, 5) Å.

(19) The first number in parentheses following an average value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviations from the average value, respectively. The fourth number represents the number of individual measurements which are included in the average value.

(20) Sato, M.; Shigeta, H.; Sekino, M.; Akabori, S. *J. Organomet. Chem.* **1993**, *458*, 199−204.

(21) (a) Lemke, F. R.; Brammer, L. *Organometallics* **1985**, *14*, 3980−87. (b) Lister, S. A.; Redhouse, A. D.; Simpson, S. J. *Acta Crystallogr.* **1992**, *C48*, 1661−63. (c) Smith, K.-T.; Rømming, C.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 8681−89.

(22) The RuH bond of Cp(PPh₃)₂RuH is anomolous in this group with an interplanar angle between its centroid−Ru−H and P−Ru−P planes of 76.5° (see Table 5 in ref 21a).

(23) Mingos, D. M. P.; Minshall, P. C.; Hursthouse, M. B.; Malik, K. M. A.; Willoughby, S. D. *J. Organomet. Chem.* **1979**, *181*, 169−82.

(24) In the solid state **2** consists of two crystallographically-independent molecules.[9] There are no significant differences in their structures relevant to a comparison with **1**, so we present only one of the structures in Figure 1b. It has been renumbered to coincide with **1**. Unfortunately, the hydride ligand on Ru could not be crystallographically located for either molecule of **2**.

(25) The close structural similarity for the immediate metal coordination spheres of **1** and **2** would seem to indicate that the differences in their chemical behavior must be due to electronic effects produced by replacing the five hydrogens on the Cp ligand in **2** by methyl groups and/or the steric effects of such substitutions on ligand atoms not bonded directly to a metal. While the electronic effects of substituting methyl for hydrogen on a cyclopentadienyl ligand are well documented and can be probed electrochemically, the steric effects of such a substitution cannot be so easily assessed.[26]

(26) Both ligands are disc-shaped with a central 2.42 Å diameter core which is 3.40 Å thick (the van der Waals diameter[27] of an aromatic carbon atom). Surrounding this central 2.42 Å disc is a ring of five hydrogens for C_5H_5 or five methyl groups for C_5Me_5. A ring of five hydrogens extends the disc radially another 2.29 Å and this annulus is 2.40 Å thick (the van der Waals diameter[27] of a hydrogen atom) while a ring of five methyls extends the disc radially another 3.54 Å and this annulus is 4.00 Å thick (the van der Waals diameter[27] of a methyl group). In terms of cone angles a value of 131° for C_5H_5 can be compared with 182° for C_5Me_5.[28]

(27) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

(28) White, D.; Coville, N. J. *Adv. Organomet. Chem.* **1994**, *36*, 95−158.

(29) This pocket contains four short H⋯H contacts between the hydride ligand and hydrogens of the surrounding ligands. These contacts are shown with dashed lines in Figure 1a and have the following separations: H_1⋯H_{25}, 2.29 Å; H_1⋯H_{32}, 2.06 Å; H_1⋯H_{66}, 2.84 Å; and H_1⋯H_{1ma}, 2.90 Å.

Figure 2. Cyclic voltammogram of **1** (0.4 mM in THF) and cobaltocene (0.4 mM, −750 mV vs NHE) with 0.1 M TBAF at a Pt-wire electrode; scan rate = 200 mV/s. A plot of i_a against the square root of the scan speed is linear across a range of 20−1000 mV/s (i_a/i_c = 0.9−1.1; correlation coefficient >0.99) for E_1 and E_2, as expected for a diffusion-controlled electrode process.

imposed structure around the hydride ligand which must retard inner-sphere reactions of its metal−hydrogen bond.

Oxidation of 1. Electrochemical oxidation of metal hydrides is rarely reversible,[30] but analysis of **1** by cyclic voltammetry reveals *two reversible oxidations* at +0.073 and +0.541 V and a quasireversible oxidation at +0.97 V vs NHE (E_1, E_2, and E_3, respectively; Figure 2). Under the same conditions Cp-(dppf)RuH shows only a quasireversible oxidation at +0.28 V, an irreversible oxidation at +.69 V, and another quasireversible redox couple at +0.97 V (Table 3). Assignment of E_1 to Ru-(III/II) and E_2 to Ru(IV/III) in **1** is supported by comparison with the oxidations of Cp*(Ph$_2$MeP)$_2$RuH (**3**) which contains no iron. For **3** both a reversible redox couple {E_1 = +0.050 V; Ru(III/II)} and an irreversible oxidation {E_2 = +0.496 V; Ru(IV/III)} at potentials similar to those of **1** must be ruthenium centered. Oxidation of iron in dppf occurs irreversibly at +0.87 V and is typically shifted positive by 0.1−0.2 V upon coordination of its phosphines in a chelate complex.[33] Comparison of the chloride derivatives reveals redox potentials for E_1 that are shifted by about 400 mV while the second oxidations all occur at ∼1.0 V, characteristic of a coordinated dppf. Because all of the dppf derivatives in Table 3 exhibit an oxidation at ∼0.97 V we assign E_3 of the hydrides and E_2 of the chlorides (Figure 2) to Fe(III/II) of the dppf ligand.

These assignments dictate an equilibrium constant for electron-transfer disproportionation of **1**$^+$ (eq 3) and predict a novel stability for this 17-electron metal hydride.

$$2[\mathbf{1}][\text{PF}_6] \underset{}{\overset{K=1.8\times10^{-8}}{\rightleftharpoons}}$$
$$[\text{Cp*(dppf)RuH}][\text{PF}_6]_2 + \text{Cp*(dppf)RuH} \quad (3)$$

In fact, a red solution of Cp*(dppf)RuH$^+$ in CH$_2$Cl$_2$ is generated by the stoichiometric oxidation of **1** with the

(30) Tilset has reported two closely related examples of near-reversibility in CpL$_2$RuH complexes,[31] but in general electrochemical oxidation of hydrides of this family are irreversible.[10] Only two examples of fully reversible electrochemical one-electron oxidations have been reported.[32]

(31) Smith, K. T.; Roemming, C.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 8681−89.

(32) (a) Sharp, P.; Frank, K. G. *Inorg. Chem.* **1985**, *24*, 1808−13. (b) Detty, M. R.; Jones, W. D. *J. Am. Chem. Soc.* **1987**, *109*, 5666−73.

(33) Zanello, P. In *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, 1995; pp 317−430.

Table 2. Selected Bond Lengths and Bond Angles in Crystalline Cp*(dppf)RuH (**1**)^a

type^b	parameter	type^b	parameter
	Bond Lengths, Å		
Ru−P$_1$	2.271(1)	Ru−P$_2$	2.259(1)
Ru−H$_1$	1.43(4)	Ru−C$_{1g}$	1.910(−)^c
Fe−C$_{2g}$	1.643(−)^c	Fe−C$_{3g}$	1.649(−)^c
P$_1$−C$_{11}$	1.847(4)	P$_2$−C$_{21}$	1.825(4)
P$_1$−C$_{31}$	1.847(4)	P$_2$−C$_{41}$	1.846(4)
P$_1$−C$_{51}$	1.862(4)	P$_2$−C$_{61}$	1.859(4)
	Bond Angle, deg		
P$_1$RuP$_2$	97.9(1)	H$_1$RuC$_{1g}$	121.0(−)^c
H$_1$RuP$_1$	82(2)	H$_1$RuP$_2$	81(2)
P$_1$RuC$_{1g}$	128.4(−)^c	P$_2$RuC$_{1g}$	129.0(−)^c
C$_{2g}$FeC$_{3g}$	176.0(−)^c		
RuP$_1$C$_{11}$	123.8(1)	RuP$_2$C$_{21}$	118.6(1)
RuP$_1$C$_{31}$	115.4(1)	RuP$_2$C$_{41}$	118.3(1)
RuP$_1$C$_{51}$	116.6(1)	RuP$_2$C$_{61}$	113.3(1)
C$_{11}$P$_1$C$_{31}$	99.7(2)	C$_{21}$P$_2$C$_{41}$	103.7(2)
C$_{11}$P$_1$C$_{51}$	97.6(2)	C$_{21}$P$_2$C$_{61}$	97.8(2)
C$_{31}$P$_1$C$_{51}$	99.6(2)	C$_{41}$P$_2$C$_{61}$	102.1(2)
P$_1$C$_{11}$C$_{12}$	128.6(3)	P$_2$C$_{21}$C$_{22}$	129.6(3)
P$_1$C$_{11}$C$_{15}$	124.8(3)	P$_2$C$_{21}$C$_{25}$	123.5(3)
P$_1$C$_{31}$C$_{32}$	120.0(3)	P$_2$C$_{41}$C$_{42}$	117.7(3)
P$_1$C$_{31}$C$_{36}$	122.2(3)	P$_2$C$_{41}$C$_{46}$	124.3(3)
P$_1$C$_{51}$C$_{52}$	123.4(3)	P$_2$C$_{61}$C$_{62}$	123.9(3)
P$_1$C$_{51}$C$_{56}$	119.0(3)	P$_2$C$_{61}$C$_{66}$	118.0(3)

^{a} The numbers in parentheses are the estimated standard deviations in the last significant digit. ^{b} Atoms are labeled in agreement with Figure 1. ^{c} See footnote 17.

Table 3. Redox Potentials of Cp*L$_2$RuH Complexes^{a,b}

	X = H			X = Cl	
	E_1	E_2	$E_3{}^c$	E_1	$E_2{}^c$
Cp*(dppf)RuX	+0.073	+0.541	(+0.975)	+0.523	+1.033
Cp*(Ph$_2$PMe)RuX	+0.050	(+0.496)		+0.480	
Cp(dppf)RuX	(+0.284)	(+0.695)	(+0.972)	+0.675	+0.967

^{a} All potentials are measured in THF solution with 0.1 M [Bu$_4$N]PF$_6$ vs cobaltocene (−0.750) and are reported vs NHE. ^{b} Values in parentheses indicate anodic peak potentials from irreversible redox couples. ^{c} E_3 of the hydrides and E_2 of the chlorides are assigned to the Fe(III/II) couple of the dppf ligand.

ferrocinium ion. This species may be reduced by cobaltocene to its parent hydride (eq 4) or precipitated by addition of pentane at low temperature, isolated, and dissolved in THF to give a purified solution of the Ru(III) hydride.[34]

$$\mathbf{1} \underset{\text{Cp}_2\text{Co}}{\overset{[\text{Fc}]\text{PF}_6}{\rightleftharpoons}} [\text{Cp*(dppf)RuH}]\text{PF}_6 \quad (4)$$
$$\mathbf{1}^+$$
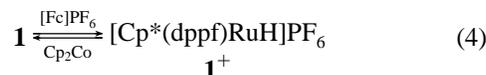
The optical spectrum of **1**$^+$ in methylene chloride contains an absorption in the NIR at 912 nm (ϵ = 486 M^{-1} cm^{-1}, Figure 3). As predicted by Hush for a weakly delocalized intervalence transition, the energy of the NIR band is sensitive to the dielectric properties of the solvent ($\nu_{max} \sim 1/n^2 - 1/D_s$)[36] and its bandwidth (3.38 × 10^3 cm^{-1}; Figure 3) is within 15% of that predicted by the analysis of Taube for an asymmetric mixed-valence ion.[37] The Ru(III) hydride, **1**$^+$, is thus characterized

(34) This procedure is analogous to that reported by Lapinte for the preparation of [Cp*(dppe)FeH]PF$_6$.[35]

(35) Hamon, P.; Toupet, L.; Hamon, J. R.; Lapinte, C. *Organometallics* **1992**, *11*, 1429−31.

(36) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391−444.

(37) Taube approximates an upper limit for the internal energy difference between two states, $\bar{\nu}_o$, as the difference in the corresponding redox potentials, $E_1 - E_2$: $\bar{\nu}_{op} - \bar{\nu}_o = (\Delta\bar{\nu}_{1/2})^2/2.31$.[38] For **1**$^+$ we use E_3 assigned to the [Fe(III/II), Ru(IV)] couple as an upper limit for the necessary [Fe-(III/II), Ru(III)] potential ($E_1 - E_3$ = 902 mV). This yields a calculated bandwidth of 2.92 × 10^3 cm^{-1} slightly less than that observed (obsvd/calcd = 1.15).
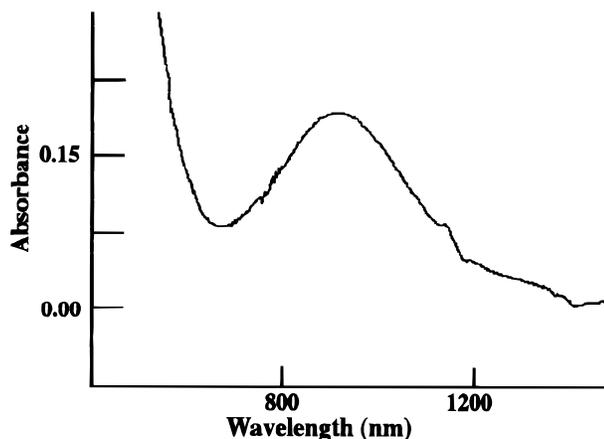
Figure 3. NIR spectrum of [**1**]PF₆ (0.6×10^{-3} M) in CH₂Cl₂. $\nu_{max} = 10.96 \times 10^3$ cm^{-1} ($\epsilon = 486$), $\nu_{1/2} = 3.38 \times 10^3$ cm^{-1}.

as a weakly delocalized [Ru(III)/Fe(II)] mixed-valence ion ($\alpha^2 = 3.3 \times 10^{-3}$, $H_{ab} = 627$ cm^{-1}).[39,41]

Reactivity of 1⁺. Atom transfer reactions readily convert **1⁺** to 18-electron Ru(IV) derivatives. For instance, reaction with Bu₃SnH yields [Cp*(dppf)RuH₂]⁺ and reactions with CCl₄, BrMn(CO)₅, or I₂ yield [Cp*(dppf)RuHX]PF₆ derivatives (eq 5). This class of reaction is well-known for M(I) 17-electron (C₅R₅)M(CO)₃ complexes (M = Cr, Mo, W), but is not for their M(III) CpL₂MX counterparts.[43]

$$[\mathbf{1}]PF_6 + XY$$
$$XY = HSnBu_3, CCl_4, BrMn(CO)_5, I_2 \longrightarrow$$
$$[Cp^*(dppf)RuX(H)]PF_6 \quad (5)$$
$$X = H, Cl, Br, I$$
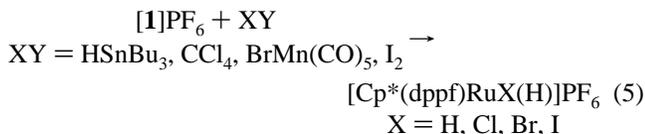
Related to these reactions is a slow process of H-atom transfer disproportionation in which **1⁺** is converted to [Cp*(dppf)Ru-(THF)]PF₆ and [Cp*(dppf)RuH₂]PF₆ (eq 6). This reaction mode is a common obstacle to the isolation of Ru(III) hydrides related to **1⁺**.[30] The disproportionation of **1⁺** (1−3 mM) in THF has a second-order dependence of the concentration of **1⁺** ($k = 3.5 \times 10^{-2}$ M^{-1} s^{-1} at 23 °C) and is retarded over 10-fold by the addition of 4 equiv of **1**. The latter observation is inconsistent with a concerted H-atom transfer or a proton transfer initiated process, but may be explained by a reversible electron-transfer disproportionation of **1⁺** (eq 3) followed by a proton transfer (a kinetic study of this reaction is in progress).[44]

$$2[\mathbf{1}]PF_6 \xrightarrow{\text{THF}} [Cp^*(dppf)Ru(THF)]PF_6 +$$
$$[Cp^*(dppf)Ru(H)_2]PF_6 \quad (6)$$

"Redox Switch" Catalysis. In our synthesis of **1⁺** the ferrocinium ion is reduced by **1** in a stoichiometric reaction (eq 4), but it can also be reduced by H₂ in the presence of a base (TMP) and a catalytic amount of **1** (eq 7). This reduction

proceeds at a modest rate (∼8.5 turnovers/min) at ambient temperature and pressure and is poisoned by stoichiometric amounts of halide or acetonitrile. As mentioned above (eq 2) the same method may be employed in the reduction of MV²⁺ to MV⁺. With the exception of hydrogenase enzymes,[45] **1** is the first example of a homogeneous catalyst for reduction of MV²⁺ with H₂. Because **1** and the H₂-activating center in hydrogenase act as templates for the conversion of a two-electron reducing agent, H₂, into one-electron equivalents (2Cp₂Fe or 2 MV⁺), we refer to them as "redox switch" catalysts.[47]

$$H_2 + 2\,TMP + [Cp_2Fe]PF_6 \xrightarrow[\text{THF}]{\mathbf{1}\,(1\%)} Cp_2Fe + 2\,[TMPH]PF_6$$
$$(7)$$
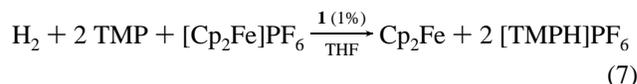
Conclusions

We report herein the discovery of Cp*(dppf)RuH (**1**), an active and well-defined catalyst for performing one-electron reductions with H₂. The unprecedented electrochemical characterization of two reversible one-electron oxidations of **1** and the reactivity of its Ru(III) hydride derivative, **1⁺**, suggest that **1⁺** is a key to the performance of **1** as a "redox switch" catalyst. The 17-electron metal hydride **1⁺** is characterized as a weakly delocalized mixed valence ion. It is the first example of such a mixed-valence ion in a dppf complex and it inspires speculation on the possible role of similar odd-electron states in the novel chemistry of dppf catalysts of Pd and Ni.[16] Likewise, as a heterobimetallic catalyst for one-electron reductions with H₂ it is a unique model for the H₂-reaction center of [NiFe] hydrogenases which may access similar delocalized oxidation states to facilitate the activation of H₂.

Supporting Information Available: A complete report of the X-ray crystallographic study of **1** (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA952206J

(38) Dowling, N.; Henry, P. M.; Lewis, N. A.; Taube, H. *Inorg. Chem.* **1981**, *20*, 2345−48.

(39) H_{ab} and α^2 values and the contribution of the mixed-valence resonance to the ground state stability of **1⁺** ($\Delta G_R = H_{ab}^2/\nu_{max} = 0.1$ kcal/mol) are calculated[40] using the Fe−Ru distance determined for **1** (4.383 Å, Figure 1).

(40) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1−74.

(41) Few examples of delocalized heterobimetallic mixed-valence complexes exist, but a similar CpRu(II) case with an acetylene bridge between ferrocene and Ru fragments has been reported ($\alpha^2 = 2.8 \times 10^{-2}$).[42a] In addition, four [(NH₃)₅Ru]²⁺−cyanoferrocene complexes ($\alpha^2 \sim 2 \times 10^{-3}$)[38,42c] and a series of complexes with Pd(II) directly bonded to the Cp ring of a substituted ferrocene are known.[42d]

(42) (a) Sato, M.; Shintate, H.; Kawata, Y.; Sekino, M.; Katada, M.; Kawata, S. *Organometallics* **1994**, *13*, 1956−62. (b) Sato, M.; Mogi, E.; Katada, M. *Organometallics* **1995**, *14*, 4837−43. (c) Dowling, N.; Henry, P. *Inorg. Chem.* **1982**, *21*, 4088−95. (d) Kotz, J. C.; Getty, E. E.; Lin, L. *Organometallics* **1985**, *4*, 610−12.

(43) Astruc, D. *Electron Transfer and Radical Processes in Transition-Metal Chemistry*; VCH: Weinheim, 1995; Chapter 5.

(44) Evidence reported by Tilset supports the proposal that Ru(III) hydrides, generated by the electrochemical oxidation of CpL₂RuH, rapidly protonate their Ru(II) parents.[30] The electrochemical stability of **1⁺**, along with the above noted effect of [**1**] on its disproportionation, rules out proton transfer from **1⁺** to **1** as a kinetically significant reaction mode. Tilset also reports that small amounts of acetonitrile accelerate the disproportionation of [CpL₂RuH]⁺ in THF.[30] We observe the same effect on **1⁺** and are pursuing a study of these H-atom disproportionation mechanisms.

(45) Woo, G.-J.; Wasserfallen, A.; Wolfe, R. S. *J. Bacteriol.* **1993**, *175*, 5970−77.

(46) Further studies of the one-electron reduction of organic substrates with H₂ catalyzed by **1** are in progress.[47]

(47) Hembre, R. T.; McQueen, J. S. In submission.