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Oxidation of $CpRu(CO)(PMe_3)H$ by $^2/_3$, 1, and 2 Electrons by the Judicious Choice of Reaction Conditions. Generation of a Bridging Hydride via the Reaction between a 17-Electron Metal Hydride Cation Radical and Its Conjugate Base

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Abstract: The hydride complex $CpRu(CO)(PMe_3)H$ (**1**) undergoes a chemically irreversible oxidation at 0.34 V vs the ferrocene/ferrocenium couple. By the judicious choice of reaction conditions, the oxidation of **1** in acetonitrile may be directed toward a $^2/_3$-, 1-, or 2-electron process. The room temperature oxidation of **1** with $Cp_2Fe^+PF_6^-$ in acetonitrile-d_3 leads to the virtually quantitative (by ^{1}H NMR) generation of $[CpRu(CO)(PMe_3)]_2(\mu\text{-H})^+$ (**5**), $HRu(CO)(PMe_3)(NCCD_3)_3^+$ (**4**-d_9), and cyclopentadiene in a 1:1:1 molar ratio, in accord with an overall $^2/_3$-electron oxidation of **1**. A trace of $CpRu(CO)(PMe_3)(NCCD_3)^+$ (**2**-d_3) was also observed. Dihydrogen complex $CpRu(CO)(PMe_3)(\eta^2\text{-}H_2)^+$ (**3**) was observed as an intermediate in the reaction, and it reacted to form **4**-d_9 and cyclopentadiene. Ferrocenium oxidation of **1** in the presence of 2,6-lutidine proceeded as a 1-electron process, yielding **5** and H^+. In the presence of pyrrolidine, a 2-electron process ensued and resulted in the formation of **2**-d_3 and H^+. Coulometry and preparative-scale experiments performed in acetonitrile proceeded somewhat differently. The electrochemical oxidation was a 1-electron process in the absence of base, yielding mostly **2** and **4**, whereas a 2-electron process took place in the presence of 2,6-lutidine or pyrrolidine, yielding **2**. The key to explaining all of the results is that an initial proton-transfer reaction from $\mathbf{1}^{\bullet+}$ to a base occurs. This transfer may take place rapidly from $\mathbf{1}^{\bullet+}$ to pyrrolidine, but only slowly to 2,6-lutidine. Proton transfer from $\mathbf{1}^{\bullet+}$ to the base yields the radical $CpRu(CO)(PMe_3)^\bullet$. The latter results in the formation of **5** via combination with $\mathbf{1}^{\bullet+}$ when $\mathbf{1}^{\bullet+}$ concentrations are relatively high. This is the case when **1** or 2,6-lutidine functions as a base. Otherwise, a second oxidation of $CpRu(CO)(PMe_3)^\bullet$ produces **2**. Pyrrolidine effects the rapid deprotonation of the cation radical, effectively depleting the solution of $\mathbf{1}^{\bullet+}$ and closing the pathway leading to **5**.

Introduction

Evidence presented by us[1] and others[2] has recently demonstrated that a number of 17-electron transition metal hydride cation radicals behave as Brønsted acids. Hydrido carbonyl metals $CpM(CO)_3H$ (M = Cr, Mo, W; Cp = $\eta^5\text{-}C_5H_5$) and $Cp^*Mo(CO)_3H$ ($Cp^* = \eta^5\text{-}C_5Me_5$) undergo spontaneous deprotonation subsequent to their oxidation.[1a] Less acidic, phosphine-substituted metal hydrides have been observed to undergo oxidatively induced reactions by an overall intermolecular proton transfer from the cation radical to the neutral parent hydride, as shown schematically in eqs 1–4. The primary observable products were MS^+ (S = solvent) and MH_2^+. Depending on the metal center in question, MH_2^+ may represent a classical dihydride [M = $CpW(CO)_2(PMe_3)$[1a] or $CpRu(PPh_3)_2$[1c]] or a nonclassical dihydrogen complex[3] [M = $CpRu(CO)(PPh_3)$[1b] or $Ir(PMe_2Ph)_3H_2$[2b]].

$$MH \rightarrow MH^{\bullet+} + e^- \qquad (1)$$

$$MH + MH^{\bullet+} \rightarrow MH_2^+ + M^\bullet \qquad (2)$$

$$M^\bullet + S \rightleftharpoons MS^\bullet \qquad (3)$$

$$MS^\bullet \rightarrow MS^+ + e^- \qquad (4)$$

Although apparently simple, the mechanisms of the initial deprotonation reactions have not been investigated in detail. For example, in view of the tendency that many 17-electron species show toward dimerization, either by metal–metal bond formation[4a] or by ligand–ligand coupling processes,[4b] relatively complicated reaction mechanisms may be conceived. We have observed on some occasions[5] that cationic, 17-electron mononuclear transition metal alkyl compounds undergo reactions via convoluted pathways involving the intermediacy of dinuclear complexes. The intricate reaction patterns often observed among organic cation radicals are also striking.[6]

We recently reported[1b] that $CpRu(CO)(PPh_3)H$ yielded $CpRu(CO)(PPh_3)(\eta^2\text{-}H_2)^+$ and $CpRu(CO)(PPh_3)(NCMe)^+$ as the first detectable (by ^{1}H NMR) products resulting from the 1-electron oxidation in acetonitrile. $CpRu(CO)(PPh_3)(NCMe)^+$ most likely arises from the oxidation of $CpRu(CO)(PPh_3)^\bullet$ via the prior coordination of acetonitrile to yield the 19-electron, readily oxidizable intermediate $CpRu(CO)(PPh_3)(NCMe)^\bullet$, in accord with the overall sequence depicted in eqs 1–4.

In this paper, we report that the oxidation of $CpRu(CO)(PMe_3)H$ (**1**) appears to result in an initial proton transfer analogous to that shown in eq 2. However, in this case the dinuclear bridging hydride $[CpRu(CO)(PMe_3)]_2(\mu\text{-H})^+$ is the predominant oxidation product in addition to the dihydrogen complex $CpRu(CO)(PMe_3)(\eta^2\text{-}H_2)^+$. Experimental evidence will be presented that suggests that the dinuclear hydride arises from a radical/cation radical coupling reaction between $CpRu(CO)(PMe_3)^\bullet$ and $CpRu(CO)(PMe_3)H^{\bullet+}$. Fine-tuning of the experimental conditions causes the oxidation to proceed as a $^2/_3$-, 1-, or 2-electron process, leading to different product mixtures. Despite the apparent complexity of this system, all results may be well-explained in terms of a primary proton transfer from $\mathbf{1}^{\bullet+}$.

Results

Electrochemical Oxidation of $CpRu(CO)(PMe_3)H$ (1). Derivative cyclic voltammetry (DCV)[7] has been demonstrated to be

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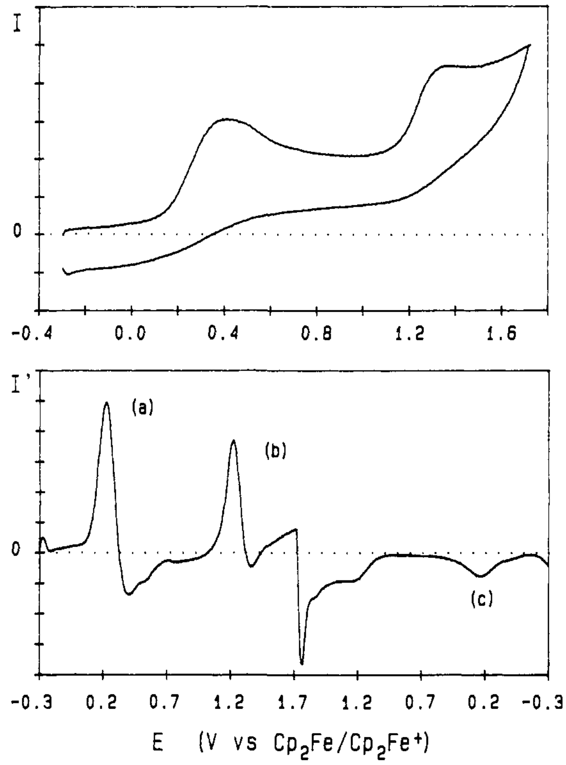

Figure 1. Cyclic voltammogram (top) and derivative cyclic voltammogram (bottom) for the oxidation of $CpRu(CO)(PMe_3)H$ (**1**; 1.0 mM) in acetonitrile/0.1 M $Bu_4N^+PF_6^-$ at a Pt disk electrode (d = 0.6 mm) at 20 °C and a voltage sweep rate ν of 1.0 V/s.

a powerful technique for the investigation of electron-transfer-induced reactions of organic[6] and organometallic[1,5,8] compounds. DCV offers enhanced resolution with respect to fine details in the voltammograms and also allows for more accurate readings of cyclic voltammetry peak potentials. DCV therefore was used for the initial investigation of the electrooxidation of **1**. Figure 1 shows a normal cyclic voltammogram (top) and a DCV trace (bottom) for the oxidation of **1** (1.0 mM substrate, acetonitrile/0.1 M $Bu_4N^+PF_6^-$, 20 °C, 0.6-mm diameter Pt disk electrode, voltage sweep rate ν = 1.0 V/s). The cyclic voltammetry oxidation peak potential, E_{ox}, corresponds to the position where the rapidly descending DCV curve crosses the base line after the first derivative peak (labeled a in Figure 1). Under these conditions, E_{ox} was located at 0.34 V vs the ferrocene/ferrocenium (FC) couple. The derivative peak width at half-height was 119 mV, indicative of a quasi-reversible electron-transfer process (the expected peak width for a Nernstian 1-electron process is 70.3 mV,[1a] and ferrocene displayed a peak width of 69 mV under the reaction conditions). The derivative peak current height was ca. 40% of the height observed for the oxidation of an equimolar solution of ferrocene under identical conditions. The shape of the oxidation peak was extremely sensitive to the electrode history in terms of cleaning and number of sweeps previously performed. Repeated scans caused severe distortion of the signal and loss of details in the voltammogram, suggestive of extensive adsorption problems at the electrode surface.

The DCV trace demonstrates that $\mathbf{1}^{\bullet+}$ undergoes complete reaction on the experimental time scale, as evidenced by the low intensity of the reverse derivative peak, labeled c. (Note that even in the event of "complete reaction", a residual DCV peak will be observed simply as a result of the shape of a normal cyclic voltammogram for a chemically irreversible electron transfer.) The intensity of the reverse peak was similarly insignificant at voltage sweep rates as high as 2000 V/s. The irreversible nature of wave a, even at high sweep rates, demonstrates that the derivative peak labeled b arises from the oxidation of products generated by the decomposition of $\mathbf{1}^{\bullet+}$ rather than from the oxidation of $\mathbf{1}^{\bullet+}$ to the dication. Seeding the solution with an equimolar amount of $CpRu(CO)(PMe_3)(NCMe)^+BF_4^-$ (**2**·BF_4) caused this peak to undergo a rough doubling in intensity, indicating the generation of an apparently quantitative yield of **2** on the time scale of the DCV measurement. However, the quantitative formation of **2** via cation radical deprotonation requires an overall 2-electron oxidation. This is in conflict with coulometry and preparative electrolysis experiments (vide infra). It is possible that peak b arises from overlapping peaks due to **2** and other reaction products, i.e., unstable $CpRu(CO)(PMe_3)(\eta^2\text{-}H_2)^+$ (**3**) or $HRu(CO)(PMe_3)(NCMe)_3^+$ (**4**).

Constant-current coulometry experiments in which the disappearance of the substrate was monitored by DCV required the passage of 1.0 ± 0.1 faradays/mol of charge for the complete consumption of **1** in acetonitrile/0.1 M $Bu_4N^+PF_6^-$. In the presence of 10 equiv of the hindered base, 2,6-lutidine, or in the presence of 2 equiv of pyrrolidine, coulometry experiments indicated the consumption of 2.0 ± 0.1 faradays/mol.

An exhaustive, preparative-scale electrochemical oxidation of **1** in acetonitrile/0.05 M $Me_4N^+BF_4^-$ also demanded the passage of 1 faraday/mol. Workup of the reaction mixture (see the Experimental Section for details) yielded **2**·BF_4 (49%) slightly contaminated with $[CpRu(CO)(PMe_3)]_2(\mu\text{-}H)^+BF_4^-$ (**5**·BF_4; 2–5%) as the only products detectable by ^1H NMR spectroscopy. Before workup, IR spectroscopy showed two CO bands of near-equal intensities at 1980 and 1950 cm^{-1}. The first band arises from **2**, and the second matches that of $HRu(CO)(PMe_3)(NCMe)_3^+$ (**4**). Attempts at isolating **4** have been unsuccessful thus far (vide infra). The dinuclear, bridging hydride **5** was produced as a mixture of cis and trans isomers. The details of its independent synthesis and characterization are presented later in this paper. A preparative-scale, 2-electron oxidation of **1** in the presence of 2 equiv of pyrrolidine but under otherwise identical conditions yielded **2**·BF_4 (54%).

Ferrocenium Oxidation of $CpRu(CO)(PMe_3)H$ in Acetonitrile-d_3. Despite the unfavorable electron-transfer equilibrium that would be attained between **1** and the ferrocenium cation, Cp_2Fe^+, we reasoned that the irreversible chemical reaction following the oxidation of **1** would drive the oxidation step to completion. Therefore, $Cp_2Fe^+PF_6^-$ (**6**) was chosen for the chemical oxidation of **1**.

A mixture of **1** and 0.85 equiv of **6** along with hexamethylbenzene (HMB; internal standard for product-yield quantification) was dissolved in acetonitrile-d_3 in a sealed NMR tube at ambient temperature. The ^1H NMR spectrum of the product mixture revealed that complete consumption of the substrate had taken place. A greenish tint to the solution suggested that the ferrocenium oxidant had not been completely consumed. This was corroborated by the ^1H NMR spectrum that, instead of the usual ferrocene singlet at δ 4.15, displayed a broad signal at δ 4.3 (peak width ca. 30 Hz) due to the signal broadening resulting from spin transfer between ferrocene and small amounts of ferrocenium. The overall integrated intensities of the PMe_3 resonances in the products, relative to the HMB internal standard, established a quantitative mass balance (within experimental errors) for ruthenium. The spectrum showed the presence of $CpRu(CO)(PMe_3)(NCCD_3)^+$ (**2**-d_3; 6% yield), $HRu(CO)(PMe_3)(NCCD_3)_3^+$ (**4**-d_9; 31%), $[CpRu(CO)(PMe_3)]_2(\mu\text{-}H)^+$ (two isomers, **5a** and **5b**, presumably cis and trans; 63%), and cyclopentadiene (29%). The products **2**-d_3, **5a**, **5b**, and cyclopentadiene were identified by comparison of their ^1H NMR spectra with those of authentic samples. Compound **4** has been independently prepared in situ (vide infra). Its identity has been inferred by comparison of its ^1H NMR and IR spectra with those of $HRu(CO)(PPh_3)(NCCD_3)_3^+$. The latter compound and cyclopentadiene were among the products resulting from the oxidation of $CpRu(CO)(PPh_3)H^{1b}$ and were believed to form in a base-catalyzed decomplexation of $CpRu(CO)(PPh_3)(\eta^2\text{-}H_2)^+$. The net results

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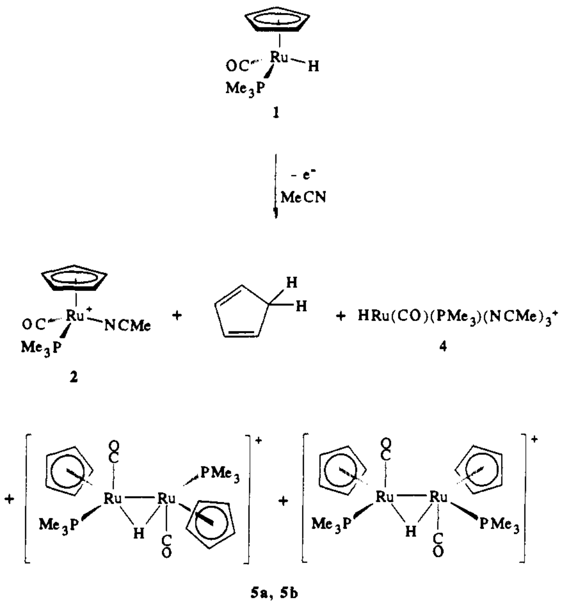
Scheme I



of the current reaction are summarized in Scheme I.

The ferrocenium oxidation of **1** was also carried out at low temperature, with recording of a ^{1}H NMR spectrum at −40 °C immediately after mixing the reactants. No internal standard was added, and the reported yields are based on overall integrated signal intensities. The spectrum showed the presence of **2**-d_3 (5%), **4**-d_9 (10%), **5** (as a mixture of the two isomers; 60%), cyclopentadiene (10%), and the known[9] dihydrogen complex CpRu(CO)(PMe$_3$)(η^2-H$_2$)$^+$ (**3**; 10%). In addition, signals of unknown origin were present at δ 5.70 (s, 8%), 3.5 (br s, 7% if derived from Cp), and −9.55 (d, J = 20 Hz, trace). After the sample had been heated to −10 °C, the signals due to **4**-d_9 and cyclopentadiene increased in intensity at the expense of the signals arising from **3** and the unknown compounds. Eventually, the product distribution was practically identical to that observed in the experiment performed at ambient temperature.

Ferrocenium oxidation of **1** was effected in the presence of the nitrogen bases 2,6-lutidine and pyrrolidine. In order to avoid erroneous conclusions regarding the product distributions due to losses during workup, the reaction mixtures were subjected to analysis by ^{1}H NMR spectroscopy without product isolation. Yields are based on combined Cp signal intensities.

In the presence of 5 equiv of 2,6-lutidine, 1 equiv of oxidant was needed for complete substrate conversion, and the only observed products from the ferrocenium oxidation were **2**-d_3 (8%) and **5** (92%). Significantly, no apparent change in the product distribution was noticed when the 2,6-lutidine concentration was increased to 10 or 20 equiv. The yields of **2**-d_3 varied between 7 and 13%, but there was no clear correlation between the quantity of base added and the resulting product distributions.

Finally, ferrocenium oxidation in the presence of 1.5 equiv of pyrrolidine required 2 equiv of the oxidant in order to effect complete consumption of the substrate and led to the total suppression of the formation of the bridging hydride **5**. The only product observed by ^{1}H NMR spectroscopy was **2**-d_3.

Ferrocenium Titrations of 1 in Acetonitrile. The intense blue color of the ferrocenium salts suggests the use of ferrocenium as an indicator in titration experiments. The oxidation of **1** was therefore performed such that a solution of **6** was slowly added with a syringe to a vigorously stirred solution of **1** (ca. 67 mM before addition of **6**) in acetonitrile. The appearance of a greenish tint to the solution signaled the presence of unreacted ferrocenium, i.e., complete oxidation of substrate. It was found that the oxidation of **1** required the addition of 0.71 equiv of **6**. This is in agreement with the results obtained from the oxidations that were performed in NMR tubes, which showed that less than 0.85 equiv of oxidant was needed.

Ferrocenium titration of a solution containing equimolar amounts of **1** and 2,6-lutidine in acetonitrile called for the addition of 1.1 equiv of oxidant before the permanent greenish tint appeared. After workup of the reaction mixture, **5**·PF$_6$ was isolated in 91% yield.

Titration of an acetonitrile solution of **1** and equimolar amounts of pyrrolidine proceeded with the consumption of 2.1 equiv of oxidant. Following workup, **2**·PF$_6$ was isolated in 71% yield.

Synthesis and Characterization of [CpRu(CO)(PMe$_3$)]$_2$(μ-H)$^+$BF$_4^-$ (5·BF$_4$). This compound has been previously reported as a product resulting from the decomposition of CpRu(CO)(PMe$_3$)(η^2-H$_2$)$^+$ in dichloromethane,[9a] but no spectroscopic details were provided. We prepared **5**·BF$_4$ by treatment of **1** with 1 equiv of the substituted trityl reagent (p-MeOC$_6$H$_4$)Ph$_2$C$^+$BF$_4^-$ (**7**) in dichloromethane at −70 °C, presumably generating an intermediate CpRu(CO)(PMe$_3$)X$^+$, where X may represent a coordinated solvent molecule[10] or a weakly bound tetrafluoroborate counterion.[11] The bridging hydride was generated by the addition of 1 equiv of **1** to the solution. Similar procedures have been recommended for the synthesis of other dinuclear, cationic bridging hydrides.[12] Analytically pure **5**·BF$_4$ was obtained in 80% yield by this method. Spectroscopic data are provided in the Experimental Section. The ^{1}H NMR spectrum revealed the presence of the two cis and trans isomers, **5a** and **5b**. It was not possible to determine which signals were due to the cis, and which to the trans, isomer on the basis of available ^{1}H NMR data. The most distinguishing feature of the ^{1}H NMR spectrum of **5** was the presence of the diagnostic, high-field triplets due to the bridging hydride ligands at δ −20.3 and −21.6. The IR spectrum (acetonitrile) displayed two barely separated CO bands at 1945 and 1950 cm^{-1}.

Acetonitrile solutions of the bridging hydride complex were remarkably stable toward bases. As indicated earlier, the complex was perfectly stable in the presence of 20 equiv of 2,6-lutidine. Even in the presence of 4 equiv of pyrrolidine, no evidence for deprotonation was observed by ^{1}H NMR spectroscopy.

In Situ Preparation of HRu(CO)(PMe$_3$)(NCCD$_3$)$_3^+$ (4-d_9). We have demonstrated[1b] that HRu(CO)(PPh$_3$)(NCMe)$_3^+$, one product arising from the oxidation of CpRu(CO)(PPh$_3$)H, could be conveniently prepared by treatment of this hydride with *aqueous* acids in acetonitrile, followed by conventional workup. In accord with this, we find that addition of aqueous HBF$_4$ to a solution of **1** in acetonitrile-d_3 causes the clean generation of cyclopentadiene and a product whose spectroscopic characteristics indicate the formation of **4**-d_9: ^{1}H NMR δ 1.43 (d, J = 10.4 Hz, 9 H), −14.6 (d, J = 33.0 Hz, 1 H). All attempts at isolating **4** have been frustrated by its rapid decomposition following removal of the solvent. The IR spectrum of solutions containing **4** displayed a CO absorption at 1948 cm^{-1}.

Reactions between Trityl Reagent (p-MeOC$_6$H$_4$)Ph$_2$C$^+$BF$_4^-$ (7) and Ruthenium Hydrides 1 and 5. Hydride abstraction from **1** with equimolar amounts of **7** in acetonitrile cleanly proceeds to give high yields of **2** as the only organometallic product.[5b] Treatment of **1** with 0.5 equiv of the trityl reagent also resulted in **2** as the only product, leaving the rest of the substrate unreacted. No evidence for **5** was observed by ^{1}H NMR spectroscopy.

When bridging hydride **5** was treated with 1 equiv of **7**, no reaction took place. Thus, as anticipated, it is clear that the absence of **5** in the reaction between **1** and substoichiometric quantities of **7** is not due to a facile secondary reaction between **5** and **7**. Most important, the experiments serve to establish that CpRu(CO)(PMe$_3$)X$^+$ (X = BF$_4^-$ or an empty coordination site), a likely intermediate for the production of **2** in the reaction between **1** and **7**, *cannot* be an intermediate for the formation of **5** during

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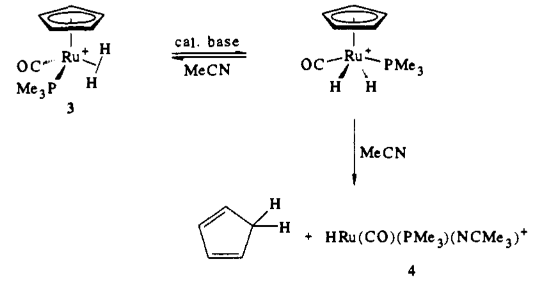
Scheme II



the oxidation of **1** in acetonitrile.

Also, the absence of **5** shows that the hydride abstraction with the trityl reagent does *not* proceed by an electron-transfer route. This is in accord with conclusions arrived at for the hydride abstraction from CpW(CO)$_2$(PMe$_3$)H.[1a] Electron-transfer mechanisms have been previously implied in the reaction between the trityl cation and iridium hydride Ir(PMe$_2$Ph)$_3$H$_3$, which, however, did *not* result in overall hydride abstraction,[2b] and for the hydride abstraction from some transition metal alkyls and other complexes.[13]

Decomposition of CpRu(CO)(PMe$_3$)(η^2-H$_2$)$^+$ (3) in Acetonitrile. Protonation of **1** with excess HBF$_4$·Et$_2$O in acetonitrile-d_3 (see the Experimental Section for details) cleanly provides a solution of **3**[9] that is stable for hours at −40 °C. Under these conditions, **3** only slowly undergoes decomposition to yield mostly **2**-d_3. On the other hand, when **3** was prepared in dichloromethane and isolated in the cold by precipitation with ether before it was dissolved in acetonitrile-d_3, a rapid reaction ensued even at −40 °C. The observed products were cyclopentadiene, **4**-d_9, and **2**-d_3. In this case, **2**-d_3 represented less than 5% of the two Ru-containing products. This behavior is analogous to that exhibited by CpRu(CO)(PPh$_3$)(η^2-H$_2$)$^+$.[1b] The decomplexation of CpRu(CO)(PPh$_3$)(η^2-H$_2$)$^+$ took place via a reversible, base-catalyzed proton transfer from the dihydrogen complex, most likely generating a transient, unobserved trans dihydride which underwent cyclopentadiene elimination by transferring a hydride ligand to the Cp ring or by a ring-slippage mechanism. The decomposition of **3** is assumed to follow an analogous mechanism and will not be discussed in more detail in this paper. The crucial point is that the observation of **4** and cyclopentadiene in oxidation reactions involving **1** indicates initial production of dihydrogen complex **3** (Scheme II).

Discussion

Qualitative Results. As was apparent in the Results Section, the outcome of the oxidation of **1** showed a great deal of variation, depending on how the experiments were performed. The nature of the products, as well as the amount of charge passed for complete substrate consumption, was highly dependent on the reaction conditions. A brief summary of the observation will be presented first.

Ferrocenium oxidations were carried out at relatively high substrate concentrations, ca. 40–70 mM. In the absence of added bases, the overall conversion (disregarding the minor amounts of **2** that were observed) may be described by eq 5. The process in theory requires the passage of 0.67 faraday/mol of charge, to be compared with the observed value by ferrocenium titration of about 0.71. The trace amount of **2** seen by ^{1}H NMR would cause a somewhat higher consumption of oxidant than the theoretical value of 0.67 equiv.

$$\underset{\mathbf{1}}{3\mathrm{CpRu(CO)(PMe_3)H}} \xrightarrow{-2e^-} \underset{\mathbf{5}}{[\mathrm{CpRu(CO)(PMe_3)}]_2(\mu\text{-H})^+} + \underset{\mathbf{3}}{\mathrm{CpRu(CO)(PMe_3)}(\eta^2\text{-H}_2)^+} \qquad (5)$$

In the presence of 2,6-lutidine (pK_a 15.4 in acetonitrile[14a]) a 1-electron process was seen, as required by the overall transformation of eq 6. Again, the traces of **2** would raise the expected demand for oxidant slightly.

$$\underset{\mathbf{1}}{2\mathrm{CpRu(CO)(PMe_3)H}} \xrightarrow{-2e^-} \underset{\mathbf{5}}{[\mathrm{CpRu(CO)(PMe_3)}]_2(\mu\text{-H})^+} + \mathrm{H}^+ \qquad (6)$$

With pyrrolidine present (pK_a 19.6[14b]), a 2-electron process generating **2** ensued, in accord with eq 7.

$$\underset{\mathbf{1}}{\mathrm{CpRu(CO)(PMe_3)H}} \xrightarrow[\mathrm{MeCN}]{-2e^-} \underset{\mathbf{2}}{\mathrm{CpRu(CO)(PMe_3)(NCMe)^+}} + \mathrm{H}^+ \qquad (7)$$

The electrochemical reactions proceeded somewhat differently. In the absence of bases, the 1-electron process depicted in eq 8 took place. The IR detection of **4** is taken as evidence for the prior generation of the unstable dihydrogen complex **3**. Finally,

$$\underset{\mathbf{1}}{2\mathrm{CpRu(CO)(PMe_3)H}} \xrightarrow[\mathrm{MeCN}]{-2e^-} \underset{\mathbf{2}}{\mathrm{CpRu(CO)(PMe_3)(NCMe)^+}} + \underset{\mathbf{4}}{\mathrm{HRu(CO)(PMe_3)(NCMe)_3^+}} + \mathrm{C_5H_6} \qquad (8)$$

the electrochemical oxidation in the presence of 2,6-lutidine or pyrrolidine appeared to proceed in the same manner as the chemical oxidation depicted in eq 7.

All of the above observations must be taken into account when discussing the reactions of $\mathbf{1}^{\bullet+}$. As will be apparent, the results may be explained in terms of proton-transfer reactions taking place from $\mathbf{1}^{\bullet+}$ to **1**, 2,6-lutidine, or pyrrolidine, with the rate of deprotonation being a decisive factor for determining the product distribution.

Estimates for the Thermodynamic Acidities of $\mathbf{1}^{\bullet+}$ and 3. Deprotonation reactions appear to be common reactions available to metal hydride cation radicals, and we first want to consider whether and under what conditions a direct deprotonation of $\mathbf{1}^{\bullet+}$ might take place. A few words concerning the acid strengths of $\mathbf{1}^{\bullet+}$ and of **3** are warranted in this context. In our previous investigation of the oxidation chemistry of groups 6 and 8 metal hydrides,[1a,b] we have noted that the difference in acid strength between several metal hydrides and their corresponding cation radicals, determined by the use of a simple thermochemical cycle,[1a] amounts to a relatively constant 21 ± 2 pK_a units. Since the thermodynamic acidity of **1** is not known, we cannot accurately determine the acidity of $\mathbf{1}^{\bullet+}$ by the usage of the thermochemical cycle. However, it is known that substituting PMe$_3$ for one CO ligand in CpW(CO)$_3$H raises the hydride pK_a value in acetonitrile solution from 16.1 to 26.5 or about 10 pK_a units.[15] Making the rather crude assumption that a similar effect pertains for CpRu(CO)$_2$H (pK_a = 20.2[15]) leads to rough estimates for the pK_a values of about 30 for **1** and of about 9 for $\mathbf{1}^{\bullet+}$, both in acetonitrile. Most likely, these estimates represent lower bounds for the true values, since the incremental effect of the added PMe$_3$ ligand should be greater for CpRu(CO)$_2$H than for CpW(CO)$_3$H. In the latter case, two CO ligands remain to accommodate the increased electron density provided by PMe$_3$, whereas in the former, only one CO ligand remains.[16]

Jia and Morris[17] recently presented valuable pK_a data for a series of ruthenium dihydride (Cp′RuL$_2$H$_2$$^+$) and dihydrogen

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[13] (a) Bodner, G. S.; Gladysz, J. A.; Nielsen, M. F.; Parker, V. D. *J. Am. Chem. Soc.* **1987**, *109*, 1757. (b) Jernakoff, P.; Cooper, N. J. *Organometallics* **1986**, *5*, 747. (c) Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1988**, 713. (d) Mandon, D.; Astruc, D. *Organometallics* **1989**, *8*, 2372. (e) Astruc, D. *Organometallics* **1990**, *9*, 341.

[14] (a) Cauquis, G.; Deronzier, A.; Serve, D.; Vieil, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *60*, 205. (b) Coetzee, J. F. *Prog. Phys. Org. Chem.* **1967**, *4*, 45.

[15] Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257.

[16] (a) A trend like the one indicated is observed when comparing the couple HMn(CO)$_5$[15]/HMn(CO)$_4$PPh$_3$[16b] (ΔpK_a = 5.3) with the couple HCo(CO)$_4$[15]/HCo(CO)$_3$PPh$_3$[15] (ΔpK_a = 7.1). (b) Kristjánsdóttir, S. S.; Moody, A. E.; Weberg, R. T.; Norton, J. R. *Organometallics* **1988**, *7*, 1983.

[17] (a) Jia, G.; Morris, R. H. *Inorg. Chem.* **1990**, *29*, 581. (b) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875.

($Cp'RuL_2(\eta^2-H_2)^+$) complexes (Cp' = Cp or Cp*; L = tertiary phosphine), obtained by equilibrium constant measurements in THF and dichloromethane solutions. The pK_a values were linked to the aqueous scale via the acid $HPCy_3^+$ (Cy = cyclohexyl), the aqueous pK_a of which was estimated to be 9.7. Making the assumption that the M–H bond dissociation energies remained constant within a series of structurally similar compounds,[18a] the data provided the linear relationship of eq 9 relating the metal

$$pK_a[Ru(\eta^2\text{-}H_2)] = -10.7E°(MH^+/MH) + 13.0 \quad (9)$$

hydride ($Cp'RuL_2H$) oxidation peak potentials $E°(MH^+/MH)$ (vs NHE) and the aqueous pK_a values of the dihydrogen complexes $Cp'RuL_2(\eta^2-H_2)^+$.[17b] The slope of −10.7 deviated from the value of −16.9 that was predicted by theory by the use of a thermochemical cycle. It was indicated that the deviation could be due to an error in the BDE assumption or to the irreversible nature of the metal hydride oxidation waves.

By employing the same conversion factors as those used by Jia and Morris [NHE = −0.6 V vs FC; $pK_a(H_2O) = pK_a(MeCN) - 7.8$], insertion of the measured E_{ox} of **3** into eq 9 provides an estimate for the acidity of **3** in acetonitrile of 10.7 pK_a units. Jia and Morris estimated the pK_a of **3** to be about 1 in water (corresponding to 8.8 in acetonitrile), not by measuring the oxidation potential of **1** but by utilizing a ligand additivity relationship[19] to find an approximate value for the oxidation potential, 1.1 V vs NHE (0.5 V vs FC).

While these pK_a estimates for $\mathbf{1}^{\bullet+}$ and **3** are associated with a high degree of uncertainty and should be used with caution, we conclude that they do suggest that proton-transfer reactions between $\mathbf{1}^{\bullet+}$ and **1** should be feasible. The exact position of a proton-transfer equilibrium between the two may be uncertain, but the presence of irreversible reactions supervening the proton-transfer step should force the proton transfer to completion. Proton transfer from $\mathbf{1}^{\bullet+}$ to any of the nitrogen bases employed should also be viable. Unfortunately, the rapid base-catalyzed decomposition of **3** precludes estimating the pK_a of **3** in acetonitrile by equilibrium measurements.

Deprotonation of $\mathbf{1}^{\bullet+}$. The direct deprotonation of $\mathbf{1}^{\bullet+}$ by an external base (other than **1**) would be expected to provide **2** as a result of an overall 2-electron oxidation. A 1-electron process might ensue if **1** acted as the base, provided that no other reactions were available to $\mathbf{1}^{\bullet+}$. In analogy with conclusions arrived at for similar systems, the generation of **2** from initially formed $CpRu(CO)(PMe_3)^\bullet$ would take place via prior coordination of acetonitrile to yield a readily oxidized 19-electron intermediate, as shown in eqs 10–12.

$$CpRu(CO)(PMe_3)H^{\bullet+} + \text{Base} \rightarrow CpRu(CO)(PMe_3)^\bullet + \text{BaseH}^+ \quad (10)$$

$$CpRu(CO)(PMe_3)^\bullet + MeCN \rightleftharpoons CpRu(CO)(PMe_3)(NCMe)^\bullet \quad (11)$$

$$CpRu(CO)(PMe_3)(NCMe)^\bullet \rightarrow CpRu(CO)(PMe_3)(NCMe)^+ + e^- \quad (12)$$

Coulometry experiments required the consumption of 1 faraday/mol. Preparative electrolysis of **1** gave a product mixture which (on the basis of IR spectroscopy) contained a near 1:1 mixture of **2** and **4** and from which **2** could be isolated in 49% yield, only slightly contaminated with **5**. Taken together, these results are consistent with an initial proton transfer as outlined in eqs 10–12, but with **1** acting as the base as in eq 13. Product **4**, arising from the decomplexation of **3**, was unstable and could not be isolated. Theoretically, the overall reaction should generate 50% of **2** on the basis of **1** consumed.

$$CpRu(CO)(PMe_3)H^{\bullet+} + CpRu(CO)(PMe_3)H \rightarrow CpRu(CO)(PMe_3)(\eta^2\text{-}H_2)^+ + CpRu(CO)(PMe_3)^\bullet \quad (13)$$

The addition of pyrrolidine or 2,6-lutidine to the electrolyte changed the oxidation of **1** to an overall 2-electron process. This may be explained in terms of efficient deprotonation of $\mathbf{1}^{\bullet+}$ by both bases under these conditions to provide $CpRu(CO)(PMe_3)^\bullet$, a precursor to **2**. Given the uncertainty in the pK_a estimate for $\mathbf{1}^{\bullet+}$, the deprotonation by 2,6-lutidine may or may not be thermodynamically favored. In any respect, the reaction could be driven by the irreversible follow-up reaction consuming $CpRu(CO)(PMe_3)^\bullet$—the oxidation to yield **2**. This should result in a quantitative formation of **2**. By IR spectroscopy, **2** was the only significant product. In accord with this, **2** was isolated in 54% yield from a preparative electrolysis with pyrrolidine present. The reason for this modest yield is not clear.

Ferrocenium oxidation of **1** in acetonitrile-d_3 at −40 °C proceeded to give substantial NMR yields of $CpRu(CO)(PMe_3)(\eta^2-H_2)^+$ (**3**, 10%), $HRu(CO)(PMe_3)(NCCD_3)_3^+$ (**4**-d_9, 10%), and cyclopentadiene (10%). Since the latter two are considered to be decomposition products from **3**, the initial yield of **3** must have been at least 20% based on **1**—higher (ca. 30%) if the unassigned ^1H NMR resonances arise from intermediates during the decomplexation of **3**. This observation is also in agreement with a rapid proton transfer from $\mathbf{1}^{\bullet+}$ to **1**, eq 13, after the oxidation. The radical $CpRu(CO)(PMe_3)^\bullet$ should then be produced in equally high initial yields. In spite of this, its anticipated decomposition product under oxidizing conditions, **2**, formed in only 6% yield. This is in stark contrast with the efficient generation of $CpRu(CO)(PPh_3)(NCMe)^+$ during the oxidation of $CpRu(CO)(PPh_3)H$ under identical conditions.[1b] For electronic reasons, the intermediate 19-electron radical $CpRu(CO)(PMe_3)(NCMe)^\bullet$ should be even more readily oxidized than the PPh_3 analogue. We tentatively attribute the inefficient transformation of $CpRu(CO)(PMe_3)^\bullet$ to **2** under these conditions to a less favorable 17-/19-electron preequilibrium, eq 11. This gives the 17-electron radical the chance to follow alternative reaction pathways. In order to account for the mass balance of the reaction, this pathway must lead to the dimeric bridging hydride complex **5**. Efficient second-order processes leading to **5** are then available under the high-concentration conditions of the experiments carried out in NMR tubes. Under the dilute conditions employed for the electrochemical oxidations, oxidation via the 19-electron intermediate is the favored reaction.

The **2**:**5** product ratio was insensitive to the presence of up to 20 equiv of 2,6-lutidine. With the possible exception of **1**, 2,6-lutidine is anticipated to be the strongest base present under these conditions. Contrasting the behavior of 2,6-lutidine, the stronger base pyrrolidine caused the exclusive formation of **2**. This observation indicates that pyrrolidine is a highly efficient base for the deprotonation of $\mathbf{1}^{\bullet+}$, essentially depleting the reaction medium of the cation radical and thereby preventing the production of **5** (vide infra). Oxidation of the resulting radical $CpRu(CO)(PMe_3)^\bullet$ then leads to **2**. Two alternative explanations for the different behavior of 2,6-lutidine may be considered. In one, relatively slow (when compared with the reaction of pyrrolidine) proton transfer occurs from $\mathbf{1}^{\bullet+}$ to **1**, generating $CpRu(CO)(PMe_3)^\bullet$ and **3**. Reaction between $CpRu(CO)(PMe_3)^\bullet$ and unreacted $\mathbf{1}^{\bullet+}$ produces **5**, and 2,6-lutidine regenerates **1** from **3**. Alternatively, $CpRu(CO)(PMe_3)^\bullet$ is produced by a slow deprotonation[20] of $\mathbf{1}^{\bullet+}$ by 2,6-lutidine, and the dimer is directly produced by combination of the radical with as yet unreacted $\mathbf{1}^{\bullet+}$. This avoids the necessity of including the extra proton-transfer step from **3** to 2,6-lutidine in the scheme and results in an overall mechanism that because of its simplicity may be more attractive.[21] In any event, the results

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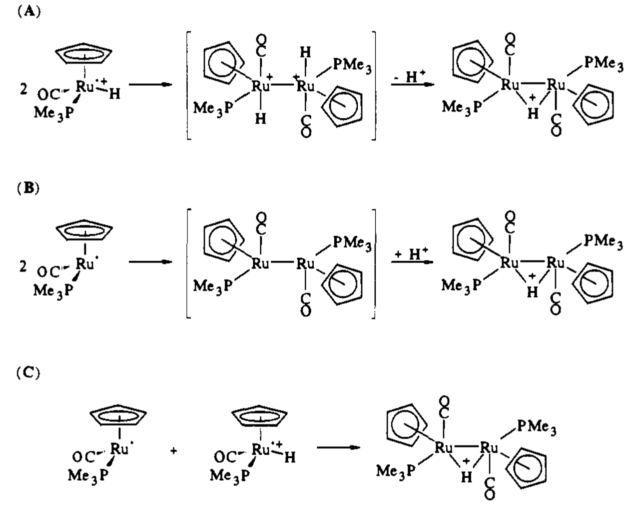
[18] (a) Slight changes in the ligand substitution patterns (Cp* for Cp; tertiary phosphine or phosphite for CO) have been found to have only modest effects on M–H bond dissociation energies. See refs 8a and 18b. (b) Kiss, G.; Zhang, K.; Mukerjee, S. L.; Hoff, C. D. *J. Am. Chem. Soc.* **1990**, *112*, 5657.

[19] Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271.

[20] Norton and co-workers have demonstrated that near-thermoneutral proton-transfer reactions from neutral metal hydrides to nitrogen bases and to metal anions proceed relatively slowly when compared with proton-transfer reactions between oxygen- and nitrogen-centered acids and bases. Proton-transfer reactions from metal hydrides to substituted anilines typically exhibit Brønsted slopes of about 0.5: Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945.

Scheme III



suggest that $1^{\bullet+}$ is also involved in the dimer-forming reaction.

Mechanism of Bridging Hydride Formation. Reactions between **1** and trityl reagent **7** in acetonitrile failed to produce detectable amounts (by ^1H NMR) of bridging hydride **5**. Furthermore, **5** was inert in the presence of **7**. These results provide solid evidence that **5**, when generated by the oxidation of **1** in acetonitrile, is not formed from the even-electron species $CpRu(CO)(PMe_3)X^+$ (X = coordinated counterion or empty coordination site[11]). Reactions involving the odd-electron species $CpRu(CO)(PMe_3)^\bullet$ and $CpRu(CO)(PMe_3)H^{\bullet+}$ appear more plausible, as was suggested in the preceding paragraph. In principle, three reaction mechanisms involving reactions between radical species may be considered for the formation of **3**, as depicted in Scheme III. All three mechanisms lead to the prediction of a 1:1 molar ratio between **3** (and secondary products arising from decomplexation of **3**) and **5** or a 1:2 ratio in the integrated Cp signal intensities of the ^1H NMR spectra. This is in good agreement with the observed ratio of 31:63.

Mechanism A involves the dimerization of two cation radicals $1^{\bullet+}$, followed by deprotonation and bridge formation. Although a cation radical/cation radical reaction may at first glance be viewed as unlikely due to the electrostatic repulsive forces that must act between the two metal centers, the mechanism should not be discounted for this reason alone. The dimerization of cationic 17-electron metal centers may be facilitated by the formation of a strong metal–metal bond and is a well-documented process in the literature.[5,22]

Mechanism B involves the dimerization of two radicals $CpRu(CO)(PMe_3)^\bullet$ to give the previously unreported dimer $[CpRu(CO)(PMe_3)]_2$, followed by rapid protonation at the Ru–Ru bond. This bond clearly must be a basic site in the dimer, since the bridging hydride is stable in the presence of excess pyrrolidine.

Mechanism C involves the reaction between $1^{\bullet+}$ and its conjugate base, the radical $CpRu(CO)(PMe_3)^\bullet$, providing direct access to **3**.

It is difficult, if not impossible, to unambiguously rule out two of the three alternatives. The base effects discussed in the preceding paragraph support the radical/cation radical combination, and in the following we will further argue that the radical/cation radical reaction C may be most consistent with the available data. The experimental evidence strongly suggests that the primary reaction of $1^{\bullet+}$ is the proton transfer of eq 13, generating $CpRu(CO)(PMe_3)^\bullet$ as an intermediate. The availability of this radical under the reaction conditions is at least indirectly confirmed by the observation of **2** as a minor product. The yield of **2** is greater than the trace amounts that would be anticipated from the thermal decomposition of **3**. $CpRu(CO)(PMe_3)^\bullet$ generated according to eq 13 then must be an intermediate for the production of **5** in order to account for the overall mass balance. This rules out the cation radical/cation radical mechanism A in Scheme III being operative.

Accepting the conclusion that $CpRu(CO)(PMe_3)^\bullet$ is indeed produced as a result of the oxidation process, mechanism B of Scheme III must be considered. Although this option cannot be rigorously ruled out, it seems less likely on the grounds that the intermediate Ru(I) dimer, $[CpRu(CO)(PMe_3)]_2$, should undergo oxidation more readily than Ru(II) hydride **1**.[23] This should lead to greater yields of **2** at the expense of **5**. A rapid protonation of the dimer could prevent such an oxidation from taking place. But if this were the case, and in conflict with the experimental results, **5** should be a major product even when pyrrolidine was present during the oxidations.

We are then left with mechanism C of Scheme III as the most plausible mechanism for the generation of **5**. The mechanism appears to be consistent with all of the experimental data. The difference in product distributions arising from the chemical and electrochemical oxidations mostly represents concentration effects. Second-order dimerization reactions are favored at the high concentrations employed for chemical oxidation, whereas further oxidation of $CpRu(CO)(PMe_3)^\bullet$ at the electrode via the postulated 19-electron acetonitrile adduct as an intermediate is favored for the electrooxidations that are performed at lower substrate concentrations.

Concluding Remarks. This work has confirmed that proton-transfer reactions appear to be fairly general reaction types available to a variety of 17-electron transition metal hydride cation radicals. In addition, the radical nature of $CpRu(CO)(PMe_3)H^{\bullet+}$ was manifested through its combination with $CpRu(CO)(PMe_3)^\bullet$ to yield the bridging hydride. Secondary reactions of the hydride cation radicals may thus cause the formation of unexpected products, the nature of which is highly dependent on the identities of the metal center, spectator ligands, and the reaction conditions. Steric effects appear to exert a major influence, since the oxidation of $CpRu(CO)(PPh_3)H$ did not lead to bridging hydride formation. Work is currently in progress in our laboratories aimed at gaining further insight into the reactions and properties of transient metal hydride cation radical species.

Experimental Section

General Procedures. All manipulations involving organometallic compounds were carried out with use of vacuum line, Schlenk, syringe, or drybox techniques. Acetonitrile and acetonitrile-d_3 were distilled from P_2O_5 and CaH_2, respectively, and dichloromethane was distilled from CaH_2. The electrochemical instrumentation, cells, data handling procedures, and electrodes have been previously described.[7a,24] Acetonitrile containing 0.1 M $Bu_4N^+PF_6^-$ was used as the solvent for electrochemical experiments and was passed through a column of active neutral alumina before use to remove water and protic impurities. The electrolyte was freed of air by purging with purified argon, and all measurements and electrolyses were carried out under a blanket of solvent-saturated argon at 293 K. ^1H NMR spectra were recorded on Varian XL-300 or Varian Gemini-200 instruments. Chemical shifts are reported in ppm relative to tetramethylsilane, with the residual solvent proton resonance as internal standard (δ 1.93 for acetonitrile, 5.32 for dichloromethane). Infrared spectra were obtained on a Perkin-Elmer 1310 infrared spectro-

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(21) We thank a referee for bringing this possibilty to our attention.

(22) (a) DeLaet, D. L.; Powell, D. R.; Kubiak, C. P. *Organometallics* **1985**, *4*, 954. (b) Droege, M. W.; Harman, W. D.; Taube, H. *Inorg. Chem.* **1987**, *26*, 1309. (c) Fonseca, E.; Geiger, W. E.; Bitterwolf, T. E.; Rheingold, A. L. *Organometallics* **1988**, *7*, 567. (d) Pufahl, D.; Geiger, W. E.; Connelly, N. G. *Organometallics* **1989**, *8*, 412. (d) Moinet, C.; Le Bozec, H.; Dixneuf, P. H. *Organometallics* **1989**, *8*, 1493. (f) Bond, A. M.; Calton, R.; Mann, D. R. *Inorg. Chem.* **1989**, *28*, 54. (g) Einstein, F. W. B.; Jones, R. H.; Zhang, X.; Yan, X.; Nagelkerke, R.; Sutton, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1424. (h) Herrmann, W. A.; Fischer, R. A.; Amslinger, W.; Herdtweck, E. *J. Organomet. Chem.* **1989**, *362*, 333. (i) Bitterwolf, T. E.; Spink, W. C.; Rausch, M. D. *J. Organomet. Chem.* **1989**, *363*, 189.

(23) For example, we have reported that $[CpMo(CO)_3]_2$ undergoes oxidation at a potential 0.25 V lower than the oxidation potential of the hydride $CpMo(CO)_3H$.[1a] We have observed similar trends for other dimer/hydride couples. Attempts at preparing $[CpRu(CO)(PMe_3)]_2$ by deprotonation of **5** have not yet been successful.

(24) (a) Ahlberg, E.; Parker, V. D. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *121*, 57. (b) Ahlberg, E.; Parker, V. D. *Acta Chem. Scand., Ser. B* **1980**, *B34*, 97.

photometer. Melting points were measured on a Büchi melting point apparatus in capillary tubes sealed under vacuum. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany.

Complexes CpRu(CO)(PMe$_3$)H,[9] CpRu(CO)(PMe$_3$)(NCMe)$^+$BF$_4^-$,[5b] CpRu(CO)(PMe$_3$)(η^2-H$_2$)$^+$BF$_4^-$,[9] Cp$_2$Fe$^+$PF$_6^-$,[25a] and (p-MeOC$_6$H$_4$)Ph$_2$C$^+$BF$_4^-$[25b] were synthesized following published procedures.

[CpRu(CO)(PMe$_3$)]$_2$(μ-H)$^+$BF$_4^-$ (5·BF$_4$). (p-MeOC$_6$H$_4$)Ph$_2$C$^+$BF$_4^-$ (66.2 mg, 0.184 mmol) was added to a solution of **1** (50.0 mg, 0.184 mmol) in dichloromethane (20 mL) at −70 °C. The mixture turned from orange-red to yellow over a 20-min period, after which **1** (50.0 mg, 0.184 mmol) was added. Stirring was continued for 15 min before the solvent was removed by vacuum transfer at 0 °C. The residue was washed with ether (5 × 5 mL). The product was recrystallized from dichloromethane/ether (93.1 mg, 80.4%): orange crystals, mp 203 °C dec (slow); ^{1}H NMR (acetonitrile-d_3) δ −21.60 (t, J = 17.8 Hz, 1 H), 1.59 (d, J = 10.6 Hz, 18 H), 5.22 (s, 10 H) for isomer **5a**, −20.27 (t, J = 19.8 Hz, 1 H), 1.61 (d, J = 10.4 Hz, 18 H), 5.19 (s, 10 H) for isomer **5b**; **5a**:**5b** ratio ca. 2:3; IR (acetonitrile) ν_{CO} 1945, 1950 cm^{-1}. Anal. Calcd for C$_{18}$H$_{29}$BF$_4$O$_2$P$_2$Ru$_2$: C, 34.41; H, 4.65. Found: C, 34.43; H, 4.80.

In Situ Preparation of HRu(CO)(PMe$_3$)(NCCD$_3$)$_3^+$ (4-d_9). An NMR tube equipped with a ground-glass joint was loaded with **1** (6 mg, 0.022 mmol) and HBF$_4$·Et$_2$O (3 μL, ca. 0.022 mmol). The latter was added as a small drop on the glass wall of the upper part of the tube, so as not to initiate a reaction with **1** before the solvent was added. The tube was connected to the vacuum line, the contents were frozen at liquid-nitrogen temperature, and the tube was evacuated. Acetonitrile-d_3 was added by vacuum transfer, and the tube was sealed. The tube was heated to ambient temperature, and the ^{1}H NMR spectrum was recorded immediately. The spectrum revealed the presence of cyclopentadiene [δ 2.97 (m, 2 H), 6.48 (m, 2 H), 6.55 (m, 2 H)], **4**-d_9 [δ 1.43 (d, J = 10.4 Hz, 9 H), −14.60 (d, J = 33.0 Hz) (cf. δ −13.70 for HRu(CO)(PPh$_3$)(NCMe)$_3^+$[1b])], and **2**-d_3 [δ 1.64 (d, J = 11.0 Hz, 9 H), 5.23 (s, 5 H)]. The cyclopentadiene:**4**-d_9:**2**-d_3 ratio was ca. 2:2:1, as judged from the integrated signal intensities.

An analogous reaction was performed with aqueous HBF$_4$ (5 μL of a 50% solution, 0.040 mmol) instead of HBF$_4$·Et$_2$O. Again, the only observable products were cyclopentadiene, **4**-d_9, and **2**-d_3, but this time the amount of **2**-d_3 was less than 5%. The hydride signal of **4**-d_9 was broad and without resolved coupling, possibly due to fast-exchange processes with excess aqueous acid, but the other signals were unaffected.

Attempted Synthesis of HRu(CO)(PMe$_3$)(NCMe)$_3^+$ (4). Aqueous HPF$_6$ (27 μL of a 75% solution, 0.26 mmol) was added to a solution of **1** (27 mg, 0.10 mmol) in acetonitrile (20 mL) that was vigorously stirred at 0 °C. The solution was stirred for 30 min. An aliquot was withdrawn for IR analysis, which showed the presence of a CO absorption at 1948 cm^{-1} (cf. 1960 cm^{-1} for HRu(CO)(PPh$_3$)(NCMe)$_3^+$[1b]) before the solvent was removed by vacuum transfer. A ^{1}H NMR spectrum of the crude product mixture did not show the expected resonances expected from the target of the synthesis. However, a signal at δ 1.63 (d, J = 12.0 Hz) matched a signal observed when solutions containing **4**, prepared in situ from **1** and HBF$_4$·Et$_2$O in acetonitrile-d_3, had undergone partial decomposition after being left for 3–4 h at ambient temperature.

Protonation of 1 with Excess HBF$_4$·Et$_2$O in Acetonitrile-d_3. An NMR tube equipped with a ground-glass joint was loaded with **1** (5 mg, 0.018 mmol) and HBF$_4$·Et$_2$O (5 μL, 0.037 mmol), the tube was cooled at liquid-nitrogen temperature, and acetonitrile-d_3 was added by vacuum transfer. At −40 °C, **3** was the only Cp-containing species present [δ −7.95 (br s, 2 H), 1.72 (d, J = 11.8 Hz, 9 H), 5.53 (s, 5 H)]. At −10 °C, the onset of a slow decomposition reaction which produced **2**-d_3 [δ 1.64 (d, J = 11.9 Hz, 9 H), 5.23 (s, 5 H)] as the only identifiable product, also verified by IR analysis (1980 cm^{-1}), was noted. Several low-intensity signals appeared in the region 5.0–5.7 ppm at ambient temperature, as well as a PMe$_3$ signal at δ 1.62 (d, J = 11.5 Hz) of unknown origin.

Decomposition of CpRu(CO)(PMe$_3$)(η^2-H$_2$)$^+$ in Acetonitrile-d_3. A solution of **1** (46 mg, 0.170 mmol) in dichloromethane (2 mL) was treated with HBF$_4$·Et$_2$O (40 μL) at −70 °C. The mixture was stirred for 5 min before the product **3**·BF$_4$ was precipitated by the addition of ether at −70 °C. The solvent was decanted, and the remaining white precipitate was washed with cold ether (3 × 3 mL) before it was transferred to two NMR tubes equipped with ground-glass joints. Dichloromethane-d_2 was added to one tube by vacuum transfer. The ^{1}H NMR spectrum (−60 °C) demonstrated the presence of **3** [δ −7.88 (br s, 2 H), 1.83 (d, J = 11.8 Hz, 9 H), 5.56 (s, 5 H)]. Acetonitrile-d_3 was added to the other tube by vacuum transfer. The ^{1}H NMR spectrum (−40 °C) showed the presence of **3**, cyclopentadiene, **4**-d_9, and a trace of **2**-d_3. The quantity of **3** rapidly decreased with a concomitant increase in the signal intensities due to the other products. The amount of **2**-d_3 was less than 5%.

Ferrocenium Oxidation of 1 in Acetonitrile-d_3 with Hexamethylbenzene as Internal Standard. A mixture of **1** (4.8 mg, 0.018 mmol) and hexamethylbenzene (0.9 mg, 0.0055 mmol) in ether (1.0 mL) was evenly distributed into two NMR tubes equipped with ground-glass joints. The solvent was carefully removed from both tubes by vacuum transfer. Cp$_2$Fe$^+$PF$_6^-$ (2.5 mg, 0.0075 mmol) was added to one tube, and acetonitrile-d_3 (0.5 mL) was added to both tubes by vacuum transfer. The oxidation reaction in the tube containing ferrocenium proceeded smoothly, as indicated by the fading blue color. A residual greenish tint to the solution indicated the incomplete conversion of the oxidant, which appeared as a broadened signal at δ 4.3 (peak width ca. 30 Hz). ^{1}H NMR spectra were recorded of both samples, and the product yields from the oxidation were determined by comparison of integrated signal intensities, relative to the hexamethylbenzene signal, with that of the substrate in the tube containing no oxidant. The ^{1}H NMR spectra revealed complete consumption of the substrate. The observable products were **2**-d_3 (6%), **4**-d_9 (31%), **5** (64% of the two isomers combined), and cyclopentadiene (29%).

Low-Temperature Ferrocenium Oxidation of 1 in Acetonitrile-d_3. An NMR tube equipped with a ground-glass joint was loaded with **1** (5.0 mg, 0.0184 mmol) and Cp$_2$Fe$^+$PF$_6^-$ (6.0 mg, 0.0181 mmol), and acetonitrile-d_3 was added by vacuum transfer. A ^{1}H NMR spectrum was recorded at −40 °C. The spectrum showed the presence of **2**-d_3 (5%), **3** (10%), **4**-d_9 (10%), **5a** and **5b** (60% combined), and cyclopentadiene (10%). In addition, signals of unknown origin were present at δ 5.71 (s, 8%), 3.5 (br s, 7% if Cp derived), and −9.55 (d, J = 20 Hz, trace). (Yields are based on total Cp present.) After the sample was heated to −10 °C, the signals due to **4**-d_9 and cyclopentadiene increased in intensity at the expense of the signals arising from **3** and the unknown compounds. Eventually, the product distribution was practically identical to that observed in the experiment carried out at ambient temperature.

Ferrocenium Oxidation of 1 in Acetonitrile-d_3 in the Presence of 2,6-Lutidine and Pyrrolidine. Acetonitrile-d_3 was added by vacuum transfer to a 10-mL round-bottom flask that was loaded with **1** (5.0 mg, 0.0184 mmol), Cp$_2$Fe$^+$PF$_6^-$ (12.2 mg, 0.0369 mmol), and 2,6-lutidine (4.3 μL, 0.0369 mmol). The ^{1}H NMR spectrum was recorded at ambient temperature and showed that the substrate had been completely consumed; the bluish green color indicated that the oxidant was incompletely consumed. The only observable Ru-containing products were **2**-d_3 (ca. 10% based on total Cp available) and **5a** and **5b** (90% combined). Experiments employing 5, 10, or 20 equiv of 2,6-lutidine led to essentially the same results. The yields of **2**-d_3 varied between 8 and 13% without obvious correlations between product distribution and base concentration. The slight variations may be due to factors like rates of mixing and dissolving of reactants that were not easily controlled. All other products observed in the absence of 2,6-lutidine were conspicuously absent.

The experiment with pyrrolidine as the base (2.3 μL, 0.027 mmol) was performed in the same fashion. The reaction led to complete consumption of the oxidant, and the ^{1}H NMR spectrum showed that **2**-d_3 was the only Ru-containing product.

Ferrocenium Titration of 1 in Acetonitrile. A solution of Cp$_2$Fe$^+$PF$_6^-$ (66.2 mg, 0.20 mmol) in acetonitrile (1.20 mL) was added slowly with a syringe to a vigorously stirred solution of **1** (54.2 mg, 0.20 mmol) in acetonitrile (3 mL). The color change to yellow-orange at first indicated the rapid consumption of added ferrocenium. However, after the addition of ca. 860 μL of the ferrocenium solution, a permanent greenish tint was apparent, signaling the presence of unconsumed ferrocenium. The amount of ferrocenium consumed at this point corresponds to 0.71 equiv of oxidant.

Ferrocenium Titration of 1 in Acetonitrile Containing 2,6-Lutidine. A solution of Cp$_2$Fe$^+$PF$_6^-$ (99.1 mg, 0.30 mmol) in acetonitrile (1.80 mL) was added slowly with a syringe to a vigorously stirred solution of **1** (54.2 mg, 0.20 mmol) and 2,6-lutidine (24 μL, 0.20 mmol) in acetonitrile (3 mL). The persistent greenish tint indicating the presence of unreacted ferrocenium was seen after the addition of ca. 1.30 mL of the ferrocenium solution, and the addition was stopped at this point. The amount of solution added corresponds to the consumption of 1.1 equiv of ferrocenium. The solvent was removed by vacuum transfer, and the residue was washed with ether (3 × 2 mL) to remove the ferrocene. The remaining waxy solid was dissolved in dichloromethane (4 mL), and the orange solution was washed with aqueous ammonium chloride (3 × 2 mL), dried (MgSO$_4$), and filtered through Celite. Recrystallization from dichloromethane/ether yielded an orange powder (62.2 mg). ^{1}H NMR analysis revealed the presence of the bridging hydride isomers **5a** and **5b**. The product yield based on **1** was 91%.

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[25] (a) Lyatifov, I. R.; Solodovnikov, S. P.; Babin, V. N.; Materikova, R. B. *Z. Naturforsch., B* **1979**, *34B*, 863. (b) Dauben, H. J.; Honnen, L. R.; Harmon, K. M. *J. Org. Chem.* **1960**, *25*, 1442.

Ferrocenium Titration of 1 in Acetonitrile Containing Pyrrolidine. A solution of $Cp_2Fe^+PF_6^-$ (165.5 mg, 0.50 mmol) in acetonitrile (2.50 mL) was added slowly with a syringe to a vigorously stirred solution of **1** (54.2 mg, 0.20 mmol) and pyrrolidine (16.7 μL, 0.20 mmol) in acetonitrile (3 mL). The persistent greenish tint indicating the presence of unreacted ferrocenium was seen after the addition of ca. 2.1 mL of the ferrocenium solution, whereupon the addition was stopped. The amount of solution added corresponds to the consumption of 2.1 equiv of the oxidizing agent. The solvent was removed by vacuum transfer, and the residue was washed with ether (3 × 2 mL) to remove the ferrocene. The remaining solid was dissolved in dichloromethane (4 mL), and the solution was washed with aqueous ammonium chloride (3 × 2 mL), dried ($MgSO_4$), and filtered through Celite. Recrystallization twice from dichloromethane/ether yielded a pale yellowish brown powder (65.1 mg). ^1H NMR analysis showed **2** to be the only product (71% yield).

Constant-Current Coulometry and Preparative Electrolysis Experiments. Constant-current electrolyses with DCV monitoring of the disappearance of substrate were performed in a H-shaped cell, the compartments of which were separated by a fritted-glass junction. A Pt-gauze working electrode was used. Solutions that contained 2.0 mM of **1** in 20 mL of acetonitrile/0.1 M $Bu_4N^+PF_6^-$ were electrolyzed with a constant current of 10 mA. The procedure was identical for coulometry experiments performed in the presence of 2,6-lutidine (20 mM).

The preparative electolyses were carried out in acetonitrile/0.05 M $Me_4N^+BF_4^-$. A solution of **1** (30 mg, 0.111 mmol) in the electrolyte solution (20 mL) was electrolyzed for the time that was required for the passage of 1.0 faraday/mol of charge. The IR spectrum of an aliquot revealed two equally intense CO absorptions at 1950 and 1980 cm^{-1}. The solution was concentrated by rotary evaporation, and the residue was extracted with dichloromethane (5 mL). The filtered extract was concentrated, and the product (21.5 mg, 49%) was precipitated by the addition of ether. ^1H NMR spectroscopy showed the product to be **2** contaminated with a trace of the two isomers of **5**.

Preparative electrolysis in the presence of 2 equiv of pyrrolidine was carried out similarly, except that a 2-electron oxidation was performed. IR analysis showed only one CO absorption at 1980 cm^{-1}. During workup, the dichloromethane extract was washed with a 5% aqueous ammonium chloride solution (2 × 3 mL) in order to remove the conjugate acid of the base. The solution was dried ($MgSO_4$), filtered, and concentrated, and the residue was crystallized from dichloromethane/ether to provide **2** in a yield of 54%.

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Registry No. 1, 87985-84-0; **2**, 136947-47-2; **2**-d_3, 136947-51-8; **3**, 110142-04-6; **4**, 136947-48-3; **4**-d_9, 136947-52-9; **5a**·BF_4, 136947-50-7; **5b**·BF_4, 137036-32-9; $Cp_2Fe^+PF_6^-$, 11077-24-0; (p-$MeOC_6H_4$)Ph_2C^+-BF_4^-, 1881-93-2.

Visible Light Photolysis of Hydrogen Iodide Using Sensitized Layered Semiconductor Particles

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Abstract: Surface sensitization of internally platinized layered oxide semiconductors $K_{4-x}H_xNb_6O_{17}\cdot nH_2O$ ($x \approx 2.5$), $H_2Ti_3O_7$, and $HTiNbO_5$ by RuL_3^{2+} (L = 4,4′-dicarboxy-2,2′-bipyridine) yields photocatalysts for the production of H_2 and I_3^- in aqueous iodide solutions. Flash photolysis experiments show that, at pH 3.0, excited-state RuL_3^{2+} injects an electron into $K_{4-x}H_xNb_6O_{17}\cdot nH_2O$ and is rapidly re-reduced by I^-. Steady-state photolysis at 450 nm in 50 mM aqueous KI (pH 3.0) yields H_2 and I_3^- in stoichiometric amounts, with an initial quantum yield of 0.3%. While H_2 and I_3^-, once formed, do not recombine at an observable rate, the rate of hydrogen evolution decreases as the concentration of I_3^- increases in the solution.

Despite the successes realized with solid-state and liquid-junction photoelectrochemical devices, there are very few chemical systems (apart from natural photosynthesis) which make energy-rich oxidized and reduced products from abundant feedstocks photochemically (i.e., without wires attached[1,2]) using light of visible wavelengths. Homogeneous or particle-based photochemical systems for hydrogen or oxygen generation typically employ "sacrificial" reducing or oxidizing agents which are irreversibly decomposed in the reaction; these systems are not of interest in practical energy conversion schemes, because in one of the half-reactions an expensive chemical (e.g., EDTA or persulfate) is consumed.

For nonsacrificial systems, i.e., those which employ chemically reversible electron donors *and* acceptors, the problem is one of spatial compartmentalization. Following photochemical charge separation, energetic oxidized and reduced products are produced at catalytic surfaces. These products must be prevented from recombining (the recombination reaction is necessarily favorable, if free energy is being stored) at the same catalyst. In photoelectrochemical cells this problem is conveniently overcome by carrying out the oxidation and reduction half-reactions at spatially well separated electrodes. However, in photochemical systems, products are made at the same particle, or in the same homogeneous solution, and keeping them separate requires sieving at the molecular level.

Recently, Domen, Onishi, and co-workers have reported that the layered semiconductor $K_4Nb_6O_{17}\cdot 3H_2O$, when internally loaded with elemental nickel or platinum as a hydrogen evolution

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[1] We are counting multipanel photoelectrode systems, which can decompose hydrohalic acids or water into their elements without input of electrical power, as internally wired photoelectrochemical devices. Examples are the Texas Instruments silicon microsphere system for HBr photolysis (Kilby, J. S.; Lathrop, J. W.; Porter, W. A. U.S. Patents 4,021,323 (1977), 4,100,051 (1978), 4,136,436 (1979); Johnson, E. L. In *Electrochemistry in Industry*; Landau, U., Yeager, E., Eds.; Plenum Press: New York, 1982; pp 299–306) and CdSe/CoS multipanel devices for water photolysis (Smotkin, E. S.; Cervera-March, S.; Bard, A. J.; Campion, A.; Fox, M. A.; Mallouk, T. E.; Webber, S. E.; White, J. M. *J. Phys. Chem.* **1987**, *91*, 6).

[2] To our knowledge there are three examples of "non-sacrificial" molecular systems which produce hydrogen or oxygen photochemically: sensitized oxygen evolution from water using Fe(III) or Hg(II) as an electron acceptor (Christensen, P. A.; Erbs, W.; Harriman, A. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 575), sensitized hydrogen evolution in which the surface of a TiO_2 colloid is oxidized to form peroxo groups (Frank, A. J.; Willner, I.; Goren, Z.; Degani, Y. *J. Am. Chem. Soc.* **1987**, *109*, 3568), and sensitized hydrogen evolution using $Ru(bpy)_3^{2+}$ or dimethoxybenzene as an electron donor with ultraviolet excitation (Slama-Schwok, A.; Avnir, D.; Ottolenghi, M. *J. Phys. Chem.* **1989**, *93*, 7544; *J. Am. Chem. Soc.* **1991**, *113*, 3984).

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