Inorg. Chem. **1995,** *34,* 6497−6504

Kinetic Isotope Effects on Metal to Nitrogen Proton Transfers

Kjell-Tore Smith and Mats Tilset*

Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway

S. Sóley Kristjánsdóttir[†] and Jack R. Norton*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Received August 24, 1994⊗

The rate constants for proton transfer from the radical cation $CpRu(PPh_3)_2H^{\bullet+}$ to pyrrolidine and piperidine have been determined by derivative cyclic voltammetry in CH_3CN. The kinetic isotope effects k_H/k_D at 20 °C are 2.7 for pyrrolidine and 2.3 for piperidine—surprisingly small for transfers that are almost thermoneutral. The rate constant for proton transfer from $CpW(CO)_3H$ to aniline in CH_3CN has been determined from the effect of the aniline concentration on the rate of W → W self-exchange; the kinetic isotope effect k_H/k_D at 25 °C is 4.2—surprisingly large for a transfer that is uphill by 5.5 pK_a units.

The size of the primary kinetic isotope effect on a proton transfer reaction is quite sensitive to the structure of the transition state, and the temperature dependence of the effect can tell us whether tunneling is involved.[1] Transition-metal hydrides rarely if ever serve as hydrogen-bond donors,[2] so their deprotonation reactions occur in single steps, with observed rate constants that are true proton transfer rate constants. The weakness of the M−H force constants means that the transferred protons experience different force constants on opposite sides of the transition state, so such deprotonation reactions provide ideal tests[3] for the various theories describing kinetic isotope effects.[4] We therefore report the first measurements of k_H/k_D for the transfer of a proton from a transition-metal acid (i.e., a hydride complex) to a nitrogen base.

One of our groups (that of M.T. at the University of Oslo) has examined the proton transfer reactions of radical cations generated by the one-electron oxidation of neutral hydride complexes,[5] whereas the other (that of J.R.N. at Colorado State University) has investigated the kinetics and thermodynamics of proton transfer from such hydride complexes to nitrogen bases.[2b] As a rule, the former are thermodynamically downhill and the latter uphill, so the combination is ideal for determining the influence of thermodynamic driving force on the isotope effect.

Results

Oxidation of $CpRu(PPh_3)_2H$ in the Absence of Base. The Tilset group recently found[5] that, contrary to previous reports,[6] the cyclic voltammetry oxidation wave of $CpRu(PPh_3)_2H$ (**1**) at −0.30 V vs the Cp_2Fe/Cp_2Fe^+ (Fc) couple exhibits virtually full chemical reversibility in dichloromethane and THF at 1 mM substrate concentration and considerable reversibility in acetonitrile. The half-life of $\mathbf{1}^{\bullet+}$ is several seconds at 20 °C in 4:1 acetonitrile/THF with 0.1 M $Bu_4N^+PF_6^-$ as the supporting electrolyte.

The disproportionation of $\mathbf{1}^{\bullet+}$ generates a 1:1 mixture of $CpRu(PPh_3)_2(NCMe)^+$ ($\mathbf{2}^+$) and $CpRu(PPh_3)_2H_2^+$ ($\mathbf{3}^+$) (eq 1).

$$\underset{\mathbf{1}}{CpRu(PPh_3)_2H} \xrightarrow[MeCN]{-e^-} 0.5\ \underset{\mathbf{2}^+}{CpRu(PPh_3)_2(NCMe)^+} + 0.5\ \underset{\mathbf{3}^+}{CpRu(PPh_3)_2H_2^+} \qquad (1)$$

A derivative cyclic voltammetry (DCV)[7] investigation of the reaction has revealed it to be second-order in total ruthenium.[5] The large solvent effects, and the k_H/k_D of unity (**1** vs **1**-*d* as substrate), imply that the reaction proceeds by a rate-limiting, acetonitrile-assisted disproportionation like that in eqs 2−5 (Scheme 1).

Scheme 1

$$\underset{\mathbf{1}}{CpRu(PPh_3)_2H} \overset{\pm e^-}{\rightleftharpoons} \underset{\mathbf{1}^{\bullet+}}{CpRu(PPh_3)_2H^{\bullet+}} \qquad (2)$$

$$\mathbf{1}^{\bullet+} + CH_3CN \rightleftharpoons \underset{\mathbf{4}^{\bullet+}}{CpRu(PPh_3)_2(NCMe)H^{\bullet+}} \qquad (3)$$

$$\mathbf{1}^{\bullet+} + \mathbf{4}^{\bullet+} \xrightarrow{k_e} \mathbf{1} + \underset{\mathbf{5}^{2+}}{CpRu(PPh_3)_2(NCMe)H^{2+}} \qquad (4)$$

$$\mathbf{1} + \mathbf{5}^{2+} \rightarrow \mathbf{2}^+ + \mathbf{3}^+ \qquad (5)$$

With the electron transfer in eq 4 as the rate-determining step, the overall rate of Scheme 1 depends upon the nature of the solvent and shows no isotope effect; with eq 3 as a rapidly

---

[†] Present address: E. I. DuPont de Nemours Co., Box 80328, Route 141, ESP 328/317B, Wilmington, DE 19888-0328.

⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1995.

(1) Melander, L.; Saunders, W. H., *Jr. Reaction Rates of Isotopic Molecules*; John Wiley & Sons: New York, 1980.

(2) (a) Kristjánsdóttir, S. S.; Norton, J. R.; Moroz, A.; Sweany, R. L.; Whittenburg, S. L. *Organometallics* **1991** *10*, 2357. (b) Kristjánsdóttir, S. S.; Norton, J. R. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; Chapter 9. (c) M⋯HB bonding, where a transition metal serves as an H-bond *acceptor*, is relatively common, e.g.: Kazarian, S. G.; Hamley, P. A.; Poliakoff, M. *J. Am. Chem. Soc.* **1993**, *115*, 9069. (d) One *cationic* hydride complex that serves as an H-bond donor has been reported: Epstein, L. M.; Shubina, E. S.; Krylov, A. N.; Kreindlin, A. Z.; Rybinskaya, M. I. *J. Organomet. Chem.* **1993**, *447*, 277.

(3) Bullock, R. M. Isotope Effects in Reactions of Transition Metal Hydrides. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; Chapter 8, and references therein.

(4) Sühnel, J. *Isotopenpraxis* **1986**, *22*, 73.

(5) Smith, K. T.; Rømming, C.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 8681, and references therein.

0020-1669/95/1334-6497$09.00/0

maintained preequilibrium, the overall rate is second-order in total ruthenium. Coordination of acetonitrile to neutral 17-electron radicals has been established,[8] and the equilibrium constant should be even larger for cationic radicals like the $\mathbf{1}^{\bullet+}$ in eq 3. The resulting 19-electron species are known[8] to be strong reducing agents (as $\mathbf{4}^{\bullet+}$ is required to be in eq 4).

Oxidation of CpRu(PPh$_3$)$_2$H in the Presence of Base. As the pK_a of $\mathbf{1}^{\bullet+}$ is between 15 and 20 in CH_3CN,[5,9] it should be deprotonated by bases like quinuclidine, piperidine, and pyrrolidine (pK_a of BH^+ = 19.5, 18.9, and 19.6, respectively).[10] The addition of these bases should therefore decrease the lifetime of $\mathbf{1}^{\bullet+}$ formed by the oxidation of **1**.

Figure 1 shows cyclic voltammograms for the oxidation of **1** (1.0 mM) in the absence (top trace) and presence (bottom trace) of pyrrolidine (12.1 mM). The addition of pyrrolidine significantly reduces the reversibility of the oxidation wave. The addition of piperidine or quinuclidine gives similar results; qualitatively, the reversibility decreases in the order quinuclidine > piperidine > pyrrolidine. These nitrogen bases thus open a reaction channel for $\mathbf{1}^{\bullet+}$ that is not available in the absence of base.

Stoichiometric oxidation with $Cp_2Fe^+PF_6^-$ in the presence of 2 equiv of pyrrolidine, piperidine, or quinuclidine in acetonitrile-d_3 showed $\mathbf{2}^+$ to be the only detectable (by ^{1}H NMR spectroscopy) Ru-containing product. The overall reaction is that in eq 6. The addition of bases has thus changed the

$$\underset{\mathbf{1}}{\mathrm{CpRu(PPh_3)_2H}} + \mathrm{Base} \xrightarrow[\mathrm{MeCN}]{-2e^-} \underset{\mathbf{2}^+}{\mathrm{CpRu(PPh_3)_2(NCMe)^+}} + \mathrm{BaseH^+} \quad (6)$$

oxidation of **1** from a one-electron process to a two-electron one. The change is apparent in Figure 1, which shows a higher peak current after the addition of the base.[11]

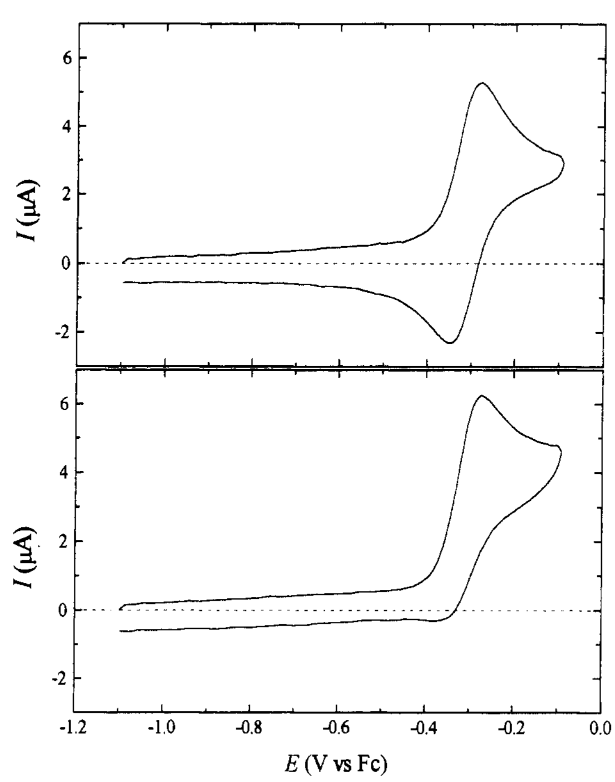

Figure 1. Cyclic voltammograms for the oxidation of CpRu(PPh$_3$)$_2$H (1.0 mM) in the absence (top) and presence (bottom) of pyrrolidine (12.1 mM). Experimental conditions: 4:1 acetonitrile/THF, 0.1 M $Bu_4N^+PF_6^-$, 0 °C, voltage sweep rate v = 10.0 V/s, Au disk electrode (d = 0.4 mm).

DCV Investigation of the Deprotonation of CpRu(PPh$_3$)$_2$H$^{\bullet+}$. The mechanism of the reactions between $\mathbf{1}^{\bullet+}$ and pyrrolidine, piperidine, and quinuclidine has been investigated by DCV. The details of the method have been thoroughly reviewed elsewhere[7] and briefly explained in a recent paper by the Tilset group,[5] and therefore will not be repeated here. The DCV analyses were performed under pseudo-first-order conditions with at least a 10-fold excess of base over **1**. The DCV reaction-order analysis data in Table 1[12] showed the reaction between $\mathbf{1}^{\bullet+}$ and piperidine or pyrrolidine to be first-order with respect to $\mathbf{1}^{\bullet+}$ and first-order with respect to the base; similar but less precise data for the less reactive quinuclidine indicated the same rate law. The results are in accord with a direct proton transfer from $\mathbf{1}^{\bullet+}$ to the bases; the mechanism appears to be the ECE one shown in Scheme 2.

Scheme 2

$$\mathbf{1} \overset{\pm e^-}{\rightleftharpoons} \mathbf{1}^{\bullet+} \quad (2)$$

$$\underset{\mathbf{1}^{\bullet+}}{\mathrm{CpRu(PPh_3)_2H^{\bullet+}}} + \mathrm{Base} \xrightarrow{k} \mathrm{CpRu(PPh_3)_2}^{\bullet} + \mathrm{BaseH^+} \quad (7)$$

$$\mathrm{CpRu(PPh_3)_2}^{\bullet} + \underset{\mathbf{1}^{\bullet+}}{\mathrm{CpRu(PPh_3)_2H^{\bullet+}}} \xrightarrow{\mathrm{MeCN}} \underset{\mathbf{2}^+}{\mathrm{CpRu(PPh_3)_2(NCMe)^+}} + \underset{\mathbf{1}}{\mathrm{CpRu(PPh_3)_2H}} \quad (8)$$

CpRu(PPh$_3$)$_2^\bullet$ may be in equilibrium with CpRu(PPh$_3$)$_2$(NCMe)$^\bullet$.[8] The latter will be a potent reducing agent (the irreversible reduction of CpRu(PPh$_3$)$_2$(NCMe)$^+$ occurs at −2.42

---

[6] (a) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875. (b) Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161.

[7] (a) Ahlberg, E.; Parker, V. D. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *121*, 73. (b) Parker, V. D. *Acta Chem. Scand., Ser. B* **1984**, *B38*, 165. (c) Parker, V. D. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1986; Vol. 14, p 1.

[8] (a) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325. (b) Trogler, W. C. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: New York, 1990; p 306. (c) Tyler, D. R. Reference 11b, p 338. (d) Philbin, C. E.; Granatir, C. A.; Tyler, D. R. *Inorg. Chem.* **1986**, *25*, 4806. (e) Tilset, M. *Inorg. Chem.* **1994**, *33*, 3121.

[9] There have been three reports of the effect on the pK_a of a carbonyl hydride complex when a CO ligand is replaced by PPh$_3$: Δ(pK_a) = 6.2 for HMn(CO)$_5$/HMn(CO)$_4$(PPh$_3$);[2b] Δ(pK_a) = 7.1 for HCo(CO)$_4$/HCo(CO)$_3$(PPh$_3$);[2b] Δ(pK_a) = 8.5 for HCr(CO)$_3$Cp/HCr(CO)$_2$(PPh$_3$)Cp (see ref 5 and Parker, V. D.; Handoo, K. L.; Roness, F.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 8681). It is evident that the increase is greater when fewer carbonyl ligands are left to accommodate the increased electron density.[5] Extrapolation to cases in which even fewer CO's remain suggests that a pK_a as high as 40 is reasonable for **1**, with both CO's in HRu(CO)$_2$Cp (pK_a 20.2)[2b] replaced by PPh$_3$. A pK_a for $\mathbf{1}^{\bullet+}$ in the range 15−20 is supported by the fact that proton transfer from $\mathbf{1}^{\bullet+}$ to Et$_3$N (pK_a 18.5)[10a] was too slow to be measured by DCV. We believe that the reactions between $\mathbf{1}^{\bullet+}$ and the bases used are almost thermoneutral−downhill by four pK_a units at most.

[10] (a) Coetzee, J. R.; Padmanabhan, G. R. *J. Am. Chem. Soc.* **1965**, *87*, 5005. (b) Beltrame, P.; Gelli, G.; Loi, A. *Gazz. Chim. Ital.* **1980**, *110*, 491, as quoted by: Izutsu, K. *Acid−Base Dissociation Constants in Dipolar Aprotic Solvents*; International Union of Pure and Applied Chemistry Chemical Data Series No. 35; Blackwell: Boston, 1990; pp 17−35.

[11] The increase is not 2-fold because not all of the $\mathbf{1}^{\bullet+}$ is deprotonated by the base at this scan rate. Digital simulation of the electrode response has confirmed that such behavior would be expected.

[12] $v_{0.5}$ is, roughly speaking, the scan rate that results in 50% conversion of the electrode-generated intermediate $\mathbf{1}^{\bullet+}$ on the measurement time scale and therefore correlates with the half-life of $\mathbf{1}^{\bullet+}$.[7] The value of $v_{0.4}$ is analogously defined and shows a similar correlation.

Table 1. Reaction-Order Data for the Reactions between $\mathbf{1}^{\bullet+}$ and Nitrogen Bases[a]

base	reaction order with respect to $\mathbf{1}^{\bullet+}$ [b]	reaction order with respect to base[c]
piperidine	1.05 (0.02)	1.11 (0.04)
pyrrolidine	1.22 (0.05)	1.22 (0.03)

[a] Measured by DCV in 4:1 acetonitrile/THF and 0.1 M $Bu_4N^+PF_6^-$ at an Au disk electrode (d = 0.6 mm) at 0 °C. [b] Obtained from slopes of log $\nu_{0.4}$ (ref 12) vs log [**1**]; 0.5–2.0 mM **1** in the presence of ca. 20 mM base. Standard deviations of linear regression lines in parentheses. [c] Obtained from slopes of log $\nu_{0.4}$ (ref 12) vs log [base]; ca. 1.0 mM **1** in the presence of 10–40 mM base. Standard deviations of linear regression lines in parentheses.

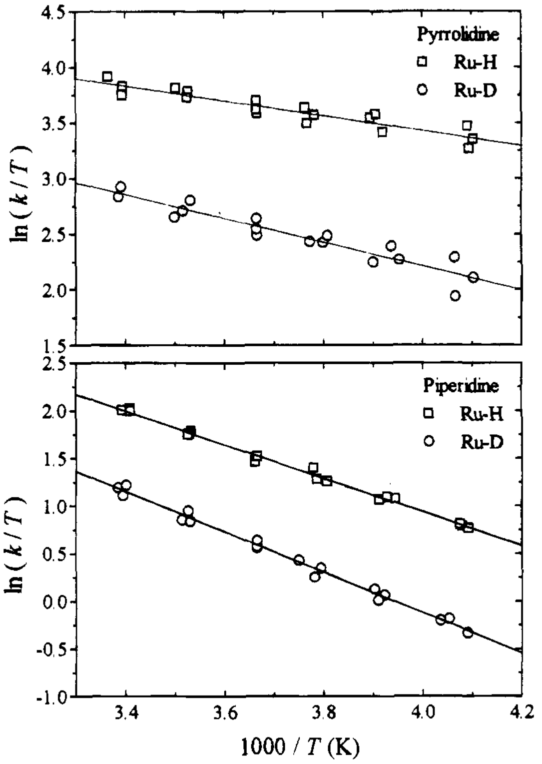

Figure 2. Eyring plots based on the second-order rate constants (M^{-1} s^{-1}) for the reactions between $CpRu(PPh_3)_2H^{\bullet+}$ and pyrrolidine (top), or piperidine (bottom), in the temperature range −30 to +25 °C.

V vs Fc)[5] toward $\mathbf{1}^{\bullet+}$, so the last step in Scheme 2 may be assisted by the solvent.

Measurement of Rates and Kinetic Isotope Effects for the Deprotonation of $\mathbf{1}^{\bullet+}$ by Various Bases. DCV measurements were performed for the reaction of **1** or **1**-*d* (1.0 mM) with pyrrolidine or piperidine (11–12 mM) in acetonitrile/0.1 M $Bu_4N^+PF_6^-$ at temperatures ranging from −30 through +25 °C. Three independent measurement series were performed for each reaction. The DCV data were transformed to second-order rate constants by comparison with available[7c] theoretical (digital simulation) data for the ECE mechanism. Figure 2 shows Eyring plots of the resulting kinetic data. Table 2 lists the activation parameters for the deprotonation of the radical cations from the oxidation of **1** and **1**-*d* and the resulting isotope effects.

The fact that k is larger for pyrrolidine than piperidine is expected from the pK_a values of their conjugate acids; the stronger base provides a greater driving force for the reaction. In contrast, although the pK_a of quinuclidineH^+ is similar to that of pyrrolidineH^+, experiments like those just described suggest that k for quinuclidine is even smaller (≈400 M^{-1} s^{-1} at 0 °C) than that for piperidine; the k_H/k_D ratio of quinuclidine, although difficult to measure with precision because both rate constants are so small, is approximately 2. The slowness with which quinuclidine reacts must be attributed to steric effects.

^{1}H NMR Measurement of the Rate of Proton Transfer from $CpW(CO)_3H$ to Aniline. The W → N proton transfer in eq 9 is uphill by 5.5 pK_a units in CH_3CN.[13] Its rate can be determined from the line widths observed for the Cp resonances of both species in the ^{1}H NMR.[14]

$$HW(CO)_3Cp + PhNH_2 \overset{k_{H+}}{\rightleftharpoons} WCp(CO)_3^- + PhNH_3^+ \qquad (9)$$

Suppose the Cp groups of $HWCp(CO)_3$ or $DWCp(CO)_3$ are observed in the presence of $WCp(CO)_3^-$. The first-order rate of exchange for $(H/D)WCp(CO)_3$, $k_{obs(H^+)}$ in eq 12 or $k_{obs(D^+)}$ in eq 13, is then the sum of the base-catalyzed exchange rate (eq 10) and the self-exchange rate (eq 11).

$$HWCp(CO)_3 + WCp(CO)_3^- \overset{PhNH_2}{\rightleftharpoons} WCp(CO)_3^- + HWCp(CO)_3 \qquad (10)$$

$$HWCp(CO)_3 + WCp(CO)_3^- \overset{k^H_{ww}}{\rightleftharpoons} WCp(CO)_3^- + HWCp(CO)_3 \qquad (11)$$

$$k_{obs(H^+)} = k^H_{ww}[WCp(CO)_3^-] + k_{H+}[PhNH_2] \qquad (12)$$

$$k_{obs(D^+)} = k^D_{ww}[WCp(CO)_3^-] + k_{D+}[PhND_2] \qquad (13)$$

The difference in chemical shift between the Cp signals of $HWCp(CO)_3$ and of $WCp(CO)_3^-$ is only 0.5 ppm, and the peaks overlap even at relatively slow exchange rates. We have therefore calculated complete lineshapes[15] for several k_{obs} values and used their line widths at half-height, Δ(Cp), to construct a calibration curve for k_{obs} as a function of Δ(Cp).

Effect of Incomplete Deuteration. We have also used calculated line shapes to quantify the effect of incomplete deuteration on $k_{obs(D^+)}$. We considered the three-site exchange in eq 14, where DW = Cp in $DWCp(CO)_3$, W^- = Cp in

$$DW \underset{k_{(W^- \to WD)}}{\overset{k_{(WD \to W^-)}}{\rightleftharpoons}} W^- \underset{k_{(WH \to W^-)}}{\overset{k_{(W^- \to WH)}}{\rightleftharpoons}} HW \qquad (14)$$

$WCp(CO)_3^-$, and HW = Cp in $HWCp(CO)_3$. The rate constant for direct exchange between $HWCp(CO)_3$ and $DWCp(CO)_3$, $k_{(WD \to WH)}$, was assumed to be zero, and the populations of the three sites were taken as $P_{WD} = 0.5$, $P_{W^-} = 0.4$, and $P_{WH} = 0.1$, corresponding to a deuterium incorporation of 83%. The separation between the Cp signal due to $HWCp(CO)_3$ or $DWCp(CO)_3$ and that due to $WCp(CO)_3^-$ was assigned its experimental value of 103.5 Hz (at 200 MHz), and the isotope effect $k_{obs(H^+)}/k_{obs(D^+)}$ was taken as 4.0, approximately the value measured below.

Figure 3 shows that the effect of incomplete deuteration is small, even for incorporation as low as 83%. The published equation[14] for correction of lineshapes in the case of incomplete deuteration is therefore incorrect for this situation. Since the deuterium incorporation in this study was better than 90%, the effect of incomplete deuteration on $k_{obs(D^+)}$ was ignored in our subsequent measurements.

Rates and Kinetic Isotope Effects for Proton Transfer from $CpW(CO)_3H$ to Aniline. The second-order rate constants

---

(13) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257.

(14) Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem.* **1987**, *109*, 3945.

(15) Sandström, J. *Dynamic NMR Spectroscopy*; Academic: New York, 1982; pp 16–20.

Table 2. Kinetic Parameters for the Deprotonation of **1** and **1**-*d*[a]

base[b]	pyrrolidine		piperidine	
substrate[c]	**1**	**1**-*d*	**1**	**1**-*d*
A	3.29 (0.85) × 10^5	4.81 (1.7) × 10^5	2.18 (0.31) × 10^6	3.09 (0.59) × 10^6
E_a (kcal/mol)	1.87 (0.1)	2.66 (0.2)	4.04 (0.07)	4.74 (0.10)
$\Delta H^\ddagger$ (kcal/mol)[d]	1.3 (0.1)	2.1 (0.2)	3.51 (0.07)	4.21 (0.10)
$\Delta S^\ddagger$ (cal/(K·mol))[d]	−35.1 (0.5)	−34.4 (0.7)	−31.3 (0.3)	−30.6 (0.4)
k(0 °C) (M^{-1} s^{-1})[e]	10 600 (170)	3590 (83)	1265 (12)	497 (6)
k_H/k_D (−20 °C)[e]	3.31 (0.16)		2.82 (0.08)	
k_H/k_D (0 °C)[e]	2.94 (0.12)		2.55 (0.06)	
k_H/k_D (20 °C)[e]	2.67 (0.17)		2.33 (0.08)	

[a] As measured by DCV in the temperature range −30 to +25 °C. [b] Base concentration 11−12 mM. [c] Substrate concentration 1.0 mM. [d] From Eyring plot of ln k/T vs $1/T$ for combined data from three independent variable-temperature runs. One standard deviation of linear regression analyses in parentheses. [e] By interpolation of Eyring data.

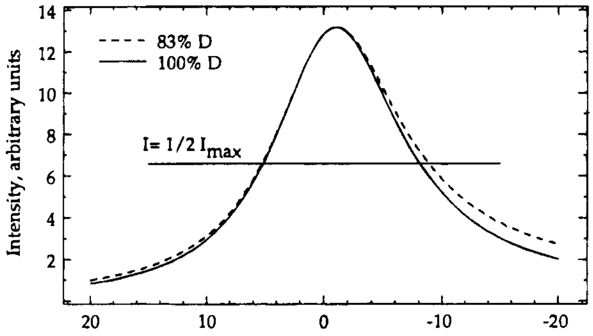

Figure 3. Simulated lineshapes for the overlapping Cp signals of $HWCp(CO)_3$ and $DWCp(CO)_3$ in the presence of $K[WCp(CO)_3]$ calculated for a deuterium incorporation of 100% (solid line) and 83% (dotted line); $k_{obs(H^-)}$ = 160 s^{-1} and $k_{obs(D^-)}$ = 40 s^{-1}.

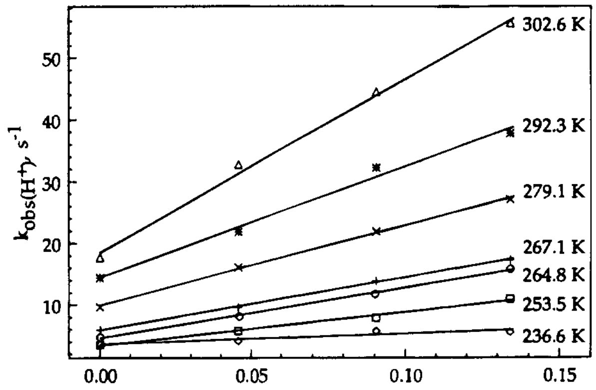

Figure 4. $k_{obs(H^+)}$ as a function of $[PhNH_2]$ in CD_3CN at several temperatures.

k_{H^+} (eq 12 and Figure 4) and k_{D^+} (eq 13 and Figure 5) were obtained at several temperatures from the slopes of plots of k_{obs} vs base concentration. The temperature dependence of these second-order rate constants gives the activation parameters in Table 3. Interpolation to 25 °C gives a k_{H^+} of 249 M^{-1} s^{-1} and a k_{D^+} of 59.8 M^{-1} s^{-1}, implying a kinetic isotope effect, k_{H^+}/k_{D^+}, of 4.2 at 25 °C. (A complete list of the k_{H^+} and k_{D^+} values at various temperatures is given in Tables 5 and 6 in the Experimental Section.)

Discussion

Three different models have been proposed to explain the different reaction rates of isotopic molecules. The most widely used one is due to Bell.[16] In it, the observed isotope effect is

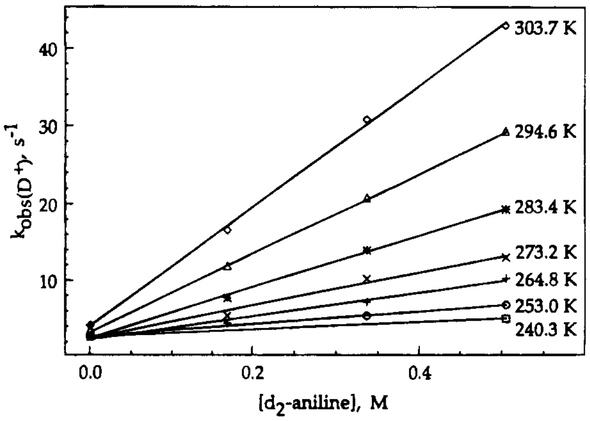

Figure 5. $k_{obs(D^-)}$ as a function of $[PhND_2]$ in CD_3CN at several temperatures.

Table 3. Rate Constants and Activation Parameters for the Reaction of $(H/D)W(CO)_3Cp$ with Aniline or Aniline-d_2 in Acetonitrile at 25 °C

	H[a]	D[a]
$k_{H^-(D^+)}$ (M^{-1} s^{-1} at 25 °C)	249 (19)	59.8 (2)
$\Delta H^\ddagger$ (kcal/mol)	5.0 (0.3)	5.9 (0.1)
$\Delta S^\ddagger$ (cal/(K·mol))	−30.7 (1.2)	−30.5 (0.5)
A	3.65 (2.2) × 10^6	3.05 (0.89) × 10^6
E_a (kcal/mol)	5.7 (0.3)	6.42 (0.15)

[a] The numbers in parentheses are estimated standard deviations.

the product of the semiclassical isotope effect[17] and a tunneling correction:

$$\frac{k_H}{k_D} = \left(\frac{k_H}{k_D}\right)_{class} \times Q_t \tag{15}$$

If isotope effects on the moment of inertia, and contributions from vibrationally excited states, are neglected, the semiclassical isotope effect depends solely upon the difference in zero-point energies between the reactants and the transition state:

$$\left(\frac{k_H}{k_D}\right)_{class} = \exp\left\{-\frac{hc}{2k_bT}\left[\sum_i^{3n^\ddagger-7}({\nu^\ddagger}_{Hi} - {\nu^\ddagger}_{Di}) - \sum_i^{3n-6}(\nu_{Hi} - \nu_{Di})\right]\right\} \tag{16}$$

The simplest model of the transition state is the three-center model shown in Figure 6. The stretching modes (i) and (ii) are usually higher in energy than the bending modes and therefore dominate the isotope effect. If the A−H and B−H force constants are equal in the transition state (the "symmetric"

---

(16) Bell, R. P. *The Proton in Chemistry*; Cornell University: Ithaca, NY, 1973.

(17) Spicer, L. D.; Poulter, C. D. In *Physical Chemistry: An Advanced Treatise*; Eyring, H., Henderson, D., Jost, W., Eds.; Academic: New York, 1975; Vol. VII, Chapter 11.

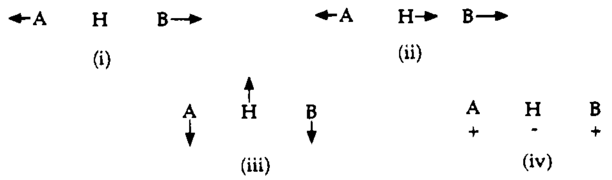

Figure 6. Vibrational modes of a three-center transition state. Mode (ii) is the reaction coordinate.

Table 4. Parameters for the H−N Bond in Aniline and the H−M Bonds in $CpRu(PPh_3)_2H^{\bullet+}$ (**1**$^{\bullet+}$) and $CpW(CO)_3H$

bond	length (Å)	stretch (cm^{-1})	bend (cm^{-1})	a_{ij} (Å)[a]	d_{ij} (Å)[a]
H−N	1.001[b]	3460[c]	1618[c]	1.66	0.30
H−Ru	1.65[d]	1968[e]	≈800[f]	1.84	0.61
H−W	1.82[g]	1845[h]	≈800[f]	1.78	0.97

[a] From ref 17c. [b] Lister, D. G.; Tyler, J. K. *J. Mol. Struct.* **1974**, *23*, 253. [c] Niu, Z.; Dunn, K. M.; Boggs, J. E. *Mol. Phys.* **1985**, *55*, 421. [d] The average terminal Ru−H bond length is given as 1.64(7) Å by Teller, R. G.; Bau, R. *Struct. Bonding* **1981**, *44*, 1−82. [e] The H−Ru stretching frequency in the radical cation **1**$^{\bullet+}$ should be approximately the same as that[33]a in neutral **1**. There is little change in the H−Fe stretching frequency between Cp*Fe(dppe)H (1869 cm^{-1}; Roger, C.; Hamon, P.; Toupet, L.; Rabaâ, H.; Saillard, J.-Y.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1991**, *10*, 1045) and its radical cation (1860/1869 cm^{-1}; Hamon, P.; Toupet, L.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1992**, *11*, 1429). [f] The bending mode has not been assigned for $H-WCp(CO)_3$, but a maximum value of 800 cm^{-1} can be estimated based on the frequency of this mode for several other hydrides: $HMn(CO)_5$, 665 cm^{-1}: Edgell, W. F.; Asato, G.; Wilson, W.; Angell, C. *J. Am. Chem. Soc.* **1959**, *81*, 2022; $HCo(CO)_4$, 703 cm^{-1}: Edgell, W. F.; Magee, C.; Gallup, G. *J. Am. Chem. Soc.* **1956**, *78*, 4185; $HCo(PF_3)_4$, 625/670 IR, 640/685 Raman: Bénazeth, S.; Loutellier, A.; Bigorgne, M. *J. Organomet. Chem.* **1970**, *24*, 479; $HRh(CO)(PPh_3)_3$, 784 cm^{-1}, $IrH(CO)(PPh_3)_3$, 822 cm^{-1}: Bath, S. S.; Vaska, L. *J. Am. Chem. Soc.* **1963**, *85*, 3500; $[Co(H)(CN)_5]^{3-}$, 774 cm^{-1}: Banks, R. G. S.; Pratt, J. M. *J. Chem. Soc. A*, **1968**, 854; $[Ir(H)(CN)_5]^{3-}$, 810 cm^{-1}: Krogmann, K.; Binder, W. *Angew. Chem., Int. Ed. Eng.* **1967**, *6*, 881; $Ir(H)(Cl)_2(PPh_3)_3$, 840/804: Vaska, L.; DiLazio, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 4989; *trans*-$[Fe(H)_2(o\text{-}C_6H_4(PEt_2)_2)_2]$, 716 cm^{-1}: Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 5507. Including bending modes in Bell's model lowers the calculated isotope effect. [g] Bueno, C.; Churchill, M. R. *Inorg. Chem.* **1981**, *20*, 2197. [h] (a) Davidson, G.; Duce, D. A. *J. Organomet. Chem.* **1976**, *120*, 229. (b) Davidson, A.; McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1963**, 1133.

case), the hydrogen is stationary in the symmetric stretch, and the maximum isotope effect is observed.

We have estimated bond lengths for bonds of order n from Pauling's[18] bond length−bond order relationship, where the length of a single bond is $r_{n=1}$ (eq 17). Badger's rule[19] (eq 18), where a_{ij} and d_{ij} are empirical parameters, can then be used

$$r_n = r_{n=1} - 0.6 \times \log_{10}(n) \qquad (17)$$

$$\sqrt[3]{F} = \frac{a_{ij} - d_{ij}}{r_n - d_{ij}} \qquad (18)$$

to evaluate the stretching force constants F_A and F_B for the partial bonds to hydrogen. Literature parameters for the H−N bond (there should be little difference between aniline and other nitrogen bases) and the H−Ru and H−W bonds are given in Table 4.

The location of the "symmetric" transition state for the proton transfer from either hydride complex to a nitrogen base can be estimated by making the reasonable assumption that the bond order to hydrogen stays 1 during the transfer (i.e., $n_N = 1 - n_M$). Substitution of eq 17 into eq 18, use of the data in Table 4, and the requirement that $F_{Ru} = F_N$ then locate the "symmetric" transition state at $n_{Ru} = 0.65$ for transfer from **1**$^{\bullet+}$ to nitrogen. Similarly, the requirement that $F_W = F_N$ locates the "symmetric" transition state at $n_W = 0.8$ for W → N transfer. (The maximum semiclassical isotope effect (eq 16), for this three-center model, depends only on the difference in zero point energies of the M−H and M−D stretches; it is 4.0 for Ru → N and 3.7 for W → N.) However, because proton transfer from $HWCp(CO)_3$ to aniline is endoergic, by 8 kcal/mol, its transition state should resemble product (i.e., n_W should be <0.5). For carbon acids, the isotope effect typically falls to two-thirds of its maximum value for such endoergic transfers.[20]

Within Bell's model (eq 15), an isotope effect larger than that expected from the semiclassical model is explained by tunneling. The tunneling contribution to the isotope effect varies with the free energy of the reaction[21] and is maximal for ergoneutral reactions. The importance of the tunneling correction can be judged by the temperature dependence of the kinetic isotope effect. A ratio of Arrhenius preexponential factors, A_D/A_H, greater than 1.4 and a difference in activation energies, $E_a^D - E_a^H$, significantly larger than that calculated from zero point energies strongly suggest tunneling.[22] These criteria, and the A_D/A_H ratio of 0.8 in Table 3, do not suggest tunneling for proton transfer from $HW(CO)_3Cp$ to aniline; the uncertainties in the A values in Table 2 are too larger to permit any conclusion about the Ru → N cases.

Kwart has suggested[23] that a large isotope effect like the one measured in this study (4.2), accompanied by an A_H/A_D ratio of close to 1, indicates a linear transition state (although MNDO calculations[24] do not support this classification). Model calculations on proton transfer from carbon acids to oxygen and nitrogen bases have shown that deviation from a linear transition state decreases the isotope effect.[25,26] The large isotope effect measured for the proton transfer from $HW(CO)_3Cp$ is therefore best explained by a linear transition state.

Quantum-Statistical Model. The origin of kinetic isotope effects has also been explained by the quantum-statistical mechanical model,[27] also called multiphonon transfer theory.[28] Within this model, the activation energy for the proton transfer is provided by low frequency solvent and intramolecular modes (the classical subsystem). The energy levels of the proton stretching vibration (the quantum subsystem) are influenced by these solvent fluctuations. When the energies of the proton donor and acceptor orbitals are equal, proton transfer occurs

---

(18) Pauling, L. *The Nature of the Chemical Bond*; Cornell University: Ithaca, NY, 1960.

(19) (a) Badger, R. M. *J. Chem. Phys.* **1934**, *2*, 128. (b) Badger, R. M. *J. Chem. Phys.* **1935**, *3*, 710. (c) Herschbach, D. R.; Laurie, V. W. *J. Chem. Phys.* **1961**, *35*, 458.

(20) (a) Bell, R. P.; Goodall, D. M. *Proc. R. Soc. A* **1966**, *294*, 273. (b) Bell, R. P.; Cox, B. G. *J. Chem. Soc., Perkin Trans.* **1971**, 738. (c) Barnes, D. J.; Bell, R. P. *Proc. R. Soc. London, Ser. A* **1970**, *318*, 421. (e) Sugimoto, N.; Sakaki, M. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 1441.

(21) (a) Sugimoto, N.; Sasaki, M. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 1441. (b) Sugimoto, N.; Sasaki, M. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 2959. (c) Sugimoto, N.; Sasaki, M.; Jiro, O. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 366. (d) Blanch, J. H.; Rogne, O.; Rossemyr, L. I. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1905.

(22) Bell, R. P. *The Proton in Chemistry*; Cornell: Ithaca, NY, 1973; pp 275−285.

(23) Kwart, H. *Acc. Chem. Res.* **1982**, *15*, 401.

(24) Anhede, B.; Bergman, N. *J. Am. Chem. Soc.* **1984**, *106*, 7636.

(25) (a) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265. (b) More O'Ferrall, R. A.; Kouba, J. *J. Chem. Soc. (B)* **1967**, 985. (c) Johnston, H. S. *Adv. Chem. Phys.* **1960**, *3*, 131.

(26) More O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, 785.

(27) (a) German, E. D.; Kuznetsov, A. M. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 397. (b) German, E. D.; Kuznetsov, A. M.; Dogonadze, R. R. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 1128. (c) German, E. D.; Kuznetsov, A. M. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 2203. (d) Levich, V. G.; Dogonadze, R. R.; German, E. D.; Kuznetsov, A. M.; Kharkats, Y. I. *Electrochim. Acta* **1970**, *15*, 353.

(28) Brüniche-Olsen, N.; Ulstrup, J. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 205.

by tunneling. This treatment has the same basis as the golden rule treatment[29] of hydrogen transfer.

This model can predict the dependence of the isotope effect, k_H/k_D, on vibrational frequencies and the free energy of transfer. For carbon acids, calculations predict that, when the initial and final force constants to the proton are different, the maximum isotope effect will occur away from ergoneutrality.[28] Although no calculations have been performed for cases where the two stretching force constants are as different as they are for an M → N proton transfer, this model plainly predicts that the maximum isotope effect in such an asymmetric case will occur at considerable exoergicity.[30]

The third model proposed to explain the different rate of reaction of isotopic molecules is due to Marcus.[31] According to this model, the intrinsic barrier, $\lambda/4$, to the reaction originates in low frequency intermolecular reorganization and solvent modes. If ΔG° in eq 19 is assumed to be isotope independent, the isotope effect, k_H/k_D, is given by eq 20, where w_r and w_p are the work terms needed to form the activated complex from reactants or products, respectively. This equation predicts a maximum isotope effect for reactions that are close to ergoneutral.[32]

$$\Delta G^{\ddagger} = [1 + (\Delta G^\circ/4\Delta G_0^{\ddagger})]^2 \Delta G_0^{\ddagger} \qquad (19)$$

$$\frac{k_H}{k_D} = \exp\left\{\frac{\lambda_D - \lambda_H}{4k_BT}\left[1 - \frac{(\Delta G_0 + w_p - w_r)^2}{\lambda_H\lambda_D}\right]\right\} \qquad (20)$$

Summary and Overview of Kinetic Isotope Effects. The W → N kinetic isotope effect from Table 3 (4.2 at 25 °C) is comparable to those reported (3.6 for M = Cr, 3.7 for M = Mo and W)[14] for M → M proton transfer in $HM(CO)_3Cp$ and $M(CO)_3Cp^-$. All of these numbers are close to the maximum classical isotope effects (3.6 for Cr, 3.7 for Mo and W) calculated from the zero-point energy differences between $HM(CO)_3Cp$ and $DM(CO)_3Cp$. However, the Ru → N kinetic isotope effects are smaller (from 2.67 to 2.33 at 20 °C in Table 2) and much less than the maximum classical isotope effect (4.0) calculated for Ru → N. The Ru → N isotope effects also vary somewhat with the nature of the base.

It is worth remembering that the Ru → N proton transfers (from **1**$^{\bullet+}$ to the nitrogen bases) are approximately thermoneutral,[9] whereas the W → N proton transfer (from $CpW(CO)_3H$ to aniline) is uphill by 5.5 pK_a units. However, as shown by the above survey of relevant theory, there is no consensus as to the effect this change in thermodynamic driving force should have on proton transfer isotope effects. None of the above three models has been explicitly used to predict the behavior of k_{H^+}/k_{D^+} with changing driving force for a M−H(D)/N system, but some predictions can be made by analogy with carbon acids. According to Marcus's model, ergoneutral transfers exhibit maximum k_{H^+}/k_{D^+} values; the quantum-statistical model and Bell's model both predict a maximum for an exoergic transfer. In Bell's model, k_{H^+}/k_{D^+} is the product of two effects (eq 15): one, the tunneling correction Q_t, peaks at ergoneutrality, while the other, the classical k_H/k_D, peaks when the *force constants* are equal in the transition state—a situation achievable in an M → N transfer only if it is quite exoergic and the transition state quite early. Nevertheless, Bell's model is more capable of explaining a maximum k_{H^+}/k_{D^+} value close to ergoneutrality than is the quantum-statistical model.

Collectively, these theories can rationalize maximal isotope effects for proton transfer reactions that range from ergoneutral to exoergic. However, our Ru → N isotope effects are far from maximal despite being approximately thermoneutral,[9] and our W → N isotope effects *are* maximal despite being *endoergic*!

It is arguable that much of the decrease in isotope effects between the $CpW(CO)_3H$/aniline case and the **1**$^{\bullet+}$ series arises from steric congestion in the latter. Such congestion will require that proton transfer occur over a longer distance in the transition state. However, if the transition state is symmetric, the semiclassical effect (eq 16) will be determined by the zero-point energies and thus remain unaffected by this longer distance. More sophisticated calculations,[33] and some experiments with hindered C → N proton transfers,[34] have suggested that steric hindrance ought to *increase* the kinetic isotope effect upon symmetric proton transfers. However, a proton transfer reaction between a metal hydride and a base is unique in that an *asymmetric* transition state will arise from the large difference in the stretching force constant of the H−M and H−N bonds *as well as* from a nonzero ΔG°. Steric hindrance may *increase* the asymmetry and thus decrease the isotope effect in the Ru → N case.

Experimental Section

General Procedures. All manipulations involving organometallic compounds were carried out with use of vacuum line, Schlenk, syringe, or drybox techniques. Acetonitrile was distilled from P_4O_{10}, and acetonitrile-d_3 was distilled from CaH_2 or P_4O_{10}. THF was distilled from sodium benzophenone ketyl.

The electrochemical instrumentation, cells, data handling procedures, and electrodes have been previously described.[7,35] Acetonitrile/THF (4:1) containing 0.1 M $Bu_4N^+PF_6^-$ was used as 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 electrolytes were carried out under a blanket of solvent-saturated argon.

^{1}H NMR spectra were recorded on a Varian Gemini 200 or an IBM-200-SY. Chemical shifts are reported in ppm relative to tetramethylsilane, with the residual solvent proton resonance as internal standards (δ 1.93 for acetonitrile-d_3). The compounds $CpRu(PPh_3)_2H$ (**1**),[36a]

---

(29) (a) Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 2418. (b) Seibrand, W.; Wildman, T. A.; Zgierski, M. Z. *J. Am. Chem. Soc.* **1984**, *106*, 4083. (c) Siebrand, W.; Wildman, T. A.; Zgierski, M. Z. *J. Am. Chem. Soc.* **1984**, *106*, 4089.

(30) The greatest differences in final and initial force constants in Ulstrup's calculations[28] were between 2600 and 3000 cm^{-1}, and between 3400 and 3000 cm^{-1}. Extrapolation of Ulstrup's results, assuming the free energy shift in the maximum k_H/k_D to be linear with the difference in force constants, to our much more asymmetric case predicts that the maximum value of k_{H^+}/k_{D^+} will occur for a transfer exoergic by ca. 16 kcal/mol. Proton transfer from $HWCp(CO)_3$ to aniline, endoergic by 8 kcal/mol, is therefore approximately 24 kcal/mol more endoergic than the transfer for which the quantum-statistical mechanical model appears to predict a maximum isotope effect.

(31) (a) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891. (b) Brunschwig, B. S.; Logan, J.; Newton, M. D.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 5798. (c) Kresge, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 7798.

(32) $\lambda_D - \lambda_H$ for a W → W proton transfer can easily be estimated as 3.03 kcal/mol from the known W → W isotope effect (3.6)[14] by using eq 20 and neglecting the work terms. The k_H/k_D for ammonia/ammonium H^+/D^+ exchange has recently been measured as 1.8 (Perrin, C. L.; Dwyer, T. J.; Baine, P. *J. Am. Chem. Soc.* **1994**, *116*, 4044); however, $\lambda_D - \lambda_H$ for an N → N transfer cannot readily be estimated from this value because the reaction is nearly encounter controlled.

(33) Wolfe, S.; Hoz, S.; Kim, C. K.; Yang, K. *J. Am. Chem. Soc.* **1990**, *112*, 4186.

(34) Pruszynski, P. *Can. J. Chem.* **1987**, *65*, 2160.

(35) (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. (c) Tilset, M. In *Energetics of Organometallics Species*; Simões, J. A. M., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1992; p 109.

(36) (a) Wilczewski, T.; Bochenska, M.; Biernat, J. F. *J. Organomet. Chem.* **1981**, *215*, 87. (b) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. (A)* **1971**, 2376. (c) Lyatifov, I. R.; Solodovnikov, S. P.; Babin, V. N.; Materikova, R. B. *Z. Naturforsch., B* **1979**, *34B*, 863.

Table 5. Values of $k_{obs(H^+)}$ for the Exchange between HWCp(CO)$_3$ and WCp(CO)$_3^-$ in the Presence of Aniline at Various Temperatures and Aniline Concentrations[a]

T (K)	[aniline] (M)	$\Delta\nu_{1/2}$ (s^{-1})	k_{obs} (s^{-1})	k_{H^+} (s^{-1} M^{-1})	intercept (s^{-1})	R
236.6	0	1.46	3.60	17.4	3.6	0.928
236.6	4.57×10^{-2}	1.62	4.17			
236.6	9.04×10^{-2}	2.12	5.75			
236.6	13.4×10^{-2}	2.08	5.62			
253.5	0	1.43	3.57	54.63	3.4	0.996
253.5	4.57×10^{-2}	2.14_5	5.83			
253.5	9.04×10^{-2}	2.82	7.95			
253.5	13.4×10^{-2}	3.78	11.0			
264.8	0	1.81	4.77	81.9	4.60	0.999
264.8	4.57×10^{-2}	2.90	8.20			
264.8	9.04×10^{-2}	4.05	11.8			
264.8	13.4×10^{-2}	5.33	15.8			
267.1	0	2.19	5.97	86.39	5.87	0.999
267.1	4.57×10^{-2}	3.36	9.64			
267.1	9.04×10^{-2}	4.74	13.94			
267.1	13.4×10^{-2}	5.83	17.32			
279.1	0	3.38	9.70	129.7	9.96	0.999
279.1	4.57×10^{-2}	5.46	16.18			
279.1	9.04×10^{-2}	7.32	21.93			
279.1	13.4×10^{-2}	8.99	27.08			
292.3	0	4.90	14.44	180.6	14.4	0.995
292.3	4.57×10^{-2}	7.32	21.93			
292.3	9.04×10^{-2}	10.68	32.27			
292.3	13.4×10^{-2}	12.5	37.82			
302.6	0	5.89	17.51	280.7	18.5	0.998
302.6	4.57×10^{-2}	10.77	32.55			
302.6	9.04×10^{-2}	14.63	44.24			
302.6	13.4×10^{-2}	18.46	55.35			

[a] At each temperature the last columns show the slope of the best line fit through k_{obs} vs [aniline], k_{H^+}; the intercept with the k_{obs} axis; and the correlation coefficient R, of this line.

Table 6. Values of $k_{obs(D^+)}$ for the Exchange between DWCp(CO)$_3$ and WCp(CO)$_3^-$ in the Presence of Aniline-*N*-d_2 at Various Temperatures and Aniline-*N*-d_2 Concentrations[a]

T (K)	[aniline-*N*-d_2] (M)	$\Delta\nu_{1/2}$ (s^{-1})	k_{obs} (s^{-1})	k_D (s^{-1} M^{-1})	intercept (s^{-1})	R
240.3	0	1.15	2.67	4.74		
240.3	0.504	1.91	5.06			
253.0	0	1.17	2.73	8.08	2.71	1.000
253.0	0.336	2.01	5.38			
253.0	0.504	2.47	6.82			
264.8	0	1.15	2.67	15.2	2.31	0.993
264.8	0.168	1.71	4.43			
264.8	0.336	2.58	7.17			
264.8	0.504	3.56	10.3			
273.2	0	1.15	2.67	21.4	2.45	0.994
273.2	0.168	2.03	5.44			
273.2	0.336	3.55	10.22			
273.2	0.504	4.46	13.07			
283.4	0	1.15	2.67	33.45	2.48	0.999
283.4	0.168	2.75	7.70			
283.4	0.336	4.74	13.95			
283.4	0.504	6.46	19.32			
294.6	0	1.36	3.33	51.5	3.23	1.000
294.6	0.168	4.02	11.7			
294.6	0.336	6.88	20.63			
294.6	0.504	9.65	29.2			
303.7	0	1.62	4.15	77.9	4.03	1.000
303.7	0.168	5.58	16.6			
303.7	0.336	10.2	30.9			
303.7	0.504	14.0	43.0			

[a] At each temperature the last columns show the slope of the best line fit through k_{obs} vs [aniline-*N*-d_2], k_{D^+}; the intercept with the k_{obs} axis; and the correlation coefficient, R, of this line.

CpRu(PPh$_3$)$_2$D (**1**-*d*),[36a] CpRu(PPh$_3$)$_2$(NCMe)$^+$,[36b] and Cp$_2$Fe$^+$PF$_6^-$ [36c] were prepared according to published procedures. HCpW(CO)$_3$ was prepared by protonating the corresponding anion[37] with trifluoroacetic acid and purified by sublimation. DWCp(CO)$_3$ was generously donated by Dr. Christophe Lawrie. K[η^5-C$_5$H$_5$)W(CO)$_3$] was prepared by deprotonation of the corresponding hydride with KH in THF.[38]

Aniline-*N*-d_2 was prepared by a published method[14] and was 96% D. Other chemicals were used as received from commercial suppliers.

Oxidation of CpRu(PPh$_3$)$_2$H with Cp$_2$Fe$^+$PF$_6^-$ in Acetonitrile-*d*$_3$ in the Presence of Bases. In a typical reaction, CpRu(PPh$_3$)$_2$H (10 mg, 0.014 mmol), quinuclidine (3.2 mg, 0.029 mmol), and Cp$_2$Fe$^+$PF$_6^-$ (9.2 mg, 0.028 mmol) were added to an NMR tube equipped with a ground-glass joint. Acetonitrile (0.5 mL) was added by vacuum transfer, and the tube was sealed under vacuum. An ^{1}H NMR (200 MHz) spectrum was immediately recorded at ambient temperature and revealed the presence of CpRu(PPh$_3$)$_2$(NCCD$_3$)$^+$ (δ 4.44), verified by comparison with an authentic sample, as the only CpRu-containing product.

The oxidation of **1** in the presence of pyrrolidine and piperidine was performed analogously and also showed the exclusive production of CpRu(PPh$_3$)$_2$(NCMe)$^+$.

Test for Retention of D Labeling during Electrochemical Measurements. After a variable-temperature kinetic measurement series, an electrolyte solution (10 mL) containing **1**-*d* and quinuclidine was concentrated to ca. 1 mL, and the supporting electrolyte was precipitated by the addition of ether. The mixture was filtered (medium-frit glass filter), and the filtrate was concentrated by vacuum transfer. An ^{1}H NMR analysis (C$_6$D$_6$) showed no hydride signal at δ −11.09, indicating that no D label had been lost within the detection limits (ca. 5%) of the method.

Constant-Current Coulometry. The constant-current coulometry measurements were performed in a H-shaped cell, the compartments of which were separated by a medium-frit glass junction. A platinum-gauze working electrode was used. Solutions of the hydride (1−2 mM) and ca. 10 equiv of the base in 20 mL of 4:1 acetonitrile/THF with 0.1 M Bu$_4$N$^+$PF$_6^-$ as the supporting electrolyte were electrolyzed at a constant current of 10 mA while the disappearance of the substrate was monitored by DCV. Three separate measurements were carried out for each base and resulted in $n = 2.0 \pm 0.1$ faraday/mol.

NMR Measurements of Proton Transfer Rate Constants and Kinetic Isotope Effect. (A) Sample Preparation. In a typical experiment, a solution of 25 mg of H(D)W(CO)$_3$Cp and 20 mg of K[W(CO)$_3$Cp] in 0.5 mL of CD$_3$CN was prepared in an inert atmosphere glovebox. An aliquot of this solution (100 μL) was syringed with a microsyringe into each of four NMR tubes. A volume of 0, 50, 100, or 150 μL of a solution of known concentration of aniline or aniline-*N*-d_2 was added to the tubes along with enough solvent to make the total solution volume in each tube 400 μL. The solution was degassed and flame sealed on a high vacuum line. The exact [HM]/[M] ratio was checked by NMR integration of the Cp signals of HM and M$^-$, using a 100 s delay time and a pulse angle of 30°. The temperature of the probe before and after each run was measured with a methanol thermometer and the use of Van Geet's equation corrected to 200 MHz.[39]

(B) Rate Constants for H$^+$ Exchange. All tubes contained a [HM]/[M$^-$] ratio of 1.13_5, corresponding to a HM population, $p_{[HM]}$, of 0.532, and a M$^-$ population, $p_{[M^-]}$, of 0.468. Since the difference in chemical shift between the Cp signals of HWCp(CO)$_3$ and of WCp(CO)$_3^-$ was only 103.53 Hz (on a 200 MHz instrument), the peaks overlapped even at fairly slow exchange rates. Complete lineshapes were therefore calculated[15] for several k_{obs} values, and their line widths at half-height, Δ(Cp), were used to construct a calibration curve for k_{obs} as a function of the observed Δ(Cp). The width at half-height, $\Delta\nu_{1/2}$, was simulated,[15] for $p_{[HM]} = 0.532$, $p_{[M^-]} = 0.468$, $\Delta\nu = 103.53$ Hz, and T_2 (for both sites) = 1.1 s, for 13 values of k_{obs} between 3.0 and 60 s^{-1}. A fourth-order polynomial was found to interpolate all the points. The value of

---

(37) King, R. B. *Organometallics Syntheses*; Academic: New York, 1965; Vol. 2, p 156.

(38) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255.

(39) Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679.

k_{obs} was, therefore, calculated from the measured $\Delta\nu_{1/2}$ using eq 21. Results are given in Table 5 and Figure 4.

$$k_{obs} = -0.9888 + 3.21152(\Delta\nu_{1/2}) - 0.018226(\Delta\nu_{1/2})^2 + 0.0013035(\Delta\nu_{1/2})^3 - (4.3035511 \times 10^{-5})(\Delta\nu_{1/2})^4 \quad (21)$$

(C) Rate Constants for D$^+$ Exchange. All the glassware used in the D$^+$ experiments was rinsed with D_2O prior to use and dried under vacuum with a heat gun. Syringes were dried in an 80 °C oven. The width at half-height, $\Delta\nu_{1/2}$, was simulated with $p_{[DM]} = 0.598$, $p_{[M^-]} = 0.402$ and $T_2 = 1.1$ s for 10 values of k_{obs} between 2 and 50 s^{-1}. A third-order polynomial was found to interpolate all the calculated points. The value of k_{obs} was, therefore, calculated from the measured $\Delta\nu_{1/2}$ using eq 22. Results are given in Table 6 and Figure 5.

$$k_{obs} = -0.95771 + 3.1542790(\Delta\nu_{1/2}) - 0.0009801(\Delta\nu_{1/2})^2 - (2.1858 \times 10^{-4})(\Delta\nu_{1/2})^3 \quad (22)$$

Acknowledgment. The work at Oslo was generously supported by Statoil under the VISTA program, administered by the Norwegian Academy of Science and Letters (stipend to K.-T.S.), and by the Norwegian Council for Science and the Humanities (NAVF); the work in Colorado was generously CHE-9120454. The authors are grateful to Profs. Branka Ladanyi and D. F. Kelley for helpful discussions and to Drs. David L. Ramage and Francis C. Rix for helping to prepare the manuscript.

IC940998X