Pulse Radiolysis Studies of Water-Soluble Tungsten Hydride Complexes: One-Electron Reduction of Metal Hydrides and Hydrogen Atom Transfer Reactions

Diane E. Cabelli,* Faisal Shafiq, Carol Creutz,* and R. Morris Bullock*

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973-5000

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The reactivity of the previously (*Organometallics* **2000**, *19*, 824−833) prepared hydride complexes $(C_5H_4CO_2H)L(CO)_2WH$ (L = CO, PMe_3) and the corresponding metal−metal dimers $[(C_5H_4CO_2H)L(CO)_2W]_2$ in pulse radiolysis studies in aqueous solution is reported. The disappearance of e_{aq}^- was monitored to determine the rate constants for one-electron reduction. The smallest reduction rate constant was obtained for the dianion $(C_5H_4CO_2)(CO)_3W^{2-}$ (4.3×10^9 M^{-1} s^{-1}), and the largest value (1.2×10^{10} M^{-1} s^{-1}) was observed for its conjugate acid $(C_5H_4CO_2)(CO)_3WH^-$. For the PMe_3-substituted complexes, the dimer reduction rate constant was about twice as large as that for the hydride ($k = 8.4 \times 10^9$ M^{-1} s^{-1}). Rate constants for reaction with CO_2^-, 3.2×10^8 (pH 5) and 3.0×10^7 (pH 9.7) M^{-1} s^{-1}, were determined for $(C_5H_4CO_2)(CO)_3WH^-$ and $(C_5H_4CO_2)(PMe_3)(CO)_2WH^-$, respectively. Rate constants for the reactions of the hydride complexes with the carbon-centered radical from *tert*-butyl alcohol and the α-hydroxy radicals from ethanol and 2-propanol radicals were in the ranges (0.9−4.8) × 10^8 and (0.3−0.6) × 10^8 M^{-1} s^{-1} for $(C_5H_4CO_2)(CO)_3WH^-$ and $(C_5H_4CO_2)(PMe_3)(CO)_2WH^-$, respectively. The transient produced in all of these reactions was the metal radical, which was observed to dimerize with $k = 2.4 \times 10^9$ and 2.2×10^8 M^{-1} s^{-1} for $(C_5H_4CO_2)(CO)_3WH^-$ and $(C_5H_4CO_2)(PMe_3)(CO)_2WH^-$, respectively.

Introduction

The chemistry and reactivity of water-soluble organometallic complexes are of increasing interest because so little is known and because of the role these complexes may come to play in environmentally benign homogeneous catalysis.[1] Replacement of one H of a cyclopentadienyl ligand (η^5-C_5H_5 = Cp) with a CO_2H group increases the water solubility of organometallic compounds. Tyler and co-workers[2] were first to characterize the photochemistry of $[(C_5H_4CO_2H)(CO)_3W]_2$ in water. Zhu and Espenson studied flash photolysis of this complex in water and reported[3] kinetics of halogen atom transfer from halocarbons to the photochemically generated tungsten-centered radical $(C_5H_4CO_2H)(CO)_3W^{\bullet}$. While earlier work probed the radicals produced from the dimers, in this paper, we report reactions of the water-soluble tungsten hydride complex $(C_5H_4CO_2H)(CO)_3WH$.

Depending upon the reaction partner, metal hydride complexes exhibit diverse modes of reactivity of the M−H bond. Some metal hydrides, such as $CpW(CO)_3H$, exhibit cleavage of the M−H bond as a proton,[4] as a hydrogen atom,[5] or as a hydride,[6] in reactions with different substrates. Oxidation of neutral metal carbonyl hydrides has been studied in detail by Tilset and coworkers[7−9] and has been shown to result in dramatic increases in the acidity of the M−H bond. In contrast, reduction of metal hydrides has received little attention. To extend our understanding of reactivity patterns of transition-metal hydride complexes, we focus here on the generation and reactivity of reduced 19 e$^-$ metal hydride species.[10] We have used pulse radiolysis to generate and study these species in aqueous solution. Pulse radiolysis is a technique by which solute molecules can be oxidized or reduced by secondary products from high-energy electron reactions with the aqueous medium; reactions are typically monitored by UV/vis spectroscopy. The technique is well-established in aqueous media, where rates of competing side reactions are known.[11,12] However, studies of organometallic compounds have been limited in number and confined to

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nonaqueous media.[13−16] Here we report on the reactivity of the previously[17] prepared hydride complexes $(C_5H_4CO_2H)L(CO)_2WH$ (L = CO, PMe_3) and the corresponding metal−metal dimers $[(C_5H_4CO_2H)L(CO)_2W]_2$ (L = CO, PMe_3) obtained via formal $H^•$ abstraction and subsequent $W^•$ dimerization.

Experimental Section

Kinetics Studies. Pulse radiolysis experiments were carried out using the BNL 2 MeV Van de Graaff accelerator. Pulse lengths were 0.04−0.5 μs, with doses ranging from 80 to 1000 rad. Dosimetry was carried out using KSCN assuming $G[(SCN)_2^-] = 6.13$ and $\epsilon[(SCN)_2^-,472\text{ nm}] = 7950\text{ M}^{-1}\text{ cm}^{-1}$.[11] The optical path length was 6.1 cm. Data analyses were carried out by nonlinear least-squares fitting of kinetic traces to kinetic equations. Solutions were deoxygenated with N_2O (Liquid Carbonic 99.999%) or argon (Praxair, 99.997%) as appropriate.

γ irradiations were carried out using a ^{60}Co source with a dose rate of ∼15 krad/min. At the doses used here, the same radicals/molecules and yields are formed upon both γ and electron irradiation in water. Observed rate constants were the average of at least four runs, with a standard deviation of ca. ±5%. The tungsten hydride concentrations were always in large excess over the radical (e_{aq}^-, $^•CO_2^-$, $^•OH$, or alcohol radical $^•ROH$).

Materials. All experiments were carried out in Millipore water. Sodium formate (Sigma Chemical Co.), monobasic potassium phosphate (Ultrex, Baker Chemical Co.), ethanol (Quantum Chemical), and 2-propanol (Burdick and Jackson) were used as purchased. *tert*-Butyl alcohol (Aldrich Chemical Co.) was purified by recrystallization. Solution pH was adjusted by the addition of $HClO_4$ (double distilled from Vycor, GFS Chemical Co.) and NaOH (puratronic, 99.999%, Baker Chemical Co.). Samples of all tungsten species used were those described previously.[17]

In a typical sample for pulse radiolysis studies, 50 mL of aqueous 0.02 M potassium phosphate was bubbled with N_2 for 15 min using a gas dispersion tube. In reactions where $^•OH$ was to be scavenged, samples also contained 0.01−0.1 M $NaHCO_2$. In the glovebox 0.1−1 mM solutions of the metal complex were prepared by the addition of a weighed sample to pH ∼12 H_2O adjusted using NaOH. Aliquots of these stock solutions were transferred in air to a modified UV/vis cell adjoining a reservoir kept under constant Ar or N_2O purge. The samples were bubbled with either Ar or N_2O, and the pH was adjusted to the desired value. The solution was degassed for an additional 15−20 min prior to the pulse radiolysis experiments. In H atom abstraction studies using carbon-centered radicals, *tert*-butyl alcohol, ethanol, or 2-propanol was added and bubbled for an additional 5 min prior to pulsing.

Results

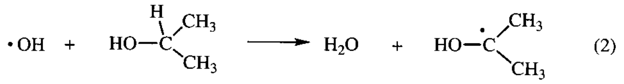
Upon radiolysis of water, the following radicals and molecules are generated:[11,12]

$$H_2O \rightsquigarrow {}^•OH\ (2.75),\ e_{aq}^-\ (2.65),\ {}^•H\ (0.65),\ H_2\ (0.45),\ H_2O_2\ (0.70)$$

where the values in parentheses are *G* values: that is, the number of atoms/molecules formed per 100 eV of energy dissipated in the solution. In most of these studies, the oxidizing $^•OH$ radical was converted to reducing radicals by reaction with appropriate added scavengers: Thus, $^•OH$ radical is converted to the $^•CO_2^-$ radical on addition of sodium formate (eq 1). Upon

$$\bullet OH + HCO_2^- \rightarrow H_2O + \bullet CO_2^- \qquad (1)$$

addition of ethanol or 2-propanol (H−ROH), the $^•OH$ radicals react to form carbon-centered alcohol radicals (eq 2), in which the radical is predominantly on the



(2)

carbon α to the hydroxyl group, 84.3% and 85.5% for ethanol and 2-propanol, respectively. A small amount of the radical at the carbon β to the hydroxyl group is formed (13.2% and 13.3%, respectively) and the remaining <3% is the O-centered radical.[18] The addition of *tert*-butyl alcohol leads to H atom abstraction on the carbon β to the hydroxyl group (95.7%) with a small amount of the O-centered radical (4.3%).[18] In an aqueous solution saturated with N_2O, the e_{aq}^- are converted to $^•OH$ radicals according to eq 3. This can be exploited to

$$e_{aq}^- + N_2O + H^+ \rightarrow {}^•OH + N_2 \qquad (3)$$

produce solutions containing only $^•CO_2^-$ radicals (reactions 1 and 3) or only $^•OH$ radicals (reaction 3 only).

The water solubility of the $C_5H_4CO_2H$ complexes arises primarily through the ionization of the carboxylate function (pK_a ca. 4.5,[2] Scheme 1). Thus, all of the species were studied as the deprotonated, carboxylate form.

Scheme 1

monomers: $HW(CO)_3(C_5H_4CO_2H) \rightleftharpoons HW(CO)_3(C_5H_4CO_2)^- + H^+$

dimers: $\{W(CO)_3(C_5H_4CO_2H)\}_2 \rightleftharpoons \{W(CO)_3(C_5H_4CO_2)\}_2^{2-} + 2H^+$

Reactions with e_{aq}^-. Argon-saturated solutions containing 0.02 M phosphate buffer, 0.01 M formate, and 0.1−0.4 mM metal complex were used, with 0.3−1.5 μM electron doses. The absorbance of e_{aq}^- (λ_{max} = 720 nm, $\epsilon = 19\,200\text{ M}^{-1}\text{ cm}^{-1}$)[19] was monitored (Figure 1). The lifetime of the electron in a “blank” solution (no added metal hydride complex) was determined to correct for the contribution of the protonation (by H^+, $H_2PO_4^-$, etc.) of the electron to the total rate of electron disappearance in the presence of the hydride complex. The second-order rate constants for the electron reactions are summarized in Table 1.

In addition to the carboxylate ionization common to all the complexes studied here, the metal hydrides can ionize to produce the metal anion. In the case of the

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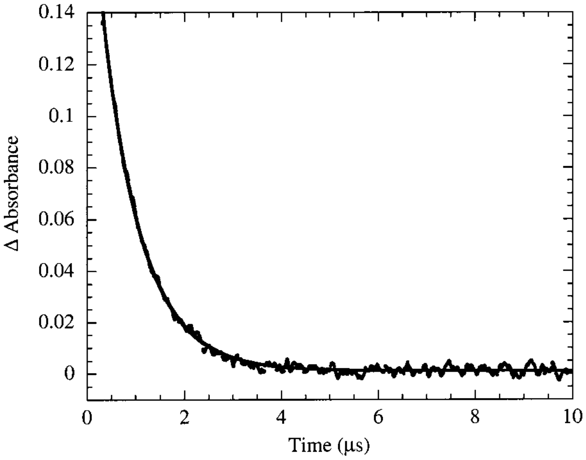


Figure 1. Decay of e_{aq}^- measured at 680 nm. Conditions: 0.25 mM $[(C_5H_4CO_2)(CO)_3WH^- + (C_5H_4CO_2)(CO)_3W^{2-}]$, 20 mM phosphate, pH 6.2, argon-saturated aqueous solution. The curve is the fit to a first-order process with a rate constant of $1.24 \times 10^6\ s^{-1}$.

Table 1. Rate Constants Determined in This Study[a]

reaction		k, $M^{-1}\ s^{-1}$ L = CO	k, $M^{-1}\ s^{-1}$ L = PMe_3
$M{-}H^- + e_{aq}^-$	k_7	1.2×10^{10}	8.4×10^9
$M^{2-} + e_{aq}^-$	k_8	4.3×10^9	
$M_2^{2-} + e_{aq}^-$	k_{10}	1.1×10^{10}	1.7×10^{10}
$^{\bullet}M^- + {}^{\bullet}M^- \rightarrow M{-}M^{2-}$	k_{11}	2.4×10^9	2.2×10^8
$M{-}H^- + {}^{\bullet}CO_2^-$		3.2×10^8	3.0×10^7
$M{-}H^- + {}^{\bullet}C(OH)(H)(CH_3)$	k_{12a}	3.8×10^8	5.9×10^7
$M{-}H^- + {}^{\bullet}C(OH)(CH_3)_2$	k_{12b}	4.8×10^8	5.9×10^7
$M{-}H^- + {}^{\bullet}CH_2C(OH)(CH_3)_2$	k_{12c}	9.3×10^7	3.0×10^7

[a] Aqueous solutions at 25 °C. $M = (C_5H_4CO_2)L(CO)_2W$.

PMe_3 complex this ionization is not observed in water ($pK_a > 12$), but in the case of $(C_5H_4CO_2)(CO)_3WH^-$ we earlier[17] found its pK_a to be ca. 6 (Scheme 2). We studied the electron reduction of $(C_5H_4CO_2)(CO)_3WH^-/(C_5H_4CO_2)(CO)_3W^{2-}$ mixtures as a function of pH to test the internal consistency of the data.

The reaction of the electron with three species (eq 6–8) connected through two ionization equilibria (eqs 4 and 5) must be considered. The expected pH dependence is given by eq 9. The pH dependence of the second-order rate constant observed for reaction with the hydrated electron is presented in Figure 2. The dependence is consistent with eq 9 if $k_6 = k_7 = 1.2 \times 10^{10}$ $M^{-1}\ s^{-1}$ and $k_8 = 4.3 \times 10^9\ M^{-1}\ s^{-1}$. The curve shown is calculated from eq 9 with the hydride and metal anion rate constants above and the pK_a of 5.8 (eq 4) determined by IR spectroscopy reported earlier.[17] The pK implicated by the kinetic data, 6.0, is in good agreement with the value 5.8 from the spectroscopic measurements. Thus, at low pH (~4.8–5.0), the complex exists as the metal hydrides $(C_5H_4CO_2)(CO)_3WH^-$ and $(C_5H_4CO_2H)(CO)_3WH$, which react faster with e_{aq}^- than the metal anion $(C_5H_4CO_2)(CO)_3W^{2-}$, the form present at higher pH (>7.0). In contrast, the rate of $(C_5H_4CO_2)(PMe_3)(CO)_2WH^-$ reduction was pH independent at pH 5–12, consistent with the very high hydride pK_a.

$$(C_5H_4CO_2H)(CO)_3WH \rightleftharpoons (C_5H_4CO_2)(CO)_3W{-}H^- + H^+ \qquad K_4 \quad (4)$$

$$(C_5H_4CO_2)(CO)_3W{-}H^- \rightleftharpoons (C_5H_4CO_2)(CO)_3W^{2-} + H^+ \qquad K_5 \quad (5)$$

$$e_{aq}^- + (C_5H_4CO_2H)(CO)_3WH \rightarrow \text{product} \qquad k_6 \quad (6)$$

$$e_{aq}^- + (C_5H_4CO_2)(CO)_3W{-}H^- \rightarrow \text{product} \qquad k_7 \quad (7)$$

$$e_{aq}^- + (C_5H_4CO_2)(CO)_3W^{2-} \rightarrow \text{product} \qquad k_8 \quad (8)$$

$$k_{obs} = \{k_6([H^+]/K_4) + k_7 + k_8(K_5/[H^+])\}/\{1 + K_5/[H^+] + [H^+]/K_4\} \quad (9)$$

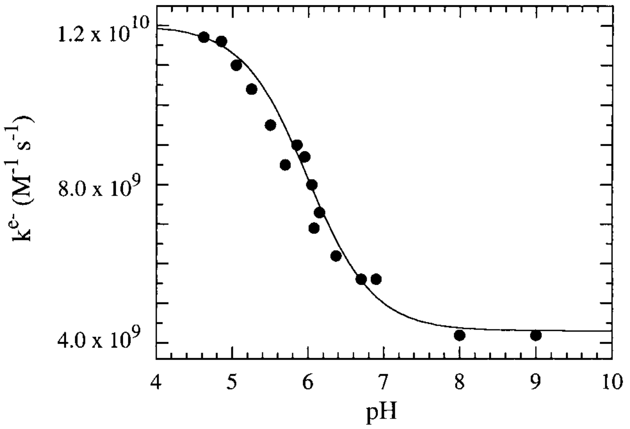
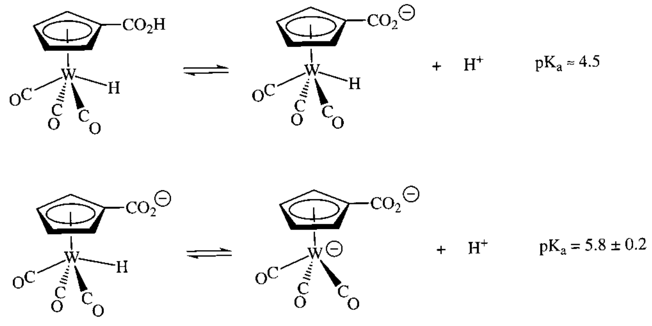


Figure 2. pH dependence of the rate constant for reduction of $(C_5H_4CO_2H)(CO)_3WH/(C_5H_4CO_2)(CO)_3WH^-/(C_5H_4CO_2)(CO)_3W^{2-}$ by the hydrated electron.

Scheme 2



In all cases, the product of reaction 6/7/8 was the metal radical within the time resolution of this experiment. Similarly, metal-dimer reduction by the electron (eq 10) also produced the metal radical. Continuous radiolysis experiments (^{60}Co source, UV–vis. monitoring) confirm the stoichiometric formation of the metal–metal-bonded dimer, viz.

$$e_{aq}^- + \{(C_5H_4CO_2)(L)(CO)_2W\}_2^{2-} \rightarrow \text{product} \qquad k_{10} \quad (10)$$

$$e_{aq}^- + W{-}H^- + H^+ \rightarrow {}^1/_2 W{-}W^{2-} + H_2$$

for both $(C_5H_4CO_2)(CO)_3WH^-$ and $(C_5H_4CO_2)(PMe_3)(CO)_2WH^-$.

Metal Radical Dimerization. The dimer formation followed second-order kinetics and varied linearly with dose as expected for eq 11 as an elementary reaction, with $k_{11} = 2.4 \times 10^9$ and $2.2 \times 10^8\ M^{-1}\ s^{-1}$ for

$(C_5H_4CO_2)(CO)_3WH^-$ and $(C_5H_4CO_2)(PMe_3)(CO)_2WH^-$, respectively. The value 3.0×10^9 M^{-1} s^{-1} was reported

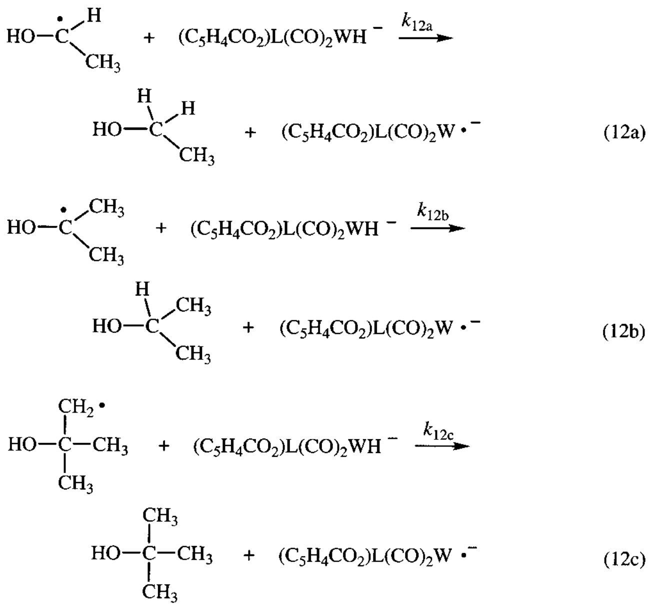
$$^{\bullet}W^- + {}^{\bullet}W^- \rightarrow W{-}W^{2-} \quad k_{11} \qquad (11)$$

for flash-photolysis work with the $(C_5H_4CO_2)(CO)_3W^{\bullet-}$ dimerization.[3] Higher values, for example 6.0×10^9 M^{-1} s^{-1} for acetonitrile,[20] are found for less viscous solvents[21] and the neutral, parent radicals.

Dimer yields for M = $(C_5H_4CO_2)(CO)_3W$ were about 80% in the pulse radiolysis experiments, possibly indicating a competing disproportionation process[10] as a minor pathway, independent of pH (pH 4.5, 9.7) and metal radical concentration. However, the fact that 100% yields are found in the longer time, continuous radiolysis experiments would require that disproportionation products comproportionate to dimer at longer times. In contrast, for M = $(C_5H_4CO_2)(PMe_3)(CO)_2W$ 100% yields of dimer were obtained in both pulse and continuous radiolysis experiments.

Reactions of $^{\bullet}CO_2^-$ Radicals with the Metal Hydride Complexes. N_2O-saturated solutions containing 0.01 M HCO_2^-, 0.02 M phosphate buffer, and hydride complex (0.2−1 mM $(C_5H_4CO_2)(CO)_3WH^-$, 0.25−2 mM $(C_5H_4CO_2)(PMe_3)(CO)_2WH^-$) were used. Rate constants 3.2×10^8 (pH 5) and 3.0×10^7 (pH 9.7) M^{-1} s^{-1} were determined for $(C_5H_4CO_2)(CO)_3WH^-$ and $(C_5H_4CO_2)(PMe_3)(CO)_2WH^-$, respectively. In both cases, the monomer metal radical was the observed primary product.

Reactions of Alcohol Radicals with the Metal Hydride Complexes. N_2O-saturated solutions containing 0.5 M alcohol, 0.02 M phosphate buffer, and hydride (0.2−1.0 mM $(C_5H_4CO_2)(CO)_3WH^-$; 0.25−2 mM $(C_5H_4CO_2)(PMe_3)(CO)_2WH^-$) were used. The alcohol radical formation (eq 2) was thus complete in less than 1 μs. The reaction (e.g., eq 12) was monitored in the visible region. Formation of the metal radical followed pseudo-first-order kinetics for 2−10 μM doses and was first order in metal hydride anion concentration. All of the carbon-centered radical reactions gave identical spectral changes at two to four wavelengths in the visible region for both hydride complexes. Rate constants for reaction of the hydride complexes with the radicals from *tert*-butyl alcohol, 2-propanol, and ethanol were in the ranges (0.9−4.8) × 10^8 M^{-1} s^{-1} for $(C_5H_4CO_2)(CO)_3WH^-$ and (0.3−0.6) × 10^8 M^{-1} s^{-1} for $(C_5H_4CO_2)(PMe_3)(CO)_2WH^-$. On a longer time scale (typically a factor of 10 longer), formation of the metal−metal-bonded dimer was observed. The transient metal radical spectrum observed is compared with that of the dimer product in Figure 3, and rate constants are summarized in Table 1.



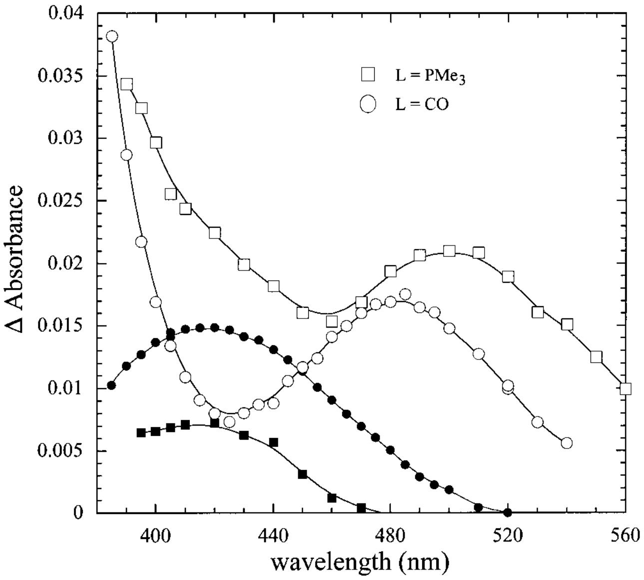


Figure 3. Comparison of $(C_5H_4CO_2)L(CO)_2W^{\bullet-}$ (lower traces) and $\{(C_5H_4CO_2)L(CO)_2W\}_2^{2-}$ (upper traces) spectra for L = CO (circles) and L = PMe_3 (squares). Transient absorbance changes have been corrected for the bleach of $(C_5H_4CO_2)(CO)_3WH^-$ absorption. Conditions: pH 4.5, 960 μM $(C_5H_4CO_2)(CO)_3WH^-$, 20 mM phosphate, 0.5 M ethanol, 4.2 μM radical, N_2O-saturated aqueous solution; pH 4.98, 1 mM $(C_5H_4CO_2)(PMe_3)(CO)_2WH^-$, 20 mM phosphate, 0.5 M *tert*-butyl alcohol, 4.2 μM radical, N_2O-saturated aqueous solution.

We studied the reaction of the hydride/anion for $(C_5H_4CO_2)(CO)_3WH^-$ with 2-propanol radical as a function of pH. The hydride form present at the lower pH values reacted rapidly with the neutral 2-propanol radical, but as the pH was increased the reaction slowed, suggesting that the metal anion $(C_5H_4CO_2)(CO)_3W^{2-}$ is unreactive. From eq 5 and eq 12b, eq 13 is obtained. In Figure 4, the observed values are compared

$$k_{obsd} = k_{12b}/(1 + K_5/[H^+]) \qquad (13)$$

with those calculated from eq 13 with $pK_a = 6.0$ for eq 5 and $k_{12b} = 4.8 \times 10^8$ M^{-1} s^{-1}. The rate constant for reaction of the metal anion $(C_5H_4CO_2)(CO)_3W^{2-}$ with $^{\bullet}C(OH)(CH_3)_2$ is thereby $<10^6$ M^{-1} s^{-1}.

Electrochemistry. In acetonitrile (0.1 M tetrabutylammonium perchlorate, Pt electrode), the cyclic voltam-

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Table 2. $(C_5H_4CO_2)L(CO)_2W^-$ (=M) **Thermodynamic Properties in or Extrapolated to Aqueous Solution**[a]

eq	value		L = CO	L = PMe$_3$
i	$E(M_2)$	$M_2 + e^- \rightarrow {}^\bullet M + M^-$	ca. −1.5 V vs aq NHE[b,c] (−1.51 vs aq NHE[c,d])	
ii	$E°(M-H)_{red}$	$M-H + e^- \rightarrow M-H^-$	<−1.6 V vs aq NHE[b,c]	
iii	$E°(M-H)_{ox}$	$M-H^+ + e^- \rightarrow M-H$	(+0.885 vs aq NHE[c,e])	+0.86 V vs NHE[b] (+0.322 vs aq NHE[c,e])
iv	$E°(M^-)_{ox}$	${}^\bullet M + e^- \rightarrow M^-$	+0.18 V vs NHE[b] (−0.252 vs aq NHE[c,f])	[j] (−0.992 vs aq NHE[c,f])
v	pK_a(M−H)	$M-H \rightleftharpoons M^- + H^+$	5.8[g] (8.0[h])	>12,[g] 16[i] (18[h])
vi	$\Delta G°(M-H)_{BDE}$	$MH \rightleftharpoons {\cdot}M + {\cdot}H$[k]	64 kcal/mol, 2.78 eV[b] (66.0 kcal/mol,[f] 2.87 eV)	(63.3,[f] 2.75 eV)

[a] Values in parentheses are for CpL(CO)$_2$W compounds measured in CH$_3$CN. [b] This study. [c] Obtained by subtracting 0.127 V from the value vs SCE in CH$_3$CN; this assumes couples are solvent-independent. [d] Kadish, K. M.; Lacombe, D. A.; Anderson, J. E. *Inorg. Chem.* **1986**, *25*, 2246−2250. [e] Ryan, O. B.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2618−2626. [f] Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711−6717, as modified in *J. Am. Chem. Soc.* **1990**, *112*, 2843. [g] Shafiq, F.; Szalda, D. J.; Creutz, C.; Bullock, R. M. *Organometallics* **2000**, *19*, 824−833. [h] Kristjánsdóttir, S. S.; Norton, J. R. *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; pp 309−359 (Chapter 9). This assumes ΔpK_a = 8 for water vs acetonitrile. [i] This assumes ΔpK_a = 10 for L = CO and PMe$_3$ complexes in water. [j] For L = PMe$_3$ in water, the value −0.4 V vs NHE is estimated from eq v (pK_a = 16) and eq vi ($\Delta G°(M-H)$ = 2.8 eV). [k] See: Wayner, D. D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287−294.

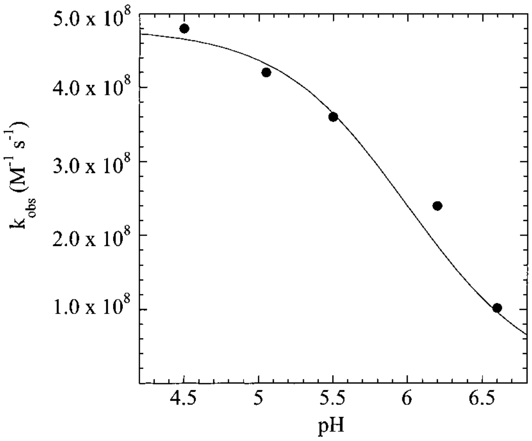

Figure 4. pH dependence of the rate constant for reaction of $(C_5H_4CO_2)(CO)_3WH^-$ with ${}^\bullet C(OH)(CH_3)_2$, produced from 2-propanol. Conditions: 0.96 mM $[(C_5H_4CO_2)(CO)_3WH^- + (C_5H_4CO_2)(CO)_3W^{2-}]$, 20 mM phosphate, 0.5 M 2-propanol, 1.5−10 μM radical, N$_2$O-saturated aqueous solution.

metry of $\{(C_5H_4CO_2H)(CO)_3W\}_2$ strongly resembles that observed for $\{(C_5H_5)(CO)_3W\}_2$ (see Kadish[22]), with the II ($W^-/W^\bullet$) and III (W_2/W^+) processes shifted ca. 0.1 V cathodic of the values found (in our hands) for the unsubstituted dimer. With $(C_5H_4CO_2H)(CO)_3WH$ in acetonitrile, no reduction was observed above −1.5 V vs SCE in initial sweeps; in subsequent sweeps the dimer was observed. A few experiments were carried out in phosphate-buffered aqueous 0.1 M NaClO$_4$: with $(C_5H_4CO_2)(CO)_3W^{2-}$ at pH 10.8, a single process, metal anion oxidation, was observed at −0.02 V vs Ag/AgCl (glassy-carbon electrode, 1 V/s); for $(C_5H_4CO_2)(PMe_3)(CO)_2WH^-$ at pH 6.3, oxidation of the hydride was found at +0.62 V vs SCE (Pt electrode, 1 V/s). Both values, +0.18 V vs NHE and +0.86 V vs NHE, are ca. 0.5 V more positive than would be predicted by extrapolation of values for the parent Cp complexes from acetonitrile.[9] All of the electrochemical processes of these systems exhibit EC mechanisms[23] as a minimum complication, and we have made no attempt to treat the data rigorously by using other techniques, by systematic sweep rate dependence studies, or by correcting for the dimerization rates. These lie beyond the scope of this study.

Discussion

Properties of the organometallic and radiation chemistry reagents used in this study are summarized in Tables 2 and 3, respectively. The parameters in Table 2 are defined in eqs i−vi (within Table 2), and those in Table 3 are defined in eqs 14 and 15. To accommodate

$$H-R(OH) = {}^\bullet R(OH) + {}^\bullet H \quad \Delta G°((OH)R-H)_{BDE} \quad (14)$$

$$RO + H^+ + e^- = {}^\bullet ROH \quad E°({}^\bullet ROH)_{ox} \quad (15a)$$

$$RO + e^- = {}^\bullet RO^- \quad E°({}^\bullet RO^-)_{ox} \quad (15b)$$

$${}^\bullet R(OH) + H^+ + e^- = RH(OH) \quad E°({}^\bullet R(OH/H^+))_{red} \quad (16a)$$

$${}^\bullet R(OH) + e^- = {:}R(OH)^- \quad E°({}^\bullet R(OH))_{red} \quad (16b)$$

$${}^\bullet R(OH) = {}^\bullet RO^- + H^+ \quad pK_a({}^\bullet R(OH)) \quad (17)$$

the various organic radicals (Table 3) used in this study, we use the abbreviations employed in an earlier study of thermodynamics of alcohols.[24] This differs from the conventional organic abbreviation in which R represents an alkyl group. In this paper, H−ROH is used to represent an alcohol (or formic acid, HC(O)OH); note, for example, that eq 16a refers to the reduction of the radical to the alcohol. Formation of the related carbanion $:R(OH)^-$ (eq 16b) has been studied,[25] and the potentials derived are ca. −1 V for ethanol and 2-propanol, reflecting the very low acidity (pK_a > 40) of the C−H bond in the conjugate acid. Details of the thermodynamic analyses are available as Supporting Information.

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Table 3. Thermodynamic Properties of the Carbon-Centered Radicals

	$^\bullet$C(OH)(H)(CH$_3$)	$^\bullet$C(OH)(CH$_3$)$_2$	$^\bullet$CH$_2$C(OH)(CH$_3$)$_2$	$^\bullet$C(O)OH
pK_a($^\bullet$R(OH))^a	11.51	12.03		1.4
$E°_{ox}$, V vs NHE^a				
RO, H$^+$/$^\bullet$ROH	−1.25	−1.39		
RO/$^\bullet$RO$^-$	−1.93	−2.10		−1.90
$E°_{red}$, V vs NHE				
$^\bullet$R(OH)/H$^{+\,c}$	+1.69	+1.65	+2.1	+1.47
$^\bullet$R(OH)^e	−1.01	−1.04		
$\Delta G°((OH)R-H)_{BDE}$, kcal/mol	91.6^d	90.6^d		86.5^d
$\Delta H°((OH)R-H)_{BDE}$, kcal/mol	96.7,^{a} 92.2^b	94.4,^{a} 89.3^b	99.1^b	95.6^a

[a] Schwarz, H. A.; Dodson, R. W. *J. Phys. Chem.* **1989**, *93*, 409−414. [b] Kanabus-Kaminska, J. M.; Gilbert, B. C.; Griller, D. *J. Am. Chem. Soc.* **1989**, *111*, 3311−3314. [c] Calculated from data given by Schwarz and Dodson (see footnote *a*); for *tert*-butyl alcohol, $\Delta G°_{f,aq}(R^\bullet) = 100$ kcal/mol was assumed. [d] From $\Delta G°_{BDE,aq} = \Delta G°_{f,aq}(R^\bullet) + \Delta G°_{f,aq}(H^\bullet) - \Delta G°_{f,aq}(HROH)$, with $\Delta G°_{f,aq}(^\bullet ROH)$ from Schwarz and Dodson (footnote *a*), $\Delta G°_{f,aq}(H^\bullet) = 52.8$ kcal/mol and $\Delta G°_{f,aq}(RH)$[29] −43.4 kcal/mol (ethanol), −89.0 kcal/mol (formic acid). For 2-propanol, $\Delta G°_{f,g} = -41.44$ kcal/mol[30] and $\Delta G°_{sol} = -3.0$ kcal/mol[24] were used. [e] Benderskii, V. A.; Benderskii, A. V. *Laser Electrochemistry of Intermediates*; CRC Press: Boca Raton, FL, 1995; pp 250−255.

Hydrated Electron Reactions. The reactions with e_{aq}^- ($E° = -2.87$ V vs NHE[26]) are rapid, with differences likely reflecting the roles of size and charge. Within our time resolution, the products of the reaction of the hydrated electron with the W−W dimers are the monomer radical (and presumably the metal anion which should undergo protonation at the metal, depending on its identity and the pH):

$$e_{aq}^- + \{(C_5H_4CO_2)(L)(CO)_2W\}_2^{2-} \rightarrow \{(C_5H_4CO_2)(L)(CO)_2W\}_2^{\bullet 3-}$$

$$\{(C_5H_4CO_2)(L)(CO)_2W\}_2^{\bullet 3-} \rightarrow (C_5H_4CO_2)(L)(CO)_2W^{\bullet -} + (C_5H_4CO_2)(L)(CO)_2W^{2-}$$

$$(C_5H_4CO_2)(L)(CO)_2W^{2-} + HA \rightarrow (C_5H_4CO_2)(L)(CO)_2WH^- + A^-$$

The related electrochemical (electron transfer) process is observed near −1.5 V vs aq. NHE (see Table 2).[22] In experiments in ethanol, analogous products have been observed for Mn$_2$(CO)$_{10}$.[13]

As noted earlier, the metal radical is also the first product observed for reduction of the metal hydride, suggesting that the primary product "$^\bullet$W−H^{2-}", formally a 19-electron reduced metal hydride, is very short-lived:

$$W-H^- + e_{aq}^- \rightarrow {}^\bullet W-H^{2-}$$

Its decay route is of some interest. Because of the low doses studied, bimolecular processes in the one-electron reduction product can be excluded ($k(^\bullet W-H^{2-} + {}^\bullet W-H^{2-})$ would have to exceed 10^{12} M^{-1} s^{-1}). Evidently H$_2$ is formed in a very rapid ($k > 10^6$ s^{-1}) sequence such as

$$^\bullet W-H^{2-} + H^+/H_2O \rightarrow {}^\bullet WH_2^- \rightarrow {}^\bullet W^- + H_2$$

although a process pseudo-first-order in the parent hydride is not excluded by the observations:

$$^\bullet W-H^{2-} + W-H^- \rightarrow {}^\bullet WH_2^- + W^{2-} \rightarrow {}^\bullet W^- + H_2$$

In support of a role for a dihydride/dihydrogen intermediate, the pK_a of structurally characterized[27] (Cp)(PMe$_3$)(CO)$_2$WH$_2^+$ in CH$_3$CN is 5.6[28] and (C$_5$H$_4$CO$_2$H)(PMe$_3$)(CO)$_2$WH is protonated to yield the dihydride by triflic acid in dichloromethane.[17]

Reactivity Patterns and Reaction Mechanism. As noted earlier, reaction of the metal hydride complexes with the organic radicals yields the metal radical, the product expected for H atom abstraction. However, since the metal radical is also observed in the reaction of the hydrated electron with the metal hydrides, careful consideration of reaction mechanism is needed. The rate constants for reaction of the hydrides with the alcohol radicals and formate radicals (Table 1) are very similar in magnitude, ranging only over about a factor of 5 for the tricarbonyl and a factor of 2 for the PMe$_3$ derivative, with the radical from *tert*-butyl alcohol being the slowest in both cases. The similarity and magnitude of the rate constants would seem to exclude electron-transfer processes, as may also be gleaned from the following considerations.

For reduction of the metal hydride by the organic radical, eq 15 (Table 3) and eq ii (Table 2) are pertinent, as are outer-sphere self-exchange rate constants, estimated as 10^{-5} M^{-1} s^{-1} for CO$_2$/$^\bullet$CO$_2^-$ and 10^5 M^{-1} s^{-1} for (CH$_3$)$_2$CO$^{0/-}$.[31] Electron transfer from the $^\bullet$R(OH) radicals to the metal hydride is thermodynamically unfavorable for the tricarbonyl ($E° < -1.6$ V) at pH 5. In addition, the variation of the rates with 2-propanol radical with pH in the range 4.6−6.6 (a drop of a factor of 7) indicates that only reaction of the hydride and the protonated form of the radical is kinetically significant. For $^\bullet$CO$_2^-$, the highly reducing deprotonated radical is the only form present in these experiments and both electron transfer and H atom abstraction seem viable. For the PMe$_3$ derivative, studied at pH 9.7, the more strongly reducing (< -1.9 V), deprotonated radicals $^\bullet$RO$^-$ could be kinetically significant for the ethanol radical (1.6% at pH 9.7) and the 2-propanol radical (0.5% at pH 9.7) if the rate constants for reduction by $^\bullet$C(O$^-$)-

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$(H)(CH_3)$ and $^{\bullet}C(O^-)(CH_3)(CH_3)$ are on the order of $(1-3) \times 10^9$ M^{-1} s^{-1}. In the case of *tert*-butyl alcohol radical (for which $E°$ values are not available), this pathway seems excluded by the observation that oxidation of the radical by the extremely potent oxidant $Ru(bpy)_3^{3+}$ proceeds at $\leq(1-2) \times 10^8$ M^{-1} s^{-1}.[32]

For completeness we consider the corresponding oxidation process, but this is excluded in the present systems because the metal "cation" product expected for this process is not observed. For oxidation of the hydride by the alcohol radical, eq 14 (Table 3) and eq iii (Table 2) bear on the thermodynamics. Although the $E°$ values suggest that the alcohol radicals are strong oxidants in acidic solution, their reactions as oxidants are expected to be slow because of proton mismatch: oxidation requires either prior protonation of the radical at carbon or formation of a highly unstable reduced form, the carbanion $:R(OH)^-$ for which the reduction potentials are quite negative[25] (followed by rapid protonation to give the alcohol). Indeed, only very strong reductants ($E° < -1.3$ V[26]) such as Cd_{aq}^{+} [33] have been reported to reduce the *tert*-butyl alcohol radical to $(CH_3)_2C{=}CH_2$.

Finally, nucleophilic addition[34,35] of alcohol radicals to the Cp ligand, as occurs for bound bipyridine and phenanthroline ligands,[36] is unlikely.

In the remaining discussion we treat the reactions as H atom abstractions.

Hydrogen Atom Transfer. Despite the centrality of organic radicals to many processes involving organometallic hydrides and radicals—e.g. olefin hydrogenation—few studies have elicited rate constants for reactions of these species.[37] Rate constants for hydrogen abstraction from metal hydrides have been estimated from competition studies involving cyclopropylstyrene radical ring opening:[38] 2.3×10^7 M^{-1} s^{-1} and $\sim 1.7 \times 10^8$ M^{-1} s^{-1} for $HCrCp(CO)_3$ and $HFeCp(CO)_2$, respectively, at 22 °C. Others reported for ca. 25 °C include 1.8×10^7 M^{-1} s^{-1} for $HCr(CO)_5^-$ to 2,2-dimethyl-3-butenyl radical[39] and 2×10^7 M^{-1} s^{-1} for $HV(CO)_3Cp^-$ to 2-allyloxyethyl radical.[40]

Recent work with $HMoCp^*(CO)_3$ ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$) as H-donor found the reactivity primary > secondary > tertiary in the ratio 26:7:1 at 25 °C in dodecane, with benzyl faster than tertiary alkyl radical.[41] For example, Franz and co-workers reported a second-order rate constant of 5.2×10^7 M^{-1} s^{-1} for hydrogen atom transfer from $HMoCp^*(CO)_3$ to the secondary radical hept-6-en-2-yl. In the present study, the order inferred for relative rate constants for hydrogen atom transfer from $(C_5H_4CO_2)(CO)_3WH$ is primary (0.2) < secondary (0.8) < tertiary (1). The rate constant for *tert*-butyl alcohol radical, our "primary" radical, is about half that found for *n*-butyl radical with $HMoCp^*(CO)_3$. For H atom transfer both thermodynamic and steric factors that vary with the radical are of concern. In terms of steric issues it is sensible to consider the OH group of the alcohols roughly equivalent to a methyl group. Then ethanol radical is sterically equivalent to 2-propyl, a secondary radical, 2-propanol radical is equivalent to *tert*-butyl radical, a tertiary radical, and *tert*-butyl alcohol radical is equivalent to neopentyl radical, a highly sterically hindered primary radical. Dimerization kinetics reflect the steric properties of the metal center. It is noteworthy that dimerization of the PMe_3-substituted radical $(C_5H_4CO_2)(PMe_3)(CO)_2W^{\bullet-}$ to form the metal−metal-bonded dimer is 10 times slower than $(C_5H_4CO_2)(CO)_3W^{\bullet-}$ dimerization.

Rate constants for hydrogen atom transfer from the phosphine-substituted metal hydride $(C_5H_4CO_2)(PMe_3)(CO)_2WH^-$ are 3−8 times lower than those for the tricarbonyl hydride $(C_5H_4CO_2)(CO)_3WH^-$. This is due in large part to the increased steric bulk of the PMe_3 ligand compared to a CO. A related hydrogen atom transfer also shows a diminished rate for a phosphine-substituted metal hydride, with $(C_5H_5)(PMe_3)(CO_2)MoH$ being 16 times slower than $(C_5H_5)(CO)_3MoH$ at hydrogen atom transfer to $(c\text{-}C_3H_5)(Ph)(CH_3)C^{\bullet}$ (100 °C, toluene solution).[38] Norton and co-workers found a large effect on hydrogen atom transfer to the extremely bulky substituted trityl radical $(p\text{-}^tBuC_6H_4)_3C^{\bullet}$, with $HMn(CO)_5$ being over 250 times more reactive than $HMn(CO)_4(PEtPh_2)$.[42] In this reaction the carbon-centered radical is already sterically demanding, and the steric congestion for the transition state is exacerbated by the phosphine ligand in the metal hydride.

Solvent Effects. While the rates and thermodynamics of many atom transfer reactions appear solvent insensitive,[43] H atom transfer reactions can be solvent sensitive through the need to disengage the H atom donor from a hydrogen bond (with solute or solvent) in a given solvent.[44] In the present systems, this factor would be important if the metal hydride complexes were to engage in solvent-dependent H bonding and would be reflected in slower rates in those solvents. Metal hydrides are now known to engage in hydrogen bonding in a variety of forms.[45] The M−H bond can function as a hydrogen bond acceptor toward conventional hydrogen bond donors such as N−H and O−H groups, forming M−H···H−N interactions.[46] The opposite sense of hydrogen bonding of metal hydrides is also known, with metal hydrides as the hydrogen bond donor. However, most examples of this type of bonding[47,48] occur with

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cationic metal hydrides and strong hydrogen bond acceptors such as phosphine oxides. Thus, there appears to be minimal likelihood that M−H···OH_2 hydrogen bonds have any effect on our kinetics of hydrogen atom transfer. As noted below, the present set of reactions in aqueous media appear, if anything, too rapid.

Linear Free Energy Relationships. Predictive linear free energy relationships, such as the Marcus cross relation for outer-sphere electron-transfer rates[49,50] and proposed Marcus expressions for atom transfer[51,52] and other reactions,[53−55] can have tremendous power. Such correlations have been demonstrated for outer-sphere electron-transfer reactions[56] and for proton-transfer reactions of metal hydride complexes.[57] At minimum, free energy plots and analyses are a helpful means to organizing data.

For H atom transfer, the cross-relation can be expressed by eq 18 in which k_{12}^{H} is the H atom transfer

$$k_{12}^{H} = (k_{11}^{H} k_{22}^{H} K_{12}^{H})^{1/2} \qquad (18)$$

rate constant for the net (cross) reaction with equilibrium constant K_{12}^{H} and k_{11}^{H} and k_{22}^{H} refer to the self-exchange reactions, e.g. Scheme 3.

Scheme 3

$$(C_5H_4CO_2)(CO)_3W^{\bullet -} + (C_5H_4CO_2)(CO)_3WH^{-} \rightarrow (C_5H_4CO_2)(CO)_3WH^{-} + (C_5H_4CO_2)(CO)_3W^{\bullet -} \quad k_{11}^{H}$$

$$^{\bullet}C(OH)(H)(CH_3) + HC(OH)(H)(CH_3) \rightarrow HC(OH)(H)(CH_3) + {}^{\bullet}C(OH)(H)(CH_3) \quad k_{22}^{H}$$

For the systems studied here, the free energy changes in aqueous solution can be assessed for the radicals from ethanol, 2-propanol, and formate because of the earlier work of Schwarz and Dodson,[24] who directly studied these radicals in redox equilibrium with Tl(0) in pulse radiolysis experiments. Values for the metal hydride complexes are derived from pK_a and electrochemical measurements (see Table 2).[4,9,58−60] The ΔG_{12}° values for H atom transfer from $(C_5H_4CO_2)(CO)_3WH^-$ to ethanol radical and 2-propanol radical are −27.6 and −24 kcal/mol, respectively, while the BDE (enthalpic) differences are −23.7 and −21.4 kcal/mol. The self-exchange rate constant for $Cp(CO)_3W{-}H/Cp(CO)_3W^{\bullet}$ hydrogen atom transfer has been found to be $k_{11}^{H} > 10^{6}$ M^{-1} s^{-1} at 25 °C.[61,62] For halogen atom transfer, self-exchange rates for the carbon-centered systems appear to be 4−5 orders of magnitude slower. For carbon-centered hydrogen exchange, such data as exist[63] suggest a rate constant k_{22}^{H} of 10^{0} M^{-1} s^{-1} at most. Thus, on the basis of ΔG°_{BDE} values and assuming a cross-relation to be applicable, diffusion-controlled rate constants would be expected with the alcohol radicals. The observed rate constants suggest a much smaller effective value of k_{22}^{H}, 10^{-5} M^{-1} s^{-1}; Mayer has given 10^{-4} M^{-1} s^{-1} for $^{\bullet}CH_3/CH_4$ in the gas phase.[54] This likely reflects the very different spatial requirements for the carbon-centered and metal-centered exchange processes,[64] much closer contact being required for the reactions involving the carbon-centered species.

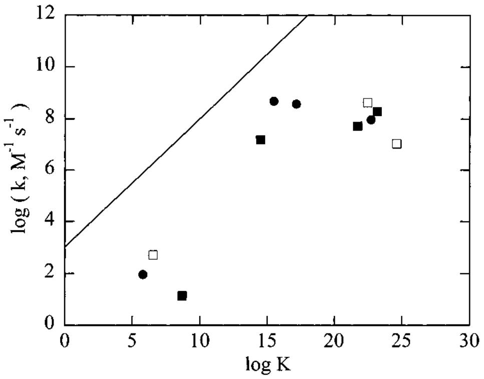

Figure 5. Logarithm of the rate constant for H abstraction from metal hydrides vs the logarithm of the equilibrium constant for the H atom transfer, estimated from the differences in BDEs: (solid circles) W complexes $HW(C_5H_4CO_2)(CO)_3$ and $HWCp(CO)_3$; (solid squares) the Mo complex $HMoCp(CO)_3$; (open squares) the Mo complex $HMoCp^*(CO)_3$. The line is calculated for eq 18 with $0.5(\log(k_{11}^{H}k_{22}^{H})) = 3$ and has not been corrected for the effects of diffusion limits (expected to be significant above log $k = 8.5$).

To see if data for the other systems are consistent with eq 18, we estimate log K_{12}^{H} values from BDE differences and plot data for H atom transfer for Mo and W complexes closely related to those studied here (Table S2), since only BDE data are generally available. (This is equivalent to assuming a constant $T\Delta S_{12}^\circ$ for the series.) The plot is shown in Figure 5. The line is calculated for eq 18 with $0.5(\log(k_{11}^{H}k_{22}^{H})) = 3$, as discussed above. The plot suggests a rough dependence on the square root of the equilibrium constant for the transfer and a *y* intercept, $0.5(\log(k_{11}^{H}\ k_{22}^{H})) \approx 0$, implicating an intrinsic barrier even greater than that inferred above. Unfortunately, the data are for very different organic radical systems and for both Cp* and Cp complexes.

Understanding of the transfer of H atom from a transition-metal center to carbon would clearly benefit from more systematic tests of the dependence of the rate constant on the free-energy change. Both rate and thermodynamic data are essential to such progress. One

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of the challenges will be to try to independently vary steric and thermodynamic factors.

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Supporting Information Available: Table of thermodynamics for $CpW(CO)_2L$ (=M) complexes in acetonitrile and a table of H atom transfer rate constants at 298 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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