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Thermodynamics of Heterolytic and Homolytic M–H Bond Cleavage Reactions of 18-Electron and 17-Electron Group 6 Hydridotris(pyrazolyl)borate Metal Hydrides

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Abstract: The energetics of the deprotonation and metal–hydrogen bond homolysis reactions of TpM(CO)$_3$H and Tp'M(CO)$_3$H (Tp = hydridotris(pyrazolyl)borate; Tp' = hydridotris(3,5-dimethylpyrazolyl)borate; M = Cr, Mo, W) and their cation radicals have been investigated, and the results are compared with available data for the analogous CpM(CO)$_3$H complexes. Proton-transfer equilibrium measurements have established that for a given metal, acetonitrile pK_a values of the metal hydrides decrease in the order CpM(CO)$_3$H > TpM(CO)$_3$H > Tp'M(CO)$_3$H. This trend is the opposite of that expected on the basis of the relative electron-richness of the metal centers, as measured by infrared ν_{CO} frequencies and oxidation potential data for the corresponding metal anions. The homolytic bond dissociation energies (BDEs) of the complexes in acetonitrile solution were obtained by the use of a known thermochemical cycle based on the pK_a and anion oxidation potential data. The BDE values decrease in the order CpM(CO)$_3$H > TpM(CO)$_3$H > Tp'M(CO)$_3$H. Steric effects significantly contribute to the ordering of the heterolytic and homolytic M–H bond strengths. The tendency of the Tp ligand to electronically favor octahedral coordination may also be of importance. Thermochemical cycles were used to probe the effect of a one-electron oxidation of the metal hydrides on the strengths of the Mo–H and W–H bonds. The oxidations led to a weakening of the bonds by a relatively constant 108–113 kJ/mol toward deprotonation, and by 25–33 kJ/mol toward homolysis.

Introduction

The hydridotris(pyrazolyl)borate (Tp) ligand and substituted derivatives, most notably hydridotris(3,5-dimethylpyrazolyl)borate (Tp'), have found widespread uses in organometallic and inorganic chemistry.[1] In terms of electron count, Tp and Tp' bear a close resemblance to the Cp (Cp = η^5-C$_5$H$_5$) ligand, and these ligands frequently yield species with closely related structures. However, the steric and electronic properties of the Tp ligands are quite different from those of Cp, and as a consequence novel chemical reactivity is commonly observed.[2]

The great differences in the steric demands of the Tp and Tp' vs Cp ligands are underscored by the fact that the radicals TpM(CO)$_3^\bullet$ and Tp'M(CO)$_3^\bullet$ (M = Cr, Mo, W) are stable toward dimerization.[2c,d,k,m] Contrasting this behavior, only the corresponding chromium radicals are persistent in solution (or in rapid equilibrium with the metal–metal bonded dimers)[3] in the realm of Cp and Cp* chemistry (Cp* = η^5-C$_5$Me$_5$). Here, the Mo and W radicals undergo dimerizations at near diffusion-controlled rates.[4] As a measure of the steric bulk, the cone angles of the Tp and Tp' ligands have been estimated to be as great as 180° and 225°, respectively.[5] The severe steric demand of the Tp and Tp' ligands presumably is a major reason that the Tp chemistry of group 6 metals is dominated by six-coordinate species TpML$_3$ that may be described as approximate three-legged piano-stool structures. In the rather limited number of known four-legged piano stool complexes TpML$_4$, the four piano stool "legs" are compressed together. The paucity of TpML$_4$ complexes is in stark contrast with the abundance of four-legged piano-stool species of the type CpML$_4$.[6]

A comparison of IR ν_{CO} data for CpM(CO)$_3^-$ and TpM(CO)$_3^-$ complexes has led to the suggestion that the Tp ligand is a better electron donor than the Cp.[7] Recent IR data for TpRu(CO)(PPh$_3$)(L)$^+$ vs CpRu(CO)(PPh$_3$)(L)$^+$ complexes, however, fail to support this conclusion.[8] The electronic effect also causes the redox potentials of the Tp'M(CO)$_3^-$/Tp'M(CO)$_3^\bullet$ [2m] and TpM(CO)$_3^-$/TpM(CO)$_3^\bullet$ (to be discussed in this paper) couples to be located at potentials less anodic than those of the CpM(CO)$_3^-$/CpM(CO)$_3^\bullet$ couples. Extended Hückel MO calculations have indicated that in addition to being a better donor than Cp, the Tp ligand promotes six-coordination by polarizing the metal orbitals into an octahedral array that is well suited for bonding.[2a,c]

From the above discussion, there may be steric as well as electronic factors that tend to destabilize seven-coordinate TpML$_4$ complexes. As a consequence, significant weakening of the M–L bonds is anticipated. The hydrides TpM(CO)$_3$H and Tp'M(CO)$_3$H (M = Mo, W)[2a,g,7] constitute some of the few examples

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of group 6 $TpML_4$ complexes. As opposed to the ubiquitous $CpM(CO)_3H$ complexes, these species still remain relatively unexplored and, as will be demonstrated, they provide a convenient entry point to the thermochemistry of this class of complexes.

Metal hydrides have played a crucial role in the development of organotransition-metal chemistry,[9] and their chemistry continues to be vigorously explored. They constitute a class of compounds for which bond strength data are relatively abundant. The important M–H bond in general may be envisioned to undergo cleavage in three fundamentally different ways: homolytic cleavage to furnish $H^•$ (eq 1), or two modes of heterolytic cleavage to yield either H^+ (eq 2) or H^- (eq 3). The energetics of the two first modes of M–H bond cleavage, in thermodynamic as well as kinetic terms, have been investigated by numerous research groups[10-12] using a variety of experimental techniques and have recently been critically reviewed.[10]

$$\text{M–H} \rightarrow \text{M}^{\bullet} + \text{H}^{\bullet} \quad (1)$$

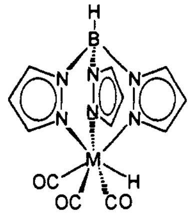
$$\text{M–H} \rightarrow \text{M}^{-} + \text{H}^{+} \quad (2)$$

$$\text{M–H} \rightarrow \text{M}^{+} + \text{H}^{-} \quad (3)$$

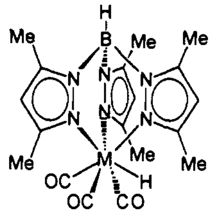
For the $CpM(CO)_3H$ complexes, all three modes of M–H cleavage are known to occur when suitable H^+, $H^•$, and H^- acceptors, respectively, are available.[10c] It has been pointed out that the hydride $TpMo(CO)_3H$ appears to be significantly more acidic than $CpMo(CO)_3H$, quite the contrary of what is expected if Tp is a better donor than Cp.[2a] On the other hand, removal of the hydride as H^- with Ph_3C^+ reportedly is not possible for $TpMo(CO)_3H$[2a] whereas it is a facile process for the $CpM(CO)_3H$ analogues.[13] To our knowledge, no quantitative bond energy or related data have been available for $TpM(CO)_3H$ (M = Cr, **1a**; Mo, **1c**; W, **1e**) and $Tp'M(CO)_3H$ (M = Cr, **1b**; Mo, **1d**; W, **1f**). In this paper, we present pK_a and BDE data for these complexes.[14a] The pK_a data have been obtained from measurements of proton-transfer equilibria. BDE values were then obtained by the use of well-known thermochemical cycles. Finally, the effect of one-electron oxidation processes on the M–H pK_a and BDE values of these complexes is investigated. The results are compared with available data for the Cp analogues.

Results

A Summary of the Methods Used for pK_a and M–H BDE Determinations. The pK_a values for **1c** and **1e** were estimated by IR (ν_{CO}) spectroscopy measurements of proton-transfer equilibria in the presence of suitable reference bases of known pK_a in acetonitrile. The method was introduced by and has been innovatively employed by Norton and co-workers.[15] Limited substrate solubilities precluded the use of this technique for **1d** and **1f**. Instead, relative pK_a data for pairs of hydrides were evaluated by monitoring proton-transfer equilibria by ^1H NMR spectroscopy in THF-d_8.



1a: M = Cr
1c: M = Mo
1e: M = W



1b: M = Cr
1d: M = Mo
1f: M = W

The determination of BDE(M–H), pK_a(M–H$^{•+}$), and BDE(M–H$^{•+}$) values was achieved by the use of thermochemical cycles[16a] related to those that were introduced by Breslow and co-workers,[16b] later to be modified and adapted by numerous research groups.[12c,16c-g]

The energetics of the homolytic cleavage of a metal hydride M–H (eq 1) and of the corresponding heterolytic cleavage (deprotonation, eq 2) are related by eq 4.[12c,17] Here, $E°_{ox}(M^-)$ is the reversible oxidation potential for the metal hydride conjugate base (anion). The magnitude of the constant term C depends on the choice of reference electrode and solvent system. For BDEs to be defined in enthalpy terms, C has been evaluated to be 249 kJ/mol (59.5 kcal/mol) when electrode potentials measured in acetonitrile solutions are referenced against the ferrocene/ferrocenium (Fc) couple.[12c]

$$\text{BDE(M–H)} = 2.301RT\text{p}K_a\text{(M–H)} + FE°_{ox}(\text{M}^-) + C \quad (4)$$

The thermodynamic acidities of a neutral metal hydride and its cation radical M–H$^{•+}$ (eq 5) are related by eq 6.[18a] The determination of pK_a(M–H$^{•+}$) requires knowledge about the oxidation potentials of the metal hydride and its conjugate base M^-. The acidities of a number of metal hydride cation radicals have been estimated and exceed the acidities of the neutral parent hydrides by 19–25 pK_a units.[11c,18] This represents activations of the M–H bonds toward heterolysis by 109–143 kJ/mol.

$$\text{M–H}^{\bullet +} \rightarrow \text{M}^{\bullet} + \text{H}^{+} \quad (5)$$

$$\text{p}K_a(\text{M–H}^{\bullet +}) = \text{p}K_a\text{(M–H)} + F[E°_{ox}(\text{M}^-) - E°_{ox}\text{(M–H)}]/2.301RT \quad (6)$$

As recently communicated,[11c] the BDEs of metal–hydride cation radicals, eq 7, may be obtained from a thermochemical cycle that results in eq 8. The oxidative activation of the Cr–H bonds in $CpCr(CO)_3H$ derivatives toward homolysis was estimated to be in the range 34–46 kJ/mol.

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$$\text{M–H}^{\bullet +} \rightarrow \text{M}^{+} + \text{H}^{\bullet} \quad (7)$$

$$\text{BDE(M–H}^{\bullet +}) = \text{BDE(M–H)} + F[E^{\circ}_{\text{ox}}(\text{M}^{\bullet}) - E^{\circ}_{\text{ox}}(\text{M–H})] \quad (8)$$

In practice, the applicability of eq 8 is severely limited due to the transient nature of most commonly encountered 17-electron organometal radicals. The fact that the $TpM(CO)_3^{\bullet}$ radicals exist as monomers means that these systems are potentially amenable to an analysis according to eq 8.

Preparation of the Metal Hydrides 1a–f. The Mo and W hydrides **1c–f** were prepared as previously described[2a,g,7] by protonation of the anions $TpM(CO)_3^-$ and $Tp'M(CO)_3^-$ (**2c–f**). Problems attributable to the rather low basicities of the corresponding anions (vide infra) were encountered during the attempted preparation of the chromium hydrides **1a** and **1b** following this procedure.

Treatment of a DMF solution of $Na^+TpCr(CO)_3^-$ (**2a**(Na^+)) with $HBF_4{\cdot}Et_2O$ caused the precipitation of an insoluble product. The ambient-temperature IR (dichloromethane, toluene, THF) and ^1H NMR (dichloromethane-d_2 and toluene-d_8) spectra of the product were consistent with the formulation of this product as $TpCr(CO)_3H$ (**1a**; see Experimental Section for spectroscopic data), contaminated with 10–20% of the radical $TpCr(CO)_3^{\bullet}$ (**3a**). The presence of **3a** always led to broadening of ^1H NMR spectra of mixtures containing metal anions, presumably due to facile electron exchange between anion and radical. When the sample of **1a** that was contaminated with **3a** was dissolved in dry acetonitrile (freshly distilled from CaH_2), an IR spectrum of the solution revealed that extensive (>60%) deprotonation to **2a** had taken place. The only other IR ν_{CO} absorptions seen could be due to **1a** and/or **3a**, for which very similar IR spectra are obtained, so we cannot conclusively say if any **1a** was left in the IR cell at all. ^1H NMR spectroscopy observation of the in situ protonation of **2a**(Bu_4N^+) with $HBF_4{\cdot}Et_2O$ in acetonitrile-d_3 failed to provide well-defined signals for **1a**. We take these observations to indicate that **1a** is highly acidic. Norton and co-workers[15b] reported that $Co(CO)_4H$ (pK_a = 8.4) underwent partial deprotonation due to the presence of basic impurities in acetonitrile. On the basis of this, we conclude that the acetonitrile pK_a of **1a** probably has a value of 8 or less but, obviously, no accurate pK_a value can be presented.

Acidification of solutions of $Tp'Cr(CO)_3^-Na^+$ never led to the precipitation of the desired hydride **1b**, nor could it ever be detected as a result of in situ protonation of **2b**(Bu_4N^+) in acetonitrile or THF.

IR Spectroscopy Determination of Metal Hydride Thermodynamic Acidities. The details of the measurements are provided in the Experimental Section. The proton-transfer equilibrium constant between $Bu_4N^+TpMo(CO)_3^-$ (**2c**(Bu_4N^+)) and an anisidine/anisidinium buffer (pK_a = 11.3[15b]) in acetonitrile was determined by IR monitoring of the relative concentrations of **1c** and **2c** and resulted in pK_a(**1c**) = 10.7 ± 0.1 (average and one standard deviation for three measurements). The use of an aniline/anilinium buffer (pK_a = 10.56[19a]) resulted in pK_a(**1c**) = 10.8 ± 0.1 (two measurements). By the use of a 4-methylpyridine/4-methylpyridinium buffer (pK_a = 14.3[19b]), pK_a(**1e**) was similarly determined to be 14.4 ± 0.1. Due to the low solubilities of **1d** and **1f** in acetonitrile, their pK_a values could not be determined by this method.

^{1}H NMR Spectroscopy Investigation of Equilibria between Metal Hydrides and Metal Anions. Measurements of proton-transfer equilibria between combinations of different metal hydrides and anions in THF-d_8 were undertaken with the hope that pK_a data would be accessible for the hydrides that could not be evaluated in acetonitrile. At sufficiently high temperatures, THF-d_8 solutions containing metal anions and hydrides displayed broadened signals due to rapid proton-exchange reactions. The equilibria were therefore measured at temperatures low enough to inhibit these exchange processes. Equilibrium constants at 25 °C were obtained by a van't Hoff analysis of ln K vs $1/T$ data. The thermodynamic parameters that are presented in the following represent values (and one standard deviation) that are based on the analysis of 4–5 data points, evenly distributed in the temperature intervals indicated.

The ^1H NMR spectrum (THF-d_8) of a mixture of **1c** and **2d**(Bu_4N^+) revealed separate signals for **1c**, **1d**, **2c**, and **2d**. The proton-transfer equilibrium constant was determined over a wide temperature range (–91 to 0 °C) and resulted in $\Delta H^{\circ} = -9 \pm 1$ kJ/mol and $\Delta S^{\circ} = -11 \pm 5$ J/K·mol for H^+ transfer from **1d** to **2c**. Extrapolation of the data to 25 °C yielded pK_a(**1c**) – pK_a(**1d**) = 1.0. This result agrees well with the recent measurements by Protasiewicz and Theopold.[14b] For a mixture of **1f** and **2e**(Bu_4N^+), separate signals for **1e**, **1f**, **2e**, and **2f** were observed over a wide temperature range. The data (–48 to +53 °C) resulted in $\Delta H^{\circ} = -6 \pm 1$ kJ/mol and $\Delta S^{\circ} = 8 \pm 2$ J/K·mol for H^+ transfer from **1f** to **2e**, and pK_a(**1e**) – pK_a(**1f**) = 1.5 at 25 °C. The near-zero values for ΔS° for the **1f**/**2e** and **1c**/**2d** equilibria are consistent with rather uncomplicated proton-transfer reactions.

For a mixture of **1d** and **2a**(Bu_4N^+), separate signals due to **1d** and **2d** were seen. Partial proton transfer from **1d** to **2a** must therefore have occurred (in a control experiment, it was shown that **1d** alone in THF-d_8 failed to show any **2d**). Unfortunately, the hydride signal anticipated for **1a** was not observed, and, in the "Tp region" of the ^1H NMR spectrum, only broadened signals were seen even at –100 °C. The failure to observe **1a** leads to considerable uncertainty as to whether it was produced at all—at least, some uncertainty exists regarding the exact site of protonation at **2a**.[20a] We are planning to further investigate the chemistry of **1a** and will report the results in due time.

In order to avoid signal overlap in the Tp region, the proton-transfer equilibrium to **2b** was performed with **1c** as the H^+ source rather than the more acidic **1d**. The observation of traces of **2c** suggested a small extent of proton transfer to **2b**, but, again, the chromium hydride was not directly observed. Because of the failure to generate **1b** in all attempts to protonate **2b**, while the reaction worked for **2a**, we infer that pK_a(**1b**) < pK_a(**1a**). In conclusion, we are unable to provide reliable quantitative data for the pK_a's of **1a** and **1b**.

Electrochemical Oxidation of the Anions 2a–f. It has been previously shown that these anions undergo one-electron oxidations that yield the stable radicals **3a–f**.[2k,m,14b] A second oxidation wave attributed to the oxidation of some of the radicals has also been noted.[2m,14b] The measurements have been repeated here in order to provide data that can be directly incorporated into the thermochemical cycles without the need for reference electrode conversions. All electrode potentials that are reported in the following were measured by derivative cyclic voltammetry (DCV)[21] due to the high precision that this method offers and are referenced against the ferrocene/ferrocenium (Fc) couple.

Figure 1 shows a cyclic voltammogram for the oxidation of **2d**(Bu_4N^+) in acetonitrile/0.1 M $Bu_4N^+PF_6^-$ at a Pt disk electrode (d = 0.6 mm) at 25 °C and a voltage sweeprate ν = 1.0 V/s. The reversible oxidation potential for **2d**, taken as the midpoint between the anodic (a) and cathodic (b) peaks, is –0.583 V vs Fc. The oxidation of the radical **3d** is observed at (c). The lack of a peak corresponding to (c) on the reverse scan is indicative of the presence of a follow-up reaction that consumes **3d**$^+$ on the time scale of

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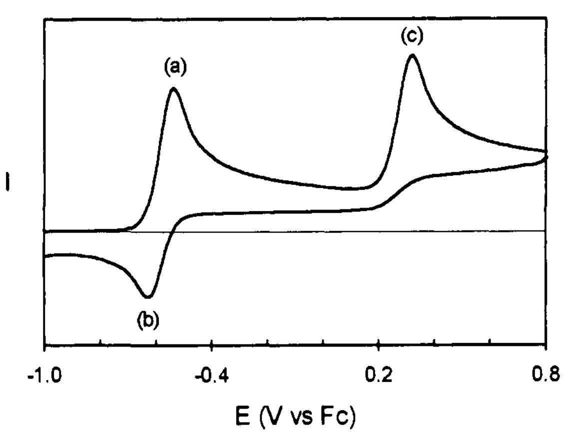

Figure 1. Cyclic voltammogram for the oxidation of $Tp'Mo(CO)_3^-Bu_4N^+$ (**2d**(Bu_4N^+)) in acetonitrile/0.1 M $Bu_4N^+PF_6^-$ at a Pt disk electrode (*d* = 0.6 mm) at 25 °C and a voltage sweep rate ν = 1.0 V/s.

Table I. Electrochemical Data for the Oxidation of Anions **2a–f**, Radicals **3a–f**, and Hydrides **1a–f**

metal center M	$E_{ox}(M^-)^{a,b}$	$E_{ox}(M^\bullet)^a$	$E_{ox}(MH)^a$
$TpCr(CO)_3$	–0.821	$0.009^{b,c}$	*d*
$Tp'Cr(CO)_3$	–0.857	$0.003^{b,f}$	*d*
$TpMo(CO)_3$	–0.521	0.311^e	0.596^e
$Tp'Mo(CO)_3$	–0.583	0.297^e	0.552^e
$TpW(CO)_3$	–0.582	0.246^e	0.586^e
$Tp'W(CO)_3$	–0.652	0.208^e	0.509^e

[a] Electrode potentials in V vs the ferrocene/ferrocenium (Fc) couple, measured by derivative cyclic voltammetry. 1.0 mM substrate in acetonitrile/0.1 M $Bu_4N^+PF_6^-$, 25 °C, Pt disk electrode (*d* = 0.6 mm), sweep rate ν = 1.0 V/s unless otherwise noted. [b] Reversible potentials, taken as the midpoint between anodic and cathodic peaks. [c] ν = 10 V/s, 0 °C. [d] See Results section for discussion. [e] Chemically irreversible waves. [f] ν = 10 V/s.

the cyclic voltammetry experiment. The oxidations of **2a–c** and **2e–f** resulted in similar voltammetric responses. The separation between the anodic and the cathodic peaks for the oxidation of **2a**, **2c**, and **2e** were identical, within ±1 mV, to that observed for ferrocene. The anodic-to-cathodic peak separations were 4–5 mV greater for **2b**, **2d**, and **2f**. The electrochemical data are summarized in Table I. For **2a** and **2b**, the waves resulting from the radical oxidations exhibited partial chemical reversibility at low temperatures and/or high voltage sweep rates.

The electrode potentials in Table I, along with the pK_a data for the hydrides, provide the BDEs of the neutral hydrides by application of eq 4. The resulting pK_a and BDE data are summarized and discussed in the Discussion section.

Electrochemical Oxidation of the Hydrides 1a–f. The oxidation potentials for the hydrides **1c–f** were measured by DCV in acetonitrile/0.1 M $Bu_4N^+PF_6^-$. The metal–hydride oxidation waves were chemically irreversible at voltage sweep rates up to 100 V/s. This behavior was anticipated in view of previous experience with the oxidation of considerably less acidic metal hydrides.[18] The cyclic voltammetry peak potentials for the oxidations of **1c–f** are included in Table I.

Attempts at measuring the oxidation potentials for **1a** and **1b** were of limited success due to the problems associated with their preparation. When a sample of synthesized **1a** (contaminated with the radical **3a**) was dissolved in the electrolyte (acetonitrile or dichloromethane solvent), several DCV peaks were observed, the major one being due to the radical **3a**. The tendency to form the radical signals that the Cr–H bond in **1a** is rather weak. The same behavior was noted when **2a** was treated with $HBF_4 \cdot Et_2O$. The oxidation of **1b** was problematic for similar reasons. The voltammograms of protonated **2a** and **2b** did show minor waves at 0.35 and 0.36 V vs Fc, respectively, which is in the potential region where the hydride oxidations were expected to occur, by comparison with $E_{ox}(M{-}H) - E_{ox}(M^-)$ differences for the Mo and W hydrides.

Table II. IR ν_{CO} and Electrochemical Oxidation Potential Data for the Anions (ligand)$M(CO)_3^-$ (ligand = Tp, Tp′, Cp; M = Cr, Mo, W)[a]

metal M =	Cr	Mo	W
$\nu_{CO}(TpM(CO)_3^-)$, cm^{-1}	1889, 1751	1888, 1752	1878, 1744
$\nu_{CO}(Tp'M(CO)_3^-)$, cm^{-1}	1881, 1742	1881, 1745	1872, 1733
$\nu_{CO}(CpM(CO)_3^-)$, cm^{-1}	1888, 1768	1891, 1770	1886, 1765
$E_{ox}(TpM(CO)_3^-)$, V vs Fc	-0.821^c	-0.521^c	-0.582^c
$E_{ox}(Tp'M(CO)_3^-)$, V vs Fc	-0.857^c	-0.583^c	-0.652^c
$E_{ox}(CpM(CO)_3^-)$, V vs Fc	-0.688^c	-0.403^d	-0.397^d

[a] Acetonitrile solutions of the Et_4N^+ salts. [b] Measured by derivative cyclic voltammetry. 1.0 mM substrate in acetonitrile/0.1 M $Bu_4N^+PF_6^-$, 25 °C, Pt disk electrode (*d* = 0.6 mm), sweep rate ν = 1.0 V/s. [c] Reversible potential, taken as the midpoint between anodic and cathodic peaks. [d] Previously reported irreversible potentials that have been corrected for kinetic potential shifts as described in ref 12c.

The metal hydride oxidation potentials for **1c–f**, along with the anion oxidation potentials, provide the pK_a values for the metal hydride cation radicals (eq 6). The hydride oxidation potentials and the radical oxidation potentials provide M–H BDEs for the cation radicals (eq 8). These data are included in the Discussion section.

Discussion

A Comparison of the Electronic Properties of Cp, Tp, and Tp′ Metal Carbonyl Anions. It is worthwhile to consider some available data concerning the electronic properties of the Tp vs the Cp ligand systems before pK_a and BDE data are discussed in detail. Table II lists relevant IR (ν_{CO}) and oxidation potential data for (ligand)$M(CO)_3^-$ (ligand = Tp, Tp′, Cp; M = Cr, Mo, W) complexes, all obtained in acetonitrile solutions under *identical* conditions.[22]

The anion oxidation potentials attest to the relative electron-richness of the $TpM(CO)_3^-$ anions, compared with the Cp analogues.[24] The $TpM(CO)_3^-$ anions are more readily oxidized than the Cp counterparts by 0.118 (Mo), 0.133 (Cr), and 0.185 (W) V. Substitution of Tp′ for Tp leads to another 0.035–0.070 V cathodic shift in the anion oxidation potentials. The IR ν_{CO} frequencies of the anions also point at the enhanced electron density at the metals. Although the high-frequency A_1 bands are only moderately affected by the substitution of Tp for Cp, the low-frequency E bands are lowered by ca. 20 cm^{-1}. Both bands are lowered by an additional 6–11 cm^{-1} when Tp′ is introduced in the place of Tp. The $E_{ox}(M^-)$ and ν_{CO} data to a first approximation suggest that the metal hydride acidities should decrease in the order $CpM(CO)_3H$ > $TpM(CO)_3H$ > $Tp'M(CO)_3H$.[26]

Thermodynamic Acidities of the Hydrides 1a–f. Table III summarizes pK_a and BDE data for compounds **1a–f**. Our value for **1c** is 0.6 pK_a units lower than Theopold's[14b] (obtained by ^1H NMR spectroscopy measurements of the proton-transfer equilibrium with aniline in acetonitrile-d_3). Data for the Cp analogues are included for comparison. Quantitative data for **1a** and **1b** are not available for reasons that have been addressed in the Results section; however, the behavior in acetonitrile strongly suggests a pK_a of 8 or less for **1a**, regardless of the site of protonation.[20a]

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(22) Trofimenko's comparison[7] of Cp vs Tp IR data is rough, because different solvents and cations—both known to strongly influence the positions of ν_{CO} bands[23]—were used for the different complexes.

(23) Darensbourg, M. Y. *Prog. Inorg. Chem.* **1985**, *33*, 221.

(24) The $E_{ox}(M^-)$ data for the $Tp'M(CO)_3^-$ anions reported herein agree well with Kochi's values[2m] assuming that SSCE data can be converted to Fc data by subtracting 312 mV,[25] and the agreement with Theopold's data[14b] for $TpMo(CO)_3^-$ and $Tp'Mo(CO)_3^-$ is better than 10 mV.

(25) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods. Fundamentals and Applications*; Wiley: New York, 1980.

(26) Although the correlation between anion oxidation potentials and metal basicities is not at all perfect, qualitatitively good correlations exist between structurally related complexes as long as the metal atom is the same.[11c,12c,17]

Table III. Acetonitrile pK_a and BDE Data for (ligand)M(CO)$_3$H (ligand = Tp, Tp′, Cp; M = Cr, Mo, W)^a

hydride M–H	pK_a(M–H)	BDE(M–H)^b, kJ/mol
TpCr(CO)$_3$H (**1a**)	*c*	*c*
Tp′Cr(CO)$_3$H (**1b**)	*c*	*c*
CpCr(CO)$_3$H	13.3^e	257^f
TpMo(CO)$_3$H (**1c**)	10.7	260
Tp′Mo(CO)$_3$H (**1d**)	9.7^d	248
CpMo(CO)$_3$H	13.9^e	290^g
TpW(CO)$_3$H (**1e**)	14.4	275
Tp′W(CO)$_3$H (**1f**)	12.9^d	260
CpW(CO)$_3$H	16.1^e	303^g

^{a} This work unless otherwise noted. ^{b} Calculated from eq 4 unless otherwise noted. ^{c} See discussions in the Results section and in the Discussion section. ^{d} From equilibrium measurements in THF-d_8 as described in text. ^{e} From ref 15a. ^{f} Calorimetry data from ref 12d. ^{g} From ref 12b.

The experimental data demonstrate that for a given metal, the acidities follow the order Tp′M(CO)$_3$H > TpM(CO)$_3$H > CpM(CO)$_3$H. In view of the previous qualitative statement by Curtis and Shiu[2a] regarding the acidity of **1c**, the ordering of TpMo(CO)$_3$H and CpMo(CO)$_3$H (and, by extension, for the Cr and W analogues) was anticipated. However, we were initially somewhat surprised to find that the Tp′ complexes are even more acidic than the Tp ones. The donor capability of Tp′ certainly exceeds that of Tp as shown by the E_{ox}(M$^-$) and ν_{CO}(M$^-$) data, a factor that should increase the pK_a for Tp′ relative to Tp. The pK_a differences between Tp′ and Tp metal hydrides probably are caused by steric effects. The expansion of the coordination sphere when the anion is protonated leads to repulsions between the methyl groups that are closest to the metal and the other ligands, causing a destabilization of the hydride for Tp′ relative to Tp.

M–H Bond Dissociation Energies of the Hydrides 1c–f. The M–H BDEs of the hydrides **1c–f** and their CpM(CO)$_3$H analogues are included in Table III. The following discussion will be based on data for M–H BDEs of CpM(CO)$_3$H that were obtained by the use of eq 4.[12c] Inspection of the BDE data reveals the same trend as the pK_a data, the M–H BDEs decreasing in the order CpM(CO)$_3$H > TpM(CO)$_3$H > Tp′M(CO)$_3$H. The reported BDE for CpCr(CO)$_3$H was obtained by direct calorimetric measurements. The excellent agreement between this value and one obtained from eq 4 with the use of a value for C that was obtained by an entirely independent method[12c] in our view attests to the reliability of BDE data that are obtained by the use of the thermochemical cycle when reversible anion oxidation potentials are available. Such is the case for the whole series **1a–f** for which the anions exhibit the desired reversible voltammetric behavior. The situation was less straightforward for CpMo(CO)$_3$H and CpW(CO)$_3$H, since the measured irreversible anion oxidation potentials had to be corrected for kinetic potential shifts. It has been pointed out[10a] that the BDEs estimated for these complexes appear to be somewhat higher than estimates arrived at by calorimetric[27] and kinetic[28] methods. However, the conclusions regarding the *trends* in BDEs are not affected by whether BDEs based on the thermochemical cycle or on other methods are used.

Table IV. pK_a and BDE Data for the Cation Radicals of the Hydrides **1c–f**

hydride MH	pK_a (M-H$^{\bullet+}$)^a	BDE (M–H$^{\bullet+}$),^{b} kJ/mol	$-\Delta\Delta G°_{het}$,^{c} kJ/mol	$-\Delta\Delta G°_{hom}$,^{d} kJ/mol
TpMo(CO)$_3$H (**1c**)	–8.2	232	108	27
Tp′Mo(CO)$_3$H (**1d**)	–9.5	223	109	25
TpW(CO)$_3$H (**1e**)	–5.4	242	113	33
Tp′W(CO)$_3$H (**1f**)	–6.7	231	112	29

^{a} From eq 6. ^{b} From eq 8. ^{c} $\Delta\Delta G°_{het} = 2.3RT\Delta(pK_a) = 2.3RT[pK_a(M\text{–}H^{\bullet+}) - pK_a(M\text{–}H)]$. ^{d} $\Delta\Delta G°_{hom} = \Delta(BDE) = BDE(M\text{–}H^{\bullet+}) - BDE(M\text{–}H)$.

Due to the uncertainties regarding the site of protonation and the pK_a of **1a** (and more so for **1b**), great caution must be exerted when the BDEs of these complexes are discussed. If the value of 8 is cautiously taken to represent an upper limit for pK_a(**1a**), as discussed in the Results section, then an upper limit to BDE(**1a**) as low as 215 kJ/mol may be calculated. The tendency that the corresponding radicals are so readily formed when **2a** and **2b** are treated with acid also indicates that the Cr–H bonds in **1a** and **1b** are extremely weak bonds. Hoff and co-workers[12a] have emphasized that M–H bonds weaker than 234 kJ/mol are thermodynamically unstable with respect to elimination of H$_2$ at room temperature.

Ligand Effects on M–H BDEs. A considerable amount of M–H BDE data is now available that allows an assessment of the effect of ligand substitutions on the BDEs to be made. Existing data allow the following conclusion to be made: Simple ligand substitutions (PR$_3$ for CO, Cp* for Cp) usually lead only to modest changes in BDEs, on the order of 10 kJ/mol or less, for closely related complexes. This applies to CpM(CO)$_3$H and derivatives for M = Cr,[12a] Mo,[12c] and W,[12c] for Co(CO)$_4$H and derivatives,[12c] and for Mn(CO)$_5$H and derivatives.[12c] This modest effect may in part be interpreted with eq 4 as a basis. Two parameters influence the BDEs: pK_a(M–H) and E_{ox}(M$^-$). For all the species within one of the series mentioned, an increase in E_{ox}(M$^-$) is accompanied by a decrease in pK_a(M–H). These two effects will cancel in part, and the BDEs obtained from eq 4 tend to be rather similar.

A different situation pertains for the compounds considered in this study. When comparing Cp vs Tp vs Tp′ for a given metal, it is seen that the tabulated E_{ox}(M$^-$) and pK_a(M–H) data in these cases do *not* counteract each other. Here, an increase in the electron density at the metal is accompanied by an increase in metal–hydride acidity. Both effects work in the same direction in eq 4, and, as a result, the BDEs have been significantly lowered. The results emphasize that the combined steric, electronic, and stereoelectronic properties of a ligand strongly influences the bonding energetics of apparently related species.

Metal Hydride Cation Radical pK_a and BDE Data. Table IV shows pK_a and BDE data for the cation radicals of **1c–f**. The values for E_{ox}(M–H) that were needed for the determination of pK_a(M–H$^{\bullet+}$) were readily available for **1c–f**. The resulting Δ(pK_a) = pK_a(M–H) – pK_a(M–H$^{\bullet+}$) and Δ(BDE) = BDE(M–H) – BDE(M–H$^{\bullet+}$) data for the whole series of cation radicals are quite consistent and in agreement with the behavior noted in our past studies[18] of metal hydride oxidation chemistry.

The one-electron oxidation of **1c–f** is seen to enhance the acidity of the respective hydrides by Δ(pK_a) = 19–20 pK_a units. This justifies the classification of these cations as *superacids*. The acidity increase is in the range of 19–25 pK_a units observed for a variety of hydrides previously.[11c,18a,c] The insensitivity of Δ(pK_a) to the nature of the metal is quite remarkable. It should be mentioned that, as in most previous cases, the Δ(pK_a) values depend on *chemically irreversible* oxidation potentials for the metal hydrides. Kinetic potential shifts have not been incorporated in the calculations, and, as a result, the Δ(pK_a) data represent *lower limits* for the acidity enhancements. The Δ(pK_a) values for **1c–f** translate to an activation of the M–H bonds toward heterolytic cleavage of 108–113 kJ/mol.

Table IV shows that the one-electron oxidation of **1c–f** leads to a decrease in the M–H BDEs of 25–33 kJ/mol. Taking into account the uncertainty introduced by the fact that E_{ox}(M$^\bullet$) and E_{ox}(M–H) were measured for chemically irreversible processes, these values are not dramatically different from the 34–46 kcal/mol differences estimated for some substituted derivatives of CpCr(CO)$_3$H.[11c]

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(27) CpMo(CO)$_3$H (66 kcal/mol): Nolan, S. P.; de la Vega, R. L.; Hoff, C. D. *J. Organomet. Chem.* **1986**, *315*, 187.

(28) CpMo(CO)$_3$H ($\leq$65 kcal/mol) and CpW(CO)$_3$H ($\leq$67 kcal/mol): Upper limits estimated at the suggestion[17] of Halpern, based on published activation parameters[29] for H$^\bullet$ transfer rates from the hyrides to conjugated alkenes.

The relative magnitudes of the heterolytic bond activation, $-\Delta\Delta G°_{het} = -2.301RT\Delta(pK_a)$, and the homolytic activation, $-\Delta\Delta G°_{hom} = -\Delta(\text{BDE})$, confirm the findings[11c] reported by us previously: The oxidation of metal hydrides activates the M–H bond toward heterolytic cleavage to a much greater extent than toward homolytic cleavage. We have shown that this may be readily understood from the thermochemical cycles involved. The definitions of $\Delta\Delta G°_{het}$ and $\Delta\Delta G°_{hom}$ and a rearrangement of eqs 6 and 8 lead to eq 9, which simply states that the heterolytic activation exceeds the homolytic activation when $E_{ox}(M^•) > E_{ox}(M^-)$. This condition should generally be fulfilled because the electron-rich, 18-electron anion M^- should be more readily oxidized than the electron-deficient, 17-electron radical $M^•$ unless significant structural changes occur as a consequence of the oxidation of M^-.[30]

$$\Delta\Delta G°_{het} - \Delta\Delta G°_{hom} = F[E_{ox}(M^-) - E_{ox}(M^•)] \qquad (9)$$

The rather modest activation of the M–H bond toward homolytic cleavage[31] may be understood in terms of simple MO arguments. The oxidation of the 18-electron hydride removes an electron from the HOMO which (for these d^4 metals) must be mostly metal d in character, and therefore little reduction in the M–H bond order results from the removal of one electron from this orbital. Equation 8 shows that $\Delta\Delta G°_{hom} < 0$, signifying a bond-weakening effect, if $E_{ox}(M\text{–}H) > E_{ox}(M^•)$. The metal hydrides M–H that have been investigated are formally M(II), whereas the radicals $M^•$ are M(I). Following a simple oxidation-state formalism, M(I) is expected to be more readily oxidized than a closely related M(II), and as a result, $\Delta\Delta G°_{hom}$ attains a negative value, however rather modest in magnitude.

The oxidation of metal hydrides frequently has led to formation of products that could arise from H^+ or $H^•$ transfer reactions from cation radicals.[18,32] The data presented in this study and in our previous communication[11c] help to resolve this dichotomy and suggest that H^+ transfer is strongly favored in these reactions, at least for thermodynamic reasons.

Concluding Remarks. We have presented extensive thermochemical data pertaining to metal–hydride bond energies in group 6 metal $TpM(CO)_3H$ complexes. Due to the electronic and/or steric properties of the Tp ligands, considerable bond weakening is observed when BDE and pK_a data are compared with available data for $CpM(CO)_3H$ analogues. The bond weakening may be understood in terms of the pronounced resistance of the $TpM(CO)_3$ against forming seven-coordinate species as a combination of steric and stereoelectronic effects. It is presently not at all clear whether similar effects will be seen for Tp derivatives of the later transition metals, which can achieve coordinative saturation with lower coordination numbers. It is our hope to address this question at some later time.

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. Ether, THF, and THF-d_8 were distilled from sodium benzophenone ketyl. The electrochemical instrumentation, cells, data handling procedures, and electrodes have been previously described.[20a,33] When used as the solvent for electrochemical experiments, acetonitrile containing 0.1 M $Bu_4N^+PF_6^-$ was passed through a column of active neutral alumina before use to remove water and protic impurities. The electrolyte was deaerated by purging with purified argon, and all electrochemical measurements were performed under a blanket of solvent-saturated argon at 298 K. ^1H NMR spectra were recorded on Varian XL-300 and Varian Gemini-200 instruments. Chemical shifts are reported in ppm relative to tetramethylsilane, with the residual solvent proton resonances as internal standards (δ 1.93 for acetonitrile-d_3; δ 1.73 for THF-d_8). Infrared spectra were obtained on a Perkin-Elmer 1310 infrared spectrophotometer.

The compounds $TpM(CO)_3^-Et_4N^+$,[7] $Tp'M(CO)_3^-Et_4N^+$,[7] $Tp'M(CO)_3^-Bu_4N^+$,[2m] $CpM(CO)_3^-Et_4N^+$,[34] (M = Cr, Mo, W), $TpM(CO)_3H$,[2a] and $Tp'M(CO)_3H$[2a] (M = Mo, W) were prepared according to published procedures.

Attempted Preparation of $TpCr(CO)_3H$ (1a). A mixture of $Cr(CO)_6$ (330 mg, 1.36 mmol) and TpNa (321 mg, 1.36 mmol) was heated in DMF at 90 °C for 20 h. The resulting solution was concentrated by vacuum transfer, and water (10% v/v) was added. The addition of $HBF_4 \cdot Et_2O$ (500 μL, ca. 3.7 mmol) at –20 °C led to the formation of a yellow precipitate. The solid was filtered and washed repeatedly with water. The remaining solid was dissolved in THF (30 mL) and filtered. The addition of water (30 mL) at 0 °C caused the formation of yellow microcrystals (221 mg, 57%). The ^1H NMR spectrum of the product (dichloromethane-d_2) revealed that the product was a ca. 5:1 mixture of **1a** (δ 8.10 (m, 3 H), 7.62 (m, 3 H), 6.26 (m, 3 H), –4.26 (s, 1 H)) and the radical $TpCr(CO)_3^•$ (**3a**; δ 3.65, –8.0, –15.7, as recently reported[2k]): IR ν_{CO}(THF) 2000, 1900 cm^{-1} (absorptions from **1a** and **3a** were not resolved).

Attempted preparations of **1b** by analogous procedures were unsuccessful.

Procedure for IR Spectroscopic Determination of Metal–Hydride Thermodynamic Acidities in Acetonitrile and THF. For the hydrides **1c** and **1e**, pK_a data were obtained by the following procedure. The Et_4N^+ or Bu_4N^+ salts of the metal anions M^- were dissolved in an acetonitrile or THF solution containing an excess of a buffer made up from known concentrations of a suitable nitrogen base (B; initial concentration $[B]_0$) and the tetrafluoroborate salt of its conjugate acid (B–H^+; initial concentration $[B\text{–}H^+]_0$). The acid–base equilibrium (eq 10) was immediately attained, and the $[M\text{–}H]/[M^-]$ ratio was measured by IR (ν_{CO}) spectroscopy, using 0.1 mm path KBr IR solution cells. $\Delta(pK_a)$, as defined by eq 11, was calculated since the buffer ratio $[B]/[B\text{–}H^+]$ was known.

$$M^- + B\text{–}H^+ \rightleftarrows M\text{–}H + B \qquad (10)$$

$$\Delta(pK_a) = pK_a(M\text{–}H) - pK_a(B\text{–}H^+) = \log([M\text{–}H][B]/[M^-][B\text{–}H^+]) \qquad (11)$$

For one of the nitrogen bases used (4-methylpyridine), the formation of the homoconjugate complex B–H–B^+ with a formation constant K_f, eqs 12 and 13, had to be taken into account.

$$B + B\text{–}H^+ \rightleftarrows B\text{–}H\text{–}B^+ \qquad (12)$$

$$[B\text{–}H\text{–}B^+] = K_f[B\text{–}H^+][B] \qquad (13)$$

The treatment of the combined equilibria is straightforward following a procedure analogous to that given by Norton and co-workers. If only M^- is added to the buffer solution (no M–H is initially added) the buffer and H^+ mass balances may be combined with eq 13 to yield eq 14, from which [B] may be extracted. $[B\text{–}H^+]$ then follows from eq 15. $[B]_{tot}$ is the total concentration of B in any form (= $[B]_0 + [B\text{–}H^+]_0$).

$$K_f[B]^2 + \{1 - K_f[B]_{tot} - 2K_f[M\text{–}H] + 2K_f[B\text{–}H^+]_0\}[B] - \{[B]_0 + [M\text{–}H]\} = 0 \qquad (14)$$

$$[B\text{–}H^+] = \{[B]_{tot} - [B]\}/\{1 + 2K_f[B]\} \qquad (15)$$

With the use of the B/B–H^+ buffer, the magnitude of K_f does not seriously affect the numerical value that is calculated for $\Delta(pK_a)$. For

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(29) Sweany, R. L.; Comberrel, D. S.; Dombourian, M. F.; Peters, N. A. *J. Organomet. Chem.* **1981**, *216*, 57.

(30) Astruc, D.; Lacoste, M.; Toupet, L. *J. Chem. Soc., Chem. Commun.* **1990**, 558.

(31) The modest homolytic bond activations found here contrasts Bordwell and Zhang's report that sizeable heterolytic *and* homolytic (typically around 150 kJ/mol for the latter) C–H bond activations occur upon oxidation of various carbon acids.[16g]

(32) (a) Klingler, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 208. (b) Detty, M. R.; Jones, W. D. *J. Am. Chem. Soc.* **1987**, *109*, 5666. (c) Westerberg, D. E.; Rhodes, L. F.; Edwin, J.; Geiger, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 1107.

(33) (a) Ahlberg, E.; Parker, V. D. *Acta Chem. Scand., Ser. B* **1980**, *B34*, 97. (b) Ahlberg, E.; Parker, V. D. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *121*, 57. (c) Tilset, M. In *Energetics of Organometallic Species*; Simões, J. A. M., Ed.; Kluwer, Academic: Dordrecht, 1992; p 109.

(34) Behrens, U.; Edelmann, F. *J. Organomet. Chem.* **1984**, *263*, 179.

the conditions used in the actual measurements the differences between calculated data when $K_f = 0$ and $K_f = 4$ amount to less than 0.6pK_a units.

For measurements on **1c** and **1e** in acetonitrile, the IR spectra indicated the presence of no other CO containing species than the particular metal hydride and its conjugate base. All measurements were performed at least three times, each time with independently prepared solutions. Δ(pK_a) data are reported as the mean value from these measurements, with the experimental uncertainty given as one standard deviation.

pK_a Determination for TpMo(CO)$_3$H (1c). $Et_4N^+TpMo(CO)_3^-$ (10.4 mg, 0.020 mmol) was dissolved in an anisidine/anisidinium (pK_a = 11.3; K_f = 0[15b]) buffer system made up from anisidine (24.6 mg, 0.20 mmol) and anisidinium tetrafluoroborate (84.3 mg, 0.40 mmol) in acetonitrile (2.0 mL) and the M–H/M$^-$ ratio was measured by IR spectroscopy. $\Delta(pK_a) = pK_a(M\text{–}H) - pK_a(B\text{–}H^+)$ was estimated to be –0.6. Measurements were repeated on independently prepared solutions with differing buffer compositions and anion/buffer concentration ratios. The combined results gave pK_a(**1c**) = 10.7 ± 0.1. The nature of the cation (Bu_4N^+ vs Et_4N^+) had no influence on the outcome. Two measurements were done analogously with an aniline/anilinium buffer (pK_a = 10.56, K_f = 0[19a]) and yielded pK_a(**1c**) = 10.8 ± 0.1.

pK_a Determination for TpW(CO)$_3$H (1e). $Et_4N^+TpW(CO)_3^-$ or $Bu_4N^+TpW(CO)_3^-$ were dissolved in a 4-methylpyridine/4-methylpyridinium buffer in acetonitrile (pK_a = 14.3;[19b] K_f is assumed to be equal to 4.0, the value reported for pyridine[19a]), and three measurements were done on independently prepared solutions. $\Delta(pK_a) = pK_a(M\text{–}H) - pK_a(B\text{–}H^+)$ was estimated to be 0.1 ± 0.1, and pK_a(**1e**) = 14.4 ± 0.1.

Measurement of the Temperature-Dependent Proton-Transfer Equilibrium between TpMo(CO)$_3$H (1c), Tp′Mo(CO)$_3$H (1d), TpMo(CO)$_3^-$ (2c), and Tp′Mo(CO)$_3^-$ (2d) in THF-d_8. An NMR tube equipped with a ground-glass joint was loaded with **1c** (4.0 mg, 0.010 mmol) and **2d**(Bu_4N^+) (10.2 mg, 0.014 mmol). THF-d_8 (0.6 mL) was added by vacuum transfer, and the tube was sealed under vacuum. ^{1}H NMR spectra showing separate signals due to **1c** (δ 8.05, 7.80, 6.28), **1d** (δ 5.89, 2.70, 2.60), **2c** (δ 7.65, 7.55, 5.99), and **2d** (δ 5.52, 2.55, 2.23) (data at –24 °C) were recorded in the temperature interval –91 to 0 °C. The relative concentrations of the species were obtained from the integration of the signals that were due to the ring protons of the Tp and Tp′ ligands. The results are summarized in the Results section.

Measurement of the Temperature-Dependent Proton-Transfer Equilibrium between TpW(CO)$_3$H (1e), Tp′W(CO)$_3$H (1f), TpW(CO)$_3^-$ (2e), and Tp′W(CO)$_3^-$ (2f) in THF-d_8. An NMR tube equipped with a ground-glass joint was loaded with **1f** (12.4 mg, 0.022 mmol) and **2e**(Bu_4N^+) (8.0 mg, 0.011 mmol). THF-d_8 (0.6 mL) was added by vacuum transfer, and the tube was sealed under vacuum. ^{1}H NMR spectra showing separate signals due to **1e** (δ 8.20, 7.88, 6.31, –2.38 at –48 °C), **1f** (δ 5.95, 2.53, 2.33, –2.42 at –48 °C), **2e** (δ 7.83, 7.62, 6.08), and **2f** (δ 5.62, 2.48, 2.27) were recorded in the temperature region –48 to +53 °C. The relative concentrations were obtained from the integration of the signals that were due to the ring protons of the Tp and Tp′ ligands. The results are summarized in the Results section. It was noted that the hydride signal of **1e**, but not that of **1f**, was temperature dependent, and this actually caused the relative positions of the two to change as the temperature increased (**1e**: δ –2.38 at –48 °C, –2.47 at 53 °C).

Attempted Measurement of the Proton-Transfer Equilibrium between TpCr(CO)$_3$H (1a), Tp′Mo(CO)$_3$H (1d), TpCr(CO)$_3^-$ (2a), and Tp′Mo(CO)$_3^-$ (2d) in THF-d_8. An NMR tube equipped with a ground-glass joint was charged with **2a**(Bu_4N^+) (10.0 mg, 0.017 mmol) and **1d** (4.7 mg, 0.010 mmol). THF-d_8 (0.6 mL) was added by vacuum transfer, and the tube was sealed under vacuum. ^{1}H NMR spectra recorded in the temperature interval –92 to –24 °C displayed separate resonances due to **1d** and **2d**, whereas only broadened resonances attributed to the Tp ligands of Cr containing species were seen. The hydride resonance of **1a** was not observable.

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