

Thermodynamic and Kinetic Studies of Hydride Transfer for a Series of Molybdenum and Tungsten Hydrides

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Abstract: The free energies for hydride donation (ΔG_{M^+}) have been determined in acetonitrile solution for a series of seven molybdenum and tungsten compounds (**1–7**) of general formula $(C_5R_5)M(CO)_2(L)H$, which yield the salts $[(C_5R_5)M(CO)_2(L)(NCMe)][BF_4]$ in these reactions. These data constitute the first thermodynamic data for hydride transfer by transition metal hydrides, and were gathered from equilibrium studies with carbenium ion salts of known hydride ion affinities in acetonitrile. The metal hydride ΔG_{M^+} values range from ca. 79 to 89 kcal/mol, and these values may be compared with pK_{as} for related compounds to demonstrate that proton-transfer processes are somewhat more sensitive to changes in co-ligands than are hydride transfer processes. Additionally, kinetic studies of hydride transfer reactions with hydride acceptor $[(p\text{-MeOPh})_2CPh][BF_4]$ exhibit second-order rate constants ranging from ca. 200 to 7500 $M^{-1} s^{-1}$. These rates show a correlation with thermodynamic driving force, and a Brønsted plot yields a slope of 0.20. The thermodynamic data may be used in conjunction with the appropriate thermodynamic cycles to calculate energies for various processes in which compounds such as **1–7** are known to function as hydride donors.

Introduction

Transition metal hydrides are key components of a variety of synthetic transformations and catalytic schemes, during which they serve to insert unsaturated species¹ or donate a hydride to an appropriate electrophile.² As such, a quantitative understanding of the kinetics and thermodynamics of hydride transfer reactions is of obvious significance. In fact, however, relatively little information is available on the energetics of hydride transfer. In an early study, efforts were made to establish a relative scale based on rates of acetone insertion; this led to the conclusion that kinetic hydricity decreased in the order $Cp_2ZrH_2 > Cp_2NbH_3 > Cp_2Nb(CO)H > Cp_2MoH_2$.³ Years later, Bursten calculated the HOMO-LUMO gaps for species such as $CpCr(CO)_3^-$ and $CpCr(NO)_2^-$ and showed that this approach could be used to predict relative tendencies for hydride and proton donation by the parent metal hydride.⁴ Ground-state effects have also been studied with the calculation of deuterium quadrupole coupling constants, which were used to assign ionic character ($M^+ H^-$) to transition metal hydrides.⁵ Finally, Bullock

has recently reported a series of kinetic studies for hydride transfer in methylene chloride,⁶ and these studies constitute the most complete determination of kinetic hydricity yet available.

Thermodynamic information on hydride transfer reactions is considerably more rare, and a recent review points out the complete lack of quantitative data.^{3b} The fundamental quantity needed here is the free energy for hydride donation (ΔG_{M^+}), as defined in eq 1. Clearly any such reaction of an 18 electron



metal hydride would yield a 16 electron cation; in a reaction of L_nMH with a hydride acceptor, the metal-containing product would bind a solvent molecule so as to relieve the electron deficiency. As such, the thermodynamic determination would be unique for the solvent chosen, but, of course, this is also true with proton-transfer studies. Solvent effects in pK_a determinations are usually dominated by proton solvation terms;⁷ in the case of hydride transfer it is clear that hydride solvation is less significant,⁸ and solvation of the 16 electron metal cation will dominate. It is, in principle, possible to derive ΔG_{M^+} from the acidity (pK_a) of the metal hydride by using the appropriate thermodynamic cycle. In this approach it would prove necessary to determine the redox potential of the M^+/M^* couple; this determination may be complicated by the kinetics of solvent

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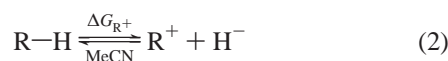
Table 1. Infrared Data for Hydrides and Cationic Acetonitrile Adducts in Acetonitrile Solution

metal hydride	hydride ν_{CO} (ϵ^a)	cation ν_{CO} (ϵ^b)
CpMo(CO) ₃ H (1)	2010 s, 1925 vs ^c	2074 (610), 1986 (1551)
Cp [*] Mo(CO) ₃ H (2)	2009 (2086), 1918 (3167) ^d	2060 (1257), 1975 (2236)
(C ₅ H ₄ CO ₂ Me)W(CO) ₃ H (3)	2026 (1262), 1932 (2606)	2075 (1112), 2059 (1685)
CpW(CO) ₃ H (4)	2008 (1780), 1915 (3420) ^e	2068 (1269), 1974 (2831)
Cp [*] W(CO) ₃ H (5)	2005 (1935), 1910 (2796)	2052 (639), 1974 (1781)
CpMo(CO) ₂ (PPh ₃)H (6)	1934 (1482), 1854 (1693)	2001 (1708), 1917 (2271)
CpMo(CO) ₂ (PMe ₃)H (7)	1927 (1838), 1842 (2429)	1992 (694), 1904 (2060)

^a Metal hydride CO stretching frequencies (cm^{-1}), extinction coefficients (ϵ) in $\text{M}^{-1} \text{cm}^{-1}$. ^b CO stretching frequencies (extinction coefficients) for cations in salts $[\text{L}_n\text{M}(\text{NCMe})][\text{BF}_4]$. ^c Data from ref 14d. ^d Data from ref 14a.

loss from M^+ and is often precluded by the rapidity with which metal radicals dimerize ($k \geq 10^6 \text{ M}^{-1} \text{ s}^{-1}$).⁹

In the current work we have chosen to measure thermodynamic hydricities directly. Parker¹⁰ and Arnett¹¹ have recently described studies designed to determine ΔG_{R^+} for a series of organic molecules RH (eq 2).



We have subsequently used a related approach to expand the list of known organic hydride acceptors, and we now have available a series of isolable carbenium ion salts for which ΔG_{R^+} spans the range 60–99 kcal/mol.¹² Herein we describe the use of this indicator series to gather both thermodynamic and kinetic information on hydride transfers involving a series of molybdenum and tungsten compounds. This allows for (a) a comparison of the energetics of proton and hydride transfer for a series of metal hydrides and (b) the correlation of thermodynamic and kinetic hydricities by way of a Brønsted analysis; while this has been done for organic hydride transfers using NADH analogues¹³ and for *proton* transfer involving metal hydrides,¹⁴ this is the first such study of hydride transfer by transition metal hydrides.

Results and Discussion

The molybdenum and tungsten hydride compounds $(\text{C}_5\text{R}_5)\text{M}(\text{CO})_2(\text{L})\text{H}$ ($\text{L} = \text{CO}, \text{PR}_3$; $\text{R} = \text{H}, \text{Me}$) are known to react with triphenylcarbenium tetrafluoroborate (Ph_3CBF_4) to give

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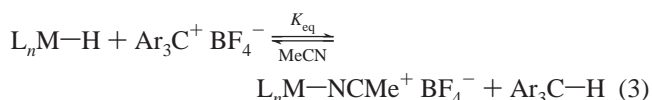
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smooth hydride transfer reactions.¹⁵ In methylene chloride solution it has been shown that the products of such a reaction are the fluoroborate complexes $(\text{C}_5\text{R}_5)(\text{CO})_2(\text{L})\text{M}-\text{F}-\text{BF}_3$.^{6,15} This reaction has been used for the kinetic studies mentioned above,⁶ but these ion-paired products are not suitable for the thermodynamic studies contemplated here. The thermodynamic methodology involves establishing an equilibrium between the metal hydride of interest and an appropriate carbenium ion. This



requires a carbenium ion whose equilibrium partner (Ar_3CH) is comparable to the unknown metal hydride in hydride donor power. Once the appropriate indicator is identified, equilibrium is established (eq 3) and ΔG_{rxn} is determined from K_{eq} . Since $\Delta G_{\text{rxn}} = \Delta G_{\text{M}^+} - \Delta G_{\text{R}^+}$ and ΔG_{R^+} is known for the indicators, ΔG_{M^+} may be calculated. The search for the appropriate indicator also confirms that a weaker acceptor Ar_3C^+ is ineffective, and that a stronger acceptor drives the equilibrium completely to the product side. Thus, these bracketing studies serve as a secondary confirmation of the equilibrium results.

Thermodynamic Studies. The determination of K_{eq} (eq 3) involves monitoring the metal hydride and cationic acetonitrile complex concentrations by infrared spectroscopy. The equilibrium constant (K_{eq}) is determined from the intensities of the metal–carbonyl stretches in the infrared spectrum. These are strong bands, and serve as convenient probes of solution concentrations; the intensities were observed to obey Beers law, and band positions and extinction coefficients are presented in Table 1. All of the resulting ΔG_{M^+} values are the result of at least three equilibrium determinations, and they are presented in Table 2 along with the indicator used and its ΔG_{R^+} value; the relative uncertainties in the measurements are small (less than 0.5 kcal/mol), but the absolute errors depend on the accuracy of the thermodynamic cycles used to determine ΔG_{R^+} for the indicator. These uncertainties are probably on the order of ca. 1–2 kcal/mol. In two of the compounds, **6** and **7**, there exists the possibility for cis–trans isomerism in the metal hydride and the cationic product. Bullock has established that the trans isomers react more rapidly with Ph_3CBF_4 than do the cis isomers (in CH_2Cl_2),⁶ and his kinetic data are reported for the trans isomers. In the present thermodynamic studies, it is necessary to consider the consequences of the cis–trans equilibrium. Fortunately, this process is well-characterized; for CpMo(CO)₂(PMe₃)H (**7**) the trans-to-cis conversion exhibits a ΔG° value of –0.11 kcal/mol,¹⁶ and for CpMo(CO)₂(PPh₃)H

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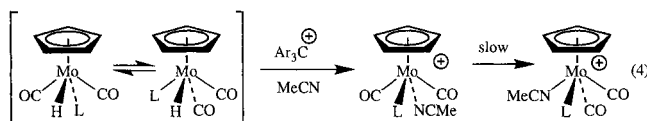
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Table 2. Thermodynamic Data for Hydride Transfer Reactions

metal hydride	indicator ($\Delta G_{R^+}^a$)	ΔG_{rxn}^b	$\Delta G_{M^+}^c$
CpMo(CO) ₃ H (1)	(<i>p</i> -MeOPh) ₂ PhC ⁺ (89.3)	-0.7 ± 0.3	88.6
Cp*Mo(CO) ₃ H (2)	(<i>p</i> -MeOPh) ₃ C ⁺ (86.1)	-1.4 ± 0.1	84.7
(C ₅ H ₄ CO ₂ Me)W(CO) ₃ H (3)	(<i>p</i> -MeOPh) ₃ C ⁺ (86.1)	-1.1 ± 0.1	85.0
CpW(CO) ₃ H (4)	(<i>p</i> -MeOPh) ₃ C ⁺ (86.1)	-2.9 ± 0.5	83.2
Cp*W(CO) ₃ H (5)	(<i>p</i> -Me ₂ NPh)Ph ₂ C ⁺ (82.9)	-1.5 ± 0.2	81.4
CpMo(CO) ₂ (PPh ₃)H (6)	(<i>p</i> -Me ₂ NPh)Ph ₂ C ⁺ (82.9)	-1.2 ± 0.5	81.7
CpMo(CO) ₂ (PMe ₃)H (7)	(<i>p</i> -Me ₂ NPh)Ph ₂ C ⁺ (82.9)	-3.5 ± 0.1	79.4

^a As the BF₄ salts. ΔG_{R^+} values (in kcal/mol) are from ref 12. ^b In kcal/mol, with uncertainties reflecting the spread in three or more determinations. ^c In kcal/mol.

(**6**) the corresponding value is -0.3 kcal/mol.¹⁷ These energy differences are smaller than the estimated uncertainties in the ΔG_{R^+} data, and may be neglected. In addition, Tilset has studied the product complexes and shown that *trans*-[CpMo(CO)₂(PR₃)-(NCMe)]⁺ is the kinetic product of hydride transfer; this *trans* isomer subsequently isomerizes to the thermodynamic *cis* isomer (in acetonitrile solution) over a period of several hours (*t*_{1/2} = 44 h at 25 °C); the overall process is summarized in eq 4.¹⁸



Since the hydride transfer reactions (eq 3) come to equilibrium in a matter of minutes (or less, *vide infra*) at 25 °C, we are observing only production of the *trans* cation isomer. In summary, then, since the starting material isomerization is rapid, the *cis/trans* energy differences are small, and only a single product isomer results, isomerism will have no measurable effect on the equilibrium studies; it is thus impossible to attribute the resulting ΔG_{M^+} value to a particular metal hydride isomer (in **6** and **7**), even though we are observing production of the *trans* product.

The ΔG_{M^+} data resulting from the aforementioned studies reside well within the range of indicators available (ΔG_{R^+} ca. 60–99 kcal/mol), spanning a range of ca. 10 kcal/mol (Table 2). A series of comparisons establishes a number of points. First, a consideration of substituent effects shows, as expected, that addition of donor co-ligands facilitates hydride loss. Hence, for the series of molybdenum compounds **1**, **6**, and **7**, hydride donor energy decreases across a series L = CO > PPh₃ > PMe₃. This is consistent with the ability of the donor co-ligand to aid in stabilizing the electron-deficient metal center. These differences, which range over 9 kcal/mol, may be compared with the energetic differences for *proton* transfer reactions. In this latter case, a related series of tungsten analogues (with identical ligand spheres) exhibits *pK_a*s ranging from 16.1 (L = CO) to 26.6 (L = PMe₃).^{14c} This corresponds to an energy difference ($\Delta\Delta G = 1.37 \Delta pK$) of ca. 14 kcal/mol, indicating that the proton transfer equilibria are roughly 1.5 times as sensitive to changes in co-ligand donor power. Similarly, both molybdenum and tungsten compounds exhibit the expected differences in Cp analogues; hydridicities increase in the order C₅H₄CO₂Me < Cp < Cp*. Notably, the Cp* co-ligands favor hydride transfer by ca. 2–4 kcal/mol relative to the Cp derivatives. This may again be compared to the acidity difference (Cp* vs Cp), which varies by 4.4 kcal/mol for (C₅R₅)Mo(CO)₃H.^{14c} Once again, the proton transfer reaction is slightly more sensitive to co-ligands than is

hydride transfer. These ligand effects on proton transfer have also been seen in the protonation enthalpies for iridium compounds; here the enthalpy difference for protonation of Cp*Ir(CO)₂ and Cp*Ir(CO)(PMe₃) is 16.6 kcal/mol, and the difference for Cp*- and CpIr(CO)(PMe₃) analogues is 4.8 kcal/mol.¹⁹

Why is proton transfer more sensitive to variations in co-ligands than is hydride transfer? Our interpretation of this consistent pattern is based on metal electron count and the nature of the ion transfer reactions. Proton transfer gives rise to an 18 electron conjugate base; this would undoubtedly exhibit some adjustment in the general solvation sphere, but this is expected to make a reasonably small contribution to the overall solvation energy. Indeed, solvation of the proton is liable to dominate the energetics of solvation in this case.⁷ Conversely, hydride transfer generates a 16 electron species that must be captured by a solvent molecule; the ligated solvent molecule provides electron density to stabilize the cationic metal center, and serves to moderate the effect resulting from changes in co-ligands.

A final, obvious, comparison involves the two metals. For both Cp*M(CO)₃H (**2** and **5**) and CpM(CO)₃H (**1** and **4**), the tungsten center functions as a better hydride donor; energy differences ($\Delta\Delta G_{M^+}$) are 5.4 (Cp) and 3.3 kcal/mol (Cp*). This is consistent with the general pattern of metal basicities, which typically increase down a transition block column.²⁰ For acidity studies in MeCN, the corresponding differences (Mo vs W) are 3.0 (CpM(CO)₃H *pK_a*) and 1.8 kcal/mol (enthalpy of protonation leading to [M(CO)₂(dppm)₂H]⁺).¹⁹ The energetic differences between molybdenum and tungsten appear comparable for hydride and proton transfer, but more studies are needed to test this suggestion.

The overall comparison of hydridicity and acidity is illustrated in Figure 1, which shows the free energies for hydride loss and proton loss for compounds **1**, **4**, and **7**. In the latter case, the *pK_a* is not available, so we have estimated it from the acidity of the known tungsten analogue CpW(CO)₂(PMe₃)H (*pK_a* = 26.6 in MeCN); the comparison of **1** and **4** and their radical cations suggests a difference of ca. 3 in *pK_a*, so we assume a *pK_a* value of ca. 24 for **7**. The *pK_a* data were converted to free energies (= 1.37 *pK_a*), and the ΔG° values for hydride and proton transfer are drawn to scale in Figure 1. The energy difference for the two processes drops from 70 (for **1**) to 47 kcal/mol (for **7**) across this series.

Kinetics of Hydride Transfer. The molybdenum–tungsten comparison is an interesting one, particularly when one considers kinetic data for hydride transfer. Bullock's studies of the reaction between metal hydrides and Ph₃CBF₄ in methylene chloride show that tungsten hydride transfer is slow relative to molyb-

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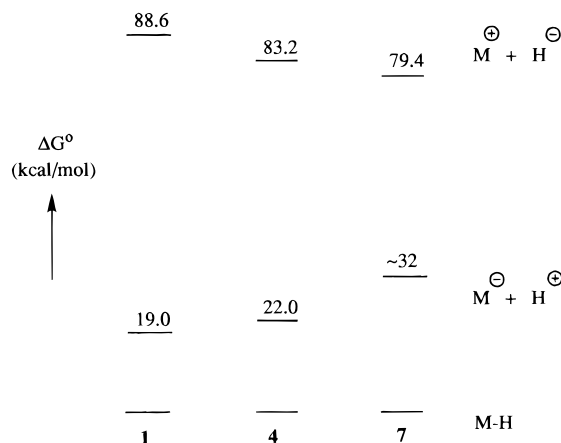


Figure 1. Free energy differences for proton loss and hydride loss from **1**, **4**, and **7**. The energy of proton loss from **7** was estimated from the tungsten analogue; see text (the energies of the parent hydrides were arbitrarily assumed to be equal so as to establish a baseline for comparison of relative energies).

denum hydride transfer.⁶ This kinetic trend does not appear to reflect thermodynamic hydride donor strength (Table 2), so we compared hydride-transfer rate constants (Table 3)⁶ and driving forces to look for any apparent correlation. This was done by plotting $\ln(k)$ vs ΔG_{M^+} , and the resulting plot is shown in Figure 2. Note that acetonitrile thermodynamic data are used as an *approximate* indicator of driving force for these methylene chloride reactions; previous work has shown that hydride transfer thermodynamics are relatively insensitive to solvent.⁸ Nonetheless, the two processes under consideration here are very different; although both equilibria involve loss of hydride, they differ in that one involves addition of an acetonitrile ligand and the other involves addition of BF_4^- anion. Tilset has estimated that the acetonitrile bond to $\text{CpM}(\text{CO})_3^+$ is worth ca. 32 kcal/mol,²¹ so this makes a significant contribution to the thermodynamics we measure in that solvent. As such, our acetonitrile data are not a reasonable measure of ΔG_{M^+} in methylene chloride. However, we have carried out a few bracketing studies in this solvent, and these suggest that the trend in *relative* ΔG_{M^+} for **1–7** is similar to that in acetonitrile. Hence, we have used the relative thermodynamic data to look for a correlation with kinetic data in methylene chloride. The resulting plot (Figure 2) shows that good, but separate, correlations exist for the two metal series. We do not attribute any theoretical significance to the slopes, but the correlation within the two metal series is quite clear. In an effort to gather kinetic data for direct comparison, we initiated a study of hydride transfer reactions (eq 3) in MeCN solution; the acceptor in these studies was (*p*-MeOC₆H₄)₂(Ph)CBF₄. We chose this acceptor because it is known to be considerably more stable in acetonitrile than is Ph_3CBF_4 ,²² and in an effort to diminish the thermodynamic driving force and (perhaps) slow the kinetics. Nonetheless, most reactions were sufficiently rapid as to require stopped-flow methods. The reactions were studied by monitoring the loss of (*p*-MeOC₆H₄)₂(Ph)CBF₄ (λ 496 nm), and pseudo-first-order conditions were employed ($[\text{MH}]_0 \geq 10[(\text{p-MeOC}_6\text{H}_4)_2(\text{Ph})\text{CBF}_4]_0$). All reactions exhibited good first-order decays through 3–4 half-lives. The resulting second-order rate constants were derived from at least three determinations, and the tabulated values (Table 3) are given with uncertainties reflecting the relative variations in these multiple runs. From these data it

becomes apparent that the molybdenum and tungsten hydrides fit the same linear Brønsted plot²³ (Figure 3, $r^2 = 0.94$). The α value is commonly used to characterize the position of the transition state along the reaction coordinate. This analysis can fail, and transition state imbalances²⁴ and solvent reorganization effects²⁵ have been observed to complicate these interpretations. However, the hydride transfer reactions studied here are significantly exothermic (ΔG_{rxn} ranges from -0.7 to -9.9 kcal/mol, Table 3), so the calculated α value of 0.20 seems entirely reasonable. Finally, we note that the good correlation of rate and driving force suggests that steric factors do not play a significant role in the reactions of **1–7**, since phosphine derivatives **6** and **7** show no tendency to deviate from the linear trend (Figure 2); this is probably the result of a kinetic preference for reaction of the trans isomers, as has been suggested for studies in methylene chloride.⁶

There are two differences apparent in the kinetic data sets from the two solvents. First, the reactions run in acetonitrile are faster, when allowance is made for driving force. The hydride transfer reaction between $\text{CpMo}(\text{CO})_3\text{H}$ (**1**) and Ph_3C^+ is exothermic by 10.5 kcal/mol and exhibits a rate constant of $380 \text{ M}^{-1} \text{ s}^{-1}$ in CH_2Cl_2 .⁶ The reaction between $\text{CpMo}(\text{CO})_2(\text{PMe}_3)\text{H}$ (**7**) and (*p*-MeOC₆H₄)Ph₂C⁺ exhibits a similar driving force, and is exothermic by 9.9 kcal/mol; however, the rate of this latter process in acetonitrile is $7500 \text{ M}^{-1} \text{ s}^{-1}$ (Table 3). An obvious explanation for this solvent difference is based on ion-pairing effects, since the starting material $\text{Ar}_3\text{C}^+\text{BF}_4^-$ is ion paired in CH_2Cl_2 . This should translate into a diminished reactivity for the carbenium ion center, which must accommodate interactions with both the counterion and the metal hydride during hydride transfer. The second obvious difference concerns the relative rates of the molybdenum and tungsten systems. As noted above, the tungsten compounds exhibit slow (relative to molybdenum) hydride transfer in methylene chloride solution.⁶ However, the data obtained herein suggest that this is not the case in acetonitrile; the comparison of rate and driving force (Figure 2) shows no evidence for an inherent reactivity difference for the two metals. Nor is there evidence in favor of an electron-transfer mechanism; it has been determined that such a process would be highly endothermic for the reactions of **1–7** with Ph_3C^+ ,⁶ and the reactions with (*p*-MeOC₆H₄)Ph₂C⁺ would be ca. 0.2 V more endothermic.¹² It is well-established that second-row transition metals undergo dissociative reactions more rapidly than do the first or third row congeners;²⁶ in the case of group VI, conversion of $\text{M}(\text{CO})_6$ to $\text{M}(\text{CO})_5(\text{PPh}_3)$ exhibits first-order rate constants (130 °C) 1.4×10^{-4} (Cr), 2.0×10^{-3} (Mo), and $4.0 \times 10^{-6} \text{ s}^{-1}$ (W).^{25,27} The hydride transfer reactions in methylene chloride would generate a 16 electron cation, a process that should, by analogy with other dissociative reactions, proceed only slowly for tungsten. Tilset has suggested that hydride transfer from **1** and derivatives involves production of the 16 electron cation, which is stereochemically rigid and is subsequently trapped by acetonitrile solvent.¹⁸ The kinetic results described here suggest a more aggressive role for acetonitrile; in view of the greater extent to which tungsten hydride transfer

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Table 3. Thermodynamic and Kinetic Data for Reactions with Carbenium Ions in Methylene Chloride or Acetonitrile

metal hydride	[(<i>p</i> -MeOPh) ₂ CPh][BF ₄]/CH ₃ CN		
	[Ph ₃ C][BF ₄]/CH ₂ Cl ₂ <i>k</i> (M ⁻¹ s ⁻¹) ^a	Δ <i>G</i> _{rxn} ^b	<i>k</i> (M ⁻¹ s ⁻¹) ^c
CpMo(CO) ₃ H (1)	380	-0.7	210(20)
Cp*Mo(CO) ₃ H (2)	6500	-4.6	810(20)
(C ₅ H ₄ CO ₂ Me)W(CO) ₃ H (3)	0.77	-4.3	1300(200)
CpW(CO) ₃ H (4)	76	-6.1	1200(200)
Cp*W(CO) ₃ H (5)	1900	-7.9	1450(150)
CpMo(CO) ₂ (PPh ₃)H (6)	5.7 × 10 ⁵	-7.6	2450(250)
CpMo(CO) ₂ (PMe ₃)H (7)	4.6 × 10 ⁶	-9.9	7500(400)

^a Second-order rate constants for reaction with [Ph₃C][BF₄] in methylene chloride; data from ref 6. ^b In kcal/mol, calculated from the values for Δ*G*_{M⁺} and a value of 89.3 kcal/mol for the Δ*G*_{R⁺} for (*p*-MeOPh)₂PhC⁺ ion (ref 12). ^c Second-order rate constants for reaction in MeCN. Uncertainties given in parentheses reflect the spread in three experimental determinations.

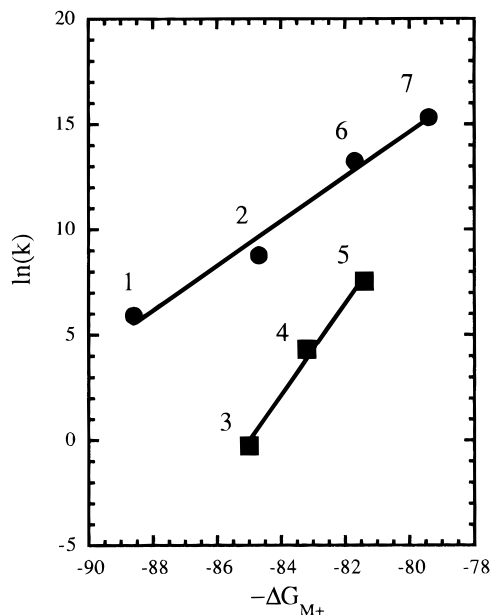


Figure 2. Plot of ln *k* vs Δ*G*_{M⁺} for reactions of 1–7 with [Ph₃C][BF₄]. Kinetic data are from ref 6 and were determined in methylene chloride solution. Equilibrium data are from acetonitrile studies (see text).

is affected by the change in solvents, we infer that hydride transfer and acetonitrile binding occur simultaneously, or before separation of the activated complex.

Applications of Thermodynamic Data. The quantities determined herein allow us to perform a thermodynamic analysis of some ionic process known to involve molybdenum or tungsten hydrides. In one such case, compounds 1 and 4 have been reported to induce ionic hydrogenation of alkenes in the presence of triflic acid; the latter was chosen because of the exceptionally poor nucleophilicity of the triflate anion, and the chemistry proceeds readily in methylene chloride solution.²⁸ We cannot assess the energetic contribution of the ion-pairing processes that occur in this solvent, but we can consider the overall reaction in acetonitrile. The proposed mechanism may be broken down into individual steps, as shown in Scheme 1 for styrene; the overall reaction is the sum of the three steps shown, and we make the assumption that acetonitrile is able to solvate the tungsten cation and triflate anion to the extent that they are not ion paired. It has been shown that, while 4 is partially protonated by triflic acid, the hydrogenation process involves the remaining free 4. In addition, 4 does not react with the alkene, so alkene protonation is therefore thought to occur

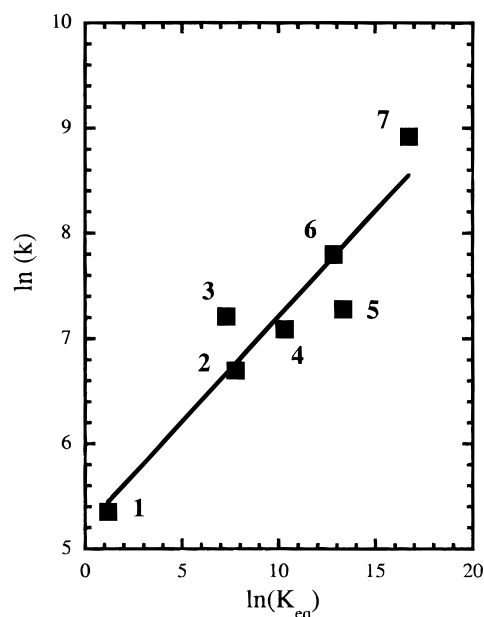
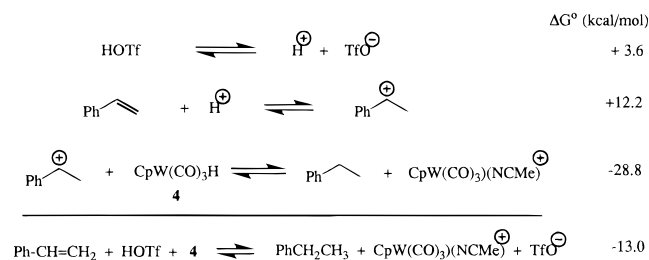


Figure 3. Bronsted plot (ln *k* vs ln *K*_{eq}) for reactions of 1–7 with [(*p*-MeOC₆H₄)₂PhC][BF₄] in acetonitrile (Table 1).

Scheme 1



before involvement of the metal hydride in the hydrogenation chemistry.²⁷ This protonation leads to a carbenium ion, which abstracts a hydride from the metal center. Obviously this latter step is conceptually similar to the reactions carried out to determine Δ*G*_{M⁺}.

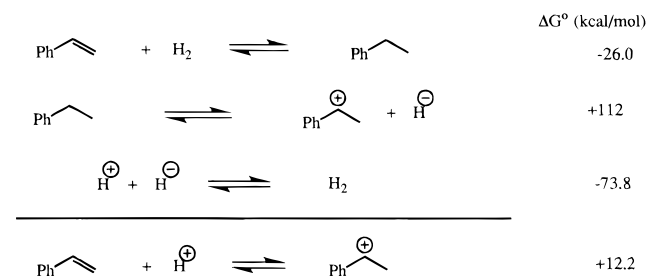
Triflic acid is known to have a *pK*_a of 2.60 in acetonitrile,²⁹ and the corresponding energy for the deprotonation step is (1.37 *pK*_a) + 3.6 kcal/mol. The energy for the second step in Scheme 1 was estimated from free energies of formation and solvation data (Scheme 2). Styrene exhibits a free energy of hydrogenation of -26.0 kcal/mol;³⁰ this involves the conversion of liquid styrene to liquid ethylbenzene, but the solvation energies of the

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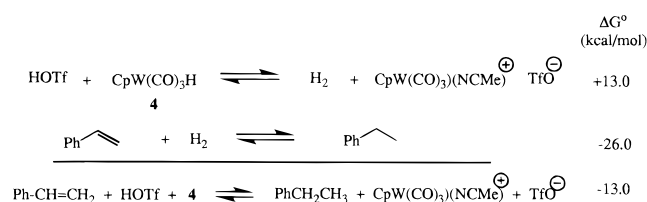
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Scheme 2



Scheme 3



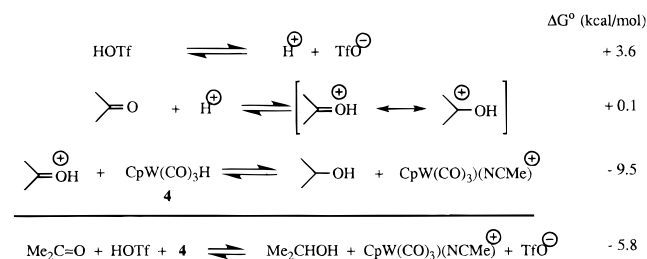
two are liable to be small (ca. 1 kcal/mol) and should cancel with very little error.³¹ We do not have an exact determination for the hydride donor power of ethylbenzene, but ΔG_R^+ is known for toluene (118 kcal/mol) and diphenylmethane (105 kcal/mol).¹⁰ We expect the number for ethylbenzene to fall between these, and we estimate 112 ± 2 kcal/mol for this process. Finally, standard potentials may be used to calculate the free energy for combination of hydride and proton in acetonitrile (-73.8 kcal/mol).³² These three reactions constitute the thermodynamic cycle for calculation of the MeCN solution proton affinity of styrene, the energy of which is thus calculated to be (-26.0 + 112 + (-73.8)) 12.2 kcal/mol. The data are combined in Scheme 2, in which all species are in acetonitrile; it includes a value of 6.6 kcal/mol for the solvation of molecular hydrogen,³¹ but this term cancels and is of no practical consequence in the final result. The overall hydrogenation reaction (Scheme 1) is comfortably exothermic for **4**, and would exhibit an overall reaction free energy of -7.6 kcal/mol for **1**; the difference reflects the greater energy associated with hydride donation by **1** (relative to **4**, Table 2).

As a check on the energy calculated in Scheme 1, we may also recognize a related thermodynamic cycle. This is represented in Scheme 3, which depicts the production of hydrogen from a reaction between hydride donor (**4**) and proton source. The second step of this cycle is simply the hydrogenation of styrene. Clearly the overall process here is the same as that in Scheme 1, so the net energies (-13.0 kcal/mol) should be the same. However, this approach points out another possible use of the ΔG_{M^+} data; these may be used to calculate the protonolysis energy, or the hydricity of **1-7** toward a proton. The protonolysis energy calculated in Scheme 3 (+13.0 kcal/mol) comes from the dissociation of triflic acid (+3.6 kcal/mol),²⁸ hydride donation by **4** (83.2 kcal/mol, Table 1), and a combination of hydride and proton to make dihydrogen (Scheme 2, -73.8 kcal/mol);³¹ a related approach for **1** yields a protonolysis energy of +18.4 kcal/mol. Ultimately, data such as these will prove useful in studies of metal hydride protonation and subsequent H₂ elimination from the cationic dihydrogen complex

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Scheme 4



or classical dihydride; for now, such studies await pK_a data for other protonation equilibria. In addition, the protonolysis data will prove useful in selecting candidates for other ionic hydrogenations; reaction with proton source (when accompanied by H₂ loss) constitutes an unwanted side reaction, which should be sufficiently endothermic so as to allow the desired reaction to proceed. This point will be discussed further below.

A related ionic hydrogenation has been reported for ketones,³³ and compounds **1** and **4** have been used for this application as well. In this reaction, treatment of acetone with a mixture of triflic acid and either **1** or **4** yields 2-propanol. The reaction may be considered in stepwise fashion (as above) by using the thermodynamic cycle given in Scheme 4. The pK_a of protonated acetone is -0.1 in acetonitrile,³⁴ so protonation of the ketone has a ΔG° (-1.37 pK_a) of only +0.1 kcal/mol. The third step of Scheme 4 involves reaction of **4** with protonated ketone, and the free energy of this step requires an estimate of the energy associated with hydride addition to protonated ketone. There are no data available for such a process, so we used an approach similar to that employed in Scheme 2; in this way one may determine the free energy of hydrogenation of acetone in acetonitrile. This calculation involved the use of free energies of formation,³⁵ from which a ΔG° value of -12.1 kcal/mol results. It is *not* appropriate to assume that solvation energies for acetone and 2-propanol will cancel, and we have used the data of Parker³⁶ and Wayner³⁷ to estimate a differential solvation free energy of 6.7 kcal/mol favoring solvation of the alcohol. This correction leads to a ΔG° value of -18.8 kcal/mol for the hydrogenation of acetone in acetonitrile. By analogy with Scheme 2, this allows us to calculate a value of -9.5 kcal/mol for the hydride transfer step in Scheme 4; this is comprised of contributions from hydride addition to protonated acetone (-92.7 kcal/mol) and hydride donation by **4** (+83.2 kcal/mol). The ketone hydrogenation reaction has a ΔG° of -5.6 kcal/mol, and is considerably less exothermic than is alkene hydrogenation; the difference reflects the fact that the C=O π bond is stronger than is the C=C π bond (as judged by hydrogenation energies). We calculate that the analogous reaction with **1** exhibits a ΔG° of only -0.4 kcal/mol; however, we note that these calculations are for acetonitrile solution, and the reaction in methylene chloride may be driven by ion pairing or complexation effects. Indeed, the first product from this reaction is an alcohol complex [CpW(CO)₃(HOR)][OTf], and

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this converts slowly to free alcohol and the triflate complex $\text{CpW}(\text{CO})_3(\text{OTf})$ in methylene chloride.³²

We noted earlier that the protonolysis reaction between metal hydride and HOTf constitutes an unwanted side reaction, one that competes with the desired protonation of the alkene. In Scheme 1 we estimated that alkene protonation is unfavorable, with a free energy of +12.2 kcal/mol. From thermodynamic considerations, then, only hydrides exhibiting a protonolysis energy higher than ca. 13–15 kcal/mol should be suitable for ionic hydrogenation of alkenes. If we accept this 2 kcal/mol range as the border region, this expectation is met. Compounds **1** (18.4 kcal/mol), **2** (14.5 kcal/mol), **4** (13.0 kcal/mol), and **6** (11.5 kcal/mol) exhibit the protonolysis energies indicated in parentheses; of these, **1** and **4** are effective in alkene hydrogenation and **2** and **6** are ineffective because of exclusive protonolysis.²⁷ The uncertainty in the range 13–15 kcal/mol presumably reflects the fact that any uphill process may be driven by a favorable following reaction; the reactivity path in this intermediate range likely depends on kinetic, rather than thermodynamic, factors. A different situation holds for ketone hydrogenation (Scheme 4). In this reaction protonation of the ketone is always favored by several kcal/mol over metal hydride protonolysis. The key thermodynamic question here is whether the hydride has sufficient donor power to reduce the protonated ketone. Compound **1** is able to support this reaction and it is the weakest donor of the compounds studied here; presumably all would function successfully in this reaction.

Conclusion

We have reported the first systematic study of the thermodynamics of hydride transfer involving transition metal hydrides. As would be expected for the cationic nature of the product, this reaction is facilitated by donor co-ligands (phosphine vs carbonyl and C_5Me_5 vs C_5H_5 vs $\text{C}_5\text{H}_4\text{CO}_2\text{Me}$); similarly, the 5d tungsten systems are more susceptible (thermodynamically) to hydride transfer than are the 4d molybdenum systems. The energies involved in hydride transfer in acetonitrile (ΔG_{M^+}) are considerably higher (79–90 kcal/mol) than are those seen for proton transfer in the same solvent (ca. 22–35 kcal/mol).¹⁴ A comparison of the two reactions shows that co-ligand effects in proton transfer show the opposite trend, since the product anions are destabilized by donors. However, it is interesting to note that, while proton transfer is less endothermic than hydride transfer, it is ca. 1.5 times as susceptible to variations in co-ligand electronic properties. These thermodynamic data also constitute a means for assessing driving force and the origin of kinetic factors associated with hydride transfer. We conclude that the slow hydride transfer seen for tungsten compounds **3–5** in methylene chloride is not the result of thermodynamic factors, but probably reflects the diminished capacity of this solvent (relative to acetonitrile) to stabilize the unsaturated intermediate.

Experimental Section

General Considerations. All manipulations involving metal complexes were carried out under an atmosphere of nitrogen that was first passed through activated BTS catalyst and molecular sieves. Standard Schlenk techniques were used to handle solutions,³⁸ and solids were transferred in a Vacuum Atmospheres Corp. glovebox under purified nitrogen. NMR spectra were obtained on a Varian Gemini 300 FT-NMR instrument, infrared spectra on a Perkin-Elmer Model 1600 FT-IR spectrophotometer, and UV–vis data on a Hewlett-Packard 8451 diode array spectrophotometer. Kinetic data were obtained with a

Durrum model D110 stopped-flow spectrometer. Acetonitrile (spectrophotometric grade) was dried with molecular sieves,³⁹ degassed, and purged with nitrogen. Metal hydrides **1**, **2**, and **4–7** were prepared according to literature procedures.^{15–18,40} Compound **3** was supplied by Dr. Morris Bullock, Brookhaven National Laboratory. Carbenium ions (as the tetrafluoroborate salts) were prepared according to literature methods.⁴¹

Thermodynamic Studies. Hydride transfer equilibria (eq 2) were studied by monitoring the carbonyl stretching frequencies of the starting hydrides, which are known to obey Beer's law in MeCN solution.¹⁴ In a typical study, acetonitrile solutions of **1** ranging in concentration from 0.012 to 0.024 M were prepared volumetrically under a nitrogen atmosphere; for reactive systems the solutions were kept cold until use and/or used without delay. Separately, acetonitrile solutions of $[(p\text{-MeOC}_6\text{H}_4)_2\text{PhC}][\text{BF}_4]$ were prepared under nitrogen. Appropriate quantities of the two solutions were mixed in a volumetric flask and diluted with acetonitrile; the resulting solution was transferred to an infrared cell with NaCl windows and the spectrum determined. Carbonyl stretching frequencies^{14–18} were used to determine the concentrations of the starting hydrides and cationic products. In all cases equilibrium was established rapidly, as confirmed by the kinetic studies. Carbenium ion salts and concentrations were chosen to keep the percent conversion of hydride to cation between 10 and 90%. The resulting equilibrium constant was calculated from $K_{\text{eq}} = [\text{L}_n\text{M} - \text{NCMe}^+][\text{Ar}_3\text{CH}]/[\text{L}_n\text{M} - \text{H}][\text{Ar}_3\text{C}^+]$ and was used to determine the free energy ($\Delta G_{\text{rxn}} = -RT \ln K_{\text{eq}}$) for the equilibrium process. This value was used with the known ΔG_{R^+} for $\text{Ar}_3\text{CH}^{10–12}$ to calculate the desired ΔG_{M^+} ($= \Delta G_{\text{rxn}} + \Delta G_{\text{R}^+}$). For **1** the resulting values of ΔG_{rxn} were –1.0, –0.43, and –0.61 kcal/mol, respectively, for three determinations. This resulted in ΔG_{M^+} values of 88.3, 88.8, and 88.7 kcal/mol for **1**.

Kinetics Experiments. In a representative experiment, a 10.0 mM solution of **7** was prepared by dissolving 74 mg (0.25 mmol) in 25 mL of CH_3CN . With use of pipet and volumetric techniques, this concentration was cut twice to 0.40 mM; 10 mL of the initial solution was diluted in a 25 mL volumetric and 1 mL of the resulting solution was diluted in a 10 mL volumetric. In a similar fashion, a 0.040 mM solution of $[(p\text{-MeOC}_6\text{H}_4)_2\text{PhC}][\text{BF}_4]$ was prepared by dissolving 156 mg (0.40 mmol) in 100 mL of CH_3CN and cutting the resulting solution by a factor of 100 with pure CH_3CN . The two solutions were loaded into the drive syringes of the stopped-flow apparatus, then injected into the mixing chamber; this gave initial concentrations $[\text{MH}]_0 = 0.2$ mM and $[\text{Ar}_3\text{C}^+][\text{BF}_4]_0 = 0.02$ mM. The absorbance of $[(p\text{-MeOC}_6\text{H}_4)_2\text{PhC}][\text{BF}_4]$ was monitored at 496 nm, and the first-order decay was analyzed by plotting $\ln(A_t - A_\infty)$ vs time. The slope of the resulting linear plot ($r^2 \geq 0.99$ in all cases) was taken as k_{obs} , and the second-order rate constant was calculated from $k_{\text{obs}}/[\text{MH}]_0$. In the case of compounds **4**, **5**, and **6**, the rate constants were also obtained under second-order conditions. In these cases, 0.04 mM solutions of hydride and $[(p\text{-MeOC}_6\text{H}_4)_2\text{PhC}][\text{BF}_4]$ were prepared and mixed as above. The initial concentrations were both 0.02 mM, and the second-order rate constant was obtained as the slope of a plot of $1/A_{496}$ vs time. These data agreed well with pseudo-first-order data and were averaged in to obtain the data provided in Table 2.

Acknowledgment. We thank Dr. Morris Bullock, Brookhaven National Laboratory, for helpful discussions and for supplying a sample of compound **3**. We also thank Dr. Rex Pratt for assistance with the stopped-flow kinetics experiments.

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