

Hydricities of BzNADH, C₅H₅Mo(PMe₃)(CO)₂H, and C₅Me₅Mo(PMe₃)(CO)₂H in Acetonitrile

William W. Ellis, James W. Raebiger, Calvin J. Curtis, Joseph W. Bruno,[†] and Daniel L. DuBois*

Contribution from the National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401

Received September 17, 2003; E-mail: ddubois@tcplink.nrel.gov

Abstract: The thermodynamic hydride donor abilities of 1-benzyl-1,4-dihydronicotinamide (BzNADH, 59 ± 2 kcal/mol), C₅H₅Mo(PMe₃)(CO)₂H (55 ± 3 kcal/mol), and C₅Me₅Mo(PMe₃)(CO)₂H (58 ± 2 kcal/mol) have been measured in acetonitrile by calorimetric and/or equilibrium methods. The hydride donor abilities of BzNADH and C₅H₅Mo(PMe₃)(CO)₂H differ by 13 and 24 kcal/mol, respectively, from those reported previously for these compounds in acetonitrile. These results require significant revisions of the hydricities reported for related NADH analogues and metal hydrides. These compounds are moderate hydride donors as compared to previously determined compounds.

Introduction

The formal transfer of a hydride ion, H⁻, is a fundamental reaction in biological and chemical catalysis. In many biological hydride transfer reactions, organic cofactors such as NADH/NAD⁺, NADPH/NADP⁺, and FADH/FAD⁺ are involved. These reactions involve the heterolytic cleavage and formation of C–H bonds. Fe-only and Fe–Ni hydrogenases contain inorganic/organometallic complexes that act as hydride acceptors/donors during heterolytic bond cleavage reactions.^{1–5} In reactions involving discrete transition-metal complexes, metal hydride bonds are frequently cleaved and formed in a heterolytic fashion. Reductions of ketones,⁶ aldehydes,⁷ alkenes,⁸ alkyl halides,⁹ imines,¹⁰ and hydrogen oxidation¹¹ are examples of reactions that have been proposed to occur via hydride transfer reactions. Because hydride transfer reactions are involved in a broad range of chemical transformations, the development of a common hydricity scale for the different classes of hydride donors is important.

The objective of this study is to establish a common hydricity scale for three different classes of compounds, [HM(diphos-

phine)₂]⁺ complexes (where M = Pt or Ni), NADH analogues, and CpMo(CO)₂(L)H complexes. The thermodynamic hydricity of a compound is defined as the free energy associated with the cleavage of M–H or C–H bonds to form the solvated hydride ion, H⁻, and the corresponding metal or organic species in solution (e.g., reaction 1). In reaction 1, a standard state is chosen in which the activity of the pure solvent, acetonitrile in this study, is unity. This choice permits a comparison of the hydride donor abilities regardless of whether the ML_n⁺ fragment interacts with the solvent to form a M–solvent bond or not, and it is the same standard state used in pK_a determinations and measurements of redox potentials where solvation effects also occur.



The absolute hydride donor abilities of a series of [HM(diphosphine)₂]⁺ complexes in acetonitrile have been determined using two independent methods. One method uses a thermodynamic cycle that requires an equilibrium measurement of the heterolytic cleavage of hydrogen to form the metal hydride of interest.^{12–14} A second method uses a cycle based on measurements of the pK_a of the hydride and the two-electron oxidation potential of the conjugate base of the metal hydride.^{11,15,16} These two methods agree within 1 kcal/mol,¹² and both provide free-energy values that do not require a reference hydride donor.

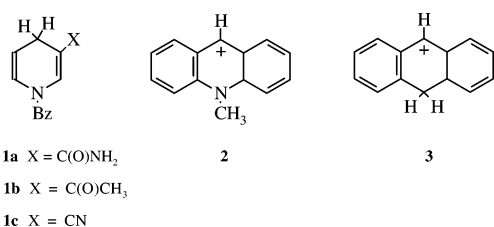
[†] Present address: Department of Chemistry, Wesleyan University, Middletown, CT 06459.

- (1) Nicolet, Y.; Cavazza, C.; Fontecilla-Camps, J. C. *J. Inorg. Biochem.* **2002**, *91*, 1–8.
- (2) Peters, J. W. *Curr. Opin. Struct. Biol.* **1999**, *9*, 670–676.
- (3) Volbeda, A.; Garcin, E.; Piras, C.; de Lacey, A. L.; Fernandez, V. M.; Hatchikian, E. C.; Frey, M.; Fontecilla-Camps, J. C. *J. Am. Chem. Soc.* **1996**, *118*, 12989–12996.
- (4) Higuchi, Y.; Ogata, H.; Miki, K.; Yasuoka, N.; Yagi, T. *Structure* **1999**, *7*, 549–556.
- (5) Garcin, E.; Vernede, X.; Hatchikian, E. C.; Volbeda, A.; Frey, M.; Fontecilla-Camps, J. C. *Structure* **1999**, *7*, 557–565.
- (6) Song, J.-S.; Szalda, D. J.; Bullock, R. M. *Organometallics* **2001**, *20*, 3337–3346.
- (7) Gaus, P. L.; Kao, S. C.; Youngdahl, K.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1985**, *107*, 2428–2434.
- (8) Bullock, R. M.; Song, J.-S. *J. Am. Chem. Soc.* **1994**, *116*, 8602–8612.
- (9) Kao, S. C.; Spillett, C. T.; Ash, C.; Lusk, R.; Park, Y. K.; Darensbourg, M. Y. *Organometallics* **1985**, *4*, 83–91.
- (10) Magee, M. P.; Norton, J. R. *J. Am. Chem. Soc.* **2001**, *123*, 1778–1779.

- (11) Curtis, C. J.; Miedaner, A.; Ciancanelli, R. F.; Ellis, W. W.; Noll, B. C.; DuBois, M. R.; DuBois, D. L. *Inorg. Chem.* **2003**, *42*, 216–227.
- (12) Curtis, C. J.; Miedaner, A.; Ellis, W. W.; DuBois, D. L. *J. Am. Chem. Soc.* **2002**, *124*, 1918–1925.
- (13) Ciancanelli, R. F.; Noll, B. C.; DuBois, D. L.; DuBois, M. R. *J. Am. Chem. Soc.* **2002**, *124*, 2984–2992.
- (14) Price, A. J.; Ciancanelli, R.; Noll, B. C.; Curtis, C. J.; DuBois, D. L. *Organometallics* **2002**, *21*, 4833–4839.
- (15) Berning, D. E.; Noll, B. C.; DuBois, D. L. *J. Am. Chem. Soc.* **1999**, *121*, 11432–11447.
- (16) Berning, D. E.; Miedaner, A.; Curtis, C. J.; Noll, B. C.; DuBois, M. R.; DuBois, D. L. *Organometallics* **2001**, *20*, 1832–1839.

As a result, these hydride complexes provide a reliable set of reference compounds for determining the hydricities of other classes of compounds.

The relative thermodynamic hydricities of NADH model compounds have been studied using equilibrium studies of hydride transfer reactions.^{17–19} Efforts to determine the hydride donor abilities of these compounds on an absolute scale have also been described. Such absolute values would allow comparisons with other classes of hydride donors. However, significantly different estimates have been presented. For example, 1-benzyl-1,4-dihydronicotinamide (BzNADH), **1a**, has reported ΔG_{H^-} values of 72 kcal/mol in acetonitrile²⁰ and 59 kcal/mol in dimethyl sulfoxide (DMSO).²¹ The estimated value of 72 kcal/mol was based on structural correlations between **2** and **3** and the relative hydricities of BzNADH and the conjugate hydride donor of **2**.²⁰ The value of 59 kcal/mol in DMSO was based on a more rigorous thermodynamic treatment that involved an enthalpy measurement and four $E_{1/2}$ values for its calculation.²¹ A more direct determination of the hydride donor ability of BzNADH in acetonitrile is therefore desirable.



The kinetic hydricities of a series of $CpM(CO)_2(L)H$ and $Cp^*M(CO)_2(L)H$ complexes (where $Cp = C_5H_5$, $Cp^* = C_5Me_5$, $M = Mo$ or W , and L is CO or a monodentate phosphine ligand) have been studied in detail by Bullock and co-workers.¹² Some of these studies have led to the development of interesting ionic hydrogenation reactions.^{6,8,22} Thermodynamic hydride donor abilities for a number of these same complexes have also been studied. For example, a hydricity of 79 kcal/mol has been reported for $CpMo(CO)_2(PMe_3)H$ in acetonitrile.²³ The thermodynamic measurements reported herein give a value of 55 ± 3 kcal/mol.

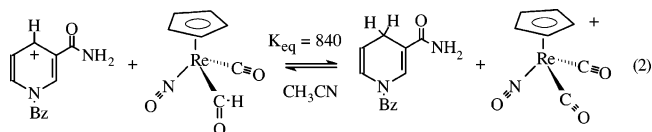
Establishing an absolute scale of hydride donor abilities requires extrathermodynamic assumptions. These assumptions have been discussed in detail in the literature by Wayner and Parker.²⁴ These authors suggested using standard redox potentials of -1.77 V for the H^+/H^\bullet redox couple and -0.60 V for the H^\bullet/H^- redox couple (potentials versus NHE(aq)). Using the ferrocene/ferrocenium couple as a reference ($+0.528$ V in acetonitrile versus NHE(aq))²⁵ gives values of -2.30 and -1.13 V for the H^+/H^\bullet and H^\bullet/H^- redox couples, respectively. Converting these potentials into kcal/mol for one-electron processes gives 53.0 kcal/mol for reducing H^+ to H^\bullet , and 26.0

kcal/mol for reducing H^\bullet to H^- using ferrocene as a reference. In addition, the free energy associated with the dissociation of hydrogen gas to form solvated hydrogen atoms in acetonitrile has been estimated to be 103.6 kcal/mol.²⁴ These values are the basis of calculations of free energies for homolytic and heterolytic bond cleavage reactions. Bruno and co-workers have used these same values for establishing the reference scale for their work.²³ The current work and previous work from our laboratory use the same values with one minor exception. A value of -2.32 V is used for the H^+/H^\bullet couple versus ferrocene (or 53.6 kcal/mol for the reduction of H^+ to H^\bullet).^{12–16} This slight modification was suggested by our previous work¹² which provides an experimental basis for determining the H_2/H^+ couple versus ferrocene in acetonitrile, as discussed in the Supporting Information. This 0.6 kcal/mol difference for the H^+/H^\bullet couple does not account for the values of ΔG_{H^-} previously reported for BzNADH²⁰ and $CpMo(PMe_3)(CO)_2H$,²³ which differ by 13 and 24 kcal/mol, respectively, from the values reported in the current work.

Results

As discussed in the Introduction, $[HM(\text{diphosphine})_2]^+$ complexes provide a good set of reference compounds for determining the hydricities of other classes of compounds. Unfortunately, cross reactions between $[HM(\text{diphosphine})_2]^+$ complexes (where $M = Pt$ or Ni) and NADH model compounds are very slow, and they are accompanied by side reactions. However, reactions of $[HM(\text{diphosphine})_2]^+$ complexes with $[CpRe(NO)(L)(CO)]^+$ (where $L = CO$ or an alkyl- or arylphosphine ligand) proceed more rapidly to produce $CpRe(NO)(L)C(O)H$ complexes. These reversible reactions have been used to establish a hydride donor scale for a series of formyl complexes.²⁶ The rhenium formyl complexes undergo clean hydride transfer reactions with NAD^+ model compounds over convenient time periods.

Studies of BzNADH. $CpRe(NO)(CO)(CHO)$ and BzNAD⁺ react cleanly at room temperature (21 °C, 294 K) with formation of an equilibrium mixture over the course of 4 h (reaction 2). The reverse reaction is slower, but equilibrium is also observed after 18 h. An equilibrium constant of 840 ± 100 was calculated for reaction 2 by integration of the 1H NMR spectra. The free energy of this reaction is -3.9 ± 0.2 kcal/mol in deuterioacetonitrile. The free energy (ΔG_{H^-}) associated with the heterolytic cleavage of the C–H bond of $CpRe(NO)(CO)(CHO)$ in acetonitrile has been previously determined to be 55 ± 2 kcal/mol.²⁶ The resulting value of $\Delta G_{H^-}(294K)$ for BzNADH is therefore 59 ± 2 kcal/mol. This calculation involves no entropy corrections or other approximations, but depends on two sequential hydride transfer equilibria to peg it to the $[HM(\text{diphosphine})_2]^+$ scale. The same value was reported for BzNADH in DMSO by Cheng et al.²¹

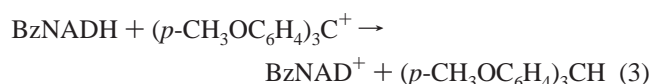


As a further check on the hydride donor ability of BzNADH, the reaction of BzNADH with the carbenium ion, ($p\text{-CH}_3\text{-}$

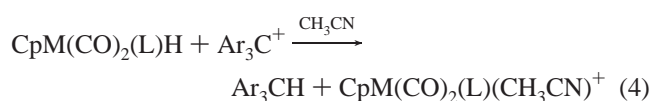
- (17) Anne, A.; Moiroux, J. *J. Org. Chem.* **1990**, *55*, 4608–4614.
 (18) Anne, A.; Moiroux, J. *Can. J. Chem.* **1995**, *73*, 531–538.
 (19) Ostovic, D.; Lee, I. S. H.; Roberts, R. M. G.; Kreevoy, M. M. *J. Org. Chem.* **1985**, *50*, 4206.
 (20) Handoo, K. L.; Cheng, J.-P.; Parker, V. D. *J. Am. Chem. Soc.* **1993**, *115*, 5067.
 (21) Cheng, J.-P.; Lu, Y.; Zhu, X.; Mu, L. *J. Org. Chem.* **1998**, *63*, 6108–6114.
 (22) Cheng, T.-Y.; Brunschwig, B. S.; Bullock, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 13121–13137.
 (23) Sarker, N.; Bruno, J. W. *J. Am. Chem. Soc.* **1999**, *121*, 2174–2180.
 (24) Wayner, D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287–294.
 (25) Parker, V. D.; Handoo, K. L.; Roness, F.; Tilset, M. *J. Am. Chem. Soc.* **1991**, *113*, 7493–7498.

- (26) Ellis, W. W.; Miedaner, A.; Curtis, C. J.; Gibson, D. H.; DuBois, D. L. *J. Am. Chem. Soc.* **2002**, *124*, 1926–1932.

$\text{OC}_6\text{H}_4)_3\text{C}^+$, in acetonitrile was studied by titration calorimetry (reaction 3). The enthalpy of this reaction was determined to be -30.7 ± 0.5 kcal/mol at 25.6 °C (298.6 K). The hydricity of $(p\text{-CH}_3\text{OC}_6\text{H}_4)_3\text{CH}$ has been reported to be 86 kcal/mol at room temperature.²⁷ A free-energy change of -27 kcal/mol is expected for reaction 3 on the basis of a ΔG_{H^-} of 59 kcal/mol for BzNADH. This is in good agreement with the measured enthalpy for this reaction, and it indicates a modest negative entropy associated with reaction 3 of -12 cal/deg mol ($T\Delta S = -3.7$ kcal/mol). A decrease in entropy is reasonable, because BzNADH is expected to have a smaller effective radius than $(p\text{-CH}_3\text{OC}_6\text{H}_4)_3\text{C}^+$. This should result in a more ordered solvation sphere for BzNADH and a decrease in entropy for reaction 3. Using the previously estimated hydride donor ability of 72 kcal/mol²⁰ leads to an expected free energy for reaction 3 of -14 kcal/mol, which is not in good agreement with the experimentally observed enthalpy change of -30.7 kcal/mol.



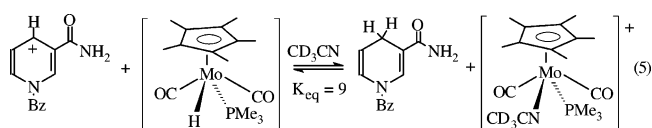
Studies of $\text{CpMo}(\text{CO})_2(\text{PMe}_3)\text{H}$ and $\text{Cp}^*\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{H}$ Complexes. Reactions of $\text{CpM}(\text{CO})_2(\text{L})\text{H}$ and $\text{Cp}^*\text{M}(\text{CO})_2(\text{L})\text{H}$ complexes (where M = Mo and W, L = CO or a phosphine ligand) with triarylcarbenium ions in acetonitrile, for example, reaction 4, have been used to calculate hydricities for this class of complexes.²³ It was assumed that these reactions were at equilibrium. On closer examination, the reverse reactions do not occur. For example, no reaction of $[\text{CpMo}(\text{CO})_3(\text{CH}_3\text{CN})]^+$ with $(p\text{-Me}_2\text{NC}_6\text{H}_4)_3\text{CH}$ is observed after 2 weeks by ^1H NMR spectroscopy in deuterioacetonitrile. The hydride donor abilities of $\text{CpMo}(\text{CO})_3(\text{H})$ and $(p\text{-Me}_2\text{NC}_6\text{H}_4)_3\text{CH}$ have reported values of 88.6 and 74.2 kcal/mol, respectively.^{23,27} Therefore, the reverse of reaction 4 is expected to be favored by nearly 15 kcal/mol, and the rates are reported to be fast enough to obtain equilibrium in a “matter of minutes”.²³ The assumption of the existence of equilibrium reactions, when the reactions are not in equilibrium, has led to large errors in the reported ΔG_{H^-} values for this class of complexes.



Reactions of $\text{CpMo}(\text{CO})_3\text{H}$ and $\text{Cp}^*\text{Mo}(\text{CO})_3\text{H}$ with $[\text{M}(\text{diphosine})_2](\text{BF}_4)_2$ complexes in acetonitrile are complicated by the well-known instability of the molybdenum complexes arising from the loss of the cyclopentadienyl rings.^{28–30} As a result of this elimination reaction and subsequent side reactions, it was not possible to obtain meaningful hydricity data from reactions of $\text{CpMo}(\text{CO})_3\text{H}$ and $\text{Cp}^*\text{Mo}(\text{CO})_3\text{H}$ with $[\text{M}(\text{diphosine})_2](\text{BF}_4)_2$ complexes. Substitution of one of the CO ligands with a phosphine ligand can retard the elimination of the cyclopentadienyl rings, but the hydride transfer reactions with $[\text{M}(\text{diphosine})_2](\text{BF}_4)_2$ are still not clean and the major

molybdenum-containing products are not those expected for simple hydride transfer reactions.

In contrast, the reaction of $\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2\text{H}$ (which exists as a 1:1 mixture of cis and trans isomers) with BzNAD⁺ proceeds slowly, but very cleanly (21 °C), in deuterioacetonitrile to form $\text{trans}-[\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2(\text{CD}_3\text{CN})]^+$, as shown in reaction 5. This reaction reaches equilibrium in about 70 days, with an equilibrium constant of 9 as determined by integration of the ^1H NMR spectrum. This corresponds to a free energy of -1.3 kcal/mol for reaction 5, and the addition of this value to ΔG_{H^-} for BzNADH gives a ΔG_{H^-} of 58 kcal/mol for $\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2\text{H}$ in acetonitrile. Although only a single determination of the equilibrium constant was made, studies of this reaction in the reverse direction over a period of 2 weeks resulted in formation of $\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2\text{H}$. This demonstrates the reversibility of reaction 5, but the reaction was not followed to equilibrium in the reverse direction.



Reaction of $\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2\text{H}$ with triphenylcarbenium ion in deuterioacetonitrile is clean (by ^1H NMR) and results in the formation of triphenylmethane and $\text{trans}-[\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2(\text{CD}_3\text{CN})]^+$, as shown in reaction 4 for $\text{CpMo}(\text{PMe}_3)(\text{CO})_2\text{H}$. Although the time required for reactions 4 and 5 is quite different, the same product, $\text{trans}-[\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2(\text{CD}_3\text{CN})]^+$, is formed. Calorimetric studies were performed by addition of an acetonitrile solution of $\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2\text{H}$ to an excess of triphenylcarbenium ion in acetonitrile and by titration of triphenylcarbenium ion into an excess of $\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2\text{H}$ in acetonitrile. The average of three determinations gave a ΔH value of -39.5 ± 1.0 kcal/mol. Based on the literature ΔG_{H^-} value of 99 kcal/mol for triphenylmethane²⁷ and a ΔG_{H^-} value of 58 kcal/mol for $\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2\text{H}$, the free energy associated with this reaction should be -41 kcal/mol. The observed enthalpy change of -39.5 kcal/mol would indicate that the entropy contribution for the reaction of $\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2\text{H}$ with triphenylcarbenium ion is small ($T\Delta S = 1$ kcal/mol).

Reaction of $\text{CpMo}(\text{PMe}_3)(\text{CO})_2\text{H}$ (for which the ΔG for the trans-to-cis conversion is -0.1 kcal/mol in toluene)³¹ with triphenylcarbenium ion in acetonitrile also results in the formation of triphenylmethane and $\text{trans}-[\text{CpMo}(\text{PMe}_3)(\text{CO})_2(\text{CH}_3\text{CN})]^+$, as shown in reaction 4. Calorimetric studies of this reaction were performed as described above for $\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2\text{H}$. The average of four determinations gave a ΔH value of -42.6 ± 3.0 kcal/mol. Adding this value to 99 kcal/mol for the hydride donor ability of triphenylmethane²⁷ gives 56 kcal/mol. Assuming the same $T\Delta S$ correction as used for $\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2\text{H}$ (1 kcal/mol) gives a ΔG_{H^-} value of 55 ± 3 kcal/mol for $\text{CpMo}(\text{PMe}_3)(\text{CO})_2\text{H}$.

The reaction of $\text{CpMo}(\text{PMe}_3)(\text{CO})_2\text{H}$ with the carbenium ion $(\text{Me}_2\text{NC}_6\text{H}_4)\text{Ph}_2\text{C}^+$ in acetonitrile to form $(\text{Me}_2\text{NC}_6\text{H}_4)\text{Ph}_2\text{CH}$ and $[\text{CpMo}(\text{PMe}_3)(\text{CO})_2(\text{CD}_3\text{CN})]^+$ was also studied by isothermal titration calorimetry. A heat of reaction of $-29.3 \pm$

(27) Zhang, X.-M.; Bruno, J. W.; Enyinnaya, E. *J. Org. Chem.* **1998**, *63*, 4671–4678.

(28) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255–1263.

(29) Keppie, S. A.; Lappert, M. F. *J. Chem. Soc. A* **1971**, 3216.

(30) Kubas, G. J.; Kiss, G.; Hoff, C. D. *Organometallics* **1991**, *10*, 2870–2876.

(31) Kalck, P.; Pince, R.; Poilblanc, R. *J. Organomet. Chem.* **1970**, *24*, 445–452.

Table 1. Hydricities of Selected Compounds in Acetonitrile

compound	ΔG_{H^-} (kcal/mol)	ref
[HRh(dppb) ₂] ⁺	34 ± 2	14
[HW(CO) ₄ (PPh ₃) ⁻	36 ± 2	35
Cp*Re(PMe ₃)(NO)(CHO)	42 ± 2	26
[HNi(dmpe) ₂] ⁺	51 ± 2	15
CpRe(CO)(NO)(CHO)	55 ± 2	26
CpMo(PMe ₃)(CO) ₂ H	55 ± 3	this work
CpMo(PMe ₃)(CO) ₂ H	58 ± 2	this work
1a	59 ± 2	this work
1b	60 ± 2 ^a	this work
[HNi(dmpp) ₂] ⁺	60 ± 2	15
1c	63 ± 2 ^a	this work
[HNi(depp) ₂] ⁺	67 ± 2	16
2	70 ± 2 ^a	this work
<i>p</i> -(Me ₂ NC ₆ H ₄) ₃ CH	74	27
Ph ₃ CH	99	27

^a Value calculated from the ΔG_{H^-} value for BzNADH and from equilibrium data given in refs 17 and 18 for hydride transfer reactions between BzNADH and the respective NAD⁺ model compounds.

2.0 kcal/mol was determined. Using ΔG_{H^-} values of 83 kcal/mol for (Me₂NC₆H₄)Ph₂CH²⁷ and 55 kcal/mol for CpMo(PMe₃)(CO)₂H gives a ΔG for this reaction of -28 kcal/mol. This is in good agreement with the observed heat of reaction and the expectation of a small entropy contribution. The observed heat of reaction is not in good agreement with the ΔG value of -3.4 kcal/mol reported previously for this reaction.²³

Discussion

The objective of this study was to determine the agreement of reported absolute hydricity values of three different classes of compounds, [HM(diphosphine)₂]⁺ complexes (where M = Pt or Ni), NADH analogues, and CpMo(CO)₂(L)H complexes. The observation of an equilibrium between BzNADH and CpRe(NO)(CO)(CHO), whose hydricity was determined previously with respect to [HPt(dmpe)₂]⁺, allows the hydride donor ability, ΔG_{H^-} , of BzNADH to be calculated (59 ± 2 kcal/mol) and linked directly to those of [HM(diphosphine)₂]⁺ complexes. The heat of reaction (-30.7 ± 0.5 kcal/mol) observed by calorimetry for the reaction between BzNADH and the carbenium ion, (*p*-CH₃OC₆H₄)₃C⁺, is in reasonable agreement with the expected free-energy change of -27 kcal/mol based on hydricities of these compounds. Our hydricity value of 59 ± 2 kcal/mol in acetonitrile is the same as that determined by Cheng and co-workers in DMSO,²¹ but it is not consistent with the previous estimates by Parker and co-workers of 72 kcal/mol for acetonitrile.²⁰ Our results lead to a revision of the hydricity values of a series of NADH model compounds²⁰ by 13 kcal/mol, as shown in Table 1 for compounds **1a–c** and **2**. The revised values indicate that NADH derivatives are significantly better hydride donors than was previously thought. Although the new ΔG_{H^-} values do not affect calculated relative homolytic bond dissociation energies for these NADH analogues,³² they will affect absolute homolytic values by 13 kcal/mol.

An enthalpy value, ΔH_{H^-} , of 64.2 kcal/mol has been reported for hydride dissociation of BzNADH in acetonitrile.³³ The calculations used to determine this enthalpy value for BzNADH

assumed that the differences in the free energies associated with $E_{1/2}(H^*/H^-)$ and $E_{1/2}(NADH^+/NADH)$ were equal to the differences in the enthalpies. This is equivalent to assuming that the entropy changes associated with electron transfer for these two redox couples, ΔS_{rc} , are the same. It is not clear how accurate these approximations are, but if they are, a $T\Delta S$ correction of approximately 5 kcal/mol is required to convert from ΔG_{H^-} to ΔH_{H^-} . This indicates a small increase in entropy upon hydride dissociation. The formation of two particles from one should lead to an increase in entropy, whereas the formation of charged species and an increased ordering of the solvent about these species should decrease the entropy. The combined result appears to be a small increase in the entropy upon hydride dissociation from BzNADH.

The enthalpy of hydride dissociation from NADH in aqueous solution of 53.6 kcal/mol³⁴ is significantly lower than the value of 64.2 kcal/mol reported for BzNADH in acetonitrile.³³ The difference in values reported for NADH and BzNADH may be caused in part by the different substituents on the nitrogen of the nicotinamide, but a major contribution to this difference likely arises from the much greater stabilization expected for the hydride ion in aqueous solutions caused by hydrogen bonding between the hydride ion and the protons of water.²⁴ Such hydrogen bonding is not possible for acetonitrile. This would lead to a more positive ΔG_{H^-} value in aqueous solutions as compared to acetonitrile. The free energy for hydride loss from [HNi(dmpp)₂]⁺ in acetonitrile ($\Delta G_{H^-} = 60$ kcal/mol) has also been compared to the enthalpy of hydride loss from NADH in water, and it was concluded the NADH is a significantly better hydride donor than [HNi(dmpp)₂]⁺.³⁴ However, a better comparison is that of BzNADH and [HNi(dmpp)₂]⁺, whose ΔG_{H^-} values in acetonitrile differ by only 1 kcal/mol (Table 1). The latter comparison has the advantages that both measurements were made in the same solvent and both measurements are free-energy measurements. Based on the data shown in Table 1, the NADH derivatives appear to be moderate hydride donors with a hydricity range that overlaps some of the less hydridic transition-metal hydrides.

Cp*Mo(PMe₃)(CO)₂H reacts slowly with BzNAD⁺ at room temperature to reach an equilibrium after 70 days. From this equilibrium measurement, ΔG_{H^-} for Cp*Mo(PMe₃)(CO)₂H can be calculated to be 58 ± 2 kcal/mol. The reaction of Cp*Mo(PMe₃)(CO)₂H with Ph₃C⁺ ($\Delta G_{H^-} = 99$ kcal/mol) is therefore expected to have a free-energy change of -41 kcal/mol. The heat of this reaction was measured to be -39.5 ± 1.0 kcal/mol. This indicates a small entropy change with $T\Delta S$ close to zero, which is consistent with previous studies of hydride transfer reactions.^{15,35} The heat of reaction of CpMo(PMe₃)(CO)₂H with Ph₃C⁺ is -43 ± 3 kcal/mol. Assuming $T\Delta S$ is also 1 kcal/mol for this reaction, as it was for Cp*Mo(PMe₃)(CO)₂H, leads to a ΔG_{H^-} value of 55 ± 3 kcal/mol for CpMo(PMe₃)(CO)₂H. This value is much different than the 79.4 kcal/mol reported previously, which was based on the assumption of an equilibrium between CpMo(PMe₃)(CO)₂H and (*p*-Me₂-NPh)Ph₂C⁺.²³ The heat of reaction for CpMo(PMe₃)(CO)₂H and (*p*-Me₂-NPh)Ph₂C⁺ is -29 kcal/mol from our calorimetry studies. This value compares well with the expected free-energy

(32) Klippenstein, J.; Arya, P.; Wayner, D. D. M. *J. Org. Chem.* **1991**, *56*, 6736–6737.

(33) Zhu, X.-Q.; Li, H.-R.; Li, Q.; Ai, T.; Lu, J.-Y.; Yang, Y.; Cheng, J.-P. *Chem.-Eur. J.* **2003**, *9*, 871–880.

(34) Zhu, X.-Q.; Yang, Y.; Zhang, M.; Cheng, J.-P. *J. Am. Chem. Soc.* **2003**, *125*, 15298–15299.

(35) Ellis, W. W.; Ciancanelli, R.; Miller, S. M.; DuBois, M. R.; DuBois, D. L. *J. Am. Chem. Soc.* **2003**, *125*, 12230–12236.

change of -28 kcal/mol using our revised value of ΔG_{H^-} for $\text{CpMo}(\text{PMe}_3)(\text{CO})_2\text{H}$. The previous ΔG value of -3.5 kcal/mol would require an extremely large $T\Delta S$ correction, 25 kcal/mol. These results lead to the conclusion that the ΔG_{H^-} values reported previously for Mo, W, Nb, and Ta hydrides^{23,36} are significantly in error. The origin of the error can be traced to the presumption of an equilibrium for reactions that are far from equilibrium.

Within experimental error, the hydride donor ability of $\text{CpMo}(\text{PMe}_3)(\text{CO})_2\text{H}$ is the same or greater than that of $\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2\text{H}$. This is not what one might expect based on electronic effects, because C_5Me_5 is more electron-donating than C_5H_5 . However, if the stabilities of the products of hydride transfer, $[\text{CpMo}(\text{PMe}_3)(\text{CO})_2(\text{CH}_3\text{CN})]^+$ and $[\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2(\text{CH}_3\text{CN})]^+$, are considered, it is reasonable that the product containing the C_5Me_5 ring may be less stable than that of the C_5H_5 ring because of steric interactions between the $\text{C}_5\text{-Me}_5$ ring and coordinated CH_3CN . This would tend to offset the electronic effects. In the hydride transfer reactions of $\text{CpM}(\text{CO})_2(\text{L})\text{H}$ and $\text{Cp}^*\text{M}(\text{CO})_2(\text{L})\text{H}$ studied by Bullock, it was found that the kinetic hydricity of these compounds follows the order expected on the basis of the electron-donating ability of the cyclopentadienyl rings²² and not the order observed in this study for the thermodynamic hydricity. This is likely due to the fact that solvation of the Mo center occurs after the hydride transfer reaction and the kinetic barrier arises from formation of unsolvated $[\text{C}_5\text{R}_5\text{Mo}(\text{PMe}_3)(\text{CO})_2]^+$ and not $[\text{C}_5\text{R}_5\text{Mo}(\text{PMe}_3)(\text{CO})_2(\text{CH}_3\text{CN})]^+$ (where $\text{R} = \text{H}$ or Me). These results illustrate the important role that solvation can play in hydride transfer reactions. However, the fact that solvation plays a role does not decrease the utility of ΔG_{H^-} values. Two compounds having the same ΔG_{H^-} value in any given solvent will have the same tendency to donate a hydride ion regardless of whether they form M -solvent bonds or not.

As seen from Table 1, the revised values of ΔG_{H^-} for $\text{CpMo}(\text{PMe}_3)(\text{CO})_2\text{H}$ and $\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2\text{H}$ indicate that these compounds are slightly better hydride donors than NADH model compounds. They are also moderate hydride donors as compared to other transition-metal hydrides studied to date, and they are somewhat less hydridic than the formyl complexes shown in Table 1. They are much better hydride donors than triaryl-methane compounds as shown by comparison with the last two entries of Table 1, and hydride transfer equilibria between these two classes of compounds are not expected.

Summary

The hydride donor abilities of BzNADH and $\text{CpMo}(\text{CO})_2(\text{PMe}_3)\text{H}$ have been reevaluated. Both of these compounds were found to be significantly better hydride donors than previously reported. For NADH analogues, this leads to a simple correction of previously reported hydride donor abilities by -13 kcal/mol.²⁰ For the Mo, W, Ta, and Nb hydrides, the situation is more complex, as our results for $\text{CpMo}(\text{PMe}_3)(\text{CO})_2\text{H}$ and $\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2$ indicate that the relative ordering of the compounds studied previously may also be incorrect.^{23,36} As a result of the studies described in this paper, the hydricities of $[\text{HM}(\text{diphosphine})_2]^+$ complexes,¹¹⁻¹⁶ $[\text{HW}(\text{L})(\text{CO})_4]^-$ complexes,³⁵ transition-metal formyl complexes,²⁶ NADH derivatives, CpMo -

$(\text{CO})_2(\text{PMe}_3)\text{H}$, and $\text{Cp}^*\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{H}$ have been cross-referenced and can now be placed on a common absolute scale.

Experimental Section

General Procedures and Materials. NMR spectra were recorded on a Varian 400 MHz spectrometer. Proton chemical shifts were recorded relative to residual protons in CD_3CN (1.93 ppm). ^{31}P NMR chemical shifts are reported relative to an external sample of H_3PO_4 (0.00 ppm). Isothermal titration calorimetry was performed on a Calorimetry Sciences Corporation ITC 4200 calorimeter. Solvents were reagent grade and were purchased from Aldrich. Acetonitrile was vacuum transferred from CaH_2 and stored in a glovebox. Reagents were purchased from Aldrich. $[\text{CpRe}(\text{NO})(\text{CO})_2](\text{BF}_4)$ and $\text{CpRe}(\text{NO})(\text{CO})(\text{CHO})$ were prepared using literature methods,³⁷⁻³⁹ as were BzNADH ,^{17,40,41} $\text{C}_5\text{R}_5\text{Mo}(\text{PMe}_3)(\text{CO})_2\text{H}$,^{22,42,43} $[(p\text{-Me}_2\text{NC}_6\text{H}_4)\text{Ph}_2\text{C}](\text{PF}_6)$,^{44,45} and $[(\text{C}_6\text{H}_5)_3\text{C}](\text{PF}_6)$.⁴⁵

Equilibration of BzNADH and $[\text{CpRe}(\text{NO})(\text{CO})_2](\text{BF}_4)$ in Acetonitrile. BzNADH (0.009 g, 0.045 mmol) and $[\text{CpRe}(\text{NO})(\text{CO})_2](\text{BF}_4)$ (0.017 g, 0.040 mmol) were dissolved in CD_3CN (0.60 mL) in an NMR tube. Over the course of 18 h, this reaction came to equilibrium with the formation of BzNAD^+ and $\text{CpRe}(\text{NO})(\text{CO})(\text{CHO})$, as determined by comparison of the ^1H NMR spectra with authentic samples prepared using literature methods.^{17,37-41} Integrations of these spectra were used to calculate an equilibrium constant of 830 ($K_2 = ([\text{BzNADH}]/[\text{BzNAD}]) \times ([\text{Re}(\text{CO})^+]/[\text{ReCHO}])$) for reaction 2. The reaction of BzNAD^+ with $\text{CpRe}(\text{NO})(\text{CO})(\text{CHO})$ was studied in a similar manner, and an equilibrium constant of 850 was obtained after 4 h.

Equilibration of $\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2\text{H}$ with BzNAD^+ in Acetonitrile. $[\text{BzNAD}](\text{PF}_6)$ (0.0155 g, 0.043 mmol) and $\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2\text{H}$ (0.019 g, 0.052 mmol) were dissolved in CD_3CN (0.7 mL) in an NMR tube. The course of the slow reaction was followed by recording ^1H NMR spectra weekly. The NMR tube was stored in the glovebox, except for the time required to collect spectra, to protect the sample from oxygen. The reaction came to equilibrium after 72 days, and the equilibrium constant ($K_5 = ([\text{BzNADH}]/[\text{BzNAD}^+]) \times ([\text{Mo}(\text{CD}_3\text{CN})^+]/[\text{MoH}])$) was evaluated using concentrations obtained from integration of the final ^1H NMR spectrum. An equilibrium constant of 9 was obtained in this way. A similar reaction in the reverse direction was not followed to equilibrium, but the formation of $\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2\text{H}$ was observed.

Calorimetry. All solutions for calorimetry were prepared in a glovebox. In a typical experiment, the reaction cell of the calorimeter was purged with a stream of N_2 for 15 min. Subsequently, it was loaded by syringe with a 30 mM solution of $[(p\text{-Me}_2\text{NC}_6\text{H}_4)\text{Ph}_2\text{C}](\text{PF}_6)$ in dry acetonitrile (cell volume = 1.3 mL), and stirring was commenced at 300 rpm. The reference cell of the calorimeter was loaded with neat acetonitrile. Next, a 250- μL syringe containing a 10.3 mM solution of $\text{CpMo}(\text{PMe}_3)(\text{CO})_2\text{H}$ in acetonitrile was inserted into the cell. After 90 min of equilibration at 25.6 $^\circ\text{C}$, 20 10- μL injections of the hydride solution were added into the cell, with an 8-min delay between injections. The first data point was discarded, and the average enthalpy/mol for the subsequent 19 injections was 29.4 ± 0.2 kcal/mol. At least three independent experiments were performed in this manner for each

- (37) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927.
 (38) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.
 (39) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 2811.
 (40) Shinkai, S.; Hamada, H.; Kusano, Y.; Manabe, O. *J. Chem. Soc., Perkin Trans. 2* **1979**, 699.
 (41) Anderson, A. C.; Berkelhammer, G. *J. Am. Chem. Soc.* **1958**, *80*, 992.
 (42) Kalck, P.; Pince, R.; Poilblanc, R.; Roussel, J. *J. Organomet. Chem.* **1970**, *24*, 445-452.
 (43) Asdar, A.; Tudoret, M.-J.; Lapinte, C. *J. Organomet. Chem.* **1988**, *349*, 353-366.
 (44) Alavosus, T. J.; Sweigart, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 985-987.
 (45) McKinley, S. V.; Rakshys, J. W., Jr.; Young, A. E.; Freedman, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 4715-4724.

(36) Sarker, N.; Bruno, J. W. *Organometallics* **2001**, *20*, 55-61.

of the hydrides studied. For $CpMo(PMe_3)(CO)_2H$, an average value of -29.3 ± 2.0 kcal/mol was obtained, which reflects a larger scatter between experiments than between injections as expected.

Acknowledgment. The support of the U.S. Department of Energy, Office of Science, Chemical and Biological Sciences Division under DOE Contract No. DE-AC36-99GO10337 is gratefully acknowledged.

Supporting Information Available: Experimental determination of the potential of the H_2/H^+ couple in acetonitrile versus ferrocene and extrathermodynamic assumptions (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA038567D