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Thermodynamic Studies of Hydride Transfer for a Series of Niobium and Tantalum Compounds

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Reported herein are the first thermodynamic hydricities (ΔG_{M+}) for a collection of niobocene and tantalocene compounds (**1**−**13**) of general formulas $(C_5R_4R')_2M(H)(L)$ (R = H, Me; R′ = H, Me, $SiMe_3$; L = CO, PEt_3, $(H)_2$, PhCCPh, $CH_2{=}O$, =O) and $(C_5H_4SiMe_3)_2Nb(Cl)(L')$ (L′ = O=C=CEtPh, $O{=}C{=}CEt_2$). The studies were carried out in acetonitrile solution, and the compounds show hydride transfer free energies ranging from 74 to 95 kcal/mol, as determined by bracketing studies involving a known series of hydride acceptors. The data indicate that the free energies of hydride transfer are heavily influenced by coligands, but less so by 4d vs 5d effects in isostructural niobium or tantalum compounds.

Introduction

Transition metal hydrides play important roles in an extraordinary range of synthetic and catalytic processes.[1] As such, quantitative data on metal hydrides are essential to understanding the diverse reaction paths available, and the study of metal hydride reactivity remains an active area of research. This is a broad field, since these compounds are potentially susceptible to proton, hydrogen atom, and hydride transfer processes, depending on reaction conditions, target substrate, and coligand set.[2] Various approaches have been used to study these reaction pathways. Most straightforward have been studies on acidity, and several reports contain quantitative data on metal hydride pK_a's and on the rates of these proton transfer reactions.[3] While this reactivity pathway seemingly conflicts with the name given to this class of compounds, spectroscopic studies suggest that susceptibility to proton transfer processes is not the result of $M^-{-}H^+$ polarization in the ground state. Indeed, both matrix isolation infrared[4] and X-ray photoelectron spectroscopic[5] data have been gathered for carbonyl hydrides such as $HCo(CO)_4$, $HMn(CO)_5$, and $H_2Fe(CO)_4$. These data have been invoked to assign hydridic character ($M^+ - H^-$) in the ground state, and the observed acidity has been attributed to the inherent weakness in the metal−hydrogen bond.[4]

There has been an increasing awareness of the role of hydride transfer in processes such as alkene reduction,[6] carbonyl reduction,[7] and redox reactions of oxometal species.[8] These have demonstrated the need for quantitative data on hydride donation and hydricity, and various approaches have been taken to address this need. For example, hydridic behavior has been correlated with the effective electronegativity of the metal center;[9] weaker, more reactive metal−hydrogen bonds are predicted for electropositive metal centers, those expected to impart appreciable hydride character to the M−H bond. Also, T_1 relaxation times have been determined for a series of metal deuterides.[10] These data allowed for the calculation of deuterium quadrupole coupling constants (DQCCs), which were then used to determine the importance of ground state ionicity in the M−D bond. Theoretical studies have been employed in the study of hydride NMR data (specifically the upfield shifts often seen with d^n metal hydrides)[11] and in ascertaining the mechanism of carbonyl reduction.[12]

There have also been various attempts to relate metal hydride hydricity and solution reactivity. An early effort involved a determination of the rates of acetone insertion into M−H bonds and led to the establishment of a relative series of kinetic hydricities.[13] From these results Labinger determined that kinetic hydricity decreased

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in the order $Cp_2ZrH_2 > Cp_2NbH_3 > Cp_2Nb(CO)H > Cp_2MoH_2$. More recently, Bullock has reported a wide series of kinetic studies involving reactions of metal hydrides with various carbenium ion salts.[14] A similar approach has been used in the study of anionic carbonyl hydrides, for which the rates of reaction with alkyl halides have been used to tabulate relative kinetic hydricity.[15] In addition, carbonyl insertion reactions have been used to establish hydride reactivity patterns,[16] and these and related studies[17] have shown that the nitrosyl coligand is very effective in promoting hydride transfer reactions. This is in accord with earlier theoretical studies on this subject, in which Bursten used calculated HOMO−LUMO gaps to predict hydride transfer activity for, for example, $CpCr(NO)_2H$.[18]

While the foregoing examples establish that there is a growing body of information on kinetic hydricity, there are but two reports of thermodynamic studies related to hydride transfer by metal hydrides. We have previously used hydride transfer to a series of carbenium ion salts to probe the hydride-donating power of a series of molybdenum and tungsten compounds of general formula $(C_5R_5)M(CO)_{3-n}L_nH$;[19] this resulted in the determination of ΔG_{M+}, the free energy for the process shown in eq 1. The compounds, which comprise a structurally

$$\mathrm{CpM(CO)}_{3-n}\mathrm{L}_n\mathrm{H} \xrightleftharpoons[\mathrm{MeCN}]{\Delta G_{\mathrm{M+}}} [\mathrm{CpM(CO)}_{3-n}\mathrm{L}_n\mathrm{(NCMe)}]^+ + \mathrm{H}^- \quad (1)$$

similar set, exhibited hydride donor powers ranging from ca. 79 to 89 kcal/mol. Donor substituents on the cyclopentadienyl ligand and the replacement of carbonyl ligands with phosphine ligands both served to lower the free energy of hydride transfer, and tungsten compounds are stronger hydride donors than are the isostructural molybdenum analogues. In addition, kinetic studies on hydride transfer showed a good Brönsted correlation between thermodynamic driving force and reaction rate. Subsequently, DuBois and co-workers used pK_a and redox data to construct the thermodynamic cycle needed to assess the hydride donor power for a series of nickel and platinum compounds of general formula $[HM(L_2)_2][PF_6]$, in which L_2 is a chelating bisphosphine.[20] Despite the postive charge on these metal centers, the compounds are strong hydride donors, with ΔG_{M+} values ranging from ca. 40 to 63 kcal/mol in nitrile solvents. In this work the platinum compounds are generally stronger hydride donors than the nickel congeners, and the stability of the square-planar products is a driving force; chelate ligands that force a tetrahedral distortion in the products raise the energy of the hydride transfer process. As pointed out by DuBois,[20] the two series of compounds considered to date comprise a collection with hydride donor powers ranging over ca. 50 kcal/mol.

In this contribution we describe further studies using our indicator series. The method has been applied to a collection of niobocene and tantalocene hydrides, and these compounds show a wide range of hydride donor power; the ΔG_{M+} values range over 74−95 kcal/mol and are influenced by such factors as 4d vs 5d effects and coligand set. Unlike the molybdenum and tungsten compounds studied earlier,[19] there are no pK_a data available for the systems studied herein. Hence the data reported herein constitute the first thermodynamic data for the metal−hydrogen bonds of these group V hydrides.

Experimental Section

General Considerations. All manipulations involving metal complexes were carried out under an atmosphere of nitrogen, which was first passed through activated BTS catalyst and molecular sieves. Standard Schlenk techniques were used to handle solutions,[21] and solids were transferred in a Vacuum Atmospheres glovebox under purified nitrogen. NMR spectra were obtained on a Varian Gemini 300 FT-NMR instrument and infrared spectra on a Perkin-Elmer Model 1600 FT-IR spectrophotometer. Acetonitrile (spectrophotometric grade) was dried with molecular sieves,[22] degassed, and purged with nitrogen. Tantalum hydrides **2**,[23] **5**,[23] **8**,[24] **12**,[25] and **13**[25] and niobium compounds **1**,[26] **3**,[27] **4**,[28] **6**,[29] **7**,[29] **9**,[30] **10**,[31] and **11**[28](see Table 1 for numbering) were prepared according to literature procedures. Carbenium ions (as the tetrafluoroborate salts) were prepared according to literature methods.[32]

Themodynamic Studies. Hydride transfer reactions were studied by monitoring the ^1H NMR spectra of the hydrides in

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Table 1. Thermodynamic Data for Hydride Transfers

metal hydride[a]	indicator (ΔG_{R+})[b]	ΔG_{M+}[c]
1 $Cp'_2Nb(H)(CO)$	$(p\text{-MeOPh})Ph_2C^+$ (93.9)	95
2 $Cp_2Ta(H)(CO)$	$(p\text{-MeOPh})Ph_2C^+$ (93.9)	95
3 $Cp_2Nb(H)(CO)$	$(p\text{-MeOPh})Ph_2C^+$ (93.9)	93
4 $Cp'_2Nb(Cl)(O{=}C{=}CEtPh)$	$(p\text{-MeOPh})_2PhC^+$ (89.3)	89
5 $Cp_2Ta(H)(PEt_3)$	$(p\text{-MeOPh})_3C^+$ (86.1)	89
6 Cp'_2NbH_3	$(p\text{-MeOPh})_3C^+$ (86.1)	86
7 Cp_2NbH_3	$(p\text{-MeOPh})_3C^+$ (86.1)	86
8 Cp_2TaH_3	$(p\text{-MeOPh})_3C^+$ (86.1)	86
9 $Cp'_2Nb(H)(PhCCPh)$	$(p\text{-Me}_2NPh)Ph_2C^+$ (82.9)	83
10 $Cp'_2Nb(H)(O{=}CH_2)$	$(p\text{-Me}_2NPh)Ph_2C^+$ (82.9)	83
11 $Cp'_2Nb(Cl)(O{=}C{=}CEt_2)$	$(p\text{-Me}_2NPh)Ph_2C^+$ (82.9)	81
12 $Cp^*_2Ta(H)({=}O)$	$(p\text{-Me}_2NPh)_2PhC^+$ (77.0)	76
13 $Cp^*_2TaH_3$	$(p\text{-Me}_2NPh)_3C^+$ (74.2)	74

[a] $Cp' = (\eta^5\text{-}C_5H_4SiMe_3)$, $Cp^* = (\eta^5\text{-}C_5Me_5)$. [b] As the BF_4 salts. Listed here is the least reactive indicator with which a reaction occurred. ΔG_{R+} values (in kcal/mol) are from ref 34. [c] In kcal/mol in acetonitrile. Estimated uncertainties are 3 kcal/mol, as discussed in the text.

MeCN-d_3 solution. In a typical study, an acetonitrile solution of **1** was prepared under a nitrogen atmosphere; for reactive systems the solutions were kept cold until use and/or used without delay. The proton NMR spectrum was obtained, and $[(p\text{-MeOC}_6H_4)Ph_2C][BF_4]$ was added under nitrogen. The spectrum was redetermined to verify that a hydride transfer reaction had occurred, as verified by the loss of signals for **1** and $[(p\text{-MeOC}_6H_4)Ph_2C][BF_4]$ and the appearance of those for **1**$^+$ (Cp′ at 5.74, 5.69, 5.59, and 5.55 ppm) and $(p\text{-MeOC}_6H_4)Ph_2CH$; for most cases the triarylmethanes exhibit a methine resonance in the range 5−5.5 ppm. Several carbenium ion salts were surveyed to identify the weakest hydride acceptor capable of effecting the desired reaction, and ΔG_{M+} values were estimated accordingly. The remaining compounds were studied in a similar fashion, and results are summarized below for reactions between the indicated species. Data for **4**$^+$ and **11**$^+$ have been published.[28]

^{1}H NMR (CD_3CN): $Cp_2Ta(CO)H$ (**2**)/[$(p\text{-MeOC}_6H_4)Ph_2C][BF_4]$, 5.6 ppm (Cp); $(p\text{-MeOC}_6H_4)Ph_2C{-}H$, 5.5 ppm.

^{1}H NMR (CD_3CN): $Cp_2Nb(CO)H$ (**3**)/[$(p\text{-MeOC}_6H_4)Ph_2C][BF_4]$, 5.61 ppm (Cp); $(p\text{-MeOC}_6H_4)Ph_2C{-}H$, 5.5 ppm.

^{1}H NMR (CD_3CN): $Cp_2Ta(PEt_3)H$ (**5**)/$[(p\text{-MeOC}_6H_4)_3C][BF_4]$, 5.54 ppm (Cp), multiplets at 4.3 and 1.2 ppm (P−Et); $(p\text{-MeOC}_6H_4)_3C{-}H$, 5.4 ppm.

^{1}H NMR (CD_3CN): Cp'_2NbH_3 (**6**)/$[(p\text{-MeOC}_6H_4)_3C][BF_4]$, overlapping resonances at 5.69, 5.61 ppm (Cp′); $(p\text{-MeOC}_6H_4)_3C{-}H$, 5.4 ppm (M−H resonances for **6**−**8** and **13** were obscured by indicator or Ar_3CH aromatics).

^{1}H NMR (CD_3CN): $[Cp_2NbH_3$ (**7**)/$[(p\text{-MeOC}_6H_4)_3C][BF_4]$, 5.57 ppm (Cp); $(p\text{-MeO}{-}C_6H_4)_3C{-}H$, 5.4 ppm.

^{1}H NMR (CD_3CN): Cp_2TaH_3 (**8**)/$[(p\text{-MeOC}_6H_4)_3C][BF_4]$, 5.54 ppm (Cp); $(p\text{-MeO}{-}C_6H_4)_3C{-}H$, 5.4 ppm.

^{1}H NMR (CD_3CN): $Cp'_2Nb(PhCCPh)H$ (**9**)/$[(p\text{-Me}_2NC_6H_4)Ph_2C][BF_4]$, 7.5−6.8 (overlapping multiplets, Ph), 6.32, 6.08, 5.66, 5.02 ppm (Cp′); $(p\text{-Me}_2NC_6H_4)Ph_2C{-}H$, 5.5 ppm.

^{1}H NMR (CD_3CN): $Cp_2Nb(OCH_2)H$ (**10**)/$[(p\text{-Me}_2NC_6H_4)Ph_2C][BF_4]$, 6.09, 5.88, 5.70, 5.49 ppm (Cp′); $(p\text{-Me}_2NC_6H_4)Ph_2C{-}H$, 5.5 ppm.

^{1}H NMR (CD_3CN): $Cp^*_2Ta(O)H$ (**12**)/$[(p\text{-Me}_2NC_6H_4)_2PhC][BF_4]$, 2.02 ppm (Cp*); $(p\text{-Me}_2NC_6H_4)_2PhC{-}H$, 5.8 ppm.

^{1}H NMR (CD_3CN): $[Cp^*_2TaH_3$ (**13**)/$[(p\text{-Me}_2NC_6H_4)_3C][BF_4]$, 2.02 ppm (Cp*); $(p\text{Me}_2NC_6H_4)_3C{-}H$, 5.7 ppm.

Results

Methodology. Just as acidity studies require indicator bases for which the pK_a of the conjugate acid is known,[3,33] the studies contemplated here require Lewis acids with known hydride affinities. In recent years, we[34] and others[35,36] have developed thermodynamic data of this kind for a wide array of carbenium ion salts, for which we defined ΔG_{R+}, the free energy of carbenium ion formation by hydride loss (eq 2). These data were

$$Ar_3C{-}H \overset{\Delta G_{R+}}{\rightleftharpoons} Ar_3C^+ + H^- \tag{2}$$

derived from a thermodynamic cycle involving pK_a data, two single-electron oxidation potentials (of R$^-$ and R$^\bullet$), and literature data for successive proton and hydrogen atom reductions.[37] This approach has led to the compilation of a hydride transfer indicator series encompassing approximately 50 compounds with ΔG_{R+} values ranging from ca. 60 to 100 kcal/mol (although data are available for stronger hydride acceptors, these carbenium ion salts are not stable and isolable). In addition, the data indicate that these values are nearly identical in dimethyl sulfoxide and acetonitrile solutions, even though acidity studies show substantial differences in pK_a for these solvents. The weak dependence of ΔG_{R+} on solvent is due to the small solvation energies for the hydride ion; indeed, the substantial solvation energy for the proton is largely responsible for the solvent effects in pK_a studies.[3c,38]

With indicators available, the determination of ΔG_{M+} requires the determination of ΔG_{rxn} for the process shown in eq 3. Clearly, this is easiest, and most reliable,

$$L_nM{-}H + Ar_3C^+ \underset{MeCN}{\rightleftharpoons} L_nM(NCMe)^+ + Ar_3C{-}H$$
$$\Delta G_{rxn} = \Delta G_{M+} - \Delta G_{R+} \tag{3}$$

for free energy changes near zero, and the availability of so many organic indicators virtually ensures that there will be a close match between an indicator and the metal hydride under study. However, an additional complication remains in the current series of compounds; specifically, they fail to undergo reversible hydride transfer. As a result, we have relied on the bracketing method, in which carbenium ion indicators of increasing strength are tested until hydride transfer occurs. In this way one defines a range of ΔG_{M+} values for the metal hydride; we note that bracketing methods are commonly used in gas phase thermodynamic studies,[39] for which the establishment and study of equilibria is difficult or impossible. Of course, this approach is potentially susceptible to the intervention of kinetic phenomena, in which a slow reaction leads one to

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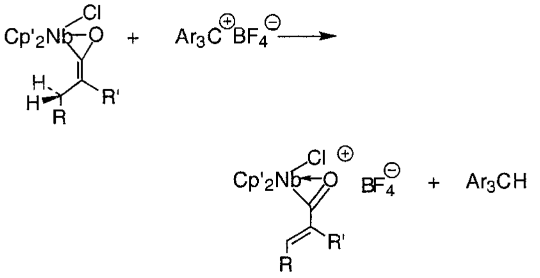
conclude that the process is endoergic. Fortunately, virtually all of the observed metal-to-carbenium ion hydride transfers occur within seconds or minutes in solution. As a consequence, unreactive systems were monitored for at least 24 h to ensure that there was no reaction in progress. Since our indicator series has substrates closely spaced (in ΔG_{R+}), we estimate that the resulting ΔG_{M+} data are accurate to within 3 kcal/mol. A few specific tests of this assertion will be discussed later.

The application of this methodology has led to the data set summarized in Table 1, which includes hydride transfer data for eight niobium compounds and five tantalum compounds. The hydrides are numbered in the table, and the products will be identified as cations using the same number. Although all are metallocene derivatives, the compounds contain a wide variety of coligands. This allows for comparison of the effects of Cp, Cp′, and Cp* ligands, as well as the effect of the other coligand (CO, phosphine, etc.) present. As the data show, the ΔG_{M+} values exhibit a range of 21 kcal/mol, reflecting the wide variability of coligands and the sensitivity of hydride transfer to these changes. Also indicated for each hydride is the least reactive indicator with which a reaction was observed. The ΔG_{M+} values were estimated from the these data, and all were assigned values within a kcal/mol of the ΔG_{R+} of the appropriate indicator. Reactions were run in CD_3CN and monitored by NMR, which was used to establish conversion to products. Interestingly, it also proved possible to monitor most of the reactions in benzene-d_6, since the reactants and products dissolved to the extent necessary to obtain spectral data. In all cases, reaction (or lack thereof) was observed with the same range of indicators (even though the product was presumably the $M^+BF_4^-$ ion pair in the absence of MeCN ligand), indicating the diminished role solvation plays in the hydride transfer reactions (relative to proton transfers).[34]

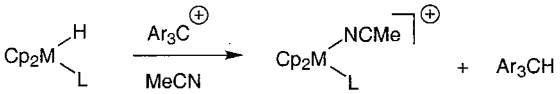
Reaction Types and Products. For reasons elaborated below, it was not always possible to ascertain with full certainty the identity of the metal-containing products. Care was taken to ensure that the metal hydride was fully consumed and that the hydride transfer led to the appropriate Ar_3CH product, thus showing that the reaction under study is truly a hydride transfer process. This eliminates alternatives such as oxidation, in which the organic product might be the $Ar_3C^\bullet$ radical or the dimer thereof. Note that this does not preclude the possibilty that the observed reactions involved a sequence of electron transfer/hydrogen atom transfer, a mechanism identified in other organometallic processes proceeding with net hydride transfer.[40] Fortunately, the thermodynamic studies reported herein do not depend on mechanism, and the identification of hydride transfer products is sufficient to establish relative hydride affinities for the reacting partners.

The reactions represented in Table 1 include 11 M−H hydride transfers and, for comparison, two C−H hydride transfers. Compounds **4** and **11** contain a η^2-C,O complexed ketene and react with trityl derivatives to transfer the hydride α to the ketene β carbon, resulting in the cationic α,β-unsaturated enacyl complexes (eq 4).[41] These latter compounds are stable and isolable, and



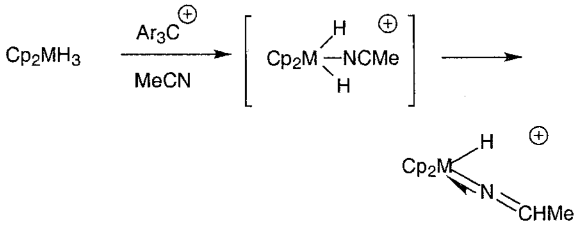
(4)

the product $4^+BF_4^-$ has been characterized by diffraction methods.[41b] Since we have previously shown that the metal center plays a key role in determining the energy of hydride transfer (and a subsequent proton transfer, by which the enacyl is converted into a vinylketene ligand),[41b] we wished to compare the energies of these C−H hydride transfers with those of the M−H processes. For the latter, hydride abstraction from an 18-electron hydride would formally produce a 16-electron cation; these compounds typically add an acetonitrile ligand (eq 5). These cationic acetonitrile



(5)

complexes, or closely related cations, are known for **1**−**3**, **4**, **9**−**11**, and **12**.[27,41,42] Conversely, the products derived from the trihydrides **6**−**8** and **13** are not expected to be stable; Moïse and co-workers have recently reported that $[(C_5H_4{}^tBu)_2TaH_2][PF_6]$ complexes an acetonitrile ligand, which then inserts to give both isomers of the azavinylidene complex (eq 6).[43] This follow-up reaction



(6)

precludes observation of the initial product of hydride transfer, but should not hinder the initial hydride transfer reaction; we note again that similar results were obtained in benzene solution, for which this follow-up reaction is unavailable.

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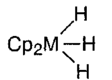
Discussion

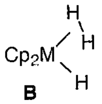
Specific Comparisons. The data for **1**−**13** allow for several comparisons on the effects of various coligands on the energetics of hydride transfer, and these will be considered sequentially. An obvious comparison involves the identity of the metal, for which we may look at isostructural compounds **2** and **3** ($Cp_2M(CO)H$) and/or **7** and **8** (Cp_2MH_3). In fact, both of these comparisons suggest there is little difference between the two metals in terms of their contribution to thermodynamic hydricity. The carbonyl derivatives show $\Delta G_{\mathrm{M+}}$ values of 93 and 95, a range that fails to exceed our estimated error limits, and the trihydrides are both determined to have $\Delta G_{\mathrm{M+}}$ values of 86 kcal/mol. This may be compared with the series $CpM(CO)_{3-n}L_nH$, for which the molybdenum−tungsten $\Delta G_{\mathrm{M+}}$ difference was typically 3−5 kcal/mol;[19] molybdenum exhibited higher values, consistent with the fact that transition metal basicities typically increase down a column.[44] Additionally, DuBois saw differences of ca. 10−15 kcal/mol in his studies of $[M(H)(P_2)_2]^+$ derivatives of nickel and platinum, with the lighter metal again showing higher values of $\Delta G_{\mathrm{M+}}$.[20] To the extent that hydricities are expected to track orbital energies and effective electronegativities,[9] it is worth noting that the difference in electronegativities increases in the order Nb/Ta < Mo/W < Ni/Pt;[45] from this we would predict that the close similarities in the electronegativities of Nb and Ta should lead to similar thermodynamic hydricities, as observed here.

Turning to the effects of coligands, compounds **1**, **3**, **8**, and **13** provide opportunities to consider the effects of various cyclopentadienyl derivatives. The first two compounds contain $C_5H_4SiMe_3$ and Cp ligands and show similar $\Delta G_{\mathrm{M+}}$ values of 93−95 kcal/mol. Conversely, **8** and **13** are $(C_5R_5)_2TaH_3$ derivatives containing Cp and C_5Me_5 ligands. The latter compound shows a substantial difference, since hydride donation is 12 kcal/mol easier for **13**. These trends are in accord with spectral data for the compounds. Infrared studies of ν_{CO} stretching modes are often used as indicators of the extent of metal−ligand back-bonding and metal π basicity. Compounds **1** and **3** were studied in toluene solution, for which the ν_{CO} frequencies are 1906 and 1907 cm^{-1}, respectively. These are identical to within instrumental uncertainty (2 cm^{-1} resolution), suggesting similar metal basicity within the bent metallocene fragments Cp_2Nb; thus, the comparable hydricities are entirely reasonable. At the same time, this type of study highlights the dangers of correlating hydricity (a σ effect) with ν_{CO} (a π effect) for different metals with different frontier orbitals (4d vs 5d) having different spatial extensions. Specifically, tantalum derivative **2** is similar to **1** and **3** in both structure and $\Delta G_{\mathrm{M+}}$, but its ν_{CO} frequency in toluene was determined as 1892 cm^{-1}. Hence, it is a better π base, even though comparable in hydride donor power. In considering **8** vs **13**, we note that Cp* is a much better donor than is Cp; it has been suggested that replacing two Cp ligands with two Cp* ligands is the electronic equivalent of lowering the metal oxidation state by one unit.[46] Hence, the dramatic increase in hydricity for **13** is fully expected.

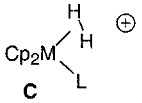
The range of coligands L in the $Cp_2M(L)H$ series allows for several comparisons of thermodynamic *cis*-influences. First, we may compare the influence of a CO ligand with that of two hydrogens in the $Cp_2M(CO)H$ and Cp_2MH_3 compounds; this requires a consideration of the hydricities of the pairs **1**/**6**, **2**/**8**, and **3**/**7**, for which the $\Delta G_{\mathrm{M+}}$ values decrease as 95/86, 95/86, and 93/86. The consistent 7−9 kcal/mol difference shows that the trihydrides are better hydride donors than are the carbonyl hydrides. This is in keeping with the acceptor capability of the carbonyl ligand and donor ability of the hydride ligand,[47] but the situation is potentially more complicated than that. First, the presence of two hydride ligands is formally accompanied by an increase in the metal oxidation state, unless one considers the importance of the dihydrogen states. In all cases, trihydrides (**A**) are more stable than dihydrogen hydride species (**B**), but the latter are thermally accessible for niobium and inaccessible for tantalum.[48] Tautomer **B** would be formulated as a trivalent system, while **A** would formally contain M(V). In fact, however, there is no discernible difference between the $\Delta G_{\mathrm{M+}}$ values of the niobium and tantalum trihydrides, so it is not clear to what extent the effects of oxidation state difference affect the CO vs 2H coligand set. It should also be noted that the cations **C** (formed prior to nitrile insertion[43]) are known to be dihydrogen complexes in both the niobium and tantalum analogues,[48] so this adds an additional energetic component to the consideration of hydride loss. Despite these complications, which remain unresolved, it is clear that there is a substantial energetic difference arising from the relative influence of hydride and CO coligands.



A



B



C

A straightforward comparison between carbonyl and phosphine ligands arises from the data for **2** and **5**. Both systems are Ta(III) analogues, and the phosphine complex proves to be a substantially stronger hydride donor ($\Delta\Delta G_{\mathrm{M+}} = 6$ kcal/mol); this is in keeping with traditional bonding formalisms defining phosphines as better σ donors and weaker π acceptors relative to carbonyl.[47] Conversely, alkynes and η^2-complexed aldehydes are expected to exhibit some π acceptor strength, and they also occupy two coordination sites. A comparison of **2** vs **9** and **1** vs **10** shows that both of these ligands facilitate hydride transfer by 12 kcal/mol relative to the

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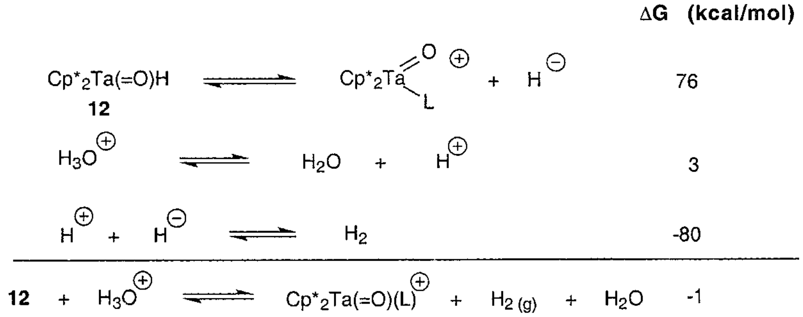
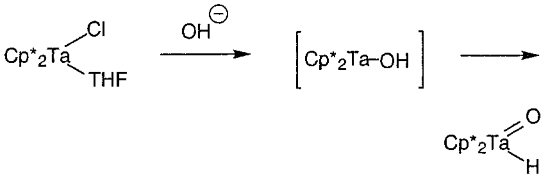
Scheme 1



carbonyl coligand. It is also clear that the C−H hydride transfer systems compare favorably with the M−H systems studied here. Ketene complexes **4** and **11** exhibit ΔG_{M+} values (89 and 81 kcal/mol, respectively) within the range seen for the metal hydrides. It is clear that the nature of the α substituent (Et vs Ph) has a large effect, as would be expected for carbenium ion generation.

Perhaps the most surprising finding in this series of compounds is that oxo compound **12** is such an effective hydride donor. This compound is clearly a tantalum(V) derivative, and the higher oxidation state might be expected to inhibit hydride donation, yet **12** is one of the most effective hydride donors of the series studied. No doubt the effects of the higher oxidation state are mitigated by the presence of Cp* rings; from the discussion above we can assume a 12 kcal/mol contribution, such that the compound $Cp_2Ta(O)H$ (which is unknown) might be expected to exhibit a ΔG_{M+} value of ca. 88 kcal/mol. This would put it into the range of the other tantalocene compounds discussed herein, but would not reflect any special effects due to the higher oxidation state.



(7)

This observation bears an interesting relationship to the known chemistry of compound **12**. This species is made by way of the route shown in eq 7, in which a tantalum(III) chloride is treated with hydroxide.[25] The presumed intermediate is a hydroxo compound which is thought to undergo an α-hydrogen transfer to give the oxo-hydride. This latter process is an intramolecular redox reaction in which a proton (in the hydroxo ligand) is reduced to a hydride while tantalum(III) is oxidized to tantalum(V); the reported chemistry of **12** and the ΔG_{M+} data herein leave little doubt about the hydridic nature of the species. This must be related to the electronic structure of the metal, and only niobium,[49] tantalum,[25,50] and rhenium[51] species have been shown to support this α-elimination process with hydroxo ligands. This chemistry also serves as an interesting model for catalytic proton reduction, a reaction of considerable importance in enzyme mechanisms[52] and the electrocatalysis of hydrogen production.[53] In the latter process metal catalysts are used to overcome kinetic barriers and reduce the overpotential needed in the electrochemical reaction. At some point in the process the metal must serve to reduce a proton to a hydride, which then reacts with another proton to liberate dihydrogen. We can envision a process like this for **12**, and the thermodynamic data allow for calculation of the free energy of the process. This is demonstrated in the thermodynamic cycle (Scheme 1, all values are for MeCN solvent), which consists of the hydricity of **12**, and literature data for hydronium ion dissociation[54] and dihydrogen production.[37] Scheme 1 shows the thermodynamic viability of such a protonolysis process, which could be converted into a catalytic cycle simply by reducing the $Cp*_2Ta({=}O)(L)^+$ product back to tantalum(III).

Competition Reactions. As a means of checking the relative order of the ΔG_{M+} data in Table 1, we wished to set up reactions such as that represented in eq 8.

$$L_nM{-}H + L'_nM^+ \rightleftharpoons L_nM^+ + L'_nM{-}H \qquad (8)$$

Here the cationic product of a weak hydride donor (high ΔG_{M+}) should react with a stronger hydride donor to give the indicated hydride transfer process. The resulting nondegenerate hydride transfer would serve to confirm the relative hydride affinities of the two metal centers. In fact, however, this approach is subject to two complications. First, many of the product cations are unstable and cannot be isolated for such a follow-up study. Second, there is a competition with an alternative process in which hydride-bridged species of the sort $[L_nM{-}H{-}ML_n]^+$ may be formed. This has been observed in closely related systems (eq 9, Cp′ = $C_5H_4{}^tBu$), in which the tantalocene cation binds the niobocene hy-

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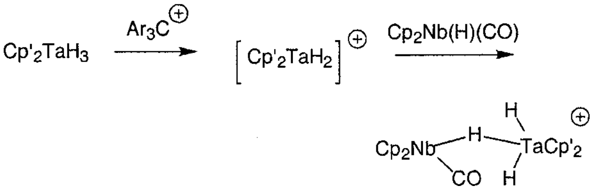
dride.[43] The intervention of this process will depend on the relative affinities of the cation for acetonitrile and another metal hydride. Thus, while the competition reactions would be useful checks on the data, we have found only a few cases in which they proceed in a straightforward fashion. In one such case, $[Cp_2Ta(CO)(NCMe)][BF_4]$ reacted with **9** to give the reaction shown in eq 10, a process calculated to have a strong driving force of ca. 12 kcal/mol. Perhaps more reliable, assuming kinetic factors are not intervening, is the negative result in which such a process fails to occur. This was observed in the reaction of $[Cp_2Nb(CO)(NCMe)][BF_4]$ with **2**, a process calculated to be endoergic by ca. 2 kcal/mol. Although the application of this competition method is limited, it does confirm the relative ordering of the systems to which it may be applied.



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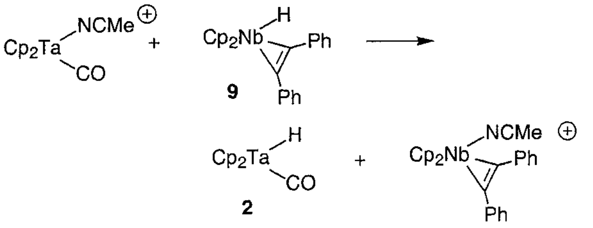

(10)

Conclusions. We have reported the first systematic studies of the thermodynamics of hydride transfer for a series of 13 niobium and tungsten compounds. The ΔG_{M+} data resulting from these studies span a range of 21 kcal/mol. Varying the identity of the metal with isostructural compounds **2**/**3** and/or **7**/**8** does not lead to large changes in the hydride transfer free energy for the species. Conversely, coligands exert a much larger effect on the hydride donor strength of a given compound. As a result, our data indicate that Cp* is a much more efficient donor than is Cp, and phosphine is a better donor than carbonyl; these observations are consistent with the known donor properties of these ligands[47] in the electron-deficient cations resulting from hydride loss. Examples of this effect include the 12 kcal/mol hydricity difference between **8** and **13** and the 6 kcal/mol difference between **2** and **5**. Compound **12**, despite the higher formal oxidation state, is found to be a good hydride donor, since the resulting positive charge is, in part, alleviated by the donor ability of the Cp* ligands. In cases in which $[L_nM-H-ML_n]^+$ formation does not intervene, competition studies have been successful in confirming the relative order of hydride transfer abilities. These data allow for the construction of a *cis*-influence series for hydride transfer, in which the various ligands L in the $(C_5R_5)_2M(L)H$ series are ranked in the order in which they facilitate hydride abstraction. Such an order is shown below, and the position of the oxo coligand is established after correcting for the Cp* donor effects discussed above. This series

$$H_2C{=}O,\ RC{\equiv}CR > O > (H)_2 > PEt_3 > CO$$

may be compared with other series compiled for organometallic reactions. For example, the *trans*-influence series derived from square-planar substitution reactions does include the sequence $H^- > PR_3 > CO$,[55] similar to the latter part of the hydride transfer series. This is largely ascribed to ground state factors related to σ-bonding ability; indeed, this order differs from the kinetic *trans*-effect series in the placement of CO (an excellent *trans*-labilizer) due to the importance of π effects in the latter series. Conversely, much less is known about *cis*-influence or *cis*-effects; the limited data available on kinetic *cis*-effects are for dissociative ligand substitution, for which the steric properties of the *cis*-ligand predominate.[55] In the current series, there may be a thermodynamic steric effect operating, since the large, polarizable hydride ligand is being replaced by the linear nitrile ligand. To the extent this is important, the η^2-bound ligands (aldehyde and alkyne) should exert a thermodynamic steric influence on the reactions. Regardless of these interpretations, the ultimate utility of the data set reported herein will derive from its use in predictions of the energetics for reactions in which **1**−**13** engage in hydride transfer, and further studies of such processes are in progress.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.

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