

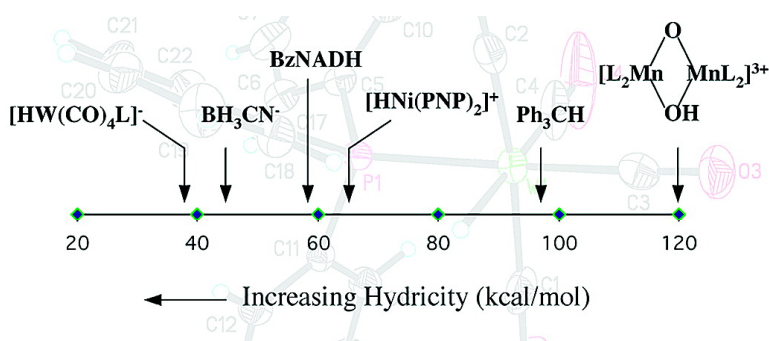
Article

Thermodynamic Hydride Donor Abilities of $[\text{HW}(\text{CO})\text{L}]$ Complexes ($\text{L} = \text{PPh}, \text{P}(\text{OMe}), \text{CO}$) and Their Reactions with $[\text{CMeRe}(\text{PMe})(\text{NO})(\text{CO})]$

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Thermodynamic Hydride Donor Abilities of $[\text{HW}(\text{CO})_4\text{L}]^-$ Complexes ($\text{L} = \text{PPh}_3, \text{P}(\text{OMe})_3, \text{CO}$) and Their Reactions with $[\text{C}_5\text{Me}_5\text{Re}(\text{PMe}_3)(\text{NO})(\text{CO})]^+$

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Abstract: The thermodynamic hydride donor abilities of $[\text{HW}(\text{CO})_5]^-$ (40 kcal/mol), $[\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3]^-$ (37 kcal/mol), and $[\text{HW}(\text{CO})_4(\text{PPh}_3)]^-$ (36 kcal/mol) have been measured in acetonitrile by either equilibrium or calorimetric methods. The hydride donor abilities of these complexes are compared with other complexes for which similar thermodynamic measurements have been made. $[\text{HW}(\text{CO})_5]^-$, $[\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3]^-$, and $[\text{HW}(\text{CO})_4(\text{PPh}_3)]^-$ all react rapidly with $[\text{Cp}^*\text{Re}(\text{PMe}_3)(\text{NO})(\text{CO})]^+$ to form dinuclear intermediates with bridging formyl ligands. These intermediates slowly form $[\text{Cp}^*\text{Re}(\text{PMe}_3)(\text{NO})(\text{CHO})]$ and $[\text{W}(\text{CO})_4(\text{L})(\text{CH}_3\text{-CN})]$. The structure of *cis*- $[\text{HW}(\text{CO})_4(\text{PPh}_3)]^-$ has been determined and has the expected octahedral structure. The hydride ligand bends away from the CO ligand trans to PPh_3 and toward PPh_3 .

Introduction

The tendency of metal hydride complexes, HML_n , to undergo heterolytic cleavage of the $\text{M}-\text{H}$ bond to form a solvated hydride ion (H^-) is an important fundamental property of these complexes. Indeed, it is for this property that they are named. The free energy associated with this heterolytic cleavage reaction, $\Delta G^\circ_{\text{H}^-}$, is a measure of the hydricity of a metal hydride, and only recently have such thermodynamic measurements been reported.¹⁻⁸ There are many important reactions in which a formal hydride transfer reaction occurs. The hydricities of NADH and NADPH determine the thermodynamic driving forces of a large number of biological reactions involved in metabolism. The heterolytic cleavage of hydrogen by hydrogenases involves a hydride transfer to iron or nickel.⁹ Stoichiometric reductions of a variety of organic compounds also involve formal hydride transfers. Finally, many catalytic processes involve heterolytic M^+-H^- bond cleavage at some point in the catalytic cycle.¹⁰ As a result, understanding those features which control a compound's hydricity is of great interest. Achieving

this goal requires quantitative measurements of this property for a range of compounds. Previous studies of transition-metal hydrides have focused mainly on the hydricity of five- and seven-coordinate complexes.¹⁻⁸ In this paper, hydride donor abilities are reported for six-coordinate octahedral complexes, one of the most common classes of transition-metal hydrides.

Six-coordinate, anionic *cis*- $[\text{HW}(\text{CO})_4(\text{L})]^-$ complexes react with a variety of organic electrophiles, including alkyl halides, acyl chlorides, ketones, aldehydes, and epoxides.¹¹⁻¹³ Each of these reactions involves a formal transfer of the hydride ligand to the substrate. In competitive studies of reactions involving hydride transfer from W to alkyl halides and organic carbonyl compounds, *cis*- $[\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3]^-$ was found to react faster than $[\text{HW}(\text{CO})_5]^-$ in all cases except for reactions with tertiary

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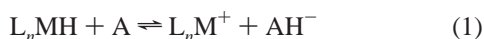
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halides, where steric demands favor reactions with less bulky hydrides.¹¹ It has been suggested that *cis*- $[\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3]^-$ is similar in reactivity to the powerful nucleophile LiBEt_3H , Super Hydride.¹¹ Because these tungsten hydrides are well-characterized and display a variety of synthetically useful hydride transfer reactions, it was of interest to determine the thermodynamic hydride donor ability of these compounds. This would permit comparison of kinetic and thermodynamic measurements of hydricity for these complexes and a thermodynamic comparison with other classes of hydride donors.

Recently, three independent methods have been developed for measuring the thermodynamic hydride donor ability, or hydricity, of transition-metal hydrides. One method is based on an equilibrium measurement of the heterolytic cleavage of hydrogen to form the metal hydride of interest.^{2–4} A second method requires a measurement of the $\text{p}K_{\text{a}}$ of the hydride and the two-electron oxidation potential of the conjugate base of the metal hydride.^{1,5,6} This method is based on an extension of a thermodynamic cycle used by a number of research groups to determine homolytic bond dissociation energies.^{14–16} These two methods have been shown to agree within experimental error (± 2 kcal/mol),² and both provide free-energy values that do not require a reference hydride donor. The third method is intuitively the simplest. It relies on equilibrium measurements of hydride transfer reactions between hydride donors, L_nMH , and hydride acceptors, A, as shown in reaction 1. In this case, eq 2 can be used to calculate $\Delta G^\circ_{\text{H}^-}$ from the equilibrium constant and the hydride donor ability of the reference compound, AH^- .



$$\Delta G^\circ(\text{L}_n\text{MH}) = \Delta G^\circ_{\text{H}^-}(\text{AH}^-) - RT \ln K_1 \quad (2)$$

This approach has been used to determine the *relative* hydride donor abilities of NADH model compounds,¹⁷ transition-metal hydrides,^{1,7,8} and formyl complexes.¹⁸ Unlike the first two methods, it requires that the hydricity of a reference compound be known to obtain absolute hydricity values.

Of these three methods, the one involving direct hydride transfer is most suitable for the study of *cis*- $[\text{HW}(\text{CO})_4(\text{L})]^-$ complexes because the appropriate tungsten derivatives do not react with hydrogen, nor do they display reversible electron-transfer waves in cyclic voltammetric experiments. This paper describes both equilibrium and calorimetric measurements of the hydricity of these complexes using hydride transfer reactions.

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 were reported relative to an external sample of H_3PO_4

(0.00 ppm). All ^{31}P NMR spectra were proton decoupled. 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. The tungsten hydride complexes, $[\text{HW}(\text{CO})_5]^-$ (**1a**), $[\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3]^-$ (**1b**), and $[\text{HW}(\text{CO})_4(\text{PPh}_3)]^-$ (**1c**), were prepared by literature methods,^{19–21} as were $[\text{Cp}^*\text{Re}(\text{PMe}_3)(\text{NO})(\text{CO})]^-$ $[\text{PF}_6]^-$ (**2**)²² and $[\text{CpRe}(\text{PMe}_3)(\text{NO})(\text{CHO})]$.¹⁸ The acetonitrile complexes $[\text{W}(\text{CO})_5(\text{CH}_3\text{CN})]$ (**4a**), $[\text{W}(\text{CO})_4(\text{CH}_3\text{CN})\text{P}(\text{OMe})_3]$ (**4b**), and $[\text{W}(\text{CO})_4(\text{CH}_3\text{CN})(\text{PPh}_3)]$ (**4c**) were also prepared using literature methods.^{23–27} X-ray quality crystals of $[\text{HW}(\text{CO})_4(\text{PPh}_3)]^+[\text{PPh}_3]_2\text{N}^-$ were grown by cooling a saturated acetonitrile solution to -40 °C in a glovebox. Equilibration reactions were performed at room temperature (21 °C).

Synthesis of $\text{Cp}^*\text{Re}(\text{PMe}_3)(\text{NO})(\text{CHO})$. The following preparation was performed under an atmosphere of N_2 on a Schlenk line. Tetramethylammonium borohydride (108 mg; 1.21 mmol) in methanol (6 mL) was added by cannula to a solution of $[\text{Cp}^*\text{Re}(\text{PMe}_3)(\text{NO})(\text{CO})]\text{PF}_6$ (420 mg; 0.700 mmol) in methanol (8 mL) in a centrifuge tube. A white precipitate formed quickly. The mixture was stirred for 10 min and then centrifuged. The yellow supernatant was removed by cannula. The precipitate was subsequently washed with 5 mL of methanol. The wash was combined with the supernatant, and the solvent was removed to form a yellow solid. The solid was extracted with 5 mL of toluene, and the resulting solution was filtered through Celite, followed by two small washes. Removal of the solvent in vacuo gave 285 mg of a yellow solid (89% yield). Because of the low thermal stability of this class of compounds, this compound was stored in a freezer at -40 °C under nitrogen. This compound is pure on the basis of ^1H NMR and ^{31}P NMR spectra. ^1H NMR (400 MHz, CD_3CN): 16.26 ppm (s, 1H, C(O)H), 1.97 ppm (d, $^4J_{\text{PH}} = 0.4$ Hz, 15 H, $\text{C}_5(\text{CH}_3)_5$), 1.49 ppm (d, $^3J_{\text{PH}} = 10$ Hz, 9 H, $\text{P}(\text{CH}_3)_3$). ^{31}P NMR (161 MHz, CD_3CN): -24.36 ppm (s). IR (Nujol mull): ν_{NO} 1643 cm^{-1} , ν_{CO} 1533 cm^{-1} . Closely related formyl complexes have been described previously.^{28–30}

Equilibration of $[\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3]^-$ and $[\text{Cp}^*\text{Re}(\text{PMe}_3)(\text{NO})(\text{CO})]^+$. **Forward Reaction.** $[\text{Cp}^*\text{Re}(\text{PMe}_3)(\text{NO})(\text{CO})]\text{PF}_6$ (**2**) (26.8 mg; 0.0446 mmol) and $[\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3][\text{PPh}_3]_2\text{N}$ (**1b**) (42 mg; 0.044 mmol) were measured into a calibrated NMR tube in a glovebox. The solids were dissolved in CD_3CN (total volume = 600 μL). The reaction was monitored by ^1H NMR and ^{31}P NMR spectroscopy, and the Cp^* signals of $[\text{Cp}^*\text{Re}(\text{PMe}_3)(\text{NO})(\text{CO})]\text{PF}_6$ and its products were used as an internal standard to determine concentrations. Formation of an intermediate $[\text{Cp}^*\text{Re}(\text{PMe}_3)(\text{NO})(\mu\text{-CHO})\text{W}(\text{CO})_4\text{P}(\text{OMe})_3]$ (**3b**) was observed immediately (~ 10 min after mixing). [^1H NMR of **3b** (CD_3CN): 14.76 ppm (s, 1 H, C(O)H), 3.65 ppm (d, 9 H, $\text{P}(\text{OCH}_3)_3$, $^3J_{\text{PH}} = 11$ Hz), 2.01 ppm (d, 14 H, $\text{C}_5(\text{CH}_3)_5$, $^4J_{\text{PH}} = 0.8$ Hz), 1.54 ppm (d, 9 H, $\text{P}(\text{CH}_3)_3$, $^2J_{\text{PH}} = 10$ Hz). ^{31}P NMR of **3b** (CD_3CN): 152.7 ppm (s, $\text{P}(\text{OCH}_3)_3$, $^1J_{\text{PW}} = 382$ Hz), -23.6 ppm (s, $\text{P}(\text{CH}_3)_3$).] The equilibrium constant for this conversion ($K = [\text{3b}]/[\text{1b}][\text{2}]$) was calculated to be 230 M^{-1} by integration of the ^1H NMR and ^{31}P NMR spectra. This value was constant for the first 3 h of the reaction, after which the concentrations of **1b** and **2** were too low to measure. Concurrent formation of $[\text{W}(\text{CO})_4(\text{CD}_3\text{CN})\text{P}(\text{OMe})_3]$ (**4b**) and $\text{Cp}^*\text{Re}(\text{PMe}_3)(\text{NO})(\text{CHO})$ (**5**) was observed. The equilibrium constant for this

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conversion ($K = [4b][5]/[3b]$) reached a constant value of 16 M over one week of observation.

Reverse Reaction. Cp*Re(PMe₃)(NO)(CHO) (**5**) (30 mg; 0.066 mmol) and [W(CO)₄(CH₃CN)P(OMe)₃] (**4b**) (30 mg; 0.065 mmol) were added to a calibrated NMR tube in a glovebox. The solids were dissolved in CD₃CN (total volume = 600 μL). As above, the reaction was monitored by ¹H NMR and ³¹P NMR spectroscopy, and the Cp* signals of Cp*Re(PMe₃)(NO)(CHO) and its products were used as an internal standard to determine concentrations. After one week of reaction, the intermediate complex **3b** could be observed, and the equilibrium constant for the reaction ($K = [4b][5]/[3b]$) had reached a constant value of 24 M.

Equilibration of [HW(CO)₅]⁻ and [Cp*Re(PMe₃)(NO)(CO)]⁺. NMR tube reactions were studied using known amounts of [Cp*Re(PMe₃)(NO)(CO)]PF₆ and [HW(CO)₅][(PPh₃)₂N]. An intermediate, [Cp*Re(PMe₃)(NO)(μ-CHO)W(CO)₅] (**3a**), was observed immediately (~10 min after mixing). ¹H NMR of **3a** (CD₃CN): 15.01 ppm (s, 1 H, C(O)H), 2.00 ppm (d, 15 H, C₅(CH₃)₅, ⁴J_{PH} = 0.4 Hz), 1.55 ppm (d, 9 H, P(CH₃)₃, ²J_{PH} = 10 Hz). The equilibrium constant for this conversion ($K = [3a]/[1a][2]$) was calculated to be 2.8 M⁻¹ by integration of the ¹H NMR spectra. Over a 20-h period, the formation of Cp*Re(PMe₃)(NO)(CHO) was observed.

Reaction of [HW(CO)₄(PPh₃)⁻ and [Cp*Re(PMe₃)(NO)(CO)]⁺. NMR tube reactions were studied using known amounts of [Cp*Re(PMe₃)(NO)(CO)]PF₆ and [HW(CO)₄(PPh₃)][(PPh₃)₂N]. An intermediate, [Cp*Re(PMe₃)(NO)(μ-CHO)W(CO)₄(PPh₃)] (**3c**), was observed immediately (~10 min after mixing). ¹H NMR of **3c** (CD₃CN): 14.7 ppm (s, 1 H, C(O)H), 1.96 ppm (s, 15 H, C₅(CH₃)₅), 1.50 ppm (d, 9 H, P(CH₃)₃, ²J_{PH} = 10 Hz). ³¹P NMR of **3c** (CD₃CN): 30.6 ppm (s, PPh₃, ¹J_{PW} = 236 Hz), -22.4 ppm (s, P(CH₃)₃). This reaction goes to completion, and no equilibrium constant could be determined. Over a 20-h period, the formation of [W(CO)₄(CD₃CN)(PPh₃)] and Cp*Re(PMe₃)(NO)(CHO) was observed.

Equilibration of [CpRe(PMe₃)(NO)(CHO)] and [Cp*Re(PMe₃)(NO)(CO)]⁺. [Cp*Re(PMe₃)(NO)(CO)](PF₆) (9.2 mg; 0.015 mmol) and [CpRe(PMe₃)(NO)(CHO)] (8.0 mg; 0.021 mmol) were measured into an NMR tube in the glovebox. The solids were dissolved in CD₃CN (600 μL), and the reaction was followed by ¹H NMR for 5 h. Equilibrium was reached after 30 min. The equilibrium constant of the reaction was determined to be 0.035 by integration of the ¹H NMR and ³¹P NMR spectra for this reaction. The reverse reaction was studied in a similar manner. ΔG° for this reaction was determined to be 2.0 kcal/mol. A ΔG°_H value of 44.1 ± 1 kcal/mol for CpRe(PMe₃)(NO)(CHO)¹⁸ results in a ΔG°_H value of 42.1 ± 1 kcal/mol for Cp*Re(PMe₃)(NO)(CHO).

Calorimetry. In a typical experiment, the reaction cell of the calorimeter was purged with a stream of N₂ for 15 min. Subsequently, it was loaded by syringe with a 5.4 mM solution of [*p*-Me₂NC₆H₄]₃C][PF₆] in dry acetonitrile (cell volume = 1.3 mL). The reference cell of the calorimeter was loaded with neat acetonitrile. Stirring was commenced at 300 rpm, and the calorimeter was allowed to equilibrate for 1.5 h. Next, a 250 μL syringe containing a 10.6 mM solution of [HW(CO)₄P(OMe)₃][(PPh₃)₂N] in acetonitrile was inserted into the cell. (Both solutions were prepared in the glovebox.) After 20 min of equilibration at 25.6 °C, 10 injections (5 μL) 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 nine injections was 34.1 kcal/mol. Next, 18 injections (10 μL) of the hydride solution were added to the cell with the same 8-min delay. Again, after discarding the first data point, the average enthalpy/mol for the following 17 injections was 34.1 kcal/mol. At least three independent experiments were performed in this manner for each of the three hydrides studied.

X-ray Diffraction Studies. X-ray diffraction data from a crystal of [HW(CO)₄(PPh₃)][(PPh₃)₂N] were recorded on a Bruker Nonius SMART CCD diffractometer employing Mo Kα radiation (graphite

Table 1. Crystallographic Data for [HW(CO)₄(PPh₃)][(PPh₃)₂N]^a

empirical formula	C ₅₈ H ₄₆ NO ₄ P ₃ W
formula weight	1097.72
crystal system	monoclinic
space group	P2(1)/c
unit cell dimensions	
<i>a</i> (Å)	11.389(2)
<i>b</i> (Å)	26.182(4)
<i>c</i> (Å)	16.820(3)
α (deg)	90
β (deg)	101.849(12)
γ (deg)	90
volume (Å ³)	4908.9(14)
<i>Z</i>	4
density (calcd) (Mg/m ³)	1.485
crystal size (mm ³)	0.60 × 0.45 × 0.40
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0340, wR2 = 0.0799
<i>R</i> indices (all data)	R1 = 0.0382, wR2 = 0.0819
extinction coefficient	0.0193(4)
largest diff. peak and hole (e ⁻ Å ⁻³)	1.985 and -0.575

^a Definitions of R1 and wR2: R1 = Σ||F_o| - |F_c||/Σ|F_o|; wR2 = {Σ[w(F_o² - F_c²)²]/Σ[w(F_o²)²]}^{1/2}.

monochromator). Selected details related to the crystallographic experiment are listed in Table 1. Unit cell parameters were obtained from a least-squares fit to the angular coordinates of all reflections, and intensities were integrated from a series of frames (3.35–23.33° ω rotation) covering more than a hemisphere of reciprocal space. Absorption and other corrections were applied by using SADABS.³¹ The structure was solved by using direct methods and refined (on F², using all data) by a full-matrix, weighted least-squares process. All nonhydrogen atoms were refined by using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined by using a riding model. Standard Bruker Nonius control (SMART) and integration (SAINT) software was employed, and Bruker Nonius SHELXTL³² software was used for structure solution, refinement, and graphics.

Results

Equilibrium Studies. The tungsten hydride complexes, [HW(CO)₅]⁻ (**1a**), *cis*-[HW(CO)₄P(OMe)₃]⁻ (**1b**), and *cis*-[HW(CO)₄(PPh₃)]⁻ (**1c**), react with [Cp*Re(PMe₃)(NO)(CO)]⁺ (**2**) (where Cp* = pentamethylcyclopentadiene), as shown in reaction 3. In each case, an intermediate formyl-bridged dinuclear complex, [Cp*Re(PMe₃)(NO)(μ-CHO)W(CO)₄(L)] (**3**), is formed. The ¹H NMR spectra of these intermediates exhibit a singlet at 14–15 ppm that is characteristic of a formyl resonance.^{28–30} These resonances are 1–2 ppm upfield from the resonance of [Cp*Re(PMe₃)(NO)(CHO)]. In addition, new ¹H NMR resonances are observed for the trimethylphosphine and Cp* ligands on rhenium, with corresponding resonances for the trimethyl phosphite and triphenylphosphine ligands on tungsten (see Experimental Section). These resonances appear and disappear in unison, and they have integration ratios consistent with the formation of mixed bimetallic species. ³¹P NMR results are also consistent with the formation of bridged species (see Experimental Section). Two coordination modes are reasonable for the bridging formyl ligand of these intermediates. In the one shown in structure **3**, the relatively basic oxygen atom of the formyl moiety is bound to tungsten. A second possible mode involves a C–H–W linkage (structure **6**). This is not unrealistic given the propensity of tungsten to form

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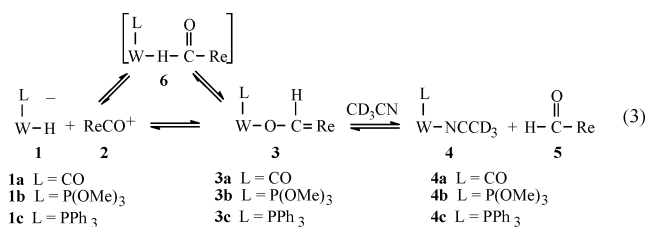
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Table 2. Thermodynamic, Kinetic, and Spectroscopic Parameters for *cis*-[HW(CO)₄(L)][−] Complexes

compound	ΔH ^o _f (kcal/mol) ^a	ΔG ^o _f (kcal/mol) ^b	k × 10 ³ (s ^{−1} M ^{−1}) ^c	νCO (cm ^{−1}) ^d
[HW(CO) ₅] [−]	−31	40	3.3	2029, 1889, 1858
[HW(CO) ₄ P(OMe) ₃] [−]	−34	37	50	1986, 1856, 1822
[HW(CO) ₄ (PPh ₃)] [−]	−35	36		1974, 1851, 1815

^a Enthalpy associated with reaction 4 at 298.6 K. ^b Free energy (at 294 K) associated with the heterolytic cleavage of the W–H bond to form solvated H[−] and *cis*-[HW(CO)₄(L)(CH₃CN)][−]. ^c Second-order rate constants taken from ref 11 for the reaction of *cis*-[HW(CO)₄(L)][−] complexes with *n*-bromobutane to form *n*-butane (299 K in THF). ^d IR data taken from refs 21 and 45.

bridging hydride complexes²¹ and the likelihood that a C–H–W interaction is involved in the initial formation of the C–H bond. However, the lack of ¹⁸³W satellites for the formyl resonances and the relatively small differences in chemical shifts between the free formyl complex and that of the intermediate argue against a direct W–H interaction in the observed intermediate. In addition, in previous hydride transfer reactions of these complexes with CO₂ and aldehydes, products or intermediates with W–O bonds were observed, e.g., WOC(O)H and WOCH₃.^{13,21} Efforts to isolate intermediates **3a–c** have been unsuccessful, and no parent ion was observed by electrospray mass spectroscopy.



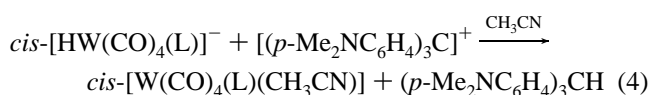
After the formation of intermediate **3**, slow release of the formyl complex, [Cp*Re(PMe₃)(NO)(CHO)] (**5**), occurs as shown in the second step of reaction 3. Formation of the corresponding *cis*-[W(CO)₄(L)(CH₃CN)] complexes, **4**, also occurs in this step. Both of the products were confirmed by comparison of the ¹H NMR spectra and ³¹P NMR spectra of authentic compounds synthesized by literature methods.^{23–27} For the reaction of the triphenylphosphine complex, [HW(CO)₄(PPh₃)][−], complete conversion to the formyl-bridged intermediate, **3c**, occurs in less than 10 min, followed by a slow dissociation to the ultimate reaction products, *cis*-[W(CO)₄(PPh₃)(CD₃CN)] and [Cp*Re(PMe₃)(NO)(CHO)], over a period of 20 h. However, for [HW(CO)₅][−] and *cis*-[HW(CO)₄P(OMe)₃][−], only partial conversion to the corresponding formyl-bridged intermediates (**3a** and **3b**) occurs initially. These reactants establish a measurable equilibrium with the intermediates within 10 min. For the reaction of *cis*-[HW(CO)₄P(OMe)₃][−] with [Cp*Re(PMe₃)(NO)(CO)]⁺, the equilibrium constant was measured to be 230 M^{−1} at 21 °C in CD₃CN by ¹H and ³¹P NMR. The same equilibrium constant is obtained over a period of 3 h, after which the concentrations of *cis*-[HW(CO)₄P(OMe)₃][−] become too small to measure because of the slow conversion of the intermediate to the final products *cis*-[W(CO)₄P(OMe)₃(CH₃CN)] and [Cp*Re(PMe₃)(NO)(CHO)]. The reaction of [HW(CO)₅][−] and [Cp*Re(PMe₃)(NO)(CO)]⁺ behaves in a similar manner. In this case, the equilibrium constant for the formation of the intermediate is 2.8 M^{−1}.

The conversion of intermediate **3b** to final products [Cp*Re(PMe₃)(NO)(CHO)] and *cis*-[W(CO)₄P(OMe)₃(CH₃CN)] is particularly interesting. Although the reaction proceeds nearly to completion, intermediate **3b** persists in low concentration after

one week. At this time the equilibrium constant ($K = [\mathbf{4b}][\mathbf{5}]/[\mathbf{3b}]$, where the activity of the solvent, acetonitrile, is taken as unity) for the conversion of intermediate **3b** to products is 24 M. To establish that this reaction is an equilibrium, the reverse reaction between [Cp*Re(PMe₃)(NO)(CHO)] and *cis*-[W(CO)₄P(OMe)₃(CH₃CN)] was studied. After one week, a small quantity of complex **3b** was observed. An equilibrium constant of 16 M for the second step of reaction 3 was determined from these data, with an average from the forward and reverse reactions of 20 M.

The overall equilibrium constant for reaction 3, starting from *cis*-[HW(CO)₄P(OMe)₃][−] and [Cp*Re(PMe₃)(NO)(CO)]⁺ to form [Cp*Re(PMe₃)(NO)(CHO)] and *cis*-[W(CO)₄P(OMe)₃(CH₃CN)] is 4600, the product of the equilibrium constants for steps 1 and 2. This corresponds to a free energy of -5 ± 1 kcal/mol for the hydride transfer from *cis*-[HW(CO)₄P(OMe)₃][−] to [Cp*Re(PMe₃)(NO)(CO)]⁺ in acetonitrile. The free energy of hydride transfer for [Cp*Re(PMe₃)(NO)(CHO)] was determined to be 42 ± 1 kcal/mol (see Experimental Section). An addition of -5 kcal/mol to this value gives a ΔG^o_H value of 37 ± 2 kcal/mol for *cis*-[HW(CO)₄P(OMe)₃][−] in acetonitrile.

Calorimetric Studies. It is likely that there is also an equilibrium in the dissociation of intermediate **3a**. However, the concentration of the acetonitrile complex, [W(CO)₅(CD₃CN)], cannot be easily measured by NMR, nor can it be assumed to be equal to the concentration of formyl product, [Cp*Re(PMe₃)(NO)(CHO)], because of the formation of bridging hydride complexes of tungsten.²¹ To overcome this problem, calorimetric studies were undertaken to determine the relative hydride donor abilities of [HW(CO)₅][−], *cis*-[HW(CO)₄P(OMe)₃][−], and *cis*-[HW(CO)₄(PPh₃)][−]. Reactions of these hydrides with crystal violet, [(*p*-Me₂NC₆H₄)₃C]⁺ (reaction 4), were found to be fast and clean by NMR spectroscopy, a necessary requirement for obtaining useful calorimetric data. Enthalpy measurements of reaction 4 were made using an isothermal calorimeter. In a typical experiment, 10–20 aliquots of a dilute acetonitrile solution of one of the hydrides were injected into a cell containing a more concentrated solution of the acceptor at 25.6 °C (see Experimental Section for details), and the heat produced was measured. The results of these experiments are shown in the second column of Table 2. The accuracy of these measurements is estimated to be ±2 kcal/mol.



The hydride donor ability of *cis*-[HW(CO)₄P(OMe)₃][−] was determined from the equilibrium measurements described above to be 37 kcal/mol. The observed enthalpy change for reaction 4 for *cis*-[HW(CO)₄P(OMe)₃][−] is -34 kcal/mol, which indicates

that addition of 71 kcal/mol is required to convert from the enthalpy of reaction 4 to $\Delta G^\circ_{\text{H}^-}$. The free energies shown in column 3 of Table 2 were obtained using this same correction for all three complexes and the heats of reaction shown in column 2. The estimated uncertainties on these values is ± 2 kcal/mol.

Using the same correction factor to convert from the heat of reaction 4 to $\Delta G^\circ_{\text{H}^-}$, we assume that the entropy contributions for hydride transfer for the three different hydride complexes are the same. This assumption seems reasonable. All of the complexes have the same charge, all of the reactions involve formation of a tungsten acetonitrile complex, and all three complexes are of roughly the same size. If acetonitrile binds to the carbonium ion on the left-hand side of reaction 4, as it does to tungsten on the right-hand side, then reaction 4 is a simple interchange of the hydride and acetonitrile ligands, with a corresponding change in charge on carbon and tungsten. For these reasons, hydride transfer reactions appear to be very similar to electron-transfer reactions. Entropy changes associated with individual redox couples can be calculated for metal complexes using a semiempirical equation developed by Weaver.³³ $T\Delta S^\circ$ values for reaction 4 of 2.3, 2.1, and 1.9 kcal/mol were calculated for $[\text{HW}(\text{CO})_5]^-$, $\text{cis-}[\text{HW}(\text{CO})_4\text{P}(\text{OMe}_3)]^-$, and $\text{cis-}[\text{HW}(\text{CO})_4(\text{PPh}_3)]^-$, respectively, using estimated radii of 6.2, 4.5, 5.2, and 6.5 Å for the radii of $(\text{Me}_2\text{NC}_6\text{H}_4)_3\text{CH}$, $[\text{HW}(\text{CO})_5]^-$, $\text{cis-}[\text{HW}(\text{CO})_4\text{P}(\text{OMe}_3)]^-$, and $\text{cis-}[\text{HW}(\text{CO})_4(\text{PPh}_3)]^-$, respectively. The similarity of these calculated values suggests that assuming the same entropy corrections for all three tungsten hydrides for reaction 4 is reasonable.

From the hydride donor ability of $(p\text{-Me}_2\text{NC}_6\text{H}_4)_3\text{CH}$ in acetonitrile (74.2 kcal/mol)^{34,35} and $\text{cis-}[\text{HW}(\text{CO})_4\text{P}(\text{OMe}_3)]^-$ (37 kcal/mol), a free energy for reaction 4 of -37 kcal/mol is expected. The observed enthalpy change of -34 kcal/mol indicates that $T\Delta S^\circ$ is approximately 3 kcal/mol. This value agrees well with the 1.9–2.3 kcal/mol range calculated in the preceding paragraph. Although this agreement may be fortuitous, good agreement between calculated and experimentally determined $T\Delta S^\circ$ values has also been observed in hydride transfer reactions of $[\text{HNi}(\text{diphosphine})_2]^+$ complexes.¹

Structure of $[\text{HW}(\text{CO})_4\text{PPh}_3]^-$. Crystals of $\text{cis-}[\text{HW}(\text{CO})_4(\text{PPh}_3)]^-[(\text{PPh}_3)_2\text{N}]$ were grown from cold acetonitrile solutions. Crystallographic data for this complex are given in Table 1. A perspective drawing is shown in Figure 1, and selected bond angles and distances are shown in Table 3. The structure of the $\text{cis-}[\text{HW}(\text{CO})_4(\text{PPh}_3)]^-$ anion is octahedral with the hydride and triphenylphosphine ligands occupying cis positions. The bond distances to the coordinated ligands are in the normal range for W(0) complexes.³⁶ The P(1)–W–C(3) bond angle is nearly linear (177.4°), but the H(1)–W–P(1) angle is significantly less than 90° (80.6°). These angles indicate a bending of the hydride ligand away from the carbonyl ligand C(3)–O(3) toward triphenylphosphine. In addition, the two carbonyl ligands cis to the hydride ligand, C(1)–O(1) and C(2)–O(2), bend toward

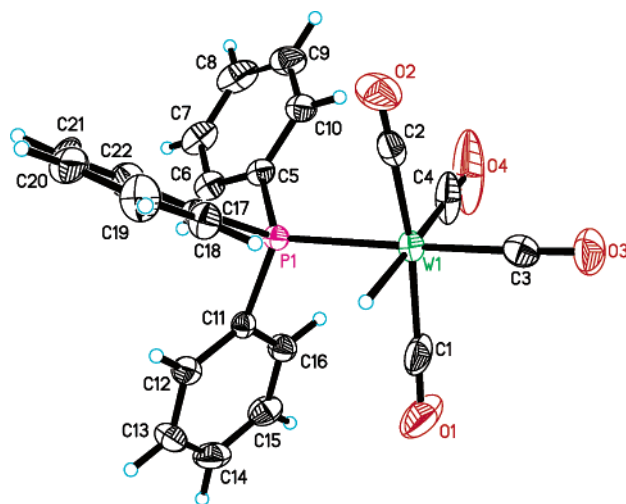


Figure 1. Drawing of the $\text{cis-}[\text{HW}(\text{CO})_4(\text{PPh}_3)]^-$ anion showing the atom numbering scheme.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $\text{cis-}[\text{HW}(\text{CO})_4(\text{PPh}_3)]^-$

bond distances (Å)		bond angles (deg)	
W(1)–H(1)	1.682(6)	H(1)–W(1)–P(1)	80.61(17)
W(1)–C(4)	1.961(5)	C(4)–W(1)–C(3)	90.07(17)
W(1)–C(3)	1.967(5)	C(4)–W(1)–C(2)	99.9(2)
W(1)–C(2)	2.003(5)	C(3)–W(1)–C(2)	89.03(16)
W(1)–C(1)	2.012(6)	C(4)–W(1)–C(1)	96.4(2)
W(1)–P(1)	2.5014(10)	C(3)–W(1)–C(1)	91.37(16)
O(1)–C(1)	1.148(6)	C(2)–W(1)–C(1)	163.8(2)
O(2)–C(2)	1.169(6)	C(4)–W(1)–P(1)	91.48(13)
O(3)–C(3)	1.170(5)	C(3)–W(1)–P(1)	177.39(12)
O(4)–C(4)	1.154(6)	C(2)–W(1)–P(1)	88.63(11)
		C(1)–W(1)–P(1)	90.55(12)

the hydride, as indicated by a C(1)–W–C(2) bond angle of 163.8°. It has been shown previously that ligands cis to a π -acceptor ligand and a σ -only ligand, such as the hydride, will tend to move away from the π -acceptor ligand toward the hydride.³⁷ This distortion is expected to reduce the hydricity of the hydride ligand compared to that of an undistorted octahedral complex because of a redistribution of negative charge from the hydride ligand to the trans carbonyl ligand.³⁸

Discussion

Comparison of Thermodynamic Hydricity and Reactivity of $\text{cis-}[\text{HW}(\text{CO})_4(\text{L})]^-$ Complexes. Although numerous $\text{p}K_{\text{a}}$ values for transition-metal hydrides have been determined,^{39–44} relatively few thermodynamic measurements of the hydricity of these complexes have been reported.^{1–8} In this study, both

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equilibrium and calorimetry measurements were used to obtain information on the energetics of hydride transfer for $[\text{HW}(\text{CO})_5]^-$, $\text{cis-}[\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3]^-$, and $\text{cis-}[\text{HW}(\text{CO})_4(\text{PPh}_3)]^-$. These data are summarized in columns 2 and 3 of Table 2. Darensbourg first prepared and studied the reactivity and relative reaction rates of these tungsten hydrides.^{11–13} In competitive studies of reactions of $[\text{HW}(\text{CO})_5]^-$ and $\text{cis-}[\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3]^-$ with *n*-bromobutane to form *n*-butane, $\text{cis-}[\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3]^-$ reacted approximately 20 times faster than $[\text{HW}(\text{CO})_5]^-$.¹¹ Similarly, on the basis of the stretching frequencies of the carbonyl ligands, the expected hydride donor ability is $[\text{HW}(\text{CO})_5]^- < \text{cis-}[\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3]^- \leq \text{cis-}[\text{HW}(\text{CO})_4(\text{PPh}_3)]^-$.^{21,45} These kinetic and spectroscopic data are shown in columns 4 and 5 in Table 2, and they correlate well with our thermodynamic measurements of hydricity shown in column 3. The observation that *tert*-butyl bromide reacts more slowly with $\text{cis-}[\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3]^-$ than with $[\text{HW}(\text{CO})_5]^-$ has been attributed to steric interactions,¹³ and this is supported by our structural studies of the $\text{cis-}[\text{HW}(\text{CO})_4(\text{PPh}_3)]^-$ anion. Not only is the hydride *cis* to the bulky phosphine ligand, there is also a significant bending of the hydride ligand toward phosphorus by about 10°. Although this bending may be less for a phosphite ligand, significant bending is still expected because CO is a better acceptor than trimethyl phosphite.³⁷ This distortion will increase the steric screening of the hydride ligand by the *cis* phosphine or phosphite ligands.

The hydricity of these tungsten complexes and their clean reactions with organic carbonyl complexes^{12,13} suggested that they might also react cleanly with metal carbonyl complexes. As discussed above, $[\text{HW}(\text{CO})_5]^-$, $\text{cis-}[\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3]^-$, and $\text{cis-}[\text{HW}(\text{CO})_4(\text{PPh}_3)]^-$ all react with $[\text{Cp}^*\text{Re}(\text{PMe}_3)(\text{NO})(\text{CO})]^+$ as shown in reaction 3 to first form observable intermediates assigned structures **3a–c**. Qualitatively, the rate and extent of formation of these intermediates parallels the hydricity of the reactants, i.e., $[\text{HW}(\text{CO})_5]^- < \text{cis-}[\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3]^- < \text{cis-}[\text{HW}(\text{CO})_4(\text{PPh}_3)]^-$. Intermediates **3a–c** ultimately convert into the final products, $\text{cis-}[\text{W}(\text{CO})_4(\text{L})(\text{CH}_3\text{CN})]$ and $[\text{Cp}^*\text{Re}(\text{PMe}_3)(\text{NO})(\text{CHO})]$. Intermediates **3a–c** are similar to those observed in other laboratories. In Darensbourg's work, alkoxide intermediates were formed as the first products resulting from hydride transfer to aldehydes.¹³ Reactions of CO₂ with these hydrides resulted in the formation of formate complexes, $\text{cis-}[\text{HCOOW}(\text{CO})_4(\text{L})]^-$.²¹ Similarly, in the reaction of the hydride acceptor 1-benzyl-3-carbamoylpyridinium cation with $\text{HRe}(\text{bpy})(\text{CO})_3$, an intermediate is observed after initial hydride transfer to the pyridinium ring.⁴⁶ This intermediate contains a bond between rhenium and the oxygen atom of the carbamoyl group. Similar intermediates have been proposed in catalytic reductions of NAD⁺.⁴⁷ These reactions all appear to occur by a common pathway of hydride transfer followed by rearrangement to form an intermediate with an M–O bond and then slow solvolysis of the M–O bond.

Comparison of Thermodynamic Hydricity and Reactivity of $\text{cis-}[\text{HW}(\text{CO})_4(\text{L})]^-$ Complexes with Other Transition-Metal Hydrides. Thermodynamic measurements of hydricity have now been reported for more than 20 transition-metal hydride complexes, and a hydride donor scale for these complexes covers a range of over 50 kcal/mol.^{1–8} These values may be correlated to observed reactions of metal hydrides, as discussed above, and used to predict reactivity.^{6,18} In general, the hydride donor abilities of metal hydride complexes are found to increase as the ligands become more electron donating or poorer π -acceptors, as the charge on the metal complex decreases, and as one moves from right to left in the Periodic Table.⁴⁸ In Table 2, a lower $\Delta G^\circ_{\text{H}^-}$ value indicates a better hydride donor, and $\text{cis-}[\text{HW}(\text{CO})_4(\text{PPh}_3)]^-$ is a better hydride donor than $[\text{HW}(\text{CO})_5]^-$ by 4 kcal/mol. This difference in hydride donor ability upon substitution of CO with triphenylphosphine is of similar magnitude to those observed for other systems. For example, for the rhenium formyl complexes, $\text{CpRe}(\text{NO})(\text{CO})\text{CHO}$ ($\Delta G^\circ_{\text{H}^-} = 55$ kcal/mol) and $\text{CpRe}(\text{NO})(\text{PPh}_3)\text{CHO}$ ($\Delta G^\circ_{\text{H}^-} = 46$ kcal/mol), the substitution of CO with triphenylphosphine increases the hydride donor ability by 9 kcal/mol.¹⁸ Similarly, $\text{CpMo}(\text{CO})_3\text{H}$ ($\Delta G^\circ_{\text{H}^-} = 89$ kcal/mol) and $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{H}$ ($\Delta G^\circ_{\text{H}^-} = 82$ kcal/mol) differ by 7 kcal/mol.⁷

Comparison of the hydride donor ability of $\text{CpW}(\text{CO})_3\text{H}$ ($\Delta G^\circ_{\text{H}^-} = 83$ kcal/mol)⁷ with $[\text{HW}(\text{CO})_5]^-$ ($\Delta G^\circ_{\text{H}^-} = 40$ kcal/mol) suggests that charge and geometry have very large effects on hydride donor abilities. The only other octahedral metal hydride for which the hydride donor ability has been determined is $[\text{H}_2\text{Co}(\text{dppe})_2]^+$, for which $\Delta G^\circ_{\text{H}^-}$ is 65 kcal/mol.³ The octahedral tungsten hydrides in this study are better hydride donors by nearly 30 kcal/mol. Certainly the fact that they are negatively charged, whereas $[\text{H}_2\text{Co}(\text{dppe})_2]^+$ is positively charged, is a major contributor to the observed differences. The most surprising and interesting comparison is that of $\text{HRh}(\text{dppb})_2$ ($\Delta G^\circ_{\text{H}^-} = 34$ kcal/mol, where *dppb* is 1,2-bis(diphenylphosphino)benzene)⁴ with $\text{cis-}[\text{HW}(\text{CO})_4(\text{PPh}_3)]^-$ ($\Delta G^\circ_{\text{H}^-} = 36$ kcal/mol). The observation that a neutral rhodium hydride containing a nonbasic diphosphine ligand is as hydridic as an anionic tungsten hydride indicates that making judgments about hydricity on the basis of the position of a metal in the Periodic Table may lead to conclusions that are not even qualitatively correct.

Comparison of Thermodynamic Hydricity and Reactivity of $\text{cis-}[\text{HW}(\text{CO})_4(\text{L})]^-$ Complexes with Other Hydride Donors. Compared with other transition-metal hydrides, the $\text{cis-}[\text{HW}(\text{CO})_4(\text{L})]^-$ complexes are among the best hydride donors. From Table 4, it can be seen that these tungsten hydrides are also more hydridic than the better organic hydride donors.^{49,50} For example, NADH model compounds are generally considered to be good hydride donors and the benzyl derivative, 1-benzyl-1,4-dihydronicotinamide, shown in Table 4, has a hydride donor ability of 59 kcal/mol in dimethyl sulfoxide.⁴⁹ Outside of some very unstable radical intermediates,⁵¹ the formyl complex, $[\text{Cp}^*\text{Re}(\text{PMe}_3)(\text{NO})(\text{CHO})]$, prepared in this study is the best

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Table 4. Hydride Donor Abilities of Different Classes of Compounds

	$\Delta G_{\text{H}^-}^{\circ}$ (kcal/mol)	ref
Heterolytic Cleavage of C–H Bonds		
Ph ₃ CH	96	50
1-benzyl-1,4-dihydronicotinamide	59	49
<i>N</i> -(4-methoxyphenyl)fluoreneamine	47	49
Cp*Re(NO)(PMe ₃)C(O)H	42	
Heterolytic Cleavage of M–H Bonds		
CpMo(CO) ₃ H	87	7
[HNi(Et ₂ PCH ₂ CH ₂ CH ₂ PEt ₂) ₂] ⁺	66	6
[HW(CO) ₄ (L)] ⁻	36–40	
HRh(dppb) ₂	34	4
Heterolytic Cleavage of O–H Bonds		
[(phen) ₂ Mn(μ-O)(μ-OH)Mn(phen) ₂] ³⁺	120	52
[(phen) ₂ Mn(μ-OH) ₂ Mn(phen) ₂] ²⁺	78	52
Heterolytic Cleavage of B–H Bonds		
NaBH ₃ (CN)	~45	34

hydride donor known involving cleavage of a C–H bond with a $\Delta G_{\text{H}^-}^{\circ}$ value of 42 kcal/mol. As expected, the *cis*-[HW(CO)₄(L)]⁻ complexes are much more hydridic than manganese complexes with bridging hydroxo ligands,⁵² but it is interesting to note that the data in Table 4 suggest that [(phen)₂Mn(μ-OH)₂Mn(phen)₂]²⁺ is a better hydride donor than some transition-metal hydride complexes. Finally, the *cis*-[HW(CO)₄(L)]⁻ complexes and HRh(dppb)₂ are better hydride donors than the commonly used reducing agent, sodium cyanoborohydride.³³ As the rhodium complex can be generated from hydrogen, this raises interesting possibilities for using hydrogen under basic conditions to carry out a variety of difficult reduction processes in a catalytic fashion.

Summary

The hydride donor abilities of [HW(CO)₅]⁻, *cis*-[HW(CO)₄P(OMe)₃]⁻, and *cis*-[HW(CO)₄(PPh₃)]⁻ have been measured in acetonitrile, and the reactions of these complexes with [Cp*Re(PMe₃)(NO)(CO)]⁺ have been studied. The thermodynamic hydride donor abilities of these tungsten complexes parallel the

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rates of reactions of these complexes with organic substrates except for cases where steric interactions are expected to contribute. The tungsten complexes are relatively powerful hydride donors, and a relative ordering of these complexes compared to other classes of metal hydrides (in kcal/mol) is as follows: CpMo(CO)₂(L)H (79–89) < CpW(CO)₂(L)H (81–83) < H₂ (76) < [HNi(diphosphine)₂]⁺ (51–67) < [HPt(diphosphine)₂]⁺ (42–55) ≈ CpRe(NO)(L)(CHO) (42–55) ≈ HCo(dppe)₂ (49) < *cis*-[HW(CO)₄(L)]⁻ (36–40) < HRh(dppb)₂ (34). Although transition-metal hydrides are generally much better hydride donors than organic, organometallic, and metal hydroxide compounds, all of these classes of compounds exhibit large ranges of hydride donor abilities, and large overlaps occur. Some of the factors that appear to contribute to the wide range of hydricities for transition-metal hydrides are metal geometry and coordination number, charge on the complex, electron-donating ability of the ligands, chelate bite size, periodic row of the transition metal, and solvation of the product formed upon hydride transfer. As a result, it should be possible to tune the hydricities of transition-metal hydrides to meet specific applications. The *cis*-[HW(CO)₄(L)]⁻ described in this study are some of the most powerful hydride donors reported to date for transition-metal hydrides.

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Supporting Information Available: Tables of crystal data, data collection parameters, structure solution and refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths, bond angles, anisotropic thermal parameters, hydrogen coordinates, and isotropic displacement parameters for [HW(PPh₃)(CO)₄](PPN) (CIF). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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