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Metal−Hydrogen Bond Dissociation Enthalpies in Series of Complexes of Eight Different Transition Metals[†]

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Abstract: Homolytic M−H bond dissociation enthalpies (BDEs) of the mononuclear cationic metal hydride complexes HML_n^+, where ML_n = $Cr(CO)_2(dppm)_2$, $Mo(CO)_2(L-L)_2$, $W(CO)_3(PR_3)_3$, $W(CO)_2(dppm)_2$, $W(CO)_3$(tripod), $W(CO)_3$(triphos), $Cp^*Re(CO)_2(PR_3)$, $Fe(CO)_3(PR_3)_2$, $Fe(CO)_3(L-L)$, Cp^*_2Ru, $CpRu(PMe_3)_2I$, $CpRu(L-L)H$, $CpRu(PPh_3)_2H$, Cp^*_2Os, $CpOs(PR_3)_2Br$, $CpOs(PPh_3)_2Cl$, $CpOs(PPh_3)_2H$, $CpIr(CO)(PR_3)$, $CpIr(CS)(PPh_3)$, $(C_5Me_nH_{5-n})Ir(COD)$, $Cp^*Ir(CO)(PR_3)$, and $Cp^*Ir(CO)_2$, have been estimated by use of a thermochemical cycle that requires a knowledge of the heats of protonation (ΔH_{HM}) and redox potentials ($E_{1/2}$) for the oxidation of the neutral metal complexes (ML_n). Excellent correlations were found between $-\Delta H_{HM}$ and $E_{1/2}$ within related series of complexes. The BDE values obtained by this method fall in the range 56−75 kcal/mol. For related complexes of a given metal, the energy required for homolytic M−H bond cleavage (BDE) increases linearly as $-\Delta H_{HM}$ for heterolytic M-H bond cleavage increases. For analogous complexes with different metals, the M−H BDE values are greater for third-row than second-row and first-row metals, the difference being 1−12 kcal/mol. Other trends in BDE values are also discussed.

Introduction

There is great interest in transition-metal hydrides, because of both their unusual reactivities and their roles as homogeneous catalysts for hydrogenation and other reactions of organic substrates.[1] In order to understand the mechanisms and thermodynamics of these catalytic reactions, a knowledge of metal−hydrogen bond enthalpies is essential. Cleavage of the M−H bond in transition metal hydrides can yield a hydrogen atom ($H^\bullet$), a proton (H^+), or a hydride (H^-) ion. The energy associated with $H^\bullet$ cleavage (eq 1) is defined as the homolytic bond dissociation enthalpy (BDE). The heterolytic cleavage

$$M-H \rightarrow M^\bullet + H^\bullet; \quad \text{BDE} \tag{1}$$

of the M−H bond (eq 2) may be described by either a pK_a or

$$M-H \rightarrow M^- + H^+; \quad -\Delta H_{HM} \text{ or } pK_a \tag{2}$$

$-\Delta H_{HM}$ value. The energies for $H^\bullet$ and H^+ cleavage from neutral M−H complexes have been determined by several research groups using a variety of experimental techniques.[2−4] One approach makes use of a thermochemical cycle which involves a redox potential, a bond dissociation enthalpy (BDE), and a pK_a value; it allows the estimation of thermodynamic quantities such as pK_a and BDE that are either difficult or impossible to obtain directly. Early work of Breslow[5] used this thermochemical cycle to estimate pK_a values of weak carbon acids in aprotic solvents. More recently, Arnold[6] made use of three different thermochemical cycles to estimate pK_a values

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[†] Dedicated to Professor The Lord Jack Lewis on the occasion of his retirement from the Department of Chemistry, University of Cambridge.

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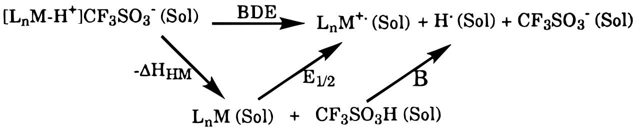
of radical cations; and Bordwell[7] estimated a large number of C−H, O−H, S−H, and N−H bond dissociation enthalpies (BDE) as well as pK_as of radical cations. Arnett[8] has combined solution calorimetry and electrochemistry to estimate homolytic and heterolytic bond energies for a number of C−C, C−O, C−S, and C−N bonds. Similar cycles were proposed by Tilset and Parker[3] to estimate metal hydride BDE and pK_a values for transition-metal hydrides and their cation radicals. In the latter studies, the BDE and pK_a values are related to each other by eq 3. The 59.5 kcal/mol constant, which applies to $E°_{ox}$ values

$$\mathrm{BDE(M-H)} = 1.37\mathrm{p}K_a + 23.06E°_{ox}(\mathrm{M}^-) + 59.5 \quad (3)$$

that are measured relative to ferrocene (Fc/Fc$^+$) in acetonitrile/ Bu_4NPF_6 (0.1M) solution, was obtained by two independent methods:[3c] (a) a calorimetric determination of the Cr−H BDE in $CpCr(CO)_3H$, and (b) thermochemical solution studies of the complex and $H^+/H^\bullet/H_2$ in acetonitrile.

Scheme 1



Solvent: 1,2-dichloroethane (DCE)
Temp: 25.0 °C

In contrast to the situation for neutral M−H complexes, there are few data available for cationic metal hydrides. In this paper, we present estimates of M-H bond dissociation enthalpies (BDEs) for 18-electron metal hydride cations (L_nMH^+); these include series of complexes of eight transition metals (M = Cr, Mo, W, Re, Fe, Ru, Os, Ir). All of the estimates are based on the thermochemical cycle in Scheme 1, which requires a knowledge of the heats of protonation (ΔH_{HM}) and redox potentials ($E_{1/2}$) for the oxidation of the neutral metal complexes (ML_n). The $-\Delta H_{HM}$ values were reported previously in a series of papers from this group.[4] In the present paper are given measured $E_{1/2}$ values for the ML_n complexes and calculated BDE values for the M−H bonds in 51 L_nMH^+ complexes.

Experimental Section

General Procedure. All preparative reactions, chromatography, and manipulations were carried out under an atmosphere of nitrogen or argon with use of vacuum line, Schlenk, syringe, or drybox techniques similar to those described in the literature.[10] The solvents were purified under nitrogen as described below using standard methods.[11] Toluene, benzene, decane, hexanes, and methylene chloride were refluxed over CaH_2 and then distilled. Diethyl ether was distilled from sodium benzophenone. 1,2-Dichloroethane (DCE) was purified by washing with concentrated sulfuric acid, distilled deionized water, 5% NaOH, and water again; the solvent was then predried over anhydrous $MgSO_4$, stored in amber bottles over molecular sieves (4 Å), and then distilled from P_4O_{10} under argon immediately before use. Neutral Al_2O_3 (Brockmann, activity I) used for chromatography was deoxygenated at room temperature under vacuum (10^{-5} mmHg) for 12 h, deactivated with 5% (w/w) N_2-saturated water, and stored under N_2.

The ^{1}H NMR spectra were obtained on samples dissolved in $CDCl_3$ or CD_2Cl_2 on a Nicolet-NT 300-MHz spectrometer using TMS (δ = 0.00 ppm) as the internal reference. Solution infrared spectra were recorded on a Nicolet 710 FT-IR spectrometer using sodium chloride cells with 0.1-mm spacers.

Materials. The complexes, decamethylruthenocene (Cp^*_2Ru) and decamethylosmocene (Cp^*_2Os), were purchased from Strem and used without purification. Ferrocene (Cp_2Fe) was purchased from Aldrich and purified by chromatography on a column of neutral alumina, eluting with hexanes. The compounds *cis*-$Cr(CO)_2(dppm)_2$,[12] *cis*-$Mo(CO)_2(L{-}L)_2$ (L−L = arphos, dppe, dppm),[12] *fac*-$W(CO)_3(PR_3)_3$ (PR_3 = $PMePh_2$, $PEtPh_2$, PEt_2Ph, PMe_3, PEt_3),[13] $W(CO)_3$(tripod),[14] $W(CO)_3$(triphos),[14] $Cp^*Re(CO)_2(PMe_2Ph)$,[13] $Cp^*Re(CO)_2(PMe_3)$,[13] $CpRu(PMe_3)_2I$,[15] $CpOs(PPh_3)_2Br$,[15] $CpOs(PPh_3)_2Cl$,[15] $CpOs(PPh_2Me)_2Br$,[15] $CpIr(CO)(PR_3)$ [PR_3 = P(*p*-$C_6H_4CF_3)_3$, P(*p*-$C_6H_4F)_3$, PPh_3, PPh_2Me, $PPhMe_2$, PMe_3, PEt_3, PCy_3],[16] $CpIr(CS)(PPh_3)$,[17] $(C_5Me_nH_{5-n})$Ir(COD)

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(n = 0, 1, 3, 4, 5),[18] $Cp^*Ir(CO)(PR_3)$ [$PR_3 = P(p\text{-}C_6H_4CF_3)_3$, $P(p\text{-}C_6H_4Cl)_3$, PPh_3, PPh_2Me, PMe_3],[16] and $Cp^*Ir(CO)_2$[16] were available from previous studies and were purified, if neccessary, before use. Ligand abbreviations are given in Table 1. The compounds $W(CO)_2(dppm)_2$,[12] $Fe(CO)_3(PR_3)_2$ ($PR_3 = PPh_3$, PPh_2Me, $PPhMe_2$, PMe_3),[17] $Fe(CO)_3(L-L)$ (L−L = dppp, dppm),[20] $CpOs(PMe_3)_2Br$,[15] and $CpOs(PPh_3)_2H$[15] were prepared according to literature procedures. We are grateful for gifts of CpRu(dppm)H, CpRu(dppe)H, and $CpRu(PPh_3)_2H$ from Professor R. H. Morris, University of Toronto.

Electrochemical Measurements. The electrochemical measurements were performed using a BAS-100 electrochemical analyzer (Bioanalytical Systems Inc., Purdue Research Park, West Lafayette, IN) equipped with a three-electrode assembly. The platinum working electrode (BAS, 1 mm) was polished with two BAS polishing aluminas (0.3 and 0.05 μm) for 1 min each and then rinsed with distilled deionized water between polishings; it was then rinsed ultrasonically in ethanol for about 5 min before use. A platinum wire (BAS) was used as the auxiliary electrode, and a SCE was used as the reference electrode. The glass electrochemical cell was dried in an oven at 110 °C for 4 h, allowed to cool to room temperature in a desiccator, and flushed with nitrogen for 10 min.

In a typical experiment, an amount of the metal complex sufficient to make 10.0 mL of a 1.0 mM solution was weighed into a small Schlenk flask capped with a rubber septum in a N_2-filled glovebox. To the electrochemical cell under nitrogen was added 330 mg (to make 0.10 M) of tetrabutylammonium tetrafluoroborate ($TBABF_4$; 99% pure, Aldrich, recrystallized twice from a 5:1 mixture of diethyl ether−ethanol and dried under vacuum overnight) and 10.0 mL of the solution of the compound in DCE via a syringe. The solution was purged with nitrogen for 1 min and stirred for 5 min under nitrogen to ensure complete dissolution. The electrochemical measurements were taken immediately after preparation of the solution. This is especially important for the $Cp^*Ir(CO)(PR_3)$ and $CpOs(PPh_3)_2H$ complexes due to their extreme air sensitivity.

The techniques used to determine $E_{1/2}$ were cyclic voltammetry (CV), second harmonic alternating current voltammetry (SHACV),[20,21] and Osteryoung square wave voltammetry (OSWV);[22] all were performed on the BAS-100 instrument. The ferrocenium/ferrocene redox couple served as the external standard for all measurements, and its $E_{1/2}$ value was checked against the reference electrode before and after each experiment. The $E_{1/2}$ value of Cp^*_2Ru was also checked against the reference electrode before and after each set of measurements, and the $E_{1/2}$ value of Cp^*_2Os was checked occasionally.

CV measurements were made at a scan speed of 100 mV/s. SHACV measurements were made at a scan rate of 5 mV/s and a frequency of 25 Hz. OSWV measurements were made at a scan speed of 60 mV/s (scan frequency 15 Hz and step voltage 4 mV). The square wave voltammetric responses for all of the compounds are peak-shaped and highly symmetrical. In general, the reproducibility of the CV measurements for a scan rate of 100 mV/s was ±10 mV. Reproducibilities of the SHACV measurements were ±20 mV, and ±15 mV for the OSWV measurements.

Table 1. $-\Delta H_{HM}$, $-\Delta H_{HP}$, $E_{1/2}$, and BDE Values of Organometallic Compounds

compd[h]	$-\Delta H_{HM}$,[a] kcal/mol	$-\Delta H_{HP}$,[b] kcal/mol	$E_{1/2}$, V[c] vs SCE	BDE,[d] kcal/mol
$Cr(CO)_2(dppm)_2$	25.5	22.0	−0.12[f,g]	56.0
$Mo(CO)_2(arphos)_2$	23.8	23.2	0.28[f]	63.6
$Mo(CO)_2(dppe)_2$	27.4	22.8	0.24[f]	66.2
$Mo(CO)_2(dppm)_2$	29.7	22.0	0.18[f]	67.2
$W(CO)_3(PMePh_2)_3$	15.1	24.7	0.48[e,f]	59.5
$W(CO)_3(PEtPh_2)_3$	16.9	25.2	0.45[e]	60.6
$W(CO)_3(PEt_2Ph)_3$	18.3	27.8	0.41[e,f]	61.0
$W(CO)_3(PMe_3)_3$	19.5	31.6	0.40[f]	62.0
$W(CO)_3(PEt_3)_3$	25.0	33.7	0.28[e,g]	64.7
$W(CO)_2(dppm)_2$	31.5	22.0	0.14[g]	68.0
$W(CO)_3(tripod)$	10.5		0.72[g]	60.4
$W(CO)_3(triphos)$	16.7		0.63[g]	64.5
$Cp^*Re(CO)_2$-(PMe_2Ph)	18.3	28.4	0.84[e,g]	71.0
$Cp^*Re(CO)_2(PMe_3)$	20.1	31.6	0.80[e,g]	71.8
$Fe(CO)_3(PPh_3)_2$	14.1	21.2	0.55[e,g]	60.1
$Fe(CO)_3(PMePh_2)_2$	17.6	24.7	0.49[e,g]	62.2
$Fe(CO)_3(PMe_2Ph)_2$	21.2	28.4	0.45[e,g]	64.9
$Fe(CO)_3(PMe_3)_2$	23.3	31.6	0.41[e,g]	66.1
$Fe(CO)_3(dppp)$	21.1	23.4	0.31[e,g]	61.5
$Fe(CO)_3(dppm)$	24.0	22.0	0.40[e,g]	66.5
Cp^*_2Ru	19.0		0.68[e−g]	68.0
$CpRu(PMe_3)_2I$	20.6	31.6	0.56[g]	66.8
CpRu(dppm)H	28.9	22.0	0.37[g]	70.7
CpRu(dppe)H	29.0	22.8	0.31[g]	69.4
$CpRu(PPh_3)_2H$	29.7	21.2	0.23[e,g]	68.3
Cp^*_2Os	26.6		0.51[e−g]	71.7
$CpOs(PPh_3)_2Br$	16.3	21.2	0.59[e,g]	63.2
$CpOs(PPh_3)_2Cl$	19.7	21.2	0.58[e,g]	66.4
$CpOs(PPh_2Me)_2Br$	20.2	24.7	0.51[e,g]	65.3
$CpOs(PMe_3)_2Br$	29.4	31.6	0.34[e,g]	70.5
$CpOs(PPh_3)_2H$	37.3	21.2	0.13[g]	73.6
CpIr(CO)-[$P(p\text{-}C_6H_4CF_3)_3$]	28.0	13.6	0.60[f,g]	75.1
CpIr(CO)-[$P(p\text{-}C_6H_4F)_3$]	29.8	19.6	0.53[f]	75.3
$CpIr(CO)(PPh_3)$	30.0	21.2	0.50[f,g]	74.9
$CpIr(CO)(PPh_2Me)$	31.5	24.7	0.45[f,g]	75.2
$CpIr(CO)(PMe_2Ph)$	32.5	28.4	0.41[g]	75.3
$CpIr(CO)(PMe_3)$	33.2	31.6	0.37[g]	75.0
$CpIr(CO)(PEt_3)$	32.9	33.7	0.35[f,g]	74.3
$CpIr(CO)(PCy_3)$	32.7	33.2	0.35[g]	74.2
$CpIr(CS)(PPh_3)$	26.5	21.2	0.51[g]	71.6
CpIr(COD)	22.8		0.69[g]	72.0
$(C_5MeH_4)Ir(COD)$	24.1		0.61[g]	71.5
$(1,2,3\text{-}C_5Me_3H_2)Ir(COD)$	26.4		0.54[g]	72.2
$(C_5Me_4H)Ir(COD)$	27.5		0.47[g]	71.6
$Cp^*Ir(COD)$	28.5		0.45[g]	72.2
$Cp^*Ir(CO)[P(p\text{-}C_6H_4CF_3)_3]$	33.8	13.6	0.30[g]	74.0
$Cp^*Ir(CO)[P(p\text{-}C_6H_4Cl)_3]$	36.9	17.9	0.20[g]	74.8
$Cp^*Ir(CO)(PPh_3)$	37.1	21.2	0.09[g]	72.4
$Cp^*Ir(CO)(PPh_2Me)$	37.1	24.7	0.08[g]	72.3
$Cp^*Ir(CO)(PMe_3)$	38.0	31.6	0.07[g]	72.9
$Cp^*Ir(CO)_2$	21.4		0.72[g]	71.3

[a] For eq 4, refs 4 and 16. [b] For protonation of the free phosphine ligand in the complex (eq 5); for the first protonation of bidentate ligands. See refs 13 and 23. [c] All $E_{1/2}$ values were obtained by CV at a scan rate of 100 mV/s; SHACV at a scan rate of 5 mV/s and a frequency of 25 Hz, and OSWV at a scan rate of 60 mV/s (scan frequency 15 Hz and step voltage 4 mV). All solutions are 1.0 mM in 1,2-dichloroethane at 23 °C using platinum as the working and auxiliary electrodes and SCE as the reference electrode with 0.10 M Bu_4NBF_4 as the electrolyte. [d] BDE ($M^+ - H$) calculated using eq 6. [e] Reversible in CV. [f] $E_{1/2}$ measured by SHACV. [g] $E_{1/2}$ measured by OSWV. [h] Ligand abbreviations: $Cp^* = C_5Me_5$; $Cp = C_5H_5$; COD = 1,5-cyclooctadiene; dppm = $Ph_2PCH_2PPh_2$; dppe = $Ph_2P(CH_2)_2PPh_2$; dppp = $Ph_2P(CH_2)_3PPh_2$; arphos = $Ph_2P(CH_2)_2AsPh_2$; tripod = $MeC(CH_2PPh_2)_3$; triphos = $PhP(CH_2CH_2PPh_2)_2$.

Results

Electrochemical Measurements. Our use of CV, SHACV,[21] and OSWV[22] techniques for the measurement of $E_{1/2}$ values for a variety of organometallic complexes follows Arnett's application of these methods to organic molecules.[8] To illustrate the results obtained by these techniques we show CV, SHACV, and OSWV traces (Figure 1) for the measurement of $E_{1/2}$ for

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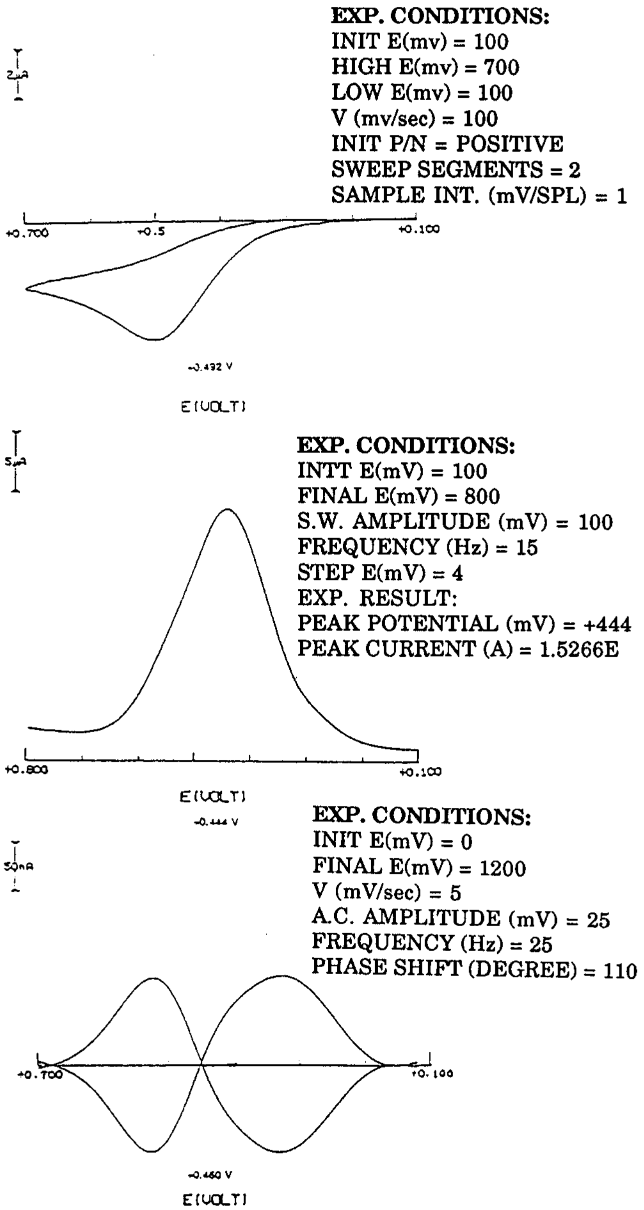

Figure 1. Irreversible cyclic voltammogram (CV, top), symmetrical Osteryoung square wave voltammogram (OSWV, middle), and second harmonic ac voltammogram (SHACV, bottom) for CpIr(CO)(PPh_2Me) in DCE at 23 °C.

CpIr(CO)(PPh_2Me). The CV trace shows that the oxidation (E_{ox} = 0.49 V) is irreversible, whereas the SHACV trace is symmetrical with a sharply delineated $E_{1/2}$ value of 0.46 ± 0.02, and OSWV yields a highly symmetrical peak with $E_{1/2}$ = 0.44 ± 0.01. In general, for complexes that are irreversible by CV, their $E_{1/2}$ values determined by SHACV and OSWV are the same within ±20 mV. The $E_{1/2}$ values for the reversible oxidation of Cp^*_2Ru obtained from CV (0.684 V), SHACV (0.676 V), and OSWV (0.682 V) are in excellent agreement, and the $E_{1/2}$ values for the reversible oxidation of Cp_2Fe (CV, 0.595; SHACV, 0.598; OSWV, 0.589) are also consistent. The errors in $E_{1/2}$ for the reversible oxidations are ±20 mV or less.[3,8] For the irreversible oxidations, the significance of the $E_{1/2}$ values determined by SHACV and OSWV is less well-defined. Although these techniques have been used extensively[7,8] to estimate reversible potentials (E_{rev}) for bond dissociation enthalpy (BDE) calculations in organic systems, it has been noted that $E_{1/2}$ may be quite different than E_{rev} depending on the rates of subsequent reactions of the oxidized species. Ahlberg and Parker[21c] showed that $E_{1/2}$ determined by SHACV may be as much as 120 mV different than E_{rev} for the oxidation of 9-phenylanthracene. And Andrieux, Hapiot, Pinson, and Savéant[21d] obtained differences between $E_{1/2}$ and E_{rev} of as much as 200 mV for the oxidation of thiophenoxide ions. Although there appear to be no analogous studies of OSWV, the errors could be similar. In addition to the effect of chemical kinetics on $E_{1/2}$, there is a possibility that electron transfer at the electrode is slow, which would also affect $E_{1/2}$.[22e] Thus, the differences between $E_{1/2}$ and E_{rev} values could be 200 mV or higher for the irreversible oxidations (Table 1). However, the similarity of the calculated M−H BDE values using these measured $E_{1/2}$ parameters to the few available BDE values determined by other methods suggests that the differences between $E_{1/2}$ and E_{rev} are less than 200 mV. Errors in BDE values are discussed below.

Table 2. Temperature Dependence of $E_{1/2}$ for the Oxidation of Cp_2Fe, Cp^*_2Ru, and CpIr(CO)(PPh_3) in DCE Solvent

compd	23 °C	40 °C	55 °C	70 °C
$Cp_2Fe^{a,b}$	0.592	0.588	0.593	0.590
$Cp^*_2Ru^{a,b}$	0.683	0.676	0.680	0.680
CpIr(CO)(PPh_3)^{b}	0.484	0.462	0.480	0.476

[a] CV, 100 mV/s. [b] OSWV, 15 Hz, 4mV.

The $E_{1/2}$ values vs SCE at room temperature (23 °C) for the oxidation of all of the complexes in DCE solution are listed in Table 1. The methods by which the $E_{1/2}$ values were determined are also indicated. All of the $E_{1/2}$ values presented in this paper are referenced to the SCE electrode; for those who wish to reference these values to the ferrocene−ferrocenium couple (Fc/Fc$^+$), the following equation may be used: $E_{1/2}$(vs Fc/Fc$^+$) = $E_{1/2}$(vs SCE) −0.59 V. In addition to the $E_{1/2}$ values, the following data are also presented in Table 1: (a) the heats of protonation ($-\Delta H_{HM}$)[4] of the neutral organometallic compounds (eq 4);

$$L_nM + CF_3SO_3H \xrightarrow[25.0\ ^\circ C]{ClCH_2CH_2Cl} L_nM(H)^+CF_3SO_3^-; \quad \Delta H_{HM} \tag{4}$$

(b) the heats of protonation ($-\Delta H_{HP}$)[13,23] of the free phosphines (PR_3) present in the metal complexes (eq 5);

$$PR_3 + CF_3SO_3H \xrightarrow[25.0\ ^\circ C]{ClCH_2CH_2Cl} HPR_3^+CF_3SO_3^-; \quad \Delta H_{HP} \tag{5}$$

and (c) the bond dissociation enthalpies (BDE) obtained from the $-\Delta H_{HM}$ and $E_{1/2}$ values as described below.

Table 2 lists potentials ($E_{1/2}$) for the oxidation of Cp_2Fe, Cp^*_2Ru, and CpIr(CO)(PPh_3) in DCE solvent as a function of temperature. The observation that $E_{1/2}$ is not temperature dependent indicates that $\Delta S_{redox} \approx 0$ within experimental error for these systems.[8c,f]

Previous Electrochemical Studies of the Compounds. Electrochemical studies of several complexes related to those in Table 1 have been reported previously. It is evident that $E_{1/2}$ values obtained in different laboratories depend on the experimental conditions. These prior electrochemical studies establish that these oxidations are one-electron processes.

cis-Cr(CO)$_2$(dppe)$_2$ undergoes a one-electron *cis*°/*cis*$^+$ oxidation at −0.59 V (vs Fc/Fc$^+$) in 0.1 M $Bu_4N(ClO_4)$/dichloromethane solution.[24ab] *cis*-Cr(CO)$_2$(dppm)$_2$ undergoes a one-electron *cis*°/*cis*$^+$ oxidation at 0.01 V (vs Ag/AgCl) in 0.1 M

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$Et_4N(ClO_4)$/acetone solution.[24c] The $E_{1/2}$ value for *cis*-$Cr(CO)_2(dppm)_2$ in 0.1 M $Bu_4N(BF_4)$/1,2-dichloroethane solution in the present study is −0.71 V (vs Fc/Fc^+).

cis-$Mo(CO)_2(dppm)_2$ and *cis*-$Mo(CO)_2(dppe)_2$ undergo one-electron oxidations at 0.30 V and 0.31 (vs Ag/AgCl), respectively, in 0.1 M $Et_4N(ClO_4)$/acetone solution.[24c] *cis*-$Mo(CO)_2(dppe)_2$ undergoes a one-electron oxidation at 0.30 V in 0.1 M $Bu_4N(PF_6)/CH_2Cl_2$ solution.[25] The $E_{1/2}$ values for the *cis*-$Mo(CO)_2(L{-}L)_2$ complexes in the present study occur at 0.28 V for L−L = arphos, 0.24 V for dppe, and 0.18 V for dppm.

The tungsten compound *cis*-$W(CO)_2(dppe)_2$ undergoes a one-electron cis°/cis^+ oxidation at 0.31 V (vs Ag/AgCl) in 0.1 M $Et_4N(ClO_4)$/acetone solution.[24c] The $E_{1/2}$ value for *cis*-$W(CO)_2(dppm)_2$ in 0.1 M $Bu_4N(BF_4)$/DCE solution in the present study is 0.14 V (vs SCE).

The iron complexes $Fe(CO)_3(PR_3)_2$ ($PR_3 = PPh_3$, 0.33 V; $PMePh_2$, 0.28 V; $(PR_3)_2$ = dppm, 0.16 V) in 0.05 M $Et_4N(ClO_4)/CH_2Cl_2$ are reported to undergo one-electron oxidations.[26] The compounds $Fe(CO)_3(PR_3)_2$ in Table 1 also undergo reversible one-electron oxidations at the following potentials: 0.55 V for L = PPh_3, 0.49 V for $PMePh_2$, 0.45 V for PMe_2Ph, 0.41 V for PMe_3, and 0.40 V for dppm.

The hydrides $CpRu(PR_3)_2H$ [$(PR_3)_2 = (PPh_3)_2$, dppm, dppe, dppp] undergo one-electron oxidations at −0.3 to −0.1 V vs Fc/Fc^+ in 0.2 M $Bu_4N(PF_6)$/THF solution;[3g,27] these are similar to the $E_{1/2}$ values obtained in the present study for $CpRu(PR_3)_2H$ [$(PR_3)_2 = (PPh_3)_2$, 0.23 V; dppm, 0.37 V; dppe, 0.31 V; all vs SCE].

The compounds Cp^*_2M (M = Ru, Os) undergo one-electron oxidations at 0.12 V for Ru and −0.06 V for Os vs Fc/Fc^+ in MeCN,[29] which are similar to 0.09 V for Ru and −0.08 V for Os vs Fc/Fc^+ in DCE in the present study.

It is well-known that high solution resistance in nonaqueous solvents can lead to large peak separations which can vary from solvent to solvent and with the reference electrode used. Using two solvents under the same conditions, ferrocene was found to exhibit the following peak separations: ΔE_p = 80−95 mV in CH_3CN and 100−120 mV in CH_2Cl_2.[28] Under our experimental conditions, the peak separations in DCE for reversible compounds, such as Cp_2Fe, Cp^*_2Ru, and Cp^*_2Os, were found to be 80−115 mV. The fact that separations between the E_{ox} (by CV) and $E_{1/2}$ (by SHACV or OSWV) peaks for all of the compounds undergoing irreversible oxidations by CV are in the 40−60 mV range indicates that they are one-electron processes.

Bond Dissociation Enthalpy (BDE) Calculations. Our method of estimating bond dissociation enthalpies of M−H bonds in $L_nM(H)^+$ complexes is closely analogous to that of Tilset and Parker.[3] It differs in that we use the heat of protonation (ΔH_{HM}) in place of pK_a and the thermochemical cycle in Scheme 1, which is summarized in eq 6; this equation applies to $E_{1/2}$ values obtained relative to SCE in DCE solvent and ΔH_{HM} values obtained by titration with CF_3SO_3H in DCE solvent (eq 4). The constant 33.3 kcal/mol in this equation was

$$\mathrm{BDE}(\mathrm{M{-}H^+}) = -\Delta H_{\mathrm{HM}} + 23.06E_{1/2}(\mathrm{M}) + 33.3 \quad \text{in kcal/mol} \quad (6)$$

calculated using our measured $-\Delta H_{HM}$ (26.6 kcal/mol) and $E_{1/2}$ (0.51 V) data and the known BDE value (71.7 kcal/mol)[29a] for $Cp^*_2OsH^+$. The BDE of 71.7 kcal/mol for $Cp^*_2OsH^+$ was determined in MeCN by Tilset using the equation

$$\mathrm{BDE}(\mathrm{M{-}H^+}) = 1.37\mathrm{p}K_a + 23.06E_{1/2}(\mathrm{M}) + 59.5 \quad \text{in kcal/mol}$$

where the pK_a is 9.9 ± 0.1 measured against the anilinium ion and $E_{1/2}$ is −0.055 V vs Fc/Fc^+. Since all BDE values (Table 1) were calculated using eq 6, any error in our method of calculating the 33.3 constant would affect all BDE values in the same way.

The major uncertainties associated with the calculations of BDE(M−H$^+$) values using eq 6 lie in the uncertainties in the ΔH_{HM} and $E_{1/2}$(M) values. In general, the average deviation from the mean value obtained from several determinations of ΔH_{HM} is ±0.3 kcal/mol or less.[4] For the complexes which undergo reversible oxidations, the $E_{1/2}$(M) values are reproducible by CV, SHAC, and OSWV within ±20 mV (1.8 kcal/mol). Thus, the uncertainties in BDE(M−H$^+$) values for complexes which undergo reversible oxidations are approximately ±2 kcal/mol.

Uncertainties in BDE(M−H$^+$) values for complexes that undergo irreversible oxidation are more difficult to define because of the unknown uncertainties in $E_{1/2}$(M), as discussed above in the Electrochemical Measurements section. As noted, kinetic factors might affect $E_{1/2}$ values by as much as 200 mV (4.6 kcal/mol). However, it seems likely that the uncertainties are not that large. For example, if one considers (Table 1) the series of complexes *fac*-$W(CO)_3(PR_3)_3$, BDE(W−H$^+$) values for complexes which undergo reversible oxidation are 59.5 ($PMePh_2$), 60.6 $(PEtPh_2)_3$, 61.0 (PEt_2Ph), and 64.7 (PEt_3) kcal/mol. Only the PMe_3 complex in this series undergoes irreversible oxidation and its BDE(W−H$^+$) value is 62.0 kcal/mol, which is very similar to the other values. And the $E_{1/2}$ value (0.40 V) for $W(CO)_3(PMe_3)_3$ is less positive than that (0.48 V) for $W(CO)_3(PMePh_2)_3$, which is the expected trend. In the $CpOs(PPh_3)_2X$ series of complexes, the reversible $E_{1/2}$ values for X = Br (0.59 V) and Cl (0.58 V) are more positive than that (0.13 V) of the irreversible $E_{1/2}$ for the X = H compound, which also follows the expected trend. Oxidations of all of the $Cp'Ir(CO)(PR_3)$ and $Cp'Ir(COD)$ compounds are irreversible; in these series, the influence of kinetic effects on the $E_{1/2}$ values is not known. In these cases, comparisons (see Discussion) with literature BDE(Ir−H) values suggest that our values are at least in the expected range.

Discussion

Correlations between $E_{1/2}$ and $-\Delta H_{HM}$. Since the $E_{1/2}$ of a metal complex is a measure of its ability to lose an electron and the heat of protonation ($-\Delta H_{HM}$) is a measure of its ability to share an electron-pair with a proton, one might reasonably expect there to be a correlation between $E_{1/2}$ and $-\Delta H_{HM}$ values.

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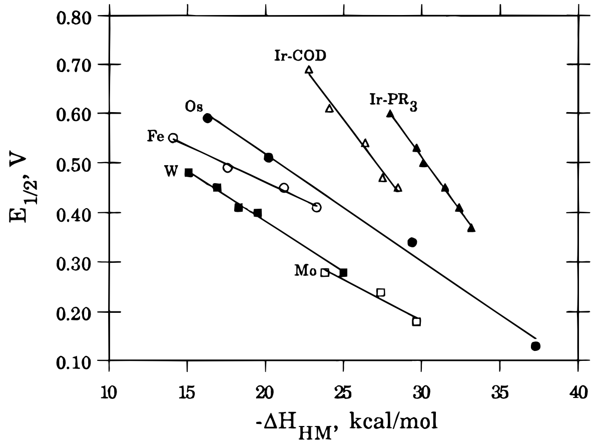

Figure 2. Plots of $E_{1/2}$ vs $-\Delta H_{HM}$ for the $Mo(CO)_2(L-L)_2$, $W(CO)_3(PR_3)_3$, $Fe(CO)_3(PR_3)_2$, $CpOs(PR_3)_2X$, $(C_5H_{5-n}Me_n)Ir(COD)$, and $CpIr(CO)(PR_3)$ series of complexes.

On the other hand, oxidation and protonation reactions are fundamentally different processes; oxidation leads to a radical cation while protonation results in a structural rearrangement which is required by the addition of a proton ligand to the coordination sphere. In fact, there are excellent correlations (Figure 2) between $E_{1/2}$ and $-\Delta H_{HM}$ within a family of compounds; the data are taken from Table 1. These correlations are expressed in eqs (7−11):

$$E_{1/2} = (0.75 \pm 0.02) - (0.015 \pm 0.001)(-\Delta H_{HM}) \quad \text{for } Fe(CO)_3(PR_3)_2 \quad (7)$$

where PR_3 = PPh_3, PPh_2Me, $PPhMe_2$, PMe_3

$$E_{1/2} = (0.68 \pm 0.11) - (0.016 \pm 0.004)(-\Delta H_{HM}) \quad \text{for } cis\text{-}Mo(CO)_2(L-L)_2 \quad (8)$$

where L−L = arphos, dppe, dppm

$$E_{1/2} = (0.79 \pm 0.02) - (0.020 \pm 0.001)(-\Delta H_{HM}) \quad \text{for } fac\text{-}W(CO)_3(PR_3)_3 \quad (9)$$

where PR_3 = PPh_2Me, PPh_2Et, $PPhEt_2$, PMe_3, PEt_3

$$E_{1/2} = (0.95 \pm 0.04) - (0.022 \pm 0.001)(-\Delta H_{HM}) \quad \text{for } CpOs(PR_3)_2X \quad (10)$$

where $(PR_3)_2X$ = $(PPh_3)_2Br$, $(PPh_2Me)_2Br$, $(PMe_3)_2Br$, $(PPh_3)_2H$

$$E_{1/2} = (1.63 \pm 0.08) - (0.042 \pm 0.003)(-\Delta H_{HM}) \quad \text{for } (C_5Me_nH_{5-n})Ir(COD) \quad (11a)$$

where n = 0, 1, 3, 4, 5

$$E_{1/2} = (1.82 \pm 0.04) - (0.044 \pm 0.001)(-\Delta H_{HM}) \quad \text{for } CpIr(CO)(PR_3) \quad (11b)$$

where PR_3 = $P(p\text{-}C_6H_4CF_3)_3$, $P(p\text{-}C_6H_4F)_3$, PPh_3, PPh_2Me, $PPhMe_2$, PMe_3.

The correlation coefficients for eqs 7−11b are >0.99; however, for the $Cp^*Ir(CO)(PR_3)$ complexes, the correlation coefficient is only 0.90; so an equation is not included. Slopes of the plots (Figure 2), which are the $-\Delta H_{HM}$ coefficients in eqs 7−11, vary considerably from one family of compounds to another. The $E_{1/2}$ values used in these correlations are for reversible oxidations (or at least most of them are reversible) of the Fe (eq 7), W (eq 9), and Os (eq 10) series of complexes. However, the $E_{1/2}$ values are for irreversible oxidations of the Mo (eq 8) and Ir (eqs 11a and 11b) complexes. For the reversible systems, the slopes of the lines are similar (0.015−0.022). For the Mo complexes, which undergo irreversible oxidation, the slope (0.016) is in the same range; but both series of Ir complexes, which are also irreversible, have significantly larger slopes (0.042 and 0.044). At this point, it is not clear whether the greater slopes for the Ir series are due to a fundamentally different behavior of these complexes or the measured $E_{1/2}$ values are determined by factors other than thermodynamics, as discussed in the Results section.

Comparison of BDE Values in Table 1 with Those in the Literature. In the present study, we report M−H BDE values for 51 different cationic metal hydride complexes (Table 1). We have used the thermochemical cycle in Scheme 1 and eq 6 to obtain our results. In the literature are reported M−H BDE values for other complexes based on different methods. The purpose of this section is to compare our results with those from related studies. Because errors and assumptions in each of the various studies may be quite different, it is difficult to draw conclusions unless the differences in BDE values are quite large. The following sections are organized according to the group of the metal in the periodic table.

(1) Cr−H BDE Values. The only BDE value for a Cr complex in Table 1 is that (56.0 kcal/mol) of $Cr(CO)_2(dppm)_2H^+$, which is based on an irreversible $E_{1/2}$ value. This BDE compares with values for the complexes $Cp'Cr(CO)_2(L)H$ which are all very similar to each other ($CpCr(CO)_3H$, 61.5 kcal/mol; $Cp^*Cr(CO)_3H$, 62.3; $CpCr(CO)_2(PPh_3)H$, 59.8; $CpCr(CO)_2(PEt_3)H$, 59.9; $CpCr(CO)_2[P(OMe)_3]H$, 62.7).[9] The BDE values (kcal/mol) for the 17-e cationic hydrides are reported to be 8−11 kcal lower than those of the neutral complexes [$Cp^*Cr(CO)_3H^{\bullet+}$ 54.3; $CpCr(CO)_2(PPh_3)H^{\bullet+}$ 49.8; $CpCr(CO)_2(PEt_3)H^{\bullet+}$ 50.9; $CpCr(CO)_2[P(OMe)_3]H^{\bullet+}$, 51.7).[3d] The BDE (56.0) of our cationic $Cr(CO)_2(dppm)_2H^+$ is between values for the neutral complexes and the 17-e cationic hydrides. The lower BDE for $Cr(CO)_2(dppm)_2H^+$ than $Cp'Cr(CO)_2(L)H$ is consistent with the lower basicity of $Cr(CO)_2(dppm)_2$ than $Cp'Cr(CO)_2(L)^-$; a correlation between basicity and BDE is discussed in the next section. The BDE value of the Cr-H bond in gas phase $CpCr(CO)_3(Me)H^+$ obtained by ion cyclotron resonance spectroscopy studies is 58 ± 5 kcal/mol,[2d] which is close to that (56.0 kcal/mol) of $Cr(CO)_2(dppm)_2H^+$.

(2) Mo-H BDE Values. The BDE values (kcal/mol) (Table 1), which are based on irreversible $E_{1/2}$ values, for $Mo(CO)_2(arphos)_2H^+$ (63.6), $Mo(CO)_2(dppe)_2H^+$ (66.2), and $Mo(CO)_2(dppm)_2H^+$ (67.2) compare with literature values for Cp_2MoH_2 (61.5),[31a] $CpMo(CO)_3H$ (69.2,[2h,3c] 69.4[32]), $Cp^*Mo(CO)_3H$ (68.5),[3c,2h] $TpMo(CO)_3H$ (62.2,[3f] 63[2h]), $Tp'Mo(CO)_3H$ (59.3,[3f] 60[2h]) and $Mo(CO)_6H^+$ (62) in the gas phase.[2d] In general, the Mo−H BDE values are higher than those of Cr−H.

(3) W-H BDE Values. The BDE values, calculated from reversible $E_{1/2}$ data, for the tungsten complexes in Table 1 range from 59.5 kcal/mol for the least basic complex $W(CO)_3(PMePh_2)_3H^+$ to 68.0 kcal/mol for the most basic complex $W(CO)_2(dppm)_2H^+$. Most of the literature values (kcal/mol) for tungsten hydride complexes fall in the same range: $Cp_2W(I)(H)$ (65.3),[31a] $CpW(CO)_3H$ (72.3,[3c] 72.5[32]), $CpW(CO)_2(PMe_3)H$ (69.6),[3c] $TpW(CO)_3H$ (65.8),[3f] $Tp'W(CO)_3H$ (62.2),[3f] and $(PPr^i_3)_2(CO)_3(SPh)W(H)$ (53.2).[2j]

(4) Re-H BDE Values. The BDE values (Table 1) for $Cp^*Re(CO)_2(PMe_2Ph)H^+$ (71.0 kcal/mol) and for $Cp^*Re(CO)_2(PMe_3)H^+$ (71.8 kcal/mol), which are based on reversible $E_{1/2}$ potentials, compare with the Re−H BDE values of 74.7 kcal/

mol for $Re(CO)_5H$[3c] and 70 ± 3 kcal/mol for $Re(CO)_5(Me)H^+$ in the gas phase.[2d]

(5) Fe−H BDE Values. The BDE values, calculated from reversible $E_{1/2}$ data, for the $Fe(CO)_3(PR_3)_2H^+$ complexes in Table 1 range from 60.1 kcal/mol for the complex $Fe(CO)_3(PPh_3)_2H^+$ to 66.1 kcal/mol for $Fe(CO)_3(PMe_3)_2H^+$. The highest value is 66.5 kcal/mol for the least acidic $Fe(CO)_3(dppm)H^+$. These compare with the following literature results: $Fe(CO)_4H_2$ (67.6 kcal/mol) and $CpFe(CO)_2H$ (57.1 kcal/mol).[3c] The reported BDE of Fe−H in gas phase Cp_2FeH^+ is 51 ± 5 kcal/mol.[2d]

(6) Ru−H BDE Values. The BDE values (kcal/mol) for the Ru complexes in Table 1 are based on reversible (r) and irreversible (i) $E_{1/2}$ values. They are 66.8 (i) for $CpRu(PMe_3)_2(I)(H)^+$, 70.7 (i) for $CpRu(dppm)(H_2)^+$, 69.4 (i) for $CpRu(dppe)H_2^+$, and 68.3 (r) for $CpRu(PPh_3)_2(H)_2^+$. These compare with 75.5 for $CpRu(dppm)(H_2)^+$, 73.8 for $CpRu(dppe)H_2^+$, and 72.0 for $CpRu(PPh_3)_2(H)_2^+$ reported by Morris and co-workers.[27] Previous values for these complexes by Tilset and co-workers[3g] are approximately 3 kcal/mol higher than those of Morris. It is not entirely clear why our values are approximately 4 kcal/mol less than those of Morris and 7 kcal/mol less than those of Tilset. All three approaches make use of thermochemical cycles but we use ΔH_{HM} values determined in DCE rather than pK_as measured in acetonitrile. Other reported Ru−H BDE values (kcal/mol) are 65 for $CpRu(CO)_2H$,[3a] 63.5 for $Ru(dmpe)_2(H)_2$,[34] and 64.8 ± 3.6 for gas-phase Cp_2RuH^+.[2d] Our value (68.0 (r)) for $Cp^*{}_2RuH^+$ is very similar to that for the same compound studied[29a] in acetonitrile solvent using pK_a measurements (68.1 kcal/mol).

(7) Os−H BDE Values. Of the BDE values for the Os complexes in Table 1 the lowest is 63.2 kcal/mol for $CpOs(PPh_3)_2(Br)H^+$ and the highest is 73.6 kcal/mol for $CpOs(PPh_3)_2(H)_2^+$; all make use of reversible $E_{1/2}$ data, except for that of $CpOs(PPh_3)_2H$. These values (kcal/mol) compare with those for $Cp^*{}_2OsH^+$ (71.7)[29a] and $OsH(L)_2(\eta^2\text{-}H_2)^+$ (L = depe, 76; dppe, 80; dtfpe, 81).[27]

(8) Ir−H BDE Values. All Ir−H BDE values (Table 1) are based on irreversible $E_{1/2}$ data. In the $CpIr(CO)(PR_3)H^+$ series, the BDE values are nearly the same (75 kcal/mol) regardless of the PR_3 ligand; likewise, the values for the $(C_5Me_nH_{5-n})Ir(COD)H^+$ series are all approximately 72 kcal/mol. Neither the basicity nor the steric size of the PR_3 or $C_5Me_nH_{5-n}$ ligands significantly affects the BDE values of the compounds in these series. Even though the oxidations are irreversible, the BDE values are all similar to those for the related compounds, $Cp^*Ir(PMe_3)(Cy)H$ (74.0 kcal/mol) and $Cp^*Ir(PMe_3)(H)_2$ (74.2 kcal/mol).[33] The average Ir−H BDE for the two Ir-H bonds in hydrogenated Vaska's-type compounds $Ir(X)(CO)(PR_3)_2(H)_2$ is 58 kcal/mol;[35] this value varies by no more than 3 kcal/mol with different X and PR_3 ligands.

Correlations between BDE and $-\Delta H_{HM}$. Since there are correlations (eqs 7−11) between $E_{1/2}$ and $-\Delta H_{HM}$, which are used to calculate BDE values from eq 6, there must be a correlation between BDE and $-\Delta H_{HM}$ values within series of compounds. Since $E_{1/2}$ values increase as $-\Delta H_{HM}$ decreases, the terms in eq 6 at least partially cancel one another; as a result, changes in BDEs may be small within a family of compounds. The correlations between $E_{1/2}$ and $-\Delta H_{HM}$ allow one to predict BDE values from known $-\Delta H_{HM}$ results. If we use eq 12

$$E_{1/2} = a(-\Delta H_{HM}) + x \qquad (12)$$

where constants a and x depend upon the specific series of compounds, to represent eqs 7−11 and substitute $E_{1/2}$ in eq 6 by $E_{1/2}$ in eq 12, we obtain eq 13 with a new constant z. Thus,

$$BDE = (1 + 23.06a)(-\Delta H_{HM}) + z \qquad (13)$$

for a series of compounds, BDE values may be predicted just from their ΔH_{HM} values. The forms of eq 13 for each of the series of compounds represented in eqs 7−11 are expressed in eqs 14−18. The correlations between BDE and $-\Delta H_{HM}$ values for the Fe, Mo, W, Os, and Ir complexes expressed in eqs 14−18 are shown in Figure 3.

$$BDE = (50.4 \pm 0.4) + (0.67 \pm 0.02)(-\Delta H_{HM}) \quad \text{for } Fe(CO)_3(PR_3)_2H^+ \qquad (14)$$

$$BDE = (48.9 \pm 2.5) + (0.62 \pm 0.09)(-\Delta H_{HM}) \quad \text{for } Mo(CO)_2(L{-}L)_2H^+ \qquad (15)$$

$$BDE = (51.6 \pm 0.4) + (0.52 \pm 0.02)(-\Delta H_{HM}) \quad \text{for } W(CO)_3(PR_3)_3H^+ \qquad (16)$$

$$BDE = (55.2 \pm 0.8) + (0.50 \pm 0.03)(-\Delta H_{HM}) \quad \text{for } CpOs(PR_3)_2(X)H^+ \qquad (17)$$

$$BDE = (71.1 \pm 1.9) + (0.038 \pm 0.075)(-\Delta H_{HM}) \quad \text{for } (C_5Me_nH_{5-n})Ir(COD)H^+ \qquad (18a)$$

$$BDE = (75.2 \pm 0.9) - (0.008 \pm 0.028)(-\Delta H_{HM}) \quad \text{for } CpIr(CO)(PR_3)H^+ \qquad (18b)$$

It should be noted in all series of compounds, except those of Ir, that the BDE values increase as the $-\Delta H_{HM}$ values increase; that is, as heterolytic bond cleavage ($-\Delta H_{HM}$) (eq 2) requires more energy, so does homolytic bond cleavage (BDE) (eq 1). However, for the Ir complexes, the BDE values do not increase even though heterolytic bond cleavage enthalpies ($-\Delta H_{HM}$) do; this divergent behavior *may* be due to the influence of kinetic factors on the irreversible $E_{1/2}$ values.

Other Trends in Bond Dissociation Enthalpies (BDE). It is evident (Table 1) for a series of complexes with the same ligands that the BDE values increase with increasing atomic weight of the metal in the same group. Thus, for the complexes $M(CO)_2(dppm)_2H^+$ (M = Cr, Mo, W), the M-H BDE (kcal/mol) increases in the order Cr−H (56.0) < Mo−H (67.2) < W−H (68.0); this is the same trend observed for the $CpM(CO)_3H$ complexes: Cr−H, 61.5 < Mo−H, 69.4 < W−H, 72.5.[3f] Similarly, the M−H BDE (kcal/mol) is larger for Os than Ru in the two types of complexes, $Cp^*{}_2MH^+$ (Ru−H, 68.0 < Os−H, 71.7) and $CpM(PPh_3)_2(H)_2^+$ (Ru−H, 68.3 < Os−H, 73.6). Thus, these data support previous reports of increasing M−H BDE values as a 3d metal is replaced by its 4d and 5d congeners.[2d,3]

In order to determine whether a cationic metal hydride complex has a significantly different BDE than a comparable neutral complex, we compare the BDE of $Cp^*Re(CO)_2(PMe_3)H^+$ (71.8 kcal/mol) with that of the isoelectronic and isosteric $CpW(CO)_2(PMe_3)H$ (69.6 kcal/mol).[3c,h] For this comparison, it would be desirable to use $Cp^*W(CO)_2(PMe_3)H$; however, its BDE has not been reported but its value is likely to be very similar to that of $CpW(CO)_2(PMe_3)H$ because replacement of

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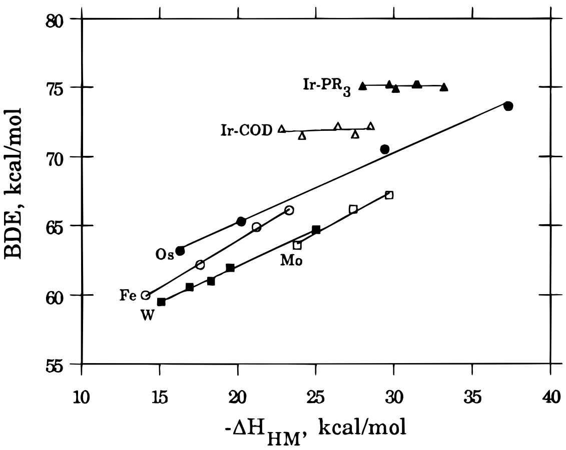

Figure 3. Plots of BDE vs $-\Delta H_{HM}$ for the $Mo(CO)_2(L-L)_2$, $W(CO)_3(PR_3)_3$, $Fe(CO)_3(PR_3)_2$, $CpOs(PR_3)_2X$, $(C_5H_{5-n}Me_n)Ir(COD)$, and $CpIr(CO)(PR_3)$ series of complexes.

Cp by Cp* changes M−H BDE values very little as seen in the complexes $CpMo(CO)_3H$ (69.2 kcal/mol)[3c] and $Cp^*Mo(CO)_3H$ (68.5)[3c]. Thus, our comparison shows that the BDE values of $Cp^*Re(CO)_2(PMe_3)H^+$ (71.8 kcal/mol) and $Cp^*W(CO)_2(PMe_3)H$ (∼69.6 kcal/mol) are very similar, which suggests that the extra positive charge in a cationic metal hydride complex does not by itself substantially strengthen or weaken a M−H bond. This is also seen in BDE values for $CpFe(CO)_2H$ (57.1 ± 3)[3c] and $CpCo(CO)_2H^+$ (58.6 ± 3)[2d] in the gas phase.

Another obvious trend in the data in Table 1 is that the heterolytic bond cleavage energy ($-\Delta H_{HM}$) for a compound is substantially less than the homolytic bond cleavage energy (BDE). However, it is important to note that heterolytic cleavage actually involves transfer of a proton (H^+) from the metal to the $CF_3SO_3^-$ base (reverse of eq 4). With stronger bases than $CF_3SO_3^-$, $-\Delta H_{HM}$ for the reverse of eq 4 would be even less positive; in these cases, heterolytic cleavage would be even more favorable than homolytic cleavage.

Summary

In the course of determining bond dissociation enthalpies (BDE) of fifty-one 18-electron cationic transition metal hydride complexes (L_nMH^+), oxidation potentials ($E_{1/2}$) for each of the conjugate Lewis base complexes (L_nM) were measured. Within a family of compounds having the same metal and types of ligands, there is an excellent correlation between the ease of oxidation ($E_{1/2}$) and the basicity ($-\Delta H_{HM}$) of the metal: the more easily oxidized the metal, the more basic it is toward protonation. Because $E_{1/2}$ and $-\Delta H_{HM}$ are used in calculations of M−H BDE values for the L_nMH^+ complexes, there are also correlations between the BDE and $-\Delta H_{HM}$ values. Thus, within a family of compounds, it is possible to estimate M−H BDE values from $-\Delta H_{HM}$. In all series of compounds, heterolytic cleavage ($-\Delta H_{HM}$) of the M−H bond is more sensitive to the nature of the ligands in the complex than is homolytic cleavage (BDE).

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