# Estimating the Acidity of Transition Metal Hydride and Dihydrogen Complexes by Adding Ligand Acidity Constants

Robert H. Morris*

Department of Chemistry, University of Toronto, 80 Saint George Street, Toronto, Ontario M5S 3H6, Canada

 Ⓢ *Supporting Information*

ABSTRACT: A simple equation ($pK_a^{THF} = \sum A_L + C_{charge} + C_{nd} + C_{d6}$) can be used to obtain an estimate of the pK_a of diamagnetic transition metal hydride and dihydrogen complexes in tetrahydrofuran, and, by use of conversion equations, in other solvents. It involves adding acidity constants A_L for each of the ligands in the 5-, 6-, 7-, or 8-coordinate conjugate base complex of the hydride or dihydrogen complex along with a correction for the charge ($C_{charge} = -15$, 0 or 30 for $x = +1$, 0 or -1 charge, respectively) and the periodic row of the transition metal ($C_{nd} = 0$ for 3d or 4d metal, 2 for 5d metal) as well as a correction for d^6 octahedral acids ($C_{d6} = 6$ for d^6 metal ion in the acid, 0 for others) that are not dihydrogen complexes. Constants A_L are provided for 13 commonly occurring ligand types; of these, nine neutral ligands are correlated with Lever's electrochemical ligand parameters E_L. This method gives good estimates of the over 170 literature pK_a values that range from less than zero to 50 with a standard deviation of 3 pK_a units for complexes of the metals chromium to nickel, molybdenum, ruthenium to palladium, and tungsten to platinum in the periodic table. This approach allows a quick assessment of the acidity of hydride complexes found in nature (e.g., hydrogenases) and in industry (e.g., catalysis and hydrogen energy applications). The pK_a values calculated for acids that have bulky or large bite angle chelating ligands deviate the most from this correlation. The method also provides an estimate of the base strength of the deprotonated form of the complex.
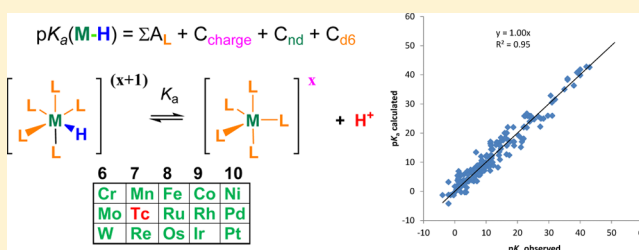
INTRODUCTION

The acidity of metal hydride and dihydrogen complexes comes into play in many important catalytic[1−10] and biological[3,11,12] processes as well as in dihydrogen storage,[13] dihydrogen generation,[3,4] photochemical water splitting,[14] fuel cell electrocatalysis,[3] and many other applications. Thus, understanding and predicting the thermodynamics of the acidity of a metal hydride complex with ligands L as in eq 1 are important objectives. Many acid dissociation equilibrium constants have been previously determined by a variety of methods including NMR,[3,15−27] IR,[15,16] calorimetry,[28,29] and DFT calculations.[8,30,31]

$$[MHL_n]^{(x+1)} \overset{K_a}{\rightleftharpoons} [ML_n]^x + H^+ \qquad (1)$$
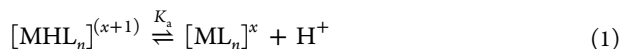
In principle, the pK_a of a metal hydride can be predicted by use of the thermochemical cycle shown in Figure 1; the free energies in this case refer to acetonitrile as the solvent.[32] One route to proton dissociation involves the free energy of the equilibrium, 1.37 pK_a for standard conditions, between the metal hydride complex and its conjugate base metal complex. An alternate route is: (1) the free energy of the homolytic cleavage of the metal−hydride bond (to produce the oxidized metal complex and a hydrogen atom), which is usually approximately 60 kcal mol^{-1};[21,29,30,32−36] (2) −53.6 kcal mol^{-1}, the energy of hydrogen atom oxidation in acetonitrile (using ferrocenium/ferrocene as the electrochemical reference); and then (3) the reduction of the oxidized conjugate
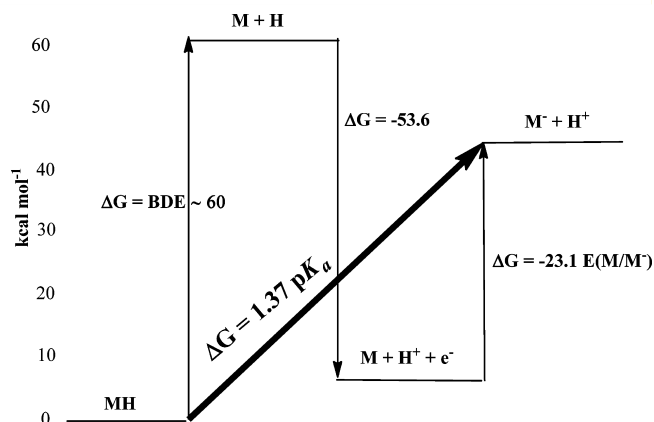

Figure 1. The thermochemical cycle showing the relationship $\Delta G(MH \rightarrow M^- + H^+) = \Delta G(MH \rightarrow M + H) - \Delta G(H \rightarrow H^+ + e^-) - 23.1 E_{1/2}(M/M^-)$ (in kcal/mol) for acetonitrile solvent with ferrocenium/ferrocene as the reference redox potential. In this case of a weak acid, $E_{1/2}(M/M^-)$ is negative. M refers to the metal in a complex.

base metal complex at the electrochemical potential $E_{1/2}(M/M^-)$. Similar cycles have been used with other solvents and references.[36,37] Therefore, because the first two energy changes

are fairly constant, the acidity depends mainly on the electrochemical potential of the conjugate base metal complex. If this can be predicted, then pK_a values can be estimated.

A similar cycle can be written for dihydrides or dihydrogen complexes with the H−H bond still intact while coordinated to the metal. Lever showed that $E_{1/2}([ML_6]^{x+1}/[ML_6]^x)$ for many octahedral metal complexes can be predicted using additive constants E_L for each type of ligand that were derived from redox potentials $E_{1/2}([Ru(III)L_6]/[Ru(II)L_6])$.[38] We showed that this method along with an estimate of a bond dissociation energy can be used to estimate the pK_a of octahedral metal dihydrogen complexes with an error of ±9 units.[37] The large error results from the uncertainty in the magnitude of the hydrogen atom dissociation energy.

This Article outlines a surprisingly simple way to obtain an estimate of the pK_a value of transition metal hydrides and dihydrogen complexes.

■ CALCULATIONS

The pK_a values for 179 transition metal hydride and dihydrogen complexes along with the solvent and a list of the generic ligand types making up each complex were tabulated on an Excel spreadsheet (see the Supporting Information). This list is believed to be comprehensive. A pK_a^{THF} value was calculated for each complex by adding the acidity constants assigned to each ligand type in the complex in a database on a linked spreadsheet plus other constants C to account for charge and d electron effects as discussed below. The pK_a^{THF} value refers to the acid dissociation constant in tetrahydrofuran. The widest range of hydride complex pK_a has been determined using this solvent.[20] For literature pK_a values that refer to acetonitrile (MeCN) or water, the pK_a^{THF} value is converted using known eqs 2−4. The equations depend on whether the acids are neutral or cationic because of different ion pairing effects in THF.[20] For acetonitrile, the conversion equations are:

$$pK_a^{MeCN} = 0.81pK_a^{THF} + 1.0 \text{ for neutral acids} \tag{2}$$

$$pK_a^{MeCN} = 1.13pK_a^{THF} + 3.7 \text{ for cationic acids} \tag{3}$$

Equation 3 is consistent with recent literature results on cationic acids measured using both THF and MeCN.[39,40] Values for cationic acids on the aqueous scale are obtained using eq 4 as reported earlier.[20] There is not enough data to make a correlation for neutral acids producing anionic bases in water.

$$pK_a^{H2O} = pK_a^{THF} - 0.7 \text{ for cationic acids} \tag{4}$$

Also included in the analysis were 43 pK_a^{THF} that were obtained indirectly via a previously reported correlation[41] between pK^{CH2Cl2} and Angelici's[28,29] enthalpies of protonation of metal complexes with trifluorosulfonic acid in dichloroethane (DCE) (eq 5). Literature values reported as pK^{CH2Cl2} or pK_a^{CH2Cl2} use the same cationic acid standards as the pK_a^{THF} scale, and cationic hydride acids are reported to give similar pK_a values in THF as in CH_2Cl_2.[42] However, it should be kept in mind that these are not absolute values but instead are relative values because absolute pK_a values would require the determination of the concentration of the protonated solvent.

$$-\Delta H^{DCE} = 1.8pK^{CH2Cl2} + 17.48 \tag{5}$$

The constants of the database were varied so that the regression coefficient of the least-squares fit of all of the calculated versus observed pK_a values was maximized. Overall, 13 constants for the ligands in these complexes and the other constants C were varied. Constants that had minimal impact were eliminated from the pK_a^{THF} equation. Three important constants were found: C_{charge} that corrected for effect of the charge of the conjugate base (Table 1), C_{d6} that corrects for the extra stability of hydride when the metal has a d^6 configuration, and C_{nd} that corrects for the added stability of hydrides of 5d transition metals. In the final analysis, eight outliers (calculated

Table 1. Constant C_{charge} Depends on the Charge of the Conjugate Base Complex[a]

x	C_{charge}
+1	−15
0	0
−1	30

[a]x in eq 1.

pK_a values with greater than two standard deviations from the observed ones; see below) were omitted from the regression. Equation 6 was the result of this fitting process along with a consistent set of values for a minimum number of ligand acidity constants A_L (Table 2). The resulting calculated pK_a values are listed in Table 3. The pK_a values refer to the solvent in which they were measured. The 43 values obtained from the correlation eq 5 are listed in parentheses in Table 3. Equations to convert pK_a values to the DMSO scale are also available but are not used here.[20]

■ RESULTS AND DISCUSSION

Description of the Additive Ligand Constant Scheme. The results of the regression analysis provided eq 6, which gives an estimate of the pK_a value in THF by adding the acidity constants A_L for each of the ligands in the conjugate base form of the hydride or dihydrogen acid and makes a correction for the charge on the conjugate base (C_{charge}), the periodic row of the transition metal (C_{nd}), and a correction for the stability of hydride complex acids with a d^6 octahedral metal (C_{d6}).

$$pK_a^{THF} = \sum A_L + C_{charge} + C_{nd} + C_{d6} \tag{6}$$

where:

(1) A_L values (Table 2) for each of the four to eight ligands around the metal in the conjugate base complex are added. When the ligand bonds to the metal at more than one coordination site (i.e., it is bi- or polydentate), the A_L value represents the contribution to each coordination site.

(2) C_{charge} depends on the charge x of the conjugate base, $[ML_n]^x$, of eq 1 as listed in Table 1. For simplicity, ion pairing and the nature of the counterion have been neglected; however, in all cases these are the weakly interacting ions BF_4^-, PF_6^-, BAr_4^-, $K(crypt)^+$, $K(18\text{-crown-6})^+$, or NEt_4^+. It is known that oxidizing a metal hydride complex to a cation decreases the pK_a of a hydride by about 15 units.[24] In fact, this value of −15 pK_a units was found to give the best fit to the data for the 12 compounds with cationic conjugate bases found in Table 3, although there was a poor correlation for these compounds, which include ligands with large bite angles and pK_a measurements with uncertainties (see the Supporting Information). The constant that reproduces pK_a values of hydrides that have anionic conjugate bases is even larger in magnitude (30 units) in the opposite direction. The value of 30 was determined from the data for 30 compounds with anionic conjugate bases (see the Supporting Information). The error in this value is large (±4) because the pK_a^{THF} values above 20 have an error of ±4 units.[20] The hydride $[FeH(CO)_4]^-$ with a dianionic conjugate base $[Fe(CO)_4]^{2-}$ is known to be a strong base in water,[43] but this one example does not allow the determination of an accurate C_{charge} value for $x = -2$.

(3) $C_{nd} = 0$ for 3d and 4d metals or $C_{nd} = 2$ for 5d metals. This recognizes the stronger M−H bonds of the 5d metals but does not discriminate between 3d and 4d metal complexes, which are known to have some differences in acidity for analogous complexes, sometimes more and sometimes less

Table 2. Additive Acidity Parameters A_L for Common Classes of Ligands and the Corresponding Average Lever Parameter E_L for That Class

class of ligand	specific ligands included[a]	number of instances	A_L parameter (pK_a units)	E_L^{38} (av.) (V)
chloride, Cl⁻	Cl	11	−6	−0.24
hydridotris(pyrazolyl)borate, Tp⁻	Tp	10	0.0^b	
hydride, H⁻	H, CH₃	88	0.2	$−0.4^c$
η^5-cyclopentadienyl, Cp⁻	C₅H₅, MeC₅H₄ (MeCp), C₅H₄CH₂CH₂NHMe₂⁺	37	0.6^b	
η^5-pentamethylcyclopentadienyl, Cp*	C₅Me₅	19	0.9^b	
carbonyl, CO	CO	68	−4.1	0.99
olefin	COD, C₂H₄	2	−2	0.76
PX₃	P(OPh)₃, P(OMe)₃, dtfpe	10	1.6	0.48
PAr₃	PPh₃; dppv; phosphorus part of PPh₂−NH−NH−PPh₂[d]	26	2.7	0.39
PAr₂R	PPh₂Me; dppe, dppm; dppp	55	3.0	0.36
PArR₂	PPhMe₂; EtXantphos	14	4.0	0.33
nitrogen donors, N	MeCN; py; oxazolyl, dach; N donor part of PPh₂−NH−NH−PPh₂[d]	7	4	0.25
PR₃	PCy₃; PⁱPr₃; PMe₃; (−PRCH₂NR′−CH₂PRCH₂NR′−)	52	4.9	0.3

[a]Abbreviations: COD = 1,5 cyclooctadiene; dtfpe = (4-CF₃C₆H₄)₂PCH₂CH₂P(4-CF₃C₆H₄)₂; dppv = PPh₂CH=CHPPh₂; dppe = PPh₂CH₂CH₂PPh₂; dppm = PPh₂CH₂PPh₂; dppp = PPh₂CH₂CH₂CH₂PPh₂; EtXantphos = 9,9-dimethyl-4,5-bis(diethylphosphino)xanthene; py = pyridine; dach = *trans*-diaminocyclohexane. [b]Assumed to occupy 3 coordination sites: $3A_L$(Tp) = 0, $3A_L$(Cp) = 1.8, $3A_L$(Cp*) = 2.7. [c]Poorly defined E_L parameter due to irreversibility of redox chemistry of hydride complexes.[37,38] [d]The total contribution from the tetradentate ligand {PPh₂C₆H₄CH₂NHCMe₂−}₂ is $2A_L$(N) + $2A_L$(PAr₃).

acidic by a few units. For example, it was reported that the acidity of 5-coordinate 18-electron metal hydrides follows the order second row > first row > third row.[33] The difference between ruthenium and osmium can be as great as 6 units,[44] and so there is some error in this simple approach. In addition, further error could result from the contribution of H−H bonding in dihydrogen complexes, although this does not appear to exceed the 3 pK_a unit error of the current method.[45]

(4) C_{d6} = 6 when the metal ion of the acidic hydride complex loses the d^6 octahedral configuration on going to the lower coordinate conjugate base form (Δ 6/5 or 6/4 in Table 3). For example, this constant is added when calculating the pK_a for the hydride Fe(Cp*)(H)(CO)₂, which is considered to have a d^6 octahedral ferrous ion, while the conjugate base, [Fe(Cp*)-(CO)₂]⁻, is considered to have a d^8 5 coordinate iron(0) atom. C_{d6} = 0 for all other cases, including dihydrogen complexes with d^6 octahedral metal centers, which remain six coordinate with a d^6 configuration in their conjugate base form (Δ 6/6). For example, C_{d6} = 0 when applying eq 6 to [Fe(H₂)H(dppe)₂]⁺ (see below). A study of the effect of introducing another parameter to account for any other change in d electron count indicated that no other parameters are warranted.

For the eight neutral ligand types listed in Table 2, eq 7 describes the relationship between the A_L parameters in pK_a units and Lever's electrochemical parameters E_L (in V):

$$A_L = −11.9E_L + 7.5$$

(regression factor R^2 = 0.97; standard deviation 0.5)

(7)

The relationship between the Lever parameters and the derived A_L values for charged ligands such as hydride and chloride is not clear because these form covalent bonds with the metals, while Lever parameters apply to electrostatic bonding of classical, "innocent" ligands. There is no obvious correlation with Pickett's electrochemical parameters.[46]

None of the conjugate base forms of the compounds treated in this study contain dihydrogen ligands. Thus, an acidity parameter for the dihydrogen ligand could not be determined.

To illustrate the simplicity of the use of eq 6, here are a few representative calculations. Entry 1 of Table 3 refers to a five coordinate d^8 cobalt hydride complex CoH(dppe)₂. Therefore, C_{d6} = 0, and C_{nd} = 0 for cobalt, a 3d metal. Its conjugate base form is the anionic complex [Co(dppe)₂]⁻ so that C_{charge} = 30. Each dppe ligand is modeled as two PAr₂R ligands with A_L 3.0 so that $\sum A_L$ = $4A_L$(PAr₂R) = 12. Therefore, from eq 6, pK_a^{THF} = 30 + 12 = 42, and by use of eq 2, pK_a^{MeCN} = 35. The observed value is 38 for acetonitrile solution.

Complex Fe(C₅Me₅)(CO)₂H (entry 8) is a d^6 iron hydride complex, so C_{d6} = 6 is used in eq 6. The conjugate base form, [Fe(Cp*)(CO)₂]⁻, is anionic. Therefore, C_{charge} = 30 and $\sum A_L$ = $3A_L$(Cp*) + $2A_L$(CO) = −5.5, pK_a^{THF} = 30 + 6 − 5.5 = 30.5. The observed value is 31.

Entry 14 refers to the cationic dihydrogen complex *trans*-[Fe(H₂)H(dppe)₂]⁺, which loses a proton to give the neutral dihydride FeH₂(dppe)₂. This conjugate base is neutral so C_{charge} = 0. $\sum A_L$ = $4A_L$(PAr₂R) + $2A_L$(H) = 12.4. C_{nd} = 0 for iron and C_{d6} = 0 because this is d^6 dihydrogen complex. Thus, from eq 6, pK_a^{THF} = 12.4. The reported value is 11.5.

A Comparison of Estimated and Literature Values. The complexes in Table 3 are ordered first alphabetically by metal symbol and then by decreasing pK_a values. Usually the hydride complexes are only isolable when they are diamagnetic and contain strong field ligands; all of the complexes involved here are diamagnetic. The use of the restrictive set of ligand parameters of Table 2 obviously neglects many factors such as finer electronic contributions, steric contributions, and bite angle considerations of bidentate ligands, and this accounts for many of the large deviations from calculated values. For example, the pK_a^{MeCN} of rhodium complexes with electronically similar ligands but with different cone angles can range from 6 (PCy₂CH₂CH₂PCy₂ with large cone angles at phosphorus, entry 117) to 18.9 (PMe₂CH₂CH₂PMe₂ with small cone angles, entry 111);[47] In our simplified scheme, both of these give the

Table 3. Observed and Calculated pK_a Values Relating the Acid and Its Conjugate Base for the Solvent(s) Specified Where the Δ Ratio Shows the Coordination Numbers of the Acid and the Base, Respectively[a]

entry	acid	base[b]	Δ	solvent[c]	pK_a obs	pK_a calcd	ref
1	CoH(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$	[Co(dppe)$_2$]$^-$	5/4	MeCN	38.0	35	48
2	CoH(CO)$_3$(PPh$_3$)	[Co(CO)$_3$(PPh$_3$)]$^-$	5/4	MeCN (H$_2$O)	15.4	18	16
3	CoH(CO)$_3$(P(OPh)$_3$)	[Co(CO)$_3$(P(OPh)$_3$)]$^-$	5/4	MeCN (H$_2$O)	11.4	16*	16
4	[CoH(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$(MeCN)]$^{2+}$	[Co(dppe)$_2$]$^+$	6/4	MeCN	11.3	7*	48
5	CoH(CO)$_4$	[Co(CO)$_4$]$^-$	5/4	MeCN (H$_2$O, MeOH)	8.4	12	16, 49
6	Cr(H)(Cp)(CO)$_3$	[Cr(Cp)(CO)$_3$]$^-$	7/6	MeCN	13.3	17	15
7	[CrH(CO)$_2$(PPh$_2$CH$_2$PPh$_2$)$_2$]$^+$	Cr(CO)$_2$(dppm)$_2$	7/6	DCE	(4)	3	29
8	Fe(Cp*)(CO)$_2$H	[Fe(Cp*)(CO)$_2$]$^-$	6/5	MeCN (THF)	31.0	29	20, 44
9	Fe(Cp)(CO)$_2$H	[Fe(Cp)(CO)$_2$]$^-$	6/5	MeCN	27.5	23*	44, 50
10	[Fe(H$_2$)(Cp)(−PPh−NPh−PPh−NPh−)]$^+$	FeH(Cp)(−PPh−NPh−PPh−NPh−)	6/6	MeCN	22.0^d	22	27
11	[FeH$_3$(PMe$_3$)$_4$]$^+$	FeH$_2$(PMe$_3$)$_4$	7/6	THF	15.9	20*	20
12	[Fe(H$_2$)H(PMe$_3$)$_4$]$^+$	FeH$_2$(PMe$_3$)$_4$	6/6	THF	15.9	20*	20
13	[Fe(CpMe)(−P^{t}Bu−N−P^{t}Bu−N−)(H$_2$)]$^+$	Fe(CpMe)(−P^{t}Bu−N−P^{t}Bu−N−)(H)	6/6	MeCN	18.9	17	3
14	trans-[Fe(H$_2$)H(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$]$^+$	cis-FeH$_2$(dppe)$_2$	6/6	THF	11.5	12	20
15	FeH$_2$(CO)$_4$	[FeH(CO)$_4$]	6/5	MeCN (H$_2$O)	11.4	17*	16
16	trans-[Fe(H$_2$)H(PAr$_2$CH$_2$CH$_2$Ar$_2$)$_2$]$^+$, Ar = p-CF$_3$C$_6$H$_4$	cis-FeH$_2$(dtfpe)$_2$	6/6	THF	6.7	6	20
17	[FeH(CO)$_3$(PMe$_2$CH$_2$PMe$_2$)]$^+$	Fe(CO)$_3$(dmpm)	6/5	DCE	(7)	4	28
18	[FeH(CO)$_3$(PCy$_2$CH$_2$CH$_2$PCy$_2$)]$^+$	Fe(CO)$_3$(dcpe)	6/5	DCE	(6)	4	28
19	[FeH(CO)$_3$(PPh$_2$CH$_2$PPh$_2$)]$^+$	Fe(CO)$_3$(dppm)	6/5	DCE	(4)	0*	29
20	[FeH(CO)$_3$(PPh$_2$CH$_2$CH$_2$PPh$_2$)]$^+$	Fe(CO)$_3$(dppe)	6/5	DCE	(3)	1	28
21	[FeH(CO)$_3$(PCy$_3$)$_2$]$^+$	Fe(CO)$_3$(PCy$_3$)$_2$	6/5	CH$_2$Cl$_2$	4.4	4	41
22	[FeH(CO)$_3$(PMe$_3$)$_2$]$^+$	Fe(CO)$_3$(PMe$_3$)$_2$	6/5	DCE	(4)	4	29
23	[FeH(CO)$_3$(PMe$_2$Ph)$_2$]$^+$	Fe(CO)$_3$(PMe$_2$Ph)$_2$	6/5	DCE	(2)	2	29
24	[FeH(CO)$_3$(PPh$_2$CH$_2$CH$_2$CH$_2$PPh$_2$)]$^+$	Fe(CO)$_3$(dppp)	6/5	DCE	(2)	0	29
25	[FeH(CO)$_3$(PMePh$_2$)$_2$]$^+$	Fe(CO)$_3$(PMePh$_2$)$_2$	6/5	DCE	(1)	0	29
26	[FeH(CO)$_3$(PPh$_3$)$_2$]$^+$	Fe(CO)$_3$(PPh$_3$)$_2$	6/5	CH$_2$Cl$_2$ (DCE)	−0.6	−1	29, 41
27	Ir(H)$_2$(Cp*)(PMe$_3$)	[IrH(Cp*)(PMe$_3$)]$^-$	6/5	THF	40.0	40	51
28	IrH$_5$(PCy$_3$)$_2$	[cis-IrH$_4$(PCy$_3$)$_2$]$^-$	7/6	THF	43.0	43	52
29	IrH$_5$(P^{i}Pr$_3$)$_2$	[cis-IrH$_4$(P^{i}Pr$_3$)$_2$]$^-$	7/6	THF	43.0	43	52
30	[IrH$_2$(CO)(PPh$_3$)$_3$]$^+$	IrH(CO)(PPh$_3$)$_3$	6/5	DCE	(12)	12	29
31	[IrH(Cp*)(PMe$_3$)(CO)]$^+$	Ir(Cp*)(PMe$_3$)(CO)	6/5	DCE	(11)	12	28
32	[IrH(Cp*)(PMe$_2$Ph)(CO)]$^+$	Ir(Cp*)(PMe$_2$Ph)(CO)	6/5	DCE	(11)	11	28
33	[IrH(Cp*)(PMePh$_2$)(CO)]$^+$	Ir(Cp*)(PMePh$_2$)(CO)	6/5	DCE	(11)	10	29
34	[IrH(Cp*)(PPh$_3$)(CO)]$^+$	Ir(Cp*)(PPh$_3$)(CO)	6/5	DCE	(11)	9	29
35	[IrH(Cp)(PMe$_3$)(CO)]$^+$	Ir(Cp)(PMe$_3$)(CO)	6/5	DCE	(9)	11	29
36	[IrH(Cp)(PEt$_3$)(CO)]$^+$	Ir(Cp)(PEt$_3$)(CO)	6/5	DCE	(9)	11	29
37	[IrH(Cp)(PPhMe$_2$)(CO)]$^+$	Ir(Cp)(PPhMe$_2$)(CO)	6/5	DCE	(8)	10	29
38	[IrH(Cp)(PPh$_2$Me)(CO)]$^+$	Ir(Cp)(PPh$_2$Me)(CO)	6/5	DCE	(8)	9	29
39	[IrH(Cp)(PPh$_3$)(CO)]$^+$	Ir(Cp)(PPh$_3$)(CO)	6/5	DCE	(7)	8	29
40	[IrH(Cp*)(COD)]$^+$	Ir(Cp*)(COD)	6/5	DCE	(6)	7	29
41	[IrH(Cp)(COD)]$^+$	Ir(Cp)(COD)	6/5	DCE	(3)	6	29
42	[IrH(CO)Cl(PMe$_2$Ph)$_2$]$^+$	IrCl(CO)(PMePh$_2$)$_2$	5/4	MeOH	2.8	7*	53
43	[IrH(CO)Cl(PPh$_3$)$_2$]$^+$	IrCl(CO)(PPh$_3$)$_2$	5/4	MeOH	2.1	2	53
44	[IrH(Cp*)(CO)$_2$]$^+$	Ir(Cp*)(CO)$_2$	6/5	DCE	(2)	3	29
45	[IrH$_3$(Cp)(PPh$_3$)]$^+$	IrH$_2$(Cp)(PPh$_3$)	7/6	DCE	(1)	7*	28
46	[IrH$_3$(Cp)(P(OPh)$_3$)]$^+$	IrH$_2$(Cp)(P(OPh)$_3$)	7/6	DCE	(−3)	6**	28
47	MnH(CO)$_4$(PPh$_3$)	[Mn(CO)$_4$(PPh$_3$)]$^-$	6/5	MeCN	20.4	19	20
48	MnH(CO)$_5$	[Mn(CO)$_5$]$^-$	6/5	MeCN	14.2	14	16, 20
49	Mo(H)(Cp*)(CO)$_3$	[Mo(Cp*)(CO)$_3$]$^-$	7/6	MeCN	17	18	16
50	Mo(H)(Cp)(CO)$_3$	[Mo(Cp)(CO)$_3$]$^-$	7/6	MeCN	13.6	17	15
51	[MoH(CO)$_2$(PMe$_2$CH$_2$CH$_2$PMe$_2$)$_2$]$^+$	Mo(CO)$_2$(dmpe)$_2$	7/6	DCE	(12)	11	28
52	[MoH(CO)$_2$(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$]$^+$	Mo(CO)$_2$(dppe)$_2$	7/6	DCE	(5)	4	28
53	[MoH(CO)$_2$(PPh$_2$CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$]$^+$	Mo(CO)$_2$(dppp)$_2$	7/6	DCE	(1)	4	28
54	[MoH(CO)$_2$(PPh$_2$CH$_2$PPh$_2$)$_2$]$^+$	Mo(CO)$_2$(dppm)$_2$	7/6	DCE	(7)	4	28
55	[NiH(PMe$_2$CH$_2$CH$_2$PMe$_2$)$_2$]$^+$	Ni(dmpe)$_2$	5/4	MeCN	24.3	26	21
56	[NiH(PMe$_2$CH$_2$CH$_2$CH$_2$PMe$_2$)$_2$]$^+$	Ni(dmpp)$_2$	5/4	MeCN	24.0	26	30

Table 3. continued

entry	acid	base[b]	Δ	solvent[c]	pK$_a$ obs	pK$_a$ calcd	ref
57	[NiH(dmpe)(depe)]$^+$	Ni(dmpe)(depe)	5/4	MeCN	24.3	26	21
58	[NiH(PEt$_2$CH$_2$CH$_2$PEt$_2$)$_2$]$^+$	Ni(depe)$_2$	5/4	MeCN	23.8	26	30
59	[NiH(PEt$_2$CH$_2$CH$_2$CH$_2$PEt$_2$)$_2$]$^+$	Ni(depp)$_2$	5/4	MeCN	23.3	26	30
60	[NiH(PEt$_2$CH$_2$NMeCH$_2$PEt$_2$)$_2$]$^+$	Ni(Et$_2$PCH$_2$NMeCH$_2$PEt$_2$)$_2$	5/4	MeCN	22.2	26	30
61	[NiH(−PMe−NPh−PMe−NPh−)$_2$]$^+$	Ni(−PMe−NPh−PMe−NPh−)$_2$	5/4	MeCN	22.5	26	54
62	[NiH(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$]$^+$	Ni(dppe)$_2$	5/4	MeCN	14.7	17	21
63	[NiH(PPh$_2$CH=CHPPh$_2$)$_2$]$^+$	Ni(dppv)$_2$	5/4	MeCN	13.2	16	30
64	Os(H$_2$)(H)$_2$(CO)(P^{i}Pr$_3$)$_2$	[OsH$_3$(CO)(P^{i}Pr$_3$)$_2$]$^-$	6/6	THF	36	38	20
65	Os(Cp)(CO)$_2$H	[Os(Cp)(CO)$_2$]$^-$	6/5	MeCN	32.7	32	44
66	OsH$_2$(CO)$_4$	[OsH(CO)$_4$]$^-$	6/5	MeCN	20.8	19	16, 55
67	[OsH$_3$(PEt$_3$)$_4$]$^+$	OsH$_2$(PEt$_3$)$_4$	7/6	THF	18.7	22	16
68	[OsH$_3$(PMe$_3$)$_4$]$^+$	OsH$_2$(PMe$_3$)$_4$	7/6	THF (MeOH)	16.9	22*	20
69	[OsH$_3$(PMe$_2$Ph)$_4$]$^+$	OsH$_2$(PMe$_2$Ph)$_4$	7/6	THF	14.9	18	56
70	[Os(H$_2$)Cl(PPh$_2$CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$]$^+$	Os(H)Cl(dppp)$_2$	6/6	CH$_2$Cl$_2$	13.8	8*	57
71	[OsH$_3$(PPh$_2$CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$]$^+$	Os(H)$_2$(dppp)$_2$	7/6	CH$_2$Cl$_2$	11.6	14	57
72	trans-[Os(H$_2$)H(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$]$^+$	cis-OsH$_2$(dppe)$_2$	6/6	THF	12.1	14	20
74	trans-[Os(H)$_2$(Cp)(PPh$_3$)$_2$]$^+$	OsH(Cp)(PPh$_3$)$_2$	7/6	DCE (CH$_2$Cl$_2$)	11.6	10	29
75	[OsH$_3$(PMePh$_2$)$_4$]$^+$	cis-OsH$_2$(PMePh$_2$)$_4$	7/6	DCE (THF)	12.4	14	20, 29
76	trans-[Os(H)$_2$(Cp)(PPh$_2$CH$_2$PPh$_2$)]$^+$	OsH(Cp)(dppm)	7/6	CH$_2$Cl$_2$	10.0	10	19
77	[OsH$_3$(P(OEt)$_3$)$_4$]$^+$	cis-OsH$_2$(P(OEt)$_3$)$_4$	7/6	DCE	(9)	8	56
78	[Os(H)$_2$(Cp)(PPh$_3$)(P(OEt)$_3$)]$^+$	Os(H)(Cp)(PPh$_3$)(P(OEt)$_3$)	7/6	DCE	(9)	8	29
79	[Os(H)$_2$(Tp)(PPh$_3$)$_2$]$^+$	OsH(Tp)(PPh$_3$)$_2$	7/6	CH$_2$Cl$_2$	8.8	8	19
80	trans-[Os(H$_2$)H(PAr$_2$CH$_2$CH$_2$Ar$_2$)$_2$]$^+$, Ar = p-CF$_3$C$_6$H$_4$	cis-OsH$_2$(dtfpe)$_2$	6/6	THF	7.3	8	20
81	Os(H$_2$)Cl(PPh$_3$)(Ph$_2$PCH$_2$py−CH$_2$PPh$_2$)]$^+$	OsHCl(PPh$_3$)(Ph$_2$PCH$_2$py−CH$_2$PPh$_2$)	6/6	CH$_2$Cl$_2$	7.2	9	58
82	[OsH$_5$(PPhMe$_2$)$_3$]$^+$	OsH$_4$(PPhMe$_2$)$_3$	8/7	DCE	(6)	17**	28
83	[OsH$_5$(PPh$_2$Me)$_3$]$^+$	OsH$_4$(PPh$_2$Me)$_3$	8/7	DCE	(4)	12**	28
84	[OsH(Cp*)$_2$]$^+$	Os(Cp*)$_2$	7/6	MeCN (DCE)	10	12	20, 29
85	[Os(Cp)(PPh$_3$)$_2$(Cl)]$^+$	Os(Cp)(PPh$_3$)$_2$(Cl)	7/6	DCE	(1)	3	29
86	[Os(H$_2$)(CO)(P^{i}Pr$_3$)(Tp)]$^+$	OsH(CO)(P^{i}Pr$_3$)(Tp)	6/6	CH$_2$Cl$_2$	2.0	3	59
87	trans-[Os(H$_2$)(MeCN)(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$]$^{2+}$	trans-[Os(H)(MeCN)(dppe)$_2$]$^+$	6/6	CH$_2$Cl$_2$	−2	3*	20
88	[PdH(PEt$_2$CH$_2$CH$_2$PEt$_2$)$_2$]$^+$	Pd(depe)$_2$	5/4	MeCN	23.9	24	60
89	[PdH(PEt$_2$CH$_2$CH$_2$CH$_2$PEt$_2$)$_2$]$^+$	Pt(depp)$_2$	5/4	MeCN	15.5	24**	60
90	[PdH(EtXantphos)$_2$]$^+$	Pd(EtXantphos)$_2$	5/4	MeCN	4.1	20**	60
91	[PtH(PMe$_2$CH$_2$CH$_2$PMe$_2$)$_2$]$^+$	Pt(dmpe)$_2$	5/4	MeCN	31.1	26*	22
92	[PtH(PEt$_2$CH$_2$CH$_2$PEt$_2$)$_2$]$^+$	Pt(depe)$_2$	5/4	MeCN	29.7	26*	22
93	[PtH(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$]$^+$	Pt(dppe)$_2$	5/4	MeCN	22.0	18*	21
94	[PtH(EtXantphos)$_2$]$^+$	Pt(EtXantphos)$_2$	6/5	MeCN	27	22*	61
95	[PtH$_2$(EtXantphos)$_2$]$^{2+}$	[PtH(EtXantphos)$_2$]$^+$	6/5	MeCN	6.8	13*	61
96	ReH$_7$(PCy$_3$)$_2$	[ReH$_6$(PCy$_3$)$_2$]$^-$	9/8	THF	42	43	20
97	ReH$_7$(PPh$_3$)$_2$	[ReH$_6$(PPh$_3$)$_2$]$^-$	9/8	THF	30	38**	20
98	ReH$_5$(PMePh$_2$)$_3$	[ReH$_4$(PMePh$_2$)$_3$]$^-$	8/7	THF	40	42	62
99	ReH$_2$(Cp)(CO)$_2$	[ReH(Cp)(CO)$_2$]$^-$	7/6	MeCN	23.0	22	28
100	ReH(CO)$_5$	[HNEt$_3$][Re(CO)$_5$]	6/5	MeCN	21.1	15*	16
101	[ReH$_2$(PMe$_3$)$_5$]$^+$	ReH(PMe$_3$)$_5$	7/6	THF	23	27*	20
102	[ReH$_4$(PMe$_3$)$_4$]$^+$	ReH$_3$(PMe$_3$)$_4$	8/7	THF	22.1	22	20
103	[ReH$_4$(PMe$_2$Ph)$_4$]$^+$	ReH$_3$(PMe$_2$Ph)$_4$	8/7	MeCN (THF)	25.3	25	20, 63
104	[ReH$_4$(PMePh$_2$)$_4$]$^+$	ReH$_3$(PMePh$_2$)$_4$	8/7	THF	14.7	15	20
105	[ReH$_2$(Cp)$_2$]$^+$	ReH(Cp)$_2$	8/7	H$_2$O	6.4	5	64
106	[ReH(Cp*)(CO)$_2$(PMe$_3$)]$^+$	Re(Cp*)(CO)$_2$(PMe$_3$)	7/6	DCE	(1)	1	29
107	[ReH(Cp*)(CO)$_2$(PMe$_2$Ph)]$^+$	Re(Cp*)(CO)$_2$(PMe$_2$Ph)	7/6	DCE	(0)	1	29
108	RhH(PEt$_2$CH$_2$C$_6$H$_4$CH$_2$PEt$_2$)$_2$	[Rh(PEt$_2$CH$_2$C$_6$H$_4$CH$_2$PEt$_2$)$_2$]$^-$	5/4	MeCN	51.0	41**	33
109	RhH(dppb)$_2$	[Rh(dppb)$_2$]$^-$	5/4	MeCN	35.0	35	23
110	[Rh(H)$_2$(PEt$_2$CH$_2$C$_6$H$_4$CH$_2$PEt$_2$)$_2$]$^+$	RhH(PEt$_2$CH$_2$C$_6$H$_4$CH$_2$PEt$_2$)$_2$	6/4	MeCN	30.6	33	33
111	[Rh(H)(PMe$_2$CH$_2$CH$_2$PMe$_2$)$_2$(MeCN)]$^{2+}$	[Rh(dmpe)$_2$]$^+$	6/4	MeCN	18.9	16	47
112	[Rh(H)(PEt$_2$CH$_2$CH$_2$PEt$_2$)$_2$(MeCN)]$^{2+}$	[Rh(depe)$_2$]$^+$	6/4	MeCN	16.6	16	47
113	[Rh(H)(PEt$_2$CH$_2$CH$_2$CH$_2$PEt$_2$)$_2$(MeCN)]$^{2+}$	[Rh(depp)$_2$]$^+$	6/4	MeCN	14.4	16	47
114	[Rh(H)(PEt$_2$CH$_2$C$_6$H$_4$CH$_2$PEt$_2$)$_2$(MeCN)]$^{2+}$	[Rh(depx)$_2$]$^+$	6/4	MeCN	11.5	16*	47
115	[RhH(dppb)$_2$(MeCN)]$^{2+}$	[Rh(dppb)$_2$]$^+$	6/4	MeCN	9.4	7	23

1952

dx.doi.org/10.1021/ja410718r | J. Am. Chem. Soc. 2014, 136, 1948−1959

Table 3. continued

entry	acid	base[b]	Δ	solvent[c]	pKa obs	pKa calcd	ref
116	[RhH(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$(MeCN)]$^{2+}$	[Rh(dppe)$_2$]$^+$	6/4	MeCN	9.0	9	23
117	[RhH(PCy$_2$CH$_2$CH$_2$PCy$_2$)$_2$(MeCN)]$^{2+}$	[Rh(dcpe)$_2$]$^+$	6/4	MeCN	6.0	16**	23
118	[RhH(PPh$_2$CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$(MeCN)]$^{2+}$	[Rh(dppp)$_2$]$^+$	6/4	MeCN	5.8	7	23
119	[RhH(CO)Cl(PPh$_3$)$_2$]$^+$	RhCl(CO)(PPh$_3$)$_2$	5/4	MeOH	3.8	1	53
120	RuH$_2$(H$_2$)$_2$(P^{i}Pr$_3$)$_2$	[RuH$_5$(P^{i}Pr$_3$)$_2$]$^-$	6/7	THF	39	41	20
121	RuH$_2$(H$_2$)(CO)(P^{i}Pr$_3$)$_2$	[RuH$_3$(CO)(P^{i}Pr$_3$)$_2$]$^-$	6/6	THF	38	36	20
122	RuH$_2$(H$_2$)(PPh$_3$)$_3$	[RuH$_3$(PPh$_3$)$_3$]$^-$	6/6	THF	36	37	20
123	Ru(Cp)(CO)$_2$H	[Ru(Cp)(CO)$_2$]$^-$	6/5	MeCN	28.3	25	20, 44
124	RuH$_2$(CO)$_4$	[RuH(CO)$_4$]$^-$	6/5	MeCN	18.7	17	16
125	[Ru(H)$_2$(Cp*)(PMe$_3$)$_2$]$^+$	RuH(Cp*)(PMe$_3$)$_2$	7/6	THF	16.5	13	20
126	trans-[Ru(H$_2$)H(PAr$_2$CH$_2$CH$_2$PAr$_2$)$_2$]$^+$, Ar = p-C$_6$H$_4$OMe	cis-RuH$_2$(dape)$_2$	6/6	THF	17.4	12*	20
127	cis-[Ru(H$_2$)H(PMe$_3$)$_4$]$^+$	RuH$_2$(PMe$_3$)$_4$	6/6	THF	16.6	20	20
128	[RuH$_3$(PEt$_3$)$_4$]$^+$	RuH$_2$(PEt$_3$)$_4$	7/6	THF	16.5	20	20
129	[Ru(H)$_2$(Cp*)(PMe$_2$Ph)$_2$]$^+$	RuH(Cp*)(PMe$_2$Ph)$_2$	7/6	THF	14.4	11	20
130	trans-[Ru(H$_2$)H(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$]$^+$	cis-RuH$_2$(dppe)$_2$	6/6	THF	14.1	12	20
131	[Ru(H)$_2$(Cp)(PMe$_3$)$_2$]$^+$	Ru(H)(Cp)(PMe$_3$)$_2$	7/6	MeCN	21.4	17*	65
132	[Ru(H)$_2$(Cp)(PMe$_2$CH$_2$CH$_2$PMe$_2$)]$^+$	Ru(H)(Cp)(dmpe)	7/6	MeCN	17.6	17	66
133	[Ru(H$_2$)H(PPh$_2$CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$]$^+$	Ru(H)$_2$(dppp)$_2$	6/6	CH$_2$Cl$_2$	11.5	12	57
134	[Ru(H)$_2$(Cp*)(PMePh$_2$)$_2$]$^+$	RuH(Cp*)(PMePh$_2$)$_2$	7/6	THF	12.3	9	20
135	[Ru(H)$_2$(Cp*)(PPh$_3$)$_2$]$^+$	RuH(Cp*)(PPh$_3$)$_2$	7/6	THF (DCE)	10.9	8	20
136	[Ru(H$_2$)H(PPh$_2$CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$]$^+$	RuH$_2$(dppp)$_2$	6/6	THF	10.2	12	20
137	[Ru(H$_2$)(Cp*)(PPh$_2$CH$_2$PPh$_2$)]$^+$	RuH(Cp*)(dppm)	6/6	THF	9.2	9	20
138	[Ru(H$_2$)(PPh$_3$)(MeCN)(Tp)]$^+$	Ru(H)(PPh$_3$)(NCMe)(Tp)	6/6	CH$_2$Cl$_2$	8.9	7	67
139	[Ru(H$_2$)(Cp*)(PPh$_2$CH$_2$PPh$_2$)]$^+$	RuH(Cp*)(dppm)	7/6	THF	8.9	9	20
140	[Ru(H$_2$)(Tp)(PPh$_3$)MeCN]$^+$	RuH(Tp)(PPh$_3$)(MeCN)	6/6	CH$_2$Cl$_2$	8.9	7	18
141	[Ru(H$_2$)(Tp)(PPh$_2$CH$_2$CH$_2$PPh$_2$)]$^+$	RuH(Tp)(dppe)	6/6	CH$_2$Cl$_2$	7.9	8	18
142	[Ru(H$_2$)(Tp)(PPh$_3$)$_2$]$^+$	RuH(Tp)(PPh$_3$)$_2$	6/6	CH$_2$Cl$_2$	7.6	6	18
143	Ru(Cp)(H$_2$)(CO)(P^{i}Pr$_3$)]$^+$	Ru(Cp)(H)(CO)(P^{i}Pr$_3$)	6/6	CH$_2$Cl$_2$	3.0	3	68
144	trans-[Ru(H$_2$)H(PAr$_2$CH$_2$CH$_2$Ar$_2$)$_2$]$^+$, Ar = p-CF$_3$C$_6$H$_4$	cis-RuH$_2$(dtfpe)$_2$	6/6	THF	8	6	20
145	[Ru(H)$_2$(Cp)(dppp)]$^+$	RuH(Cp)(dppp)	7/6	THF	8.7	8	20
146	[Ru(H)$_2$(Cl)(dach)(PPh$_3$)$_2$]$^+$	RuHCl(dach)(PPh$_3$)$_2$	6/6	CH$_2$Cl$_2$	8.6	8	69
147	[Ru(H$_2$)(Cp)(PPh$_3$)$_2$]$^+$	RuH(Cp)(PPh$_3$)$_2$	7/6	THF (CH$_2$Cl$_2$, DCE)	8.0	7	20, 29
148	[Ru(H$_2$)(PPh$_2$CH$_2$CH$_2$PPh$_2$)(Tp)]$^+$	RuH(dppe)(Tp)	6/6	CH$_2$Cl$_2$	7.9	6	42
149	[Ru(H$_2$)(PPh$_3$)$_2$(Tp)]$^+$	RuH(PPh$_3$)$_2$(Tp)	6/6	CH$_2$Cl$_2$	7.6	6	42
150	[Ru(H$_2$)(Cp)(PPh$_2$CH$_2$PPh$_2$)]$^+$	RuH(Cp)(dppm)	6/6	THF (DCE)	7.2	8	20, 29
151	[Ru(H)$_2$(Cp)(PPh$_2$CH$_2$CH$_2$PPh$_2$)]$^+$	RuH(Cp)(dppe)	7/6	THF (DCE)	6.4	8	20, 29
152	[Ru(H$_2$)(Cp)(PPh$_2$CH$_2$CH$_2$PPh$_2$)]$^+$	RuH(Cp)(dppe)	6/6	THF	7.2	8	20, 29
153	[Ru(H$_2$)(Cp)(PPh$_2$CH$_2$CH$_2$CH$_2$PPh$_2$)]$^+$	RuH(Cp)(dppp)	7/6	DCE	(7)	8	28
154	Ru(C$_5$H$_4$CH$_2$CH$_2$NHMe$_2$)(H$_2$)(PPh$_2$CH$_2$PPh$_2$)$^{2+}$	Ru(C$_5$H$_4$CH$_2$CH$_2$NHMe$_2$)(H)(dppm)]$^+$	6/6	CH$_2$Cl$_2$	7.1	8[d]	18
155	[Ru(H)(Cl)(Cp*)(PMe$_3$)$_2$]$^+$	Ru(Cl)(Cp*)(PMe$_3$)$_2$	7/6	DCE	(7)	7	28
156	[Ru(H$_2$)Cl{PPh$_2$C$_6$H$_4$CH$_2$NHCMe$_2$−}$_2$]$^+$	RuHCl(PPh$_2$−NH−NH−PPh$_2$)	6/6	CH$_2$Cl$_2$	6.9	8	69
157	[Ru(H$_2$)Cl(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$]$^+$	RuHCl(dppe)$_2$	6/6	CH$_2$Cl$_2$	4.7	6	69
158	[Ru(H$_2$)Cl(PPh$_2$CH$_2$pyCH$_2$PPh$_2$)(PPh$_3$)]$^+$	RuHCl(pmp)(PPh$_3$)	6/6	CH$_2$Cl$_2$	4.0	7	69
159	[Ru(H$_2$)(PPh$_3$)$_2$(Cn)]$^{2+}$	RuH(PPh$_3$)$_2$(Cn)]$^+$	6/6	CH$_2$Cl$_2$	3.2	3	18
160	Ru(H$_2$)Cl(dppp)$_2$]$^+$	RuHCl(dppp)$_2$	6/6	CH$_2$Cl$_2$	5.6	6	57
161	[RuCp(H$_2$)Cl(PMe$_3$)$_2$]$^+$	RuHCpCl(PMe$_3$)$_2$	6/6	DCE	(2)	6*	57
162	[RuH(Cp*)$_2$]$^+$	Ru(Cp*)$_2$	7/6	DCE	(1)	5*	20, 29
163	[Ru(H$_2$)(PPh$_3$)(CO)(Tp)]$^+$	Ru(H)(PPh$_3$)(CO)(Tp)	6/6	CH$_2$Cl$_2$	−2	−1	18
164	[Ru(H$_2$)(PPh$_3$)(CO)(Cn)]$^{2+}$	RuH(PPh$_3$)(CO)(Cn)]$^+$	6/6	CH$_2$Cl$_2$	−2	−4	18
165	[WH$_6$(PMe$_2$Ph)$_3$]	[WH$_5$(PMe$_2$Ph)$_3$]$^-$	9/8	THF	42	43	62
166	W(Cp)(CO)$_2$(PMe$_3$)H	[W(Cp)(CO)$_2$(PMe$_3$)]$^-$	7/6	MeCN	26.6	26	16
167	W(H)(Cp)(CO)$_3$	[W(Cp)(CO)$_3$]$^-$	7/6	MeCN (H$_2$O, CH$_3$OH)	16.1	18	15
168	[WH(CO)$_2$(PPh$_2$CH$_2$PPh$_2$)$_2$]$^+$	W(CO)$_2$(dppm)$_2$	7/6	DCE	(8)	6	29
169	[WH(CO)$_2$(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$]$^+$	W(CO)$_2$(dppe)$_2$	7/6	DCE	(4)	6	29
170	[W(H)$_2$(CO)$_2$(Cp)(PMe$_3$)]$^+$	W(H)(CO)$_2$(Cp)(PMe$_3$)	8/7	MeCN	5.6	4	70
171	[WH(CO)$_3$(PEt$_3$)$_3$]$^+$	W(CO)$_3$(PEt$_3$)$_3$	7/6	DCE	(4)	4	29
172	[WH(CO)$_3$(PMe$_3$)$_3$]$^+$	W(CO)$_3$(PMe$_3$)$_3$	7/6	DCE	(1)	4	29

Table 3. continued

entry	acid	base[b]	Δ	solvent[c]	pK_a obs	pK_a calcd	ref
173	[WH(CO)$_3$(bpy)(PMePh$_2$)]$^+$	W(CO)$_3$(bpy)(PMePh$_2$)	7/6	DCE	(1)	1	28
174	[WH(CO)$_3$(PEt$_2$Ph)$_3$]$^+$	W(CO)$_3$(PEt$_2$Ph)$_3$	7/6	DCE	(1)	2	29
175	[WH(CO)$_3$(PMe$_2$Ph)$_3$]$^+$	W(CO)$_3$(PMe$_2$Ph)$_3$	7/6	DCE	(0)	2	28
176	[WH(CO)$_3$(PEtPh$_2$)$_3$]$^+$	W(CO)$_3$(PEtPh$_2$)$_3$	7/6	DCE	(0)	−1	29
177	[WH(CO)$_3$(PMePh$_2$)$_3$]$^+$	W(CO)$_3$(PMePh$_2$)$_3$	7/6	DCE	(−1)	−1	29
178	[WH(CO)$_3${PhP(CH$_2$CH$_2$PPh$_2$)$_2$}]$^+$	W(CO)$_3$(triphos)	7/6	DCE	(0)	−1	29
179	[WH(CO)$_3$(MeC(CH$_2$PPh$_2$)$_3$]$^+$	W(CO)$_3$(tripod)	7/6	DCE	(−4)	−1	29

[a]Values with one asterisk are within 2 standard deviations, and those with two are above 2 standard deviations. [b]Abbreviations. Tp = hydridotris(pyrazolyl)borate, Cn = 1,4,7-triazacyclononane, tmeP$_2$NH$_2$ = PPh$_2$C$_6$H$_4$CH$_2$NHCMe$_2$−CMe$_2$NHCH$_2$C$_6$H$_4$PPh$_2$. [c]A second determination was done in the bracketed solvent by another group, and the values agree. [d]The conjugate base is considered neutral with a positive charge of the ammonium that is remote from the metal.

same acidity contribution of 2A_L(PR$_3$), and the calculated pK_a^{MeCN} is 16 for both compounds. The direction of the deviation can often be predicted by considering how the change in geometry on going from the acid to base forms will affect the relative stability of the two (see below).

Discussion of the Correlation. A plot of the 171 calculated versus observed pK_a values has a regression factor R^2 of 0.95 with a standard deviation of 3 pK_a units (Figure 2). Equation 6 along with the 13 ligand constants provides pK_a values within ±3 pK_a units for 147 complexes with pK_a values ranging from −1 to 51. Of these, 79 complexes are made up completely of ligands that fall in a group of six common ligand classes (CO, PR$_3$, Cp, Cp*, H, PAr$_3$). There are 24 compounds with deviations of between 4 and 6 units that are marked with an asterisk in Table 3.

Eight hydrides that deviate from between 7 and 16 units (pK_a^{obs} − pK_a^{calc}) marked with a double asterisk, and these are not included in the final regression shown in Figure 2. Six of the eight large deviations (beyond two standard deviations, i.e., beyond 6 pK_a units) are for cationic complexes where the pK_a is overestimated by eq 6. The largest are for [PdH-(PEt$_2$CH$_2$CH$_2$CH$_2$PEt$_2$)$_2$]$^+$ (entry 89, pK_a^{MeCN} 15.5, pK_a^{calc} 24), [PdH(EtXantphos)$_2$]$^+$ (entry 90, pK_a^{MeCN} 4.1, pK_a^{calc} 20), and [RhH(dcpe)$_2$(MeCN)]$^{2+}$ (entry 117, pK_a^{MeCN} 6, pK_a^{calc} 16). The first two are attributed to the large bite angle ligands preferentially stabilizing the tetrahedral Pd(0) conjugate base over the five coordinate acid form (the bite angle of the ligand EtXantphos can vary from 110° to 140°[60]), while the last appears to be a steric effect where the bulky 1,2-dicyclohexylphosphino ethane ligands destabilize the six coordinate complex over the four coordinate conjugate base, making the complex more acidic than expected. The pK_a values of the other three cationic complex outliers (entries 46, 82, and 83) were derived from enthalpies of protonation of the conjugate base forms with trifluorosulfonic acid in dichloroethane using eq 5 and are assumed to be [CpIrH$_3$[P(OPh)$_3$]]$^+$, [OsH$_5$(PPhMe$_2$)$_3$]$^+$, and [OsH$_5$(PPh$_2$Me)$_3$]$^+$. Complex [OsH$_5$(PPhMe$_2$)$_3$]$^+$ is expected on the basis of eq 6 to have a pK_a^{CH2Cl2} of 15, while its pK_a is 6 from its enthalpy of protonation in DCE. It is deprotonated by triethylamine (pK_a^{CH2Cl2} 12.5)[20] in CD$_2$Cl$_2$,[71] and so our approach is not accounting completely for the acidity of these cationic osmium polyhydrides. The pK_a^{THF} of ReH$_7$(PPh$_3$)$_2$ is also overestimated, by 8 units in this case (entry 97). However, the method is successful at providing good estimates of the acidity of 11 other cationic and neutral polyhydrides of Ir, Os, Re, Ru, and W (entries 28, 29, 96, 98, 102−104, 120−122, 165).
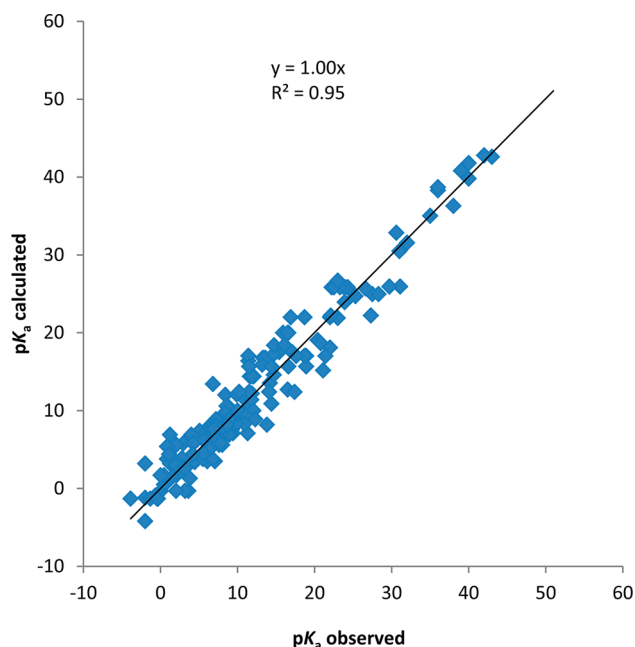

Figure 2. A plot of the calculated pK_a values versus the literature pK_a values.

The observed pK_a^{MeCN} of 51 for the neutral hydride acid RhH(depx)$_2$ (entry 108) is significantly underestimated by eq 6 (pK_a^{MeCN} 41). The two large bite angle depx ligands destabilize the square planar conjugate base [Rh(depx)$_2$]$^−$ more than the five coordinate acid, making the acid 10 units less acidic than expected. It is worth pointing out that [Rh(depx)$_2$]$^−$ is likely to be too basic to exist in the MeCN, and this might complicate the thermochemical cycle used to derive the pK_a^{MeCN} value.[33]

Looking Down Table 3. Equation 6 is consistent with the pK_a^{MeCN} of five acids of general formula CoHL$_4$ (entries 1−3 and 5) . The one cobalt(III) complex [CoHL$_5$]$^{2+}$ complex (entry 4) deviates by 6 units. The equation works for the two chromium examples with formulas CrH(Cp)(CO)$_3$ and [CrH(L)$_6$]$^+$ where each L represents a neutral donor group at one coordination site (i.e., a dppe ligand is L$_2$). The 19 iron complex acids that are represented in the table have the general formulas FeH(Cp or Cp*)(CO)$_2$, [Fe(Cp)(H$_2$)L$_2$]$^+$, [Fe-(H)$_3$L$_4$]$^+$, [Fe(H$_2$)HL$_4$]$^+$, FeH$_2$(CO)$_4$, and [FeHL$_5$]$^+$. For the calculation, the C_{d6} factor of 6 of eq 6 is added for the iron(II) complexes that are not dihydrogen complexes. The equation works for all of the iron complexes except that two isomers of the complex [FeH$_3$(PMe$_3$)$_4$]$^+$ (entries 11 and 12) and

Table 4. Less Well-Defined Acidity Constant Values Not Used in the Correlation

class of ligand	specific ligands included	number of conjugate bases with the ligand	A_L (pK_a units)	E_L (V)[a]
cyanide, CN⁻	CN	1	−11	0.02
(S,S)-N-tosyl-1,2-diphenylethylenediamine	TsNCHPhCPhNH₂⁻(TsDPEN)	1	2[b]	
nitrosyl, NO	NO	1	−5	~0[c]
NHC	N-heterocyclic carbene IMes, NHC part of chelating ligands	3	4	0.29[d]
H₂O	H₂O	1	6	0.04
hydrogen isocyanide, CNH	CNH	1	−2	

[a]Reference 38. [b]Bidentate TsDPEN has a total acid contribution of 2 × 2. [c]NO complexes have variable redox chemistry. [d]Reference 73.

Table 5. Other Acidic Hydride Complexes of Note with Unique Ligand Representatives or Estimated pK_a Values Not Used in the Correlation

entry	acid[a]	base	Δ	solvent	pK_a obs	pK_a calcd	ref
1	[Fe(H){ᵗBuSi(CH₂PMe₂)₃}(PMe₂CH₂PMe₂)]⁺	Fe(H){ᵗBuSi(CH₂PMe₂)₃}(dmpm)	6/5	C₆D₆ (MeCN)	~25	31	74
2	trans-[Fe(H₂)(PEt₂CH₂CH₂PEt₂)₂(CO)]²⁺	trans-[Fe(H)(PEt₂CH₂CH₂PEt₂)₂(CO)]⁺	6/6	CD₂Cl₂	~0	1	75
3	trans-[Fe(H₂)(PPh₂CH₂CH₂PPh₂)₂(CO)]²⁺	trans-[Fe(H)(PPh₂CH₂CH₂PPh₂)₂(CO)]⁺	6/6	CD₂Cl₂	< −5	−7	75
4	trans-[Fe(H₂)(CN)(PEt₂CH₂CH₂PEt₂)₂]⁺	trans-FeH(CN)(depe)₂	6/6	CH₂Cl₂	9	9	76
5	trans-[Fe(H₂)(CNH)(PEt₂CH₂CH₂PEt₂)₂]²⁺	trans-[FeH(CNH)(depe)₂]⁺	6/6	CH₂Cl₂	3	3	76
6	[Ir(H)₄(C₂H₄)(NHC−oxaz)]⁺	IrH₃(C₂H₄)(NHC−oxaz)	7/6	MeCN	17	15	8
7	[Ir(H)₄(C₂H₄)(PPh₂−oxaz)]⁺	IrH₃(C₂H₄)(PPh₂−oxaz)	7/6	MeCN	11	12	8
8	[Ir(H)₄(py)(PCy₃)(C₂H₄)]⁺	IrH₃(C₂H₄)(PCy₃)(py)	7/6	MeCN	11	14	8
9	[Ir(H)₄(C₂H₄)(PPh₂O-oxaz)]⁺	IrH₃(C₂H₄)(PPh₂O−oxaz)	7/6	MeCN	10	12	8
10	[Ir(H₂)(Cp*)(TsDPEN)]⁺	IrH(Cp*)(TsDPEN)	6/6	MeCN	14	14	77
11	[Ir(H₂)(Cp*)(NHC−NHC)]²⁺	[Ir(H)(Cp*)(NHC−NHC)]⁺	6/6	CH₂Cl₂	<0	0	78
12	[Re(H₂)(CO)₅]⁺	[Re(H)(CO)₅]	6/6	PhF	−3[b]	−18	79
13	Re(H)₄(NO)(PⁱPr₃)₂	[ReH₃(NO)(PⁱPr₃)₂]⁻	7/6	THF	38	38	20
14	[Ru(H₂)(OH₂)₅]²⁺	[RuH(OH₂)₅]⁺	6/6	H₂O	11	14	80
15a	[Ru(H₂)(cymene)(TsDPEN)]⁺	Ru(H)(cymene)(TsDPEN)	6/6	MeOH	~0[c]	−1.3[d]	81
15b	[Ru(H₂)(cymene)(TsDPEN)]⁺	Ru(H)(cymene)(TsDPEN)	6/6	MeCN	16	16[e]	77
16	W(Cp)(CO)₂(IMes)H	[W(Cp)(CO)₂(IMes)]⁻	7/6	MeCN	32	37	32
17	W(H₂)(CO)₅	[W(H)(CO)₅]⁻	6/6	PhF	~0[f]	12	79, 37

[a]Abbreviations: NHC−oxaz = 2,5-ⁱPr₂C₆H₃NC₃H₂NCH₂CH₂C₃H₃NO(2-(1-adamantyl)); PPh₂−oxaz = 2-PPh₂C₆H₄C₃H₃NO(3-ᵗBu); PPh₂O−oxaz = PPh₂OCMe₂C₃HNO(2-Ph)(5-Me); TsDPEN = 4-MeC₆H₄SO₂NCHPhCHPhNH₂; η⁶-cymene = para-isopropyltoluene; NHC−NHC = methylenebis(N-methylimidazol-2-ylidene); IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene. [b]Protonates Et₂O in PhF. [c]This acid as the triflate (CF₃SO₃⁻) salt is proposed to protonate MeOH solvent under pressures of hydrogen. [d]The acid constant for the η⁶-cymene ligand is taken to be 3 times the olefin parameter (−6). [e]The acid constant for the η⁶-cymene ligand would have to be 2.5 × 3 (see Results and Discussion). [f]Protonates excess water in PhF.

FeH₂(CO)₄ (entry 15) are more acidic than expected by 4−5 units. Of the 20 iridium complexes, there are only two that deviate by more than 3 units, entries 45 and 46. These are unidentified hydrides produced by protonating IrH₂(Cp)L complexes with triflic acid as discussed above. Heinekey et al. have shown that the complex [Ir(H)₃Cp(PPh₃)]BF₄ is a trihydride.[72] The C_{d6} constant is applied in eq 6 for the iridium(III) acids (entries 30−44). The two manganese(I) complexes of the type MnHL₅ (the C_{d6} factor applies for these), the six molybdenum(II) complexes of the type MoH(Cp or Cp*)(CO)₃ and [MoHL₆]⁺, and the nine nickel(II) complexes are treated correctly. The method works for 22 of the 25 osmium complexes: those with formulas Os(H₂)H₂L₃, OsH-(Cp)(CO)₂, and OsH₂(CO)₄ (the C_{d6} correction is applied for these two), [OsH₃L₄]⁺, [Os(H₂)HL₄]⁺, [OsH₂(Cp or Tp)L₂]⁺, [Os(H₂)ClL₄]⁺, [OsH(Cp)Cl(L)₂]⁺, and [OsH(Cp*)₂]⁺. The large deviations for the two [OsH₅L₃]⁺ were discussed above, and there is a deviation of 6 units for the very acidic complex trans-[Os(H₂)(MeCN)(dppe)₂]²⁺ (entry 87), although the experimental value was only an estimate. Deviations for two of the three palladium complexes [PdHL₄]⁺ result from large

bite angle ligands as discussed. Of the five platinum complexes, four are Pt(II) complexes of the type [PtHL₄]⁺ (entries 91−94); these are 3−5 units less acidic than expected. The Pt(IV) complex [PtH₂L₄]²⁺ (entry 95) is 6 units more acidic than predicted by eq 6; this can be explained by the large bite angle ligand EtXantphos (110−140°)[60] stabilizing the 5-coordinate conjugate base form and destabilizing the octahedral Pt(IV) acid form.

There are 12 rhenium complexes of the types ReH₇L₂, ReH₅L₃, ReH₂(Cp)(CO)₂, ReH(CO)₅, [ReH₂L₅]⁺, [ReH₄L₄]⁺, [ReH₂(Cp)₂]⁺, and [ReH(Cp)L₃] with good agreement for 11 of these. Of the 12 rhodium complexes with forms RhHL₄, [RhHL₅]²⁺, and [RhH(Cl)L₃],⁺ deviations are only observed when the ligand (L₂) has a large bite angle as discussed above. Ruthenium complexes are the most prevalent with 46 members representing the formulas Ru(H₂)₂H₂L₂, Ru(H₂)H₂L₃, RuH-(Cp)(CO)₂, RuH₂(CO)₄, [RuH₂(Cp* or Cp or Tp)L₂]⁺, [RuH(H₂)L₄]⁺, [RuH₃L₄]⁺, [Ru(H₂)ClL₄]⁺, [RuH₂ClL₄]⁺, [RuH(Cp)ClL₂]⁺, [RuH(Cp*)₂]⁺, and [Ru(H₂)(Cn)L₂]²⁺. Of these, 42 have deviations of 3 units or less. Entries 126 and 131 are less acidic than expected by 4 units, while entries 161−162

Table 6. Prediction of pK_a^{THF} Values for Classes of 18-Electron Metal Carbonyl Hydrides and Metal Trimethylphosphine Hydrides[a]

Cr, Mo, W	Mn, Tc, Re	Fe, Ru, Os	Co, Rh, Ir	Ni, Pd, Pt	pK_a^{THF}, L = CO (5d metal)	pK_a^{THF}, L = PMe$_3$ (5d metal)	add for d^6 octahedral acids
MH$_2$L$_5$	**MHL$_5$**				12	57	+6 (Re)
MH$_4$L$_4$	MH$_3$L$_4$	**MH$_2$L$_4$**	**MHL$_4$**		16	52	+6 (Os)
WH$_6$L$_3$	**ReH$_5$L$_3$**	**MH$_4$L$_3$**	MH$_3$L$_3$		21	48	+6 (Ir)
MH$_8$L$_2$	**ReH$_7$L$_2$**	**RuH$_6$L$_2$**	**IrH$_5$L$_2$**	MH$_4$L$_2$	25	43	+6 (Pt)
WHL$_6^+$					−23	31	
MH$_3$L$_5^+$	**ReH$_2$L$_5^+$**	**MHL$_5^+$**			−18	27	+6 (Os)
MH$_5$L$_4^+$	**ReH$_4$L$_4^+$**	**MH$_3$L$_4^+$**	**MH$_2$L$_4^+$**	**MHL$_4^+$**	−14	22	+6 (Ir)
MH$_7$L$_3^+$	MH$_6$L$_3^+$	**OsH$_5$L$_3^+$**	MH$_4$L$_3^+$	MH$_3$L$_3^+$	−10	17	+6 (Pt)
MH$_9$L$_2^+$	MH$_8$L$_2^+$	MH$_7$L$_2^+$	MH$_6$L$_2^+$	MH$_5$L$_2^+$	−5	13	
MH$_2$L$_6^{2+}$	MHL$_6^{2+}$				−37	17	
MH$_4$L$_5^{2+}$	MH$_3$L$_5^{2+}$	**MH$_2$L$_5^{2+}$**	MHL$_5^{2+}$		−33	12	+6 (Ir)
MH$_6$L$_4^{2+}$	MH$_5$L$_4^{2+}$	MH$_4$L$_4^{2+}$	MH$_3$L$_4^{2+}$	**PtH$_2$L$_4^{2+}$**	−29	7	+6 (Pt)

[a]The formulas in bold have representatives in Table 3.

are 4 units more acidic than expected. The 15 tungsten complexes all have good agreement. They have the form WH$_6$L$_3$, WH(Cp)L$_3$, [WHL$_6$]$^+$, and [WH$_2$(Cp)L$_3$]$^+$.

Peliminary Ligand Constants. Some classes of ligands appear only a few times in the hydride acidity literature, or the pK_a values of their complexes are only approximate. A preliminary acidity constant (Table 4) was determined from the observed pK_a (Table 5) and eq 6, where the A_L for one ligand is the only unknown. Where more than one complex has this class of ligand, the A_L values were averaged. The A_L values for the class of N-heterocyclic carbenes and water also fit the correlation eq 7.

The first entry of Table 5 is an unusual, weakly acidic cationic hydride complex of iron(II) containing five trialkylphosphine ligands of the class PR$_3$ with A_L 4.9.[74] The calculated pK_a^{THF} is 31 ($5 \times 4.9 + 6$ because the metal of this acid loses its d^6 octahedral configuration), and this value is consistent with the high reactivity of the conjugate base iron(0) complex, which partially deprotonates acetonitrile (pK_a^{DMSO} 31.3[82]) and ethylacetate (pK_a^{DMSO} 24.4[82]). Table 5 lists synthetic iron carbonyl and hydrogen isocyanide complexes that have very acidic dihydrogen ligands (entries 2, 3, and 5). The A_L value for the HNC ligand is negative (−2) as expected for a ligand with π-acceptor properties like carbon monoxide. The pK_a reported for an iron cyanide dihydrogen complex (entry 4) indicates that the cyanide ligand is very acidifying (A_L −11). As noted above, there is no correlation between the Lever parameter and such anionic ligands. In contrast to the very low pK_a values of these iron dihydrogen complexes, the $pK_a(H_2/H^-)^{MeCN}$ of hydrogen gas in acetonitrile can be calculated[79] to be 55 (=76/1.37 log(1)) from the reported free energy of 76 kcal/mol for the dissociation of a dihydrogen into a proton and a hydride.[33] The very negative values for cyanide and carbonyl (A_L values of −11 and −4.1, respectively) help to explain how nature brings the pK_a of free dihydrogen down to neutral pH for efficient hydrogen oxidation or proton reduction in the NiFe or FeFe hydrogenases.[83,84] The active sites of these enzymes are bimetallic where a dihydrogen or hydride ligand is likely to be coordinated at iron with carbonyl and cyanide ligands as well as thiolate ligands.

Complexes of N-heterocyclic ligands are becoming common, but only a few pK_a values have been reported or estimated. An A_L value of 4 is estimated for these in keeping with the expectation that they are donating like trialkylphosphine (PR$_3$) ligands. The acidity of hydrides on iridium(III) complexes with

chelating NHC ligands (entries 6[8] and 11[78]) is of relevance to the catalytic hydrogenation activity of these complexes and can be estimated using the additivity model. The low acidity of a tungsten complex (entry 16) is predicted by eq 6 after conversion to the MeCN scale.

The tosyl-1,2-diphenylethylenediamine ligand is given its own treatment due to its importance as a supporting ligand on Ru(II) (the compound of entries 15a and 15b) for the asymmetric transfer hydrogenation of prochiral ketones in isopropanol under basic or neutral conditions,[85,86] and of imines in formic acid/triethylamine,[87] as well as the pressure hydrogenation of ketones under acidic conditions.[81] The Ir(III) complex containing this ligand (entry 10) also catalyzes the pressure hydrogenation of ketones. The ligand value represents a net contribution to the pK_a of 4 ($2A_L$) when it is bidentate on Ir(III) on the basis of the pK_a^{MeCN} of 13.9 measured indirectly for the Ir(III) complex (entry 10). For this value to be transferred to the Ru(II) hydride (entry 15a or 15b are two differing studies), an acidity constant is needed for the η^6-arene ligand. If it is assumed that it will be similar to that of 3 η^2-olefins ($3 \times -2 = -6$), then the pK_a^{THF} predicted for the Ru(II) complex is about −1. The complex was thought to be fairly acidic because it forms from a triflate complex under a pressure of hydrogen and protonates the triflate ion or MeOH (entry 15a, pK_a approximately 0 in MeOH).[81] This behavior does not seem to be consistent with the pK_a^{MeCN} value of 16 measured indirectly for this ruthenium complex in MeCN and then converted to pK_a^{MeOH} 8 (entry 15b).[77] Given the pK_a^{MeCN} value for this ruthenium complex, the total A_L value for the arene contribution needs to be 7.5. More work in this area is required.

The acidic dihydrogen complexes [Re(H$_2$)(CO)$_5$][B-(C$_6$F$_5$)$_4$] and W(H$_2$)(CO)$_5$ (entries 12 and 17) were synthesized by the Heinekey group by use of the non-coordinating solvent fluorobenzene and the large, weakly interacting anion B(C$_6$F$_5$)$_4^-$. These were shown to react with weak bases such as water and diethyl ether, with the rhenium complex displaying the greater acidity.[79] The estimated pK_a values of −18 for Re(I) and 12 for W(0) are in fair agreement with these observations, although the first value appears to be too low and the second appears too high. However, these are unusually small acids. In the solvent of low dielectric constant (PhF), the rhenium complex exists as a tight ion pair in the acid form, while the tungsten exists as a tight ion pair in the anionic conjugate form, and this may shift the pK_a by several units. In

addition, the nature of carbonyl−metal bonding changes when there are more than three CO ligands on the metalbecause this will result in competition for $d\pi$ orbitals for π-backbonding and therefore nonadditive effects.

The nitrosyl is not expected to have a constant A_L value because of its variable coordination in the continuum between NO^+ and NO^-. The rhenium complex $Re(H)_4(NO)(P^iPr_3)_2$ with a pK_a^{THF} of 38 (entry 13) contains an NO^+ with $A_L = -5$ that acidifies the complex like the carbonyl ligand ($A_L = -4.1$).

Other acidity measurements do not yet lead to ligand constants. Cobalt bis(dimethylgloxime) complexes are of interest in photochemical hydrogen generation, and so estimating the acidity of the hydrides produced is useful.[14,31] The hydride complex $CoH(dmgH)_2(PBu_3)$ has been reported to have a pK_a of 13 in water.[31,88] A reliable equation to convert the pK_a of acids with anionic conjugate bases between nonaqueous solvents and water is needed before an acidity constant for the $(dmgH)_2^{2-}$ tetradentate ligand can be determined.

Implications. The success of eq 6 implies that the acidity of metal hydride or dihydrogen complexes goes up or down from a constant starting level as ligands are added to a diamagnetic metal ion. Becuse isolable metal hydride complexes typically have ligands with low electronegativity atoms as donors (P, C, H; see Table 2), the conjugate base form has one or more nonbonding d electron pairs in the highest occupied molecular orbitals that can be protonated to produce the hydride acid. The energy of this lone pair responds to the additive effect of the predominantly electrostatic field contributed by the ligand−metal bonds and increases or decreases as ligands are added around the metal. A higher energy lone pair gives, upon protonation, a less acidic hydride complex and vice versa.

The results of this study suggest that groups of structures will have very similar pK_a^{THF} values. For example, Table 6 shows the approximate values for $[MH_x(CO)_y]^{z+}$ and $[MH_x(PMe_3)_y]^{z+}$ complexes for periodic groups of metals represented in Table 3. All of these formulas give the metal an 18-electron count and make the complex diamagnetic. The structural types represented by complexes found in Table 3 are printed in bold. Because the hydride ligand has the A_L close to 0.0 (actually 0.2), all polyhydride complexes on the same row of Table 6 with the same charge and same number of the same ligand L will have very similar acidities except the d^6 octahedral hydride acids, which are expected to be 6 units less acidic. For example, $WH_6(PMe_3)_3/[WH_5(PMe_3)_3]^-$, $ReH_5(PMe_3)_3/[ReH_4(PMe_3)_3]^-$, and $OsH_4(PMe_3)_3/[OsH_3(PMe_3)_3]^-$ are expected to have a pK_a^{THF} of approximately 48; $IrH_3(PMe_3)_3/[IrH_2(PMe_3)_3]^-$ would be 6 higher, or 54. The table shows that cationic polycarbonyl complexes would be extremely difficult or impossible to make due to their high acidity (and probable instability with respect to the loss of H_2).[89] Only $[Re(H_2)(CO)_5]^+$ is known (Table 5). Of course, mixed carbonylphosphine complexes would have pK_a^{THF} values between these two extremes.

The method can be used to explain several reactions. The complex $[Ir(Cp)(H)(bpy)]^+$ is reported to be stable in pH 7 water.[90] We calculate its pK_a^{H2O} to be 17, a very weak acid. The related protonated complex, $[Ir(Cp)(H_2)(bpy)]^{2+}$, forms at pH 3 but is unstable.[91] Its pK_a^{H2O} is predicted to be −3 (a strong acid in water). These results help to explain the mechanism of action of this iridium system in the catalysis of CO_2 reduction,[91] electrochemical hydrogen evolution,[90] and aerobic alcohol oxidation.[92] The related ruthenium complex $[Ru$-

$(C_6Me_6)(H)(bpy)]^+$ is also postulated to catalyze CO_2 hydrogenation[91] and is expected from our calculation to have a pK_a^{H2O} somewhat higher than 2 if the C_6Me_6 ligand is given the same acidity constant as 3 times the olefin value of −2. The dihydrogen complex $[Os(bpy)(PPh_3)_2(H_2)(CO)]^{2+}$ is deprotonated by diethylether.[93] Its pK^{CH2Cl2} is expected from eq 6 to be −3.5. The rhenium dihydrogen complex $[Re(H_2)(PCy_3)_2(CO)_3]^+$ is deprotonated by 1,8-bis(dimethylamino)naphthalene (Proton-Sponge, pK_a^{THF} 12)[94] or 2,6-di-*tert*-butyl-4-methylpyridine, but not pentafluoropyridine and 2,6-diisopropylaniline (pK_a^{THF} approximately 6).[95] Equation 6 provides a pK_a^{THF} of 0. This complex has a short, strong H−H bond, which might make deprotonation less thermodynamically favorable than expected. The dihydrogen complexes $[Ir(Cp^*)(PMe_2CH_2PMe_2)(H_2)]^{2+}$ and $[Ir(Cp^*)(PPh_2CH_2PPh_2)(H_2)]^{2+}$ are reported to be highly acidic so that they are deprotonated by small amounts of water in CD_2Cl_2.[96] Their pK_a^{THF} values from eq 6 are −1 and −4, respectively. Of the series of dihydrogen complexes $[OsH_4(P^iPr_3)_2(MeCN)_2]^{2+}$, $[OsH_3(P^iPr_3)_2(MeCN)_2]^+$, and $[OsH_2(P^iPr_3)_2(MeCN)_3]^{2+}$, only the dicationic species are deprotonated by piperidine (pK_a^{THF} approximately 10).[97] These observations are explained successfully by the pK_a^{THF} for the three calculated from eq 6 to be 5, 20, and 9, respectively.

■ CONCLUSIONS

Equation 6 represents a surprisingly simple recipe for estimating pK_a values of hydride and dihydrogen complexes. It provides the pK_a for 147 complexes of this type within ±3 units. Another 24 are predicted with two standard deviations, while a remaining eight have large deviations caused by a variety of possible factors. Charge on the conjugate base complex, either positive or negative, has a large contribution to the pK_a^{THF} of the metal hydride acid, −15 and +30, respectively. The disruption of a d^6 octahedral metal center in the acid form on going to the base form results in a weaker acid than expected, by 6 units. An interesting finding is that the acidity of hydrides is determined mainly by the sum of the acidity constants of the non-hydrogen ligands because the acidity constant for hydride is 0.2, which is almost a negligible contribution to the acidity. Very high pK_a values indicate that the conjugate base forms will be very basic and reactive. This information can be used in many ways, including whether the base form will react with protic solvents such as water, methanol, or even acetonitrile.

In the future, DFT calculations might be used to better understand the trends revealed here and why ligand additivity might apply in such a general way, as well as to refine this method.[30] The method has the potential to predict useful catalyst structures that utilize the heterolytic splitting of dihydrogen in hydrogenation and electrochemical processes.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Excel spreadsheet containing data for Tables 2 and 3. Data for acids with anionic and cationic conjugate bases. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
rmorris@chem.utoronto.ca

■ REFERENCES

(1) Wang, W. H.; Muckerman, J. T.; Fujita, E.; Himeda, Y. *ACS Catal.* **2013**, *3*, 856−860.

(2) Stewart, M. P.; Ho, M. H.; Wiese, S.; Lindstrom, M. L.; Thogerson, C. E.; Raugei, S.; Bullock, R. M.; Helm, M. L. *J. Am. Chem. Soc.* **2013**, *135*, 6033−6046.

(3) Liu, T.; Dubois, D. L.; Bullock, R. M. *Nat. Chem.* **2013**, *5*, 228−233.

(4) Luca, O. R.; Blakemore, J. D.; Konezny, S. J.; Praetorius, J. M.; Schmeier, T. J.; Hunsinger, G. B.; Batista, V. S.; Brudvig, G. W.; Hazari, N.; Crabtree, R. H. *Inorg. Chem.* **2012**, *51*, 8704−8709.

(5) Espino, G.; Caballero, A.; Manzano, B. R.; Santos, L.; Perez-Manrique, M.; Moreno, M.; Jalon, F. A. *Organometallics* **2012**, *31*, 3087−3100.

(6) von der Hoh, A.; Berkessel, A. *ChemCatChem* **2011**, *3*, 861−867.

(7) Dobereiner, G. E.; Nova, A.; Schley, N. D.; Hazari, N.; Miller, S. J.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 7547−7562.

(8) Zhu, Y.; Fan, Y.; Burgess, K. *J. Am. Chem. Soc.* **2010**, *132*, 6249−6253.

(9) Heiden, Z. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2009**, *131*, 3593−3600.

(10) Guan, H.; Saddoughi, S. A.; Shaw, A. P.; Norton, J. R. *Organometallics* **2005**, *24*, 6358−6364.

(11) Camara, J. M.; Rauchfuss, T. B. *Nat. Chem.* **2012**, *4*, 26−30.

(12) Kimmich, B. F. M.; Fagan, P. J.; Hauptman, E.; Marshall, W. J.; Bullock, R. M. *Organometallics* **2005**, *24*, 6220−6229.

(13) Maj, L.; Grochala, W. *Adv. Funct. Mater.* **2006**, *16*, 2061−2076.

(14) Du, P. W.; Schneider, J.; Luo, G. G.; Brennessel, W. W.; Eisenberg, R. *Inorg. Chem.* **2009**, *48*, 4952−4962.

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

(16) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257−2263 and references therein.

(17) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875−883.

(18) Ng, S. M.; Fang, Y. Q.; Lau, C. P.; Wong, W. T.; Jia, G. C. *Organometallics* **1998**, *17*, 2052−2059.

(19) Ng, W. S.; Jia, G. C.; Huang, M. Y.; Lau, C. P.; Wong, K. Y.; Wen, L. B. *Organometallics* **1998**, *17*, 4556−4561.

(20) Abdur-Rashid, K.; Fong, T. P.; Greaves, B.; Gusev, D. G.; Hinman, J. G.; Landau, S. E.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 9155−9171.

(21) Berning, D. E.; Noll, B. C.; DuBois, D. L. *J. Am. Chem. Soc.* **1999**, *121*, 11432−11447.

(22) Curtis, C. J.; Miedaner, A.; Ellis, W. W.; DuBois, D. L. *J. Am. Chem. Soc.* **2002**, *124*, 1918−1925.

(23) Price, A. J.; Ciancanelli, R.; Noll, B. C.; Curtis, C. J.; DuBois, D. L.; Rakowski-DuBois, M. *Organometallics* **2002**, *21*, 4833−4839.

(24) Curtis, C. J.; Miedaner, A.; Ciancanelli, R.; Ellis, W. W.; Noll, B. C.; Rakowski-DuBois, M.; DuBois, D. L. *Inorg. Chem.* **2003**, *42*, 216−227.

(25) Curtis, C. J.; Miedaner, A.; Raebiger, J. W.; DuBois, D. L. *Organometallics* **2004**, *23*, 511−516.

(26) Helm, M. L.; Stewart, M. P.; Bullock, R. M.; DuBois, M. R.; DuBois, D. L. *Science* **2011**, *333*, 863−866.

(27) Liu, T. B.; Chen, S. T.; O'Hagan, M. J.; DuBois, M. R.; Bullock, R. M.; DuBois, D. L. *J. Am. Chem. Soc.* **2012**, *134*, 6257−6272.

(28) Angelici, R. J. *Acc. Chem. Res.* **1995**, *28*, 51−60.

(29) Wang, D. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 935−942.

(30) Chen, S. T.; Rousseau, R.; Raugei, S.; Dupuis, M.; DuBois, D. L.; Bullock, R. M. *Organometallics* **2011**, *30*, 6108−6118.

(31) Solis, B. H.; Hammes-Schiffer, S. *Inorg. Chem.* **2011**, *50*, 11252−11262.

(32) Roberts, J. A. S.; Appel, A. M.; Dubois, D. L.; Bullock, R. M. *J. Am. Chem. Soc.* **2011**, *133*, 14604−14613.

(33) Raebiger, J. W.; DuBois, D. L. *Organometallics* **2005**, *24*, 110−118.

(34) Fu, X. F.; Wayland, B. B. *J. Am. Chem. Soc.* **2005**, *127*, 16460−16467.

(35) van der Eide, E. F.; Helm, M. L.; Walter, E. D.; Bullock, R. M. *Inorg. Chem.* **2013**, *52*, 1591−1603.

(36) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711−6717.

(37) Morris, R. H. *Inorg. Chem.* **1992**, *31*, 1471−1478.

(38) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271−1285.

(39) Haav, K.; Saame, J.; Kutt, A.; Leito, I. *Eur. J. Org. Chem.* **2012**, 2167−2172 and references therein.

(40) Garrido, G.; Koort, E.; Rafols, C.; Bosch, E.; Rodima, T.; Leito, I.; Roses, M. *J. Org. Chem.* **2006**, *71*, 9062−9067.

(41) Li, T.; Lough, A. J.; Morris, R. H. *Chem.—Eur. J.* **2007**, *13*, 3796−3803.

(42) Jia, G. C.; Lau, C. P. *Coord. Chem. Rev.* **1999**, *192*, 83−108.

(43) Krumholz, P.; Galembeck, F. *J. Am. Chem. Soc.* **1971**, *93*, 1909−1913.

(44) Estes, D. P.; Vannucci, A. K.; Hall, A. R.; Lichtenberger, D. L.; Norton, J. R. *Organometallics* **2011**, *30*, 3444−3447.

(45) Chin, B.; Lough, A. J.; Morris, R. H.; Schweitzer, C. T.; Dagostino, C. *Inorg. Chem.* **1994**, *33*, 6278−6288.

(46) Chatt, J.; Kan, C. T.; Leigh, G. J.; Pickett, C. J.; Stanley, D. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2032−2038.

(47) Wilson, A. D.; Miller, A. J. M.; DuBois, D. L.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **2010**, *49*, 3918−3926.

(48) Ciancanelli, R.; Noll, B. C.; DuBois, D. L.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **2002**, *124*, 2984−2992.

(49) Vidal, J. L.; Walker, W. E. *Inorg. Chem.* **1981**, *20*, 249−254.

(50) Felton, G. A. N.; Vannucci, A. K.; Okumura, N.; Lockett, L. T.; Evans, D. H.; Glass, R. S.; Lichtenberger, D. L. *Organometallics* **2008**, *27*, 4671−4679.

(51) Peterson, T. H.; Golden, J. T.; Bergman, R. G. *Organometallics* **1999**, *18*, 2005−2020.

(52) Landau, S. E.; Groh, K. E.; Lough, A. J.; Morris, R. H. *Inorg. Chem.* **2002**, *41*, 2995−3007.

(53) Pearson, R. G.; Kresge, C. T. *Inorg. Chem.* **1981**, *20*, 1878−1882.

(54) Wiese, S.; Kilgore, U. J.; Dubois, D. L.; Bullock, R. M. *ACS Catal.* **2012**, *2*, 720−727.

(55) Walker, H. W.; Pearson, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1983**, *105*, 1179−1186.

(56) Rottink, M. K.; Angelici, R. J. *Inorg. Chem.* **1993**, *32*, 3282−3286.

(57) Rocchini, E.; Mezzetti, A.; Ruegger, H.; Burckhardt, U.; Gramlich, V.; Del Zotto, A.; Martinuzzi, P.; Rigo, P. *Inorg. Chem.* **1997**, *36*, 711−720.

(58) Liu, S. H.; Lo, S. T.; Wen, T. B.; Zhou, Z. Y.; Lau, C. P.; Jia, G. *Organometallics* **2001**, *20*, 667−672.

(59) Bohanna, C.; Esteruelas, M. A.; Gomez, A. V.; Lopez, A. M.; Martinez, M. P. *Organometallics* **1997**, *16*, 4464−4468.

(60) Raebiger, J. W.; Miedaner, A.; Curtis, C. J.; Miller, S. M.; Anderson, O. P.; DuBois, D. L. *J. Am. Chem. Soc.* **2004**, *126*, 5502−5514.

(61) Miedaner, A.; Raebiger, J. W.; Curtis, C. J.; Miller, S. M.; DuBois, D. L. *Organometallics* **2004**, *23*, 2670−2679.

(62) Hinman, J. G.; Lough, A. J.; Morris, R. H. *Inorg. Chem.* **2007**, *46*, 4392−4401.

(63) Kristjansdottir, S. S.; Loendorf, A. J.; Norton, J. R. *Inorg. Chem.* **1991**, *30*, 4470−4471.

(64) Green, M. L. H.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1958**, 3916.

(65) Lemke, F. R.; Brammer, L. *Organometallics* **1995**, *14*, 3980−3987.

(66) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166−5175.

(67) Chan, W.-C.; Lau, C.-P.; Chen, Y.-Z.; Fang, Y.-Q.; Ng, S.-M.; Jia, G. *Organometallics* **1997**, *16*, 34−44.

(68) Esteruelas, M. A.; Gomez, A. V.; Lahoz, F. J.; Lopez, A. M.; Onate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423−3435.

(69) Li, T. S.; Lough, A. J.; Zuccaccia, C.; Macchioni, A.; Morris, R. H. *Can. J. Chem.* **2006**, *84*, 164−175.

(70) Papish, E. T.; Rix, F. C.; Spetseris, N.; Norton, J. R.; Williams, R. D. *J. Am. Chem. Soc.* **2000**, *122*, 12235−12242.

(71) Bruno, J. W.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 1663−1669.

(72) Heinekey, D. M.; Hinkle, A. S.; Close, J. D. *J. Am. Chem. Soc.* **1996**, *118*, 5353−5361.

(73) Mercs, L.; Labat, G.; Neels, A.; Ehlers, A.; Albrecht, M. *Organometallics* **2006**, *25*, 5648−5656.

(74) Thoreson, K. A.; Follett, A. D.; McNeill, K. *Inorg. Chem.* **2010**, *49*, 3942−3949.

(75) Landau, S. E.; Morris, R. H.; Lough, A. J. *Inorg. Chem.* **1999**, *38*, 6060−6068.

(76) Fong, T. P.; Forde, C. E.; Lough, A. J.; Morris, R. H.; Rigo, P.; Rocchini, E.; Stephan, T. *J. Chem. Soc., Dalton Trans.* **1999**, 4475−4486.

(77) Heiden, Z. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2009**, *131*, 3593−3600.

(78) Vogt, M.; Pons, V.; Heinekey, D. M. *Organometallics* **2005**, *24*, 1832−1836.

(79) Matthews, S. L.; Pons, V.; Heinekey, D. M. *J. Am. Chem. Soc.* **2005**, *127*, 850−851.

(80) Grundler, P. V.; Yazyev, O. V.; Aebischer, N.; Helm, L.; Laurenczy, G.; Merbach, A. E. *Inorg. Chim. Acta* **2006**, *359*, 1795−1806.

(81) Ohkuma, T.; Utsumi, N.; Tsutsumi, K.; Murata, K.; Sandoval, C.; Noyori, R. *J. Am. Chem. Soc.* **2006**, *128*, 8724−8725.

(82) Bordwell, F. B. *Acc. Chem. Res.* **1988**, *21*, 456−463.

(83) Nicolet, Y.; Fontecilla-Camps, J. C. *J. Biol. Chem.* **2012**, *287*, 13532−13540.

(84) Carroll, M. E.; Barton, B. E.; Rauchfuss, T. B.; Carroll, P. J. *J. Am. Chem. Soc.* **2012**, *134*, 18843−18852.

(85) Hashiguchi, S.; Fujii, A.; Takehara, J.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 7562−7563.

(86) Ikariya, T.; Murata, K.; Noyori, R. *Org. Biomol. Chem.* **2006**, *4*, 393−406.

(87) Uematsu, N.; Fujii, A.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 4916−4917.

(88) Jacques, P.-A.; Artero, V.; Pacautb, J.; Fontecave, M. *Proc. Nat. Acad. Sci. U.S.A.* **2009**, *106*, 20627−20632.

(89) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155−284.

(90) Ladwig, M.; Kaim, W. *J. Organomet. Chem.* **1992**, *439*, 79−90.

(91) Ogo, S.; Kabe, R.; Hayashi, H.; Harada, R.; Fukuzumi, S. *Dalton Trans.* **2006**, 4657−4663.

(92) Gabrielsson, A.; van Leeuwen, P.; Kaim, W. *Chem. Commun.* **2006**, 4926−4927.

(93) Heinekey, D. M.; Luther, T. A. *Inorg. Chem.* **1996**, *35*, 4396−4399.

(94) Rodima, T.; Kaljurand, I.; Pihl, A.; Mäemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2002**, *67*, 1873−1881.

(95) Heinekey, D. M.; Radzewich, C. E.; Voges, M. H.; Schomber, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 4172−4181.

(96) Gelabert, R.; Moreno, M.; Lluch, J. M.; Lledos, A.; Pons, V.; Heinekey, D. M. *J. Am. Chem. Soc.* **2004**, *126*, 8813−8822.

(97) Smith, K. T.; Tilset, M.; Kuhlman, R.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 9473−9480.